CH275 FOUNDATIONS OF INORGANIC



Amanda Bowman
Colorado College

LibreTexts™

CH275 Foundations of Inorganic

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide an accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by NICE CXone Expert and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org or visit our main website at https://LibreTexts.org.

This text was compiled on 05/15/2026

TABLE OF CONTENTS

Licensing

1: Introduction

2: Chemical Structure and Periodic Trends (Review)

- 2.1: Atomic Structure
- 2.2: Molecular and Ionic Compounds
- 2.3: Chemical Nomenclature
- 2.4: Electron Configurations (Atoms)
- 2.5: Electron Configurations (Ions)
- 2.6: Redox Reactions and Oxidation State
- 2.7: Periodic Trends
- 2.8: Electronegativity
- 2.9: Electron-Dot Structures
- 2.10: Formal Charges and Resonance
- 2.11: Molecular Orbitals

3: Acid-Base Chemistry

- 3.1: Acid-Base Theories
- 3.2: Brønsted-Lowry Model
- 3.3: Acidity of Binary Hydrides
- 3.4: Acidity of Oxoacids
- 3.5: Acidity of Metal Cations

4: Redox Reactivity

- 4.1: Redox Reactions
- 4.2: Balancing Redox Reactions
- 4.3: Electrochemical Potentials
- 4.4: Pourbaix Diagrams
- 4.5: Electrochemical Corrosion

5: Electrochemistry

- 5.1: Electrolysis
- 5.2: Cyclic Voltammetry
- 5.3: CV Electrodes

6: Ionic Compounds

- 6.1: Unit Cells
- 6.2: Ionic Radii and Radius Ratios
- 6.3: Lattice Energy
- 6.4: Born-Haber Cycles
- 6.5: Ionic Lattices - Examples
  - 6.5A: Structure - Rock Salt (NaCl)

- 6.5B: Structure - Caesium Chloride (CsCl)
- 6.5C: Structure - Fluorite and Antifluorite
- 6.5D: Structure - Zinc Blende (ZnS)
- 6.6: Lattice Energy and Solubility
- 6.7: Solubility Equilibria

7: Coordination Compounds

- 7.1: Coordination Compounds
- 7.2: Lewis Acids and Bases
- 7.3: Nomenclature and Ligands
- 7.4: Structures
- 7.5: Isomerism
- 7.6: Complex-Ion Equilibria
- 7.7: Hard-Soft Acid-Base Theory

8: NMR and IR Spectroscopy

- 8.1: Infrared (IR) Spectroscopy
- 8.2: Interpreting Infrared Spectra
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
- 8.4: Chemical Shifts
- 8.5: Proton Equivalence
- 8.6: Chemical Shifts in \(^1H\) NMR Spectroscopy
- 8.7: Peak Integration
- 8.8: Peak Splitting

9: Symmetry

- 9.1: Symmetry Elements
- 9.2: Point Groups
- 9.3: Assigning Point Groups
- 9.4: Character Tables
- 9.5: Applications of Symmetry - Chirality

10: Molecular Orbital Theory

- 10.1: Molecular Orbitals
  - 10.1.1: s-Orbital MOs
  - 10.1.2: p-Orbital MOs
  - 10.1.3: d-Orbital MOs
- 10.2: Non-bonding Orbitals
- 10.3: Molecular Orbital Diagrams
- 10.4: Orbital Mixing
- 10.5: Diatomic Molecules
- 10.6: Polar Diatomic Molecules
- 10.7: Polyatomic Molecules
  - 10.7.1: Bifluoride anion
  - 10.7.2: Carbon Dioxide
  - 10.7.3: H_2O
  - 10.7.4: NH_3

- 10.7.5: CO_2 (Revisted with Projection Operators)
- 10.7.6: BF_3

11: Coordination Compound Bonding

- 11.1: Crystal Field Theory
- 11.2: Crystal Field Stabilization Energy
- 11.3: Crystal Field Splitting
- 11.4: Ligand Field Theory
- 11.5: Metal-Metal Bonding
- 11.6: Spectrochemical Series
- 11.7: Colors of Coordination Compounds
- 11.8: Magnetic Moments

12: Coordination Compound Spectroscopy

- 12.1: Molecular Vibrations
- 12.2: Identifying Active Vibrations
- 12.3: Carbonyl Vibrational Modes

13: Substitution Reactivity

- 13.1: Reactions of Metal Complexes
- 13.2: Substitution Reactions
- 13.3: Inert and Labile Complexes
- 13.4: Chelate Effects
- 13.5: Substitution Mechanisms
  - 13.5.1: Dissociative Mechanism
  - 13.5.2: Interchange Mechanism
  - 13.5.3: Associative Mechanism
- 13.6: Activation Parameters
- 13.7: Dissociation
- 13.8: Association
- 13.9: The Trans Effect

Index

Glossary

Detailed Licensing

Detailed Licensing

Detailed Licensing

Licensing

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

1: Introduction

CH275 - Foundations of Inorganic

Course Overview

Inorganic chemistry covers a broad range of topics with applications to everything from water purification to medicine to industrial catalysis. Foundations of Inorganic will provide a foundation in the fundamental concepts of inorganic chemistry, and will explore the structure, bonding, and reactivity of different types of (often colorful!) inorganic compounds and materials. We will study these concepts through the lens of different real-world applications and problems. In particular, the lab component of the course will focus on an ongoing lab project with a central theme, the selective solvent extraction of copper metal. Through lab, you will also gain first-hand experience with the experimental skills and techniques necessary to study inorganic chemistry.

Learning Outcomes

By the end of the course, you should be able to:

1) **Use** periodicity to explain properties and reactivity of inorganic ions.

2) **Explain** bonding interactions in inorganic compounds and materials using electrostatics, acid-base properties, and/or molecular orbital theory.

3) **Predict** the reactivity of inorganic compounds and ions using knowledge of structure and bonding.

4) **Predict** the reactivity of coordination compounds, including reaction rates, using thermodynamics, kinetics, and reduction potential.

5) **Apply** knowledge of inorganic compounds and reactions to real-world cases.

6) **Use** standard inorganic techniques to gather experimental data.

7) **Analyze** data collected using standard inorganic experimental techniques.

8) **Construct** a testable hypothesis that addresses a specific research question

This page titled 1: Introduction is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

CHAPTER OVERVIEW

2: Chemical Structure and Periodic Trends (Review)

2.1: Atomic Structure
2.2: Molecular and Ionic Compounds
2.3: Chemical Nomenclature
2.4: Electron Configurations (Atoms)
2.5: Electron Configurations (Ions)
2.6: Redox Reactions and Oxidation State
2.7: Periodic Trends
2.8: Electronegativity
2.9: Electron-Dot Structures
2.10: Formal Charges and Resonance
2.11: Molecular Orbitals

This page titled 2: Chemical Structure and Periodic Trends (Review) is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

2.1: Atomic Structure

Learning Objectives

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

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

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 2.1.1).



Figure 2.1.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

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

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton). The properties of these fundamental particles are summarized in Table 2.1.1. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00 amu. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 2.1.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	$-1.602\ 10^{-19}$	1−	0.00055	$0.00091\ 10^{-24}$
proton	nucleus	$1.602\ 10^{-19}$	1+	1.00727	$1.67262\ 10^{-24}$
neutron	nucleus	0	0	1.00866	$1.67493\ 10^{-24}$

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

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

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

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

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

Example 2.1.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.1.2).



(a) (b)

Figure 2.1.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by “Almazi”/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world’s population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 − 53 = 74). Since the iodine is added as a 1− anion, the number of electrons is 54 [53 – (1–) = 54].

? Exercise 2.1.1

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 2.1.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure 2.1.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The symbols for several common elements and their atoms are listed in Table 2.1.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table (also found in Appendix A).

Table 2.1.2: Some Common Elements and Their Symbols

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

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

Link to Learning

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

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 2.1.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

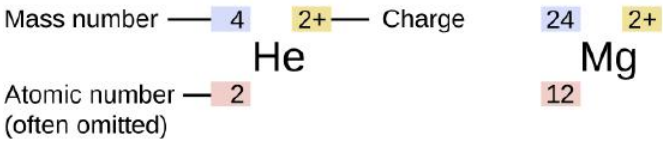


Figure 2.1.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 2.1.3. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table 2.1.3: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}H$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}H$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}H$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}He$	2	2	1	3.01603	0.00013
	$^{4}_{2}He$	2	2	2	4.0026	100
lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}Be$	4	4	5	9.0122	100
boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}N$	7	7	7	14.0031	99.63
	$^{15}_{7}N$	7	7	8	15.0001	0.37
oxygen	$^{16}_{81}O$	8	8	8	15.9949	99.757
	$^{17}_{81}O$	8	8	9	16.9991	0.038
	$^{18}_{81}O$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}F$	9	9	10	18.9984	100
neon	$^{20}_{10}Ne$	10	10	10	19.9924	90.48
	$^{21}_{10}Ne$	10	10	11	20.9938	0.27
	$^{22}_{10}Ne$	10	10	12	21.9914	9.25

Link to Learning

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

Atomic Mass

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

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

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

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

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

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

Example 2.1.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass } &= (0.9184 \times 19.9924\,\text{amu}) + (0.0047 \times 20.9940\,\text{amu}) + (0.0769 \times 21.9914\,\text{amu} \\ &= (18.36 + 0.099 + 1.69)\,\text{amu} \\ &= 20.15\,\text{amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Exercise 2.1.2

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

Answer

24.31 amu

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

Example 2.1.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\text{average mass } = \left(\text{ fraction of } {}^{35}Cl \times \text{ mass of } {}^{35}Cl\right) + \left(\text{ fraction of } {}^{37}Cl \times \text{ mass of } {}^{37}Cl\right)$$

If we let *x* represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by 1.00 − *x*.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 − the fraction of ^{35}Cl.)

Substituting this into the average mass equation, we have:

$$\begin{aligned} 35.453amu &= (x \times 34.96885amu) + [(1.00 - x) \times 36.96590amu] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576 \end{aligned}$$

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

Exercise 2.1.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer

69.15% Cu-63 and 30.85% Cu-65

Link to Learning

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

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

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. **Mass spectrometry** (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 2.1.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball rolling

past a magnet is deflected to a lesser extent that that of a small steel ball). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.

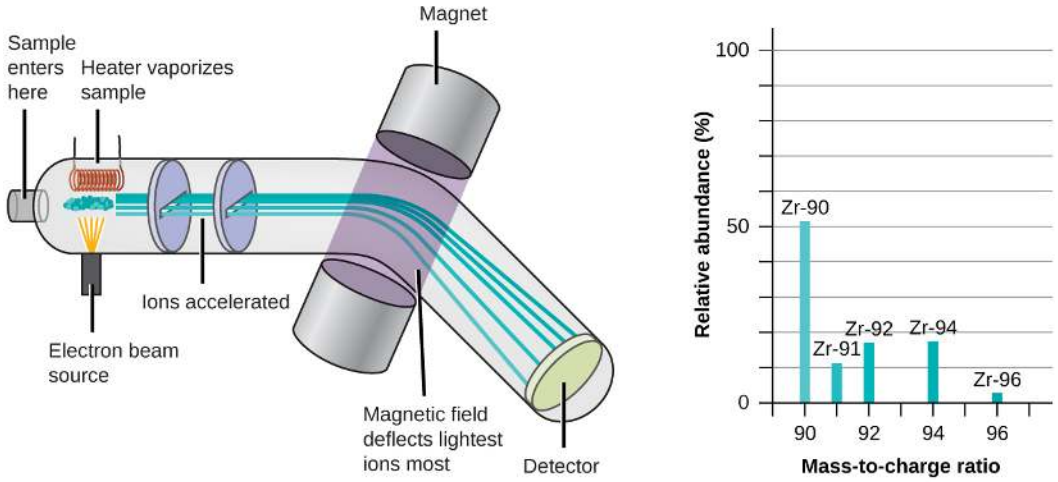


Figure 2.1.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

Link to Learning

See an animation that explains mass spectrometry. Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

This page titled 2.1: Atomic Structure is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **2.3: Atomic Structure and Symbolism** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.2: Molecular and Ionic Compounds

Learning Objectives

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

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 2.2.1).

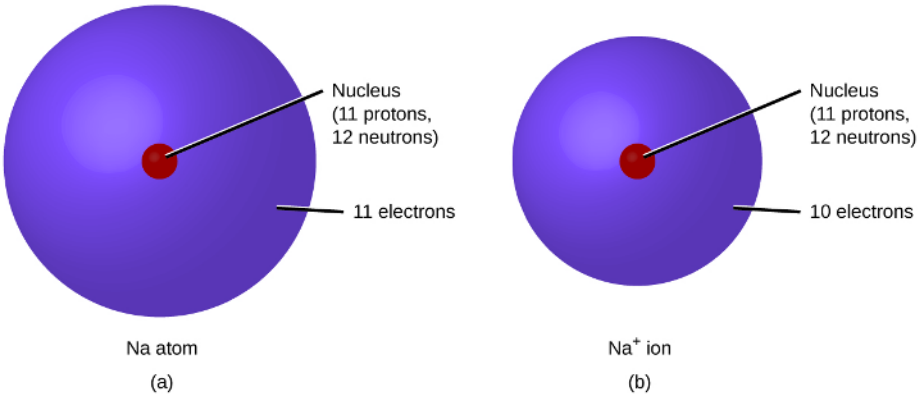


Table 2.2.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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

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

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 2.2.2). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic

table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

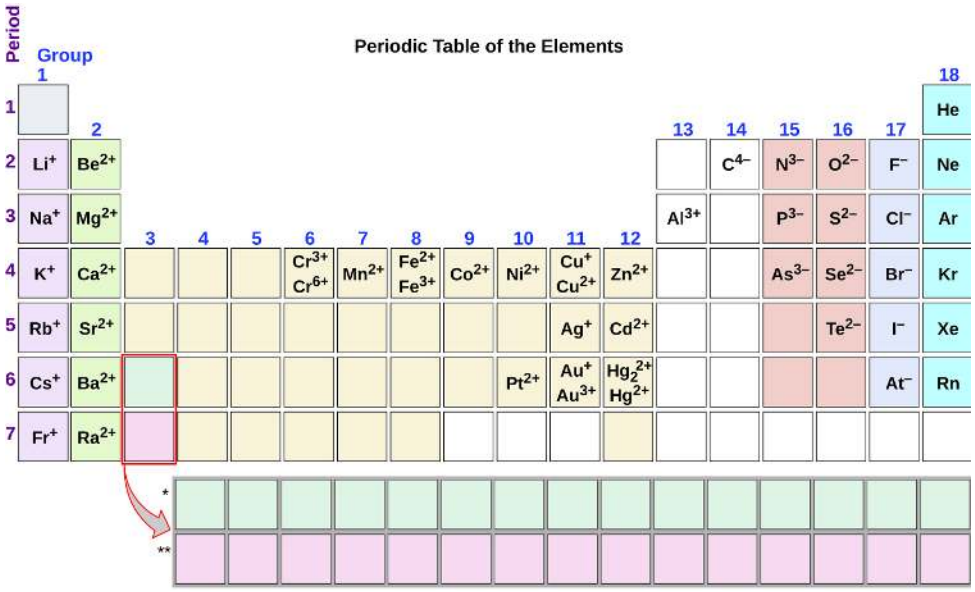


Table 2.2.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 2.2.1: Composition of Ions

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

Solution

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

Exercise 2.2.1

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

Answer

Se^{2-}, the selenide ion

Example 2.2.2: Formation of Ions

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

Solution

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

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

Exercise 2.2.2

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

Answer

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

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 2.2.1. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table 2.2.1: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_{42}^-	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

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

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are “shared” and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei

of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

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

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

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 2.2.3).

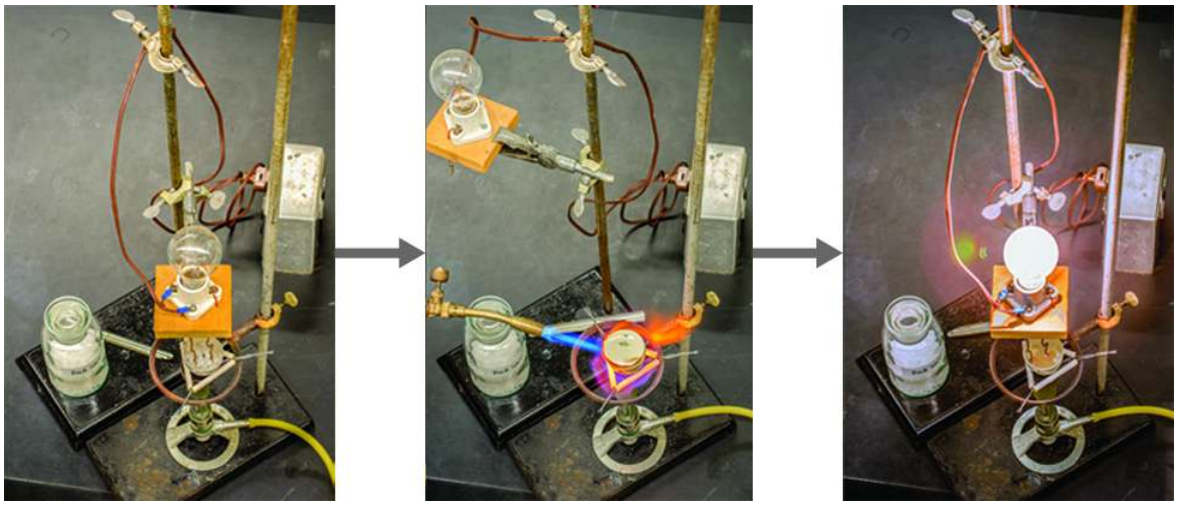


Table 2.2.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Link to Learning

Watch this video to see a mixture of salts melt and conduct electricity.

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

Example 2.2.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 2.2.4) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Table 2.2.4: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko via Wikipedia)

Solution

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

Exercise 2.2.3

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

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table 2.2.1) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 2.2.4: Predicting the Formula of a Compound with a Polyatomic Anion

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

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 2.2.4

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

Answer

Li_2O_2

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

Molecular Compounds

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

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

✔ Example 2.2.5: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

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

Solution

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

? Exercise 2.2.5

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

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer

a. molecular
b. ionic

c. molecular
d. ionic

This page titled 2.2: Molecular and Ionic Compounds is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **2.6: Molecular and Ionic Compounds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.3: Chemical Nomenclature

Learning Objectives

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

- Derive names for common types of inorganic compounds using a systematic approach

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

Ionic Compounds

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

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table 2.3.1.

Table 2.3.1: Names of Some Ionic Compounds

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

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in Table 2.3.2.

Table 2.3.2: Names of Some Polyatomic Ionic Compounds

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

Chemistry in Everyday Life: Ionic Compounds in Your Cabinet

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 2.3.3. Look at the label or ingredients list on the various products that you use during

the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 2.3.3: Everyday Ionic Compounds

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

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see Figure 2.29), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 2.3.4.

Table 2.3.4: Some Ionic Compounds with Variably Charged Metal Ions

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

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the anhydrous (meaning "not hydrated") compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see Table 2.3.5) and ends with "hydrate." For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

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

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

$$\text{sodium carbonate decahydrate} \quad Na_2CO_3 \cdot 10\,H_2O$$

Table 2.3.5: Nomenclature Prefixes

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

Example 2.3.1: Naming Ionic Compounds

Name the following ionic compounds

a. Fe_2S_3
b. CuSe
c. GaN
d. $MgSO_4{\cdot}7H_2O$
e. $Ti_2(SO_4)_3$

Solution

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

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

Exercise 2.3.1

Write the formulas of the following ionic compounds:

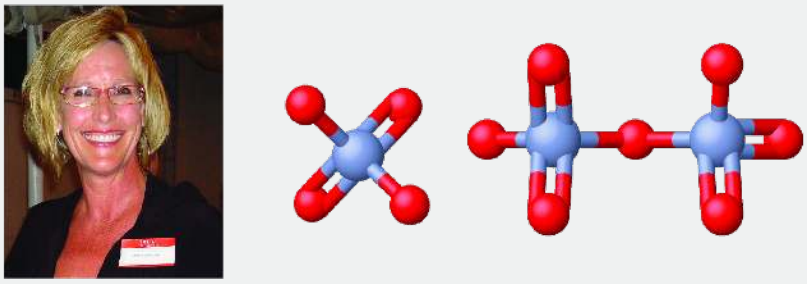
a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. iron(III) chloride dihydrate

Answer

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

Chemistry in Everyday Life: Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 2.3.1) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brockovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a) (b)

Figure 2.3.1: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, (left), and dichromate, (right).

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

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

Molecular (Covalent) Compounds

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

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 2.3.5.

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 2.3.6.

Table 2.3.6: Names of Some Molecular Compounds Composed of Two Elements

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

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

✔ Example 2.3.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

? Exercise 2.3.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer

(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

Link to Learning

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

Binary Acids

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

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

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 2.3.7.

Table 2.3.7: Names of Some Simple Acids

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

Oxyacids

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

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

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 2.3.8. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 2.3.8: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

This page titled 2.3: Chemical Nomenclature is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **2.7: Chemical Nomenclature** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.4: Electron Configurations (Atoms)

Learning Objectives

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

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

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

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 2.4.1: depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

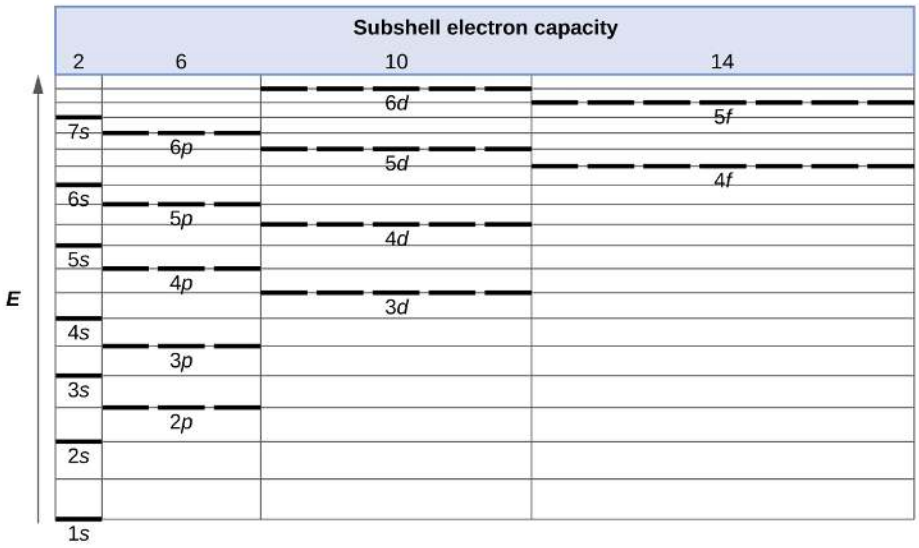


Figure 2.4.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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

significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 2.4.2):

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

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

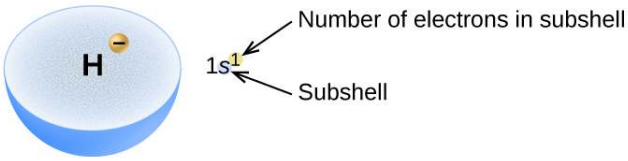


Figure 2.4.2: The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 2.4.1), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 2.4.3 illustrates the traditional way to remember the filling order for atomic orbitals.

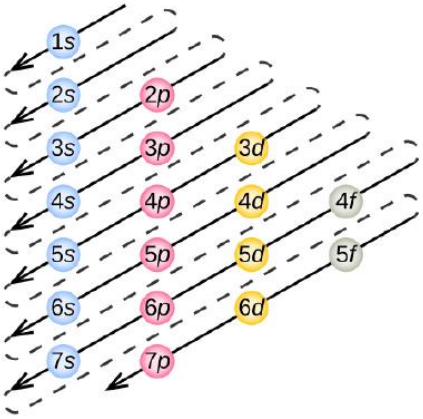


Figure 2.4.3: This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, Figure 2.4.4 provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

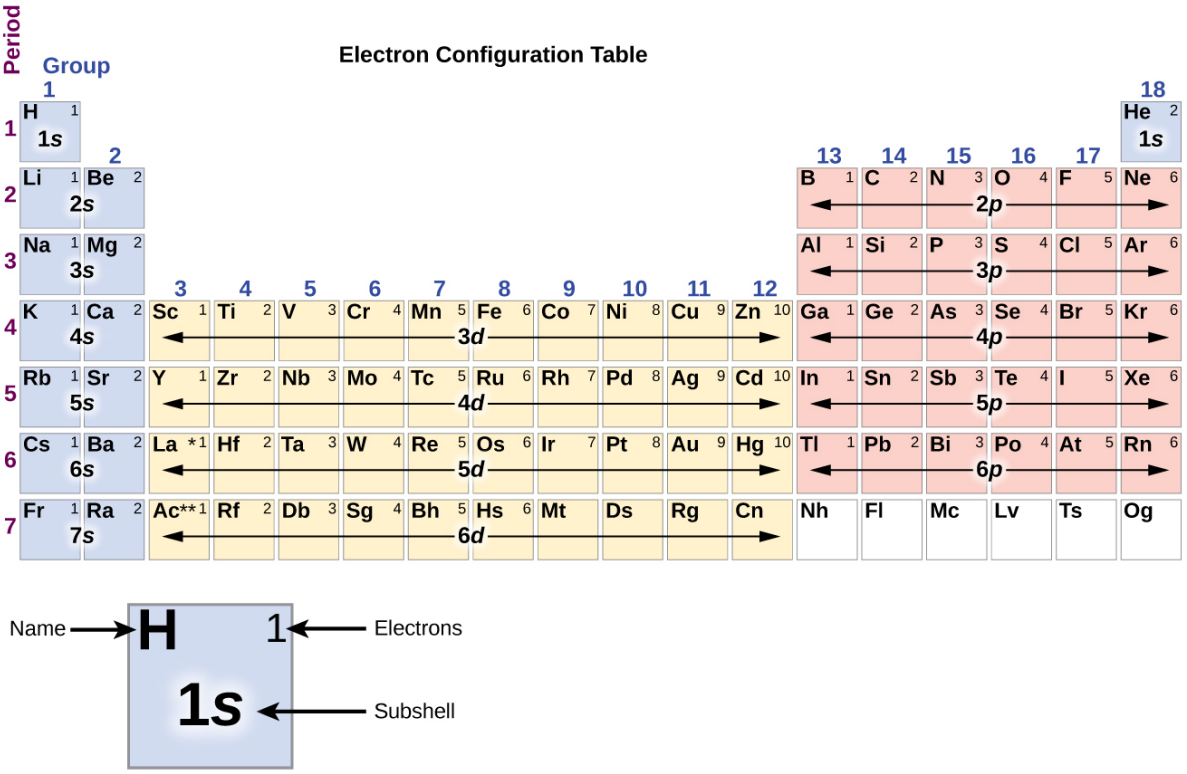
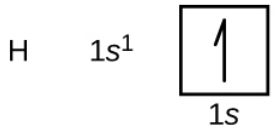
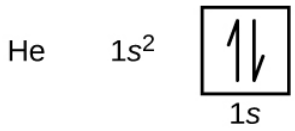


Figure 2.4.4: This partial periodic table shows electron configurations for the valence subshells of atoms. By "building up" from hydrogen, this table can be used to determine the electron configuration for atoms of most elements in the periodic table. (Electron configurations of the lanthanides and actinides are not accurately predicted by this simple approach. See Figure 2.4.6:

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 2.4.3 or Figure 2.4.4, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



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

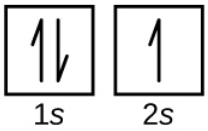


The $n = 1$ shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next

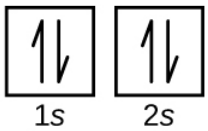
lowest energy, the 2*s* orbital (Figure 2.4.3 or Figure 2.4.4). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



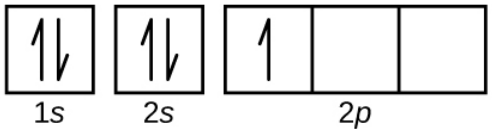
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



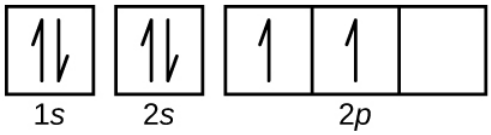
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There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

B $1s^2 2s^2 2p^1$

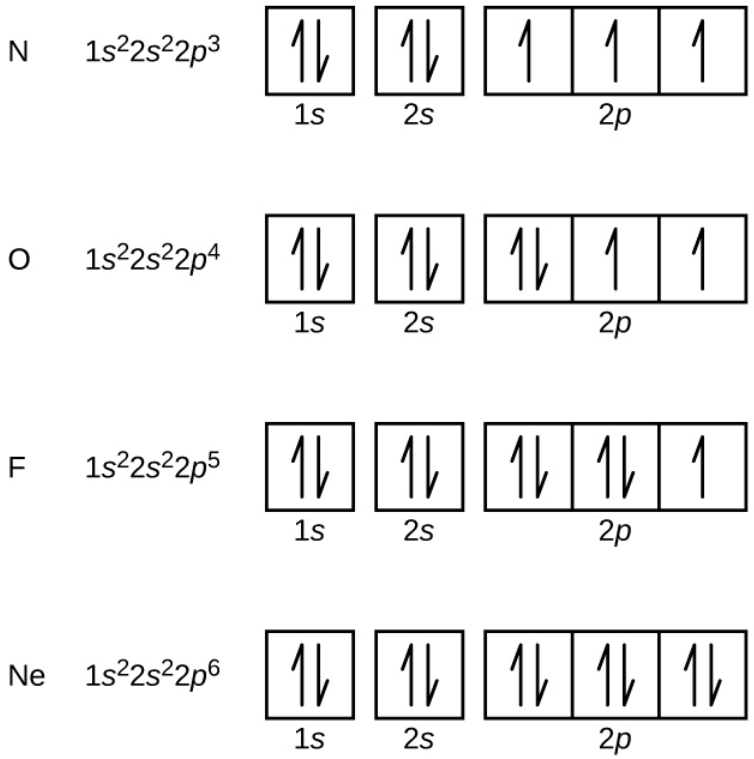


Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p*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

C $1s^2 2s^2 2p^2$



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



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 2.4.5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

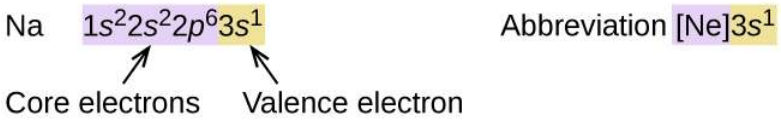


Figure 2.4.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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

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

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

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 2.4.6: shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

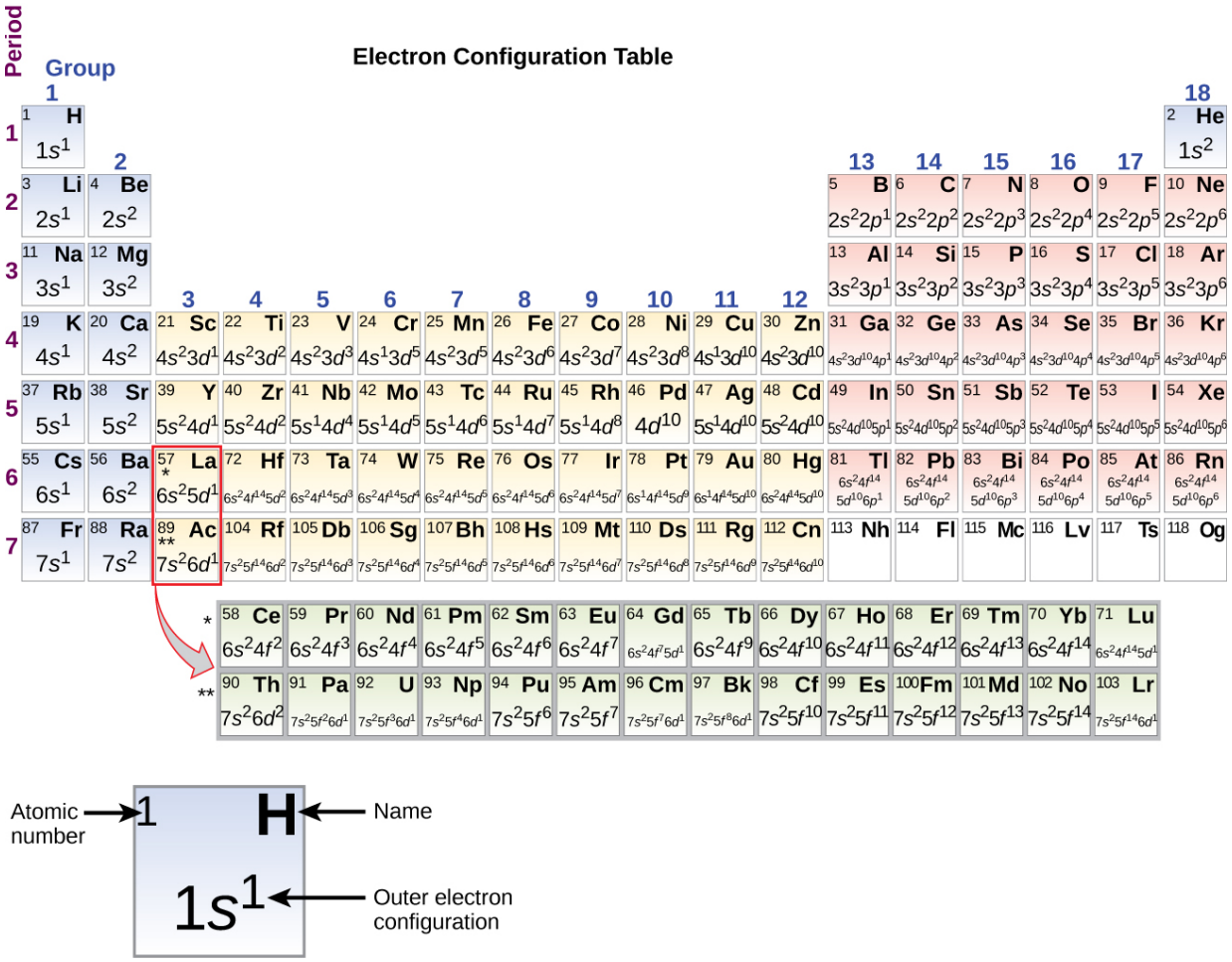


Figure 2.4.6: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 2.4.6). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of [Ar]$4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of [Ar]$4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

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

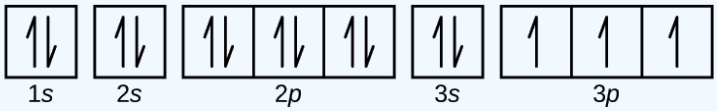
Example 2.4.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

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

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



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

Exercise 2.4.1

Identify the atoms from the electron configurations given:

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

Answer

a. Mn
b. Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 2.4.3: or Figure 2.4.4. For instance, the electron configurations (shown in Figure 2.4.6) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

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

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 2.4.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

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

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 2.4.6: , which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 2.4.6: show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 2.4.6. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 2.4.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 2.4.6), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 2.4.6. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    a. The lanthanide series: lanthanum (La) through lutetium (Lu)
    b. The actinide series: actinium (Ac) through lawrencium (Lr)

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

Electron Configurations of Ions

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

Example 2.4.2: Predicting Electron Configurations of Ions

What is the electron configuration of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

? Exercise 2.4.21

Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$? Which ion with a +3 charge has this configuration?

Answer

Tc^{2+}, Ru^{3+}

This page titled 2.4: Electron Configurations (Atoms) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **6.4: Electronic Structure of Atoms (Electron Configurations)** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.5: Electron Configurations (Ions)

Learning Objectives

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

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 2.5.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 2.5.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3,

indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, (2 +3) + (3 –2) = 0].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 2.5.2).

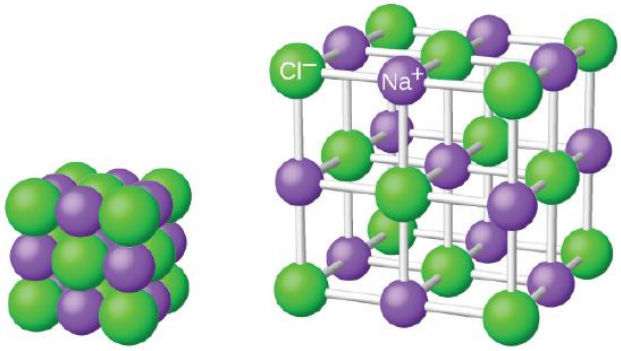


Figure 2.5.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl\,(s)} \longrightarrow \mathrm{Na^+\,(g) + Cl^-\,(g)} \qquad \Delta H = 769\,\mathrm{kJ}$$

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons.

Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 2.5.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[Ar]3d^{10}4s^2$

Cr: $[Ar]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

Zn^{2+}: $[Ar]3d^{10}$

Cr^{3+}: $[Ar]3d^3$

Exercise 2.5.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 2.5.1: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^2 4p^6$

I^-: $[Kr]4d^{10}5s^2 5p^6$

Exercise 2.5.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: [Ne]$3s^2 3p^3$; P^{3-}: [Ne]$3s^2 3p^6$

This page titled 2.5: Electron Configurations (Ions) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **7.1: Ionic Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.6: Redox Reactions and Oxidation State

Learning Objectives

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

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in a later chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table 2.6.1).

Table 2.6.1

	contain these ions	exceptions
Soluble Ionic Compounds	NH_4^+ group I cations: Li^+ Na^+ K^+ Rb^+ Cs^+	none
	Cl^- Br^- I^-	compounds with Ag^+, Hg_2^{2+}, and Pb^{2+}
	F^-	compounds with group 2 metal cations, Pb^{2+}, and Fe^{3+}
	$C_2H_3O_2^-$ HCO_3^- NO_3^- ClO_3^-	none
	SO_4^{2-}	compounds with Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+} and Sr^{2+}
Insoluble Ionic Compounds	contain these ions	exceptions
	CO_3^{2-} CrO_4^{2-} PO_4^{3-} S^{2-}	compounds with group 1 cations and NH_4^+
	OH^-	compounds with group 1 cations and Ba^{2+}

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$2\,KI\,(aq) + Pb(NO_3)_2\,(aq) \longrightarrow PbI_2\,(s) + 2\,KNO_3\,(aq)$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$Pb^{2+}\,(aq) + 2\,I^-\,(aq) \longrightarrow PbI_2\,(s)$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 2.6.1). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.

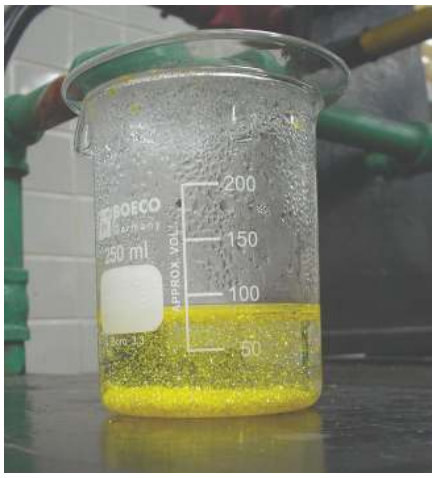


Figure 2.6.1: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table 2.6.1 may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium chloride will yield a solution containing Ag^+, NO_3^-, Na^+, and Cl^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaCl, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgCl. The solubility guidelines indicate all nitrate salts are soluble but that AgCl is one of insoluble. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$\mathrm{NaCl\,(aq) + AgNO_3\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)} \quad \text{(molecular)}$$

$$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)} \quad \text{(net ionic)}$$

Example 2.6.1: Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)}$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)}$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Pb^{2+}\,(aq) + CO_3{}^{2-}\,(aq) \longrightarrow PbCO_3\,(s)}$$

? Exercise 2.6.1

Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Answer

sodium sulfate, $BaSO_4$

Acid-Base Reactions

An acid-base reaction is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

$$HCl\,(aq) + H_2O\,(aq) \longrightarrow Cl^-\,(aq) + H_3O^+\,(aq)$$

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (Figure 2.6.2).

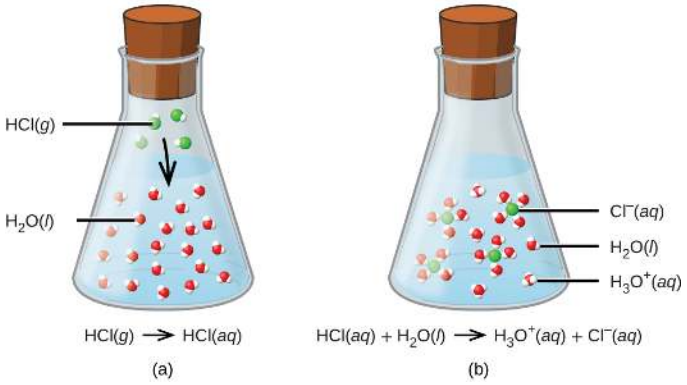
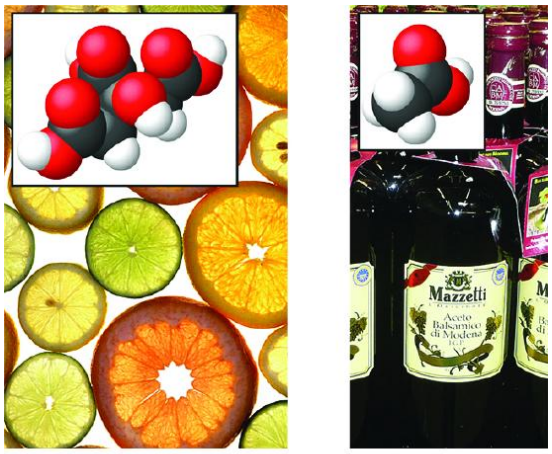


Figure 2.6.2: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong (Table 2.6.2). A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

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

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form,



(a) (b)

Figure 2.6.3: (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

Table 2.6.2: Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

A base is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

$$\mathrm{NaOH\,(s)} \longrightarrow \mathrm{Na^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure 2.6.4). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{NH_4{}^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as ions.



Figure 2.6.4: Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a salt and water

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$Mg(OH)_2\,(s) + 2\,HCl\,(aq) \longrightarrow MgCl_2\,(aq) + 2\,H_2O\,(l)$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example 2.6.2: Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

a. the weak acid hydrogen hypochlorite reacts with water
b. a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$HOCl\,(aq) + H_2O\,(l) \rightleftharpoons OCl^-\,(aq) + H_3O^+\,(aq)$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion

$$Ba(OH)_2\,(aq) + 2\,HNO_3\,(aq) \longrightarrow Ba(NO_3)_2\,(aq) + 2\,H_2O\,(l)$$

Exercise 2.6.2

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer

$$H_3O^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,H_2O\,(l)$$

Chemistry in Everyday Life: Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3\,(s) + 2\,HCl\,(aq) \rightleftharpoons CaCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O\,(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Chemistry in Everyday Life: Culinary Aspects of Chemistry

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 2.6.5). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.



$CH_3COOH + NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow CH_3COO^- + NH_3^+CH_2CH_2CH_2CH_2NH_2$

Acetic acid + Putrescine → Acetate ion + Putrescinium ion

Figure 2.6.5: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

Link to Learning

Explore the microscopic view of strong and weak acids and bases.

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\,\mathrm{Na\,(s)} + \mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{NaCl\,(s)}$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2\,\mathrm{Na\,(s)} \longrightarrow 2\,\mathrm{Na^+\,(s)} + 2\,\mathrm{e^-}$$
$$\mathrm{Cl_2\,(g)} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-\,(s)}$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\text{oxidation} = \text{loss of electrons}$$
$$\text{reduction} = \text{gain of electrons}$$

In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent** (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent** (oxidant), as it effectively removes electrons from (oxidizes) sodium.

$$\text{reducing agent} = \text{species that is oxidized}$$
$$\text{oxidizing agent} = \text{species that is reduced}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound were ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
   - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
   - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, very rarely (so-called superoxides, positive values when combined with F (values vary)
   - Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 2.6.3: Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. $\mathrm{H_2S}$
b. $\mathrm{SO_3^{2-}}$
c. $\mathrm{Na_2SO_4}$

Solution

(a) According to guideline 3, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$
$$x = 0 - (2 \times +1) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } {SO_3}^{2-} = -2 = (3 \times -2) + (1 \times x)$$
$$x = -2 - (3 \times -2) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on } {SO_4}^{2-} = -2 = (4 \times -2) + (1 \times x)$$
$$x = -2 - (4 \times -2) = +6$$

? Exercise 2.6.3

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

a. $\mathrm{K}\underline{N}\mathrm{O}_3$
b. $\underline{Al}\mathrm{H}_3$
c. $\underline{N}\mathrm{H}_4{}^+$
d. $\mathrm{H}_2\underline{P}\mathrm{O}_4{}^-$

Answer

a. N, +5;
b. Al, +3;
c. N, −3;
d. P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist Example 4.6.) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\begin{aligned} \text{oxidation} &= \text{increase in oxidation number} \\ \text{reduction} &= \text{decrease in oxidation number} \end{aligned}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$\begin{aligned} \text{oxidation} &= \text{increase in oxidation number} \\ \text{reduction} &= \text{decrease in oxidation number} \end{aligned}$$

Link to Learning

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\mathrm{Cu\,(s) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,Ag\,(s)}$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 2.6.6).

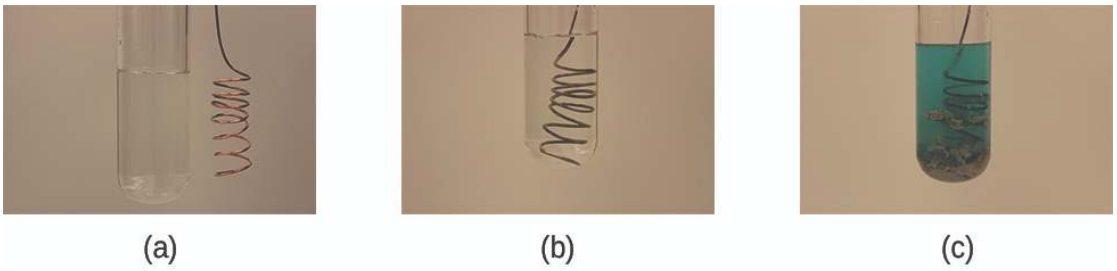


Figure 2.6.6: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 2.6.4: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $\mathrm{ZnCO_3\,(s) \longrightarrow ZnO\ (s)^+\ CO_2\,(g)}$
b. $\mathrm{2\,Ga\,(l) + 3\,Br_2\,(l) \longrightarrow 2\,GaBr_3\,(s)}$
c. $\mathrm{2\,H_2O_2\,(aq) \longrightarrow 2\,H_2O\,(l) + O_2\,(g)}$
d. $\mathrm{BaCl_2\,(aq) + K_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2\,KCl\,(aq)}$
e. $\mathrm{C_2H_4\,(g) + 3\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)}$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in $GaBr_3$(s). The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(l) to −1 in $GaBr_3$(s). The oxidizing agent is Br_2(l).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in H_2O_2(aq) to 0 in O_2(g). Oxygen is also reduced, its oxidation number decreasing from −1 in H_2O_2(aq) to −2 in H_2O(l). For disproportionation reactions, the same substance functions as an oxidant and a reductant.
d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C_2H_4(g) to +4 in CO_2(g). The reducing agent (fuel) is C_2H_4(g). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(g) to −2 in H_2O(l). The oxidizing agent is O_2(g).

Exercise 2.6.4

This equation describes the production of tin(II) chloride:

$$\mathrm{Sn\,(s) + 2\,HCl\,(g) \longrightarrow SnCl_2\,(s) + H_2\,(g)}$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. $\mathrm{Sn(s)}$ is the reductant and $\mathrm{HCl(g)}$ is the oxidant.

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
   a. Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
   b. On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
   c. Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges[1] are balanced.

Example 2.6.5: Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$$\mathrm{Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}}$$

Solution

Step 1.Write the two half-reactions.

Each half-reaction will contain one reactant and one product with one element in common.

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} \longrightarrow Cr^{3+}}$$

Step 2. Balance oxygen atoms by adding $\mathrm{H_2O}$ molecules.

The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+}}$$

Step 3. Balance charge by adding electrons.

The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Step 4. Balance hydrogen atoms by adding $\mathrm{H^+}$ ions.

The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+}}$$

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Step 5. Balance charge by adding electrons.

The iron half-reaction shows a total charge of 2+ on the left side (1 $\mathrm{Fe^{2+}}$ ion) and 3+ on the right side (1 $\mathrm{Fe^{3+}}$ ion). Adding one electron to the right side brings that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved.

The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 $\mathrm{Cr_2O_7^{2-}}$ ion and 14 $\mathrm{H^+}$ ions). The total charge on the right side is (2 × 3+) = 6 + (2 $\mathrm{Cr^{3+}}$ ions). Adding six electrons to the left side will bring that side's total charge to (12+ + 6−) = 6+, and charge balance is achieved.

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + e^-}$$

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Step 6: Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction.

To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$$\mathrm{6\,Fe^{2+} \longrightarrow 6\,Fe^{3+} + 6\,e^-}$$

$$\mathrm{Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Step 7. Add the balanced half-reactions and cancel species that appear on both sides of the equation.

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \longrightarrow 6\,Fe^{3+} + 6\,e^- + 2\,Cr^{3+} + 7\,H_2O}$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O}$$

A final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

? Exercise 2.6.5

In basic solution, molecular chlorine, $\mathrm{Cl_2}$, reacts with hydroxide ions, $\mathrm{OH^-}$, to yield chloride ions, $\mathrm{Cl^-}$. and chlorate ions, $\mathrm{ClO_3^-}$. HINT: This is a *disproportionation reaction* in which the element chlorine is both oxidized and reduced. Write a balanced equation for this reaction.

Answer

$$\mathrm{3\,Cl_2\,(aq) + 6\,OH^-\,(aq) \longrightarrow 5\,Cl^-\,(aq) + ClO_3^-\,(aq) + 3\,H_2O\,(l)}$$

Footnotes

- 1The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

This page titled 2.6: Redox Reactions and Oxidation State is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **4.2: Classifying Chemical Reactions** is licensed CC BY 4.0.

2.7: Periodic Trends

Learning Objectives

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

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

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

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

Link to Learning

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

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 2.7.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 2.7.1 and Figure 2.7.1. The trends for the entire periodic table can be seen in Figure 2.7.2.

Table 2.7.1: Covalent Radii of the Halogen Group Elements

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

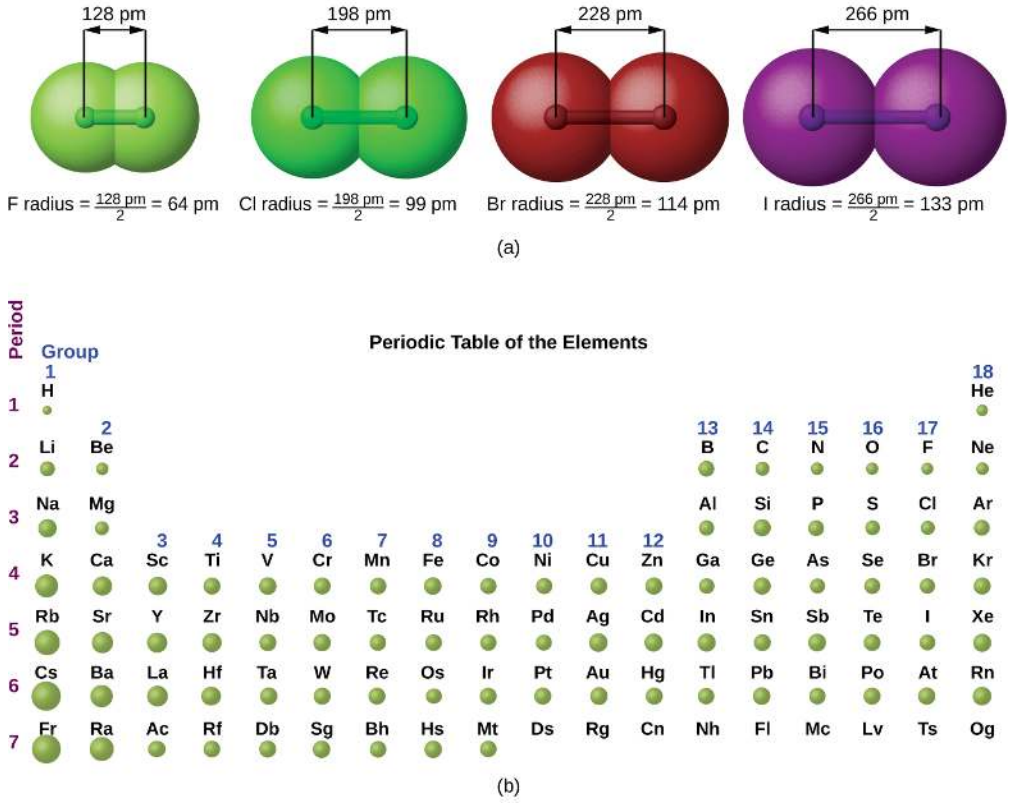


Figure 2.7.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

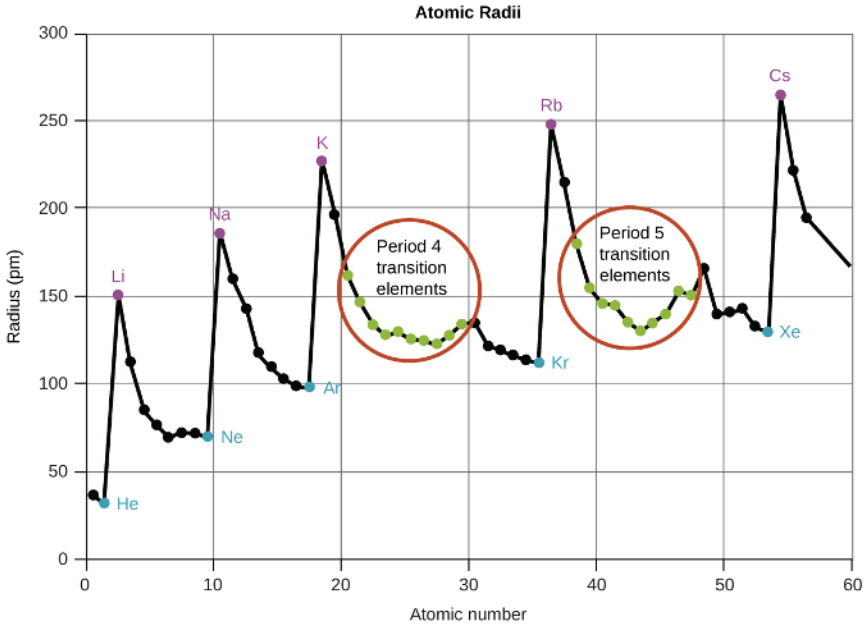


Figure 2.7.2: Within each period, the trend in atomic radius decreases as *Z* increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as *Z* increases.

As shown in Figure 2.7.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge**, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and

so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

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

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

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

Example 2.7.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Exercise 2.7.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 2.7.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 2.7.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

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

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 2.7.3). For example, a sulfur atom

($[Ne]3s^23p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^23p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^22s^22p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^23p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

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

$$\mathrm{X(g)} \longrightarrow \mathrm{X^+(g)} + \mathrm{e^-} \qquad IE_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X^+(g)} \longrightarrow \mathrm{X^{2+}(g)} + \mathrm{e^-} \qquad IE_2$$

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

Figure 2.7.4 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 2.7.5. Within a period, the IE_1 generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[He]2s^22p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

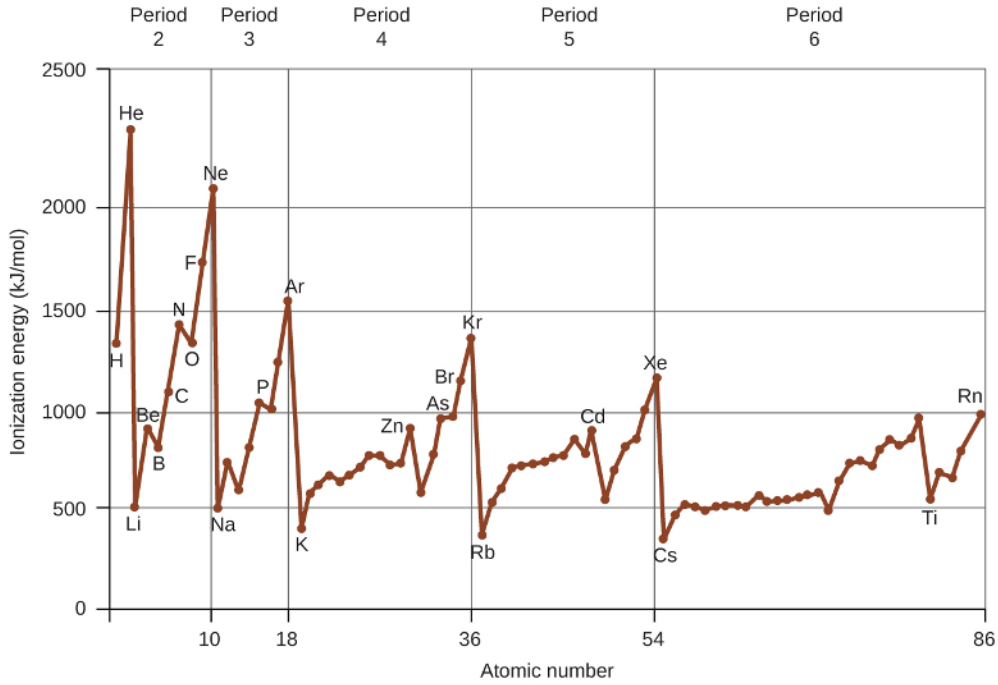


Figure 2.7.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

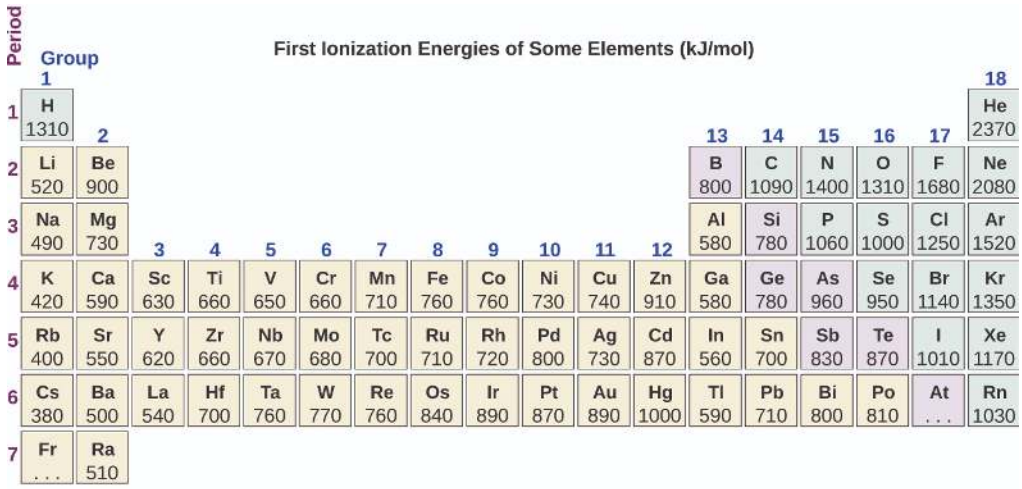
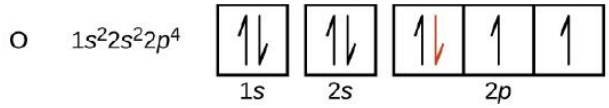


Figure 2.7.5: This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 2.7.5).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 2.7.2, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the

core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 2.7.2: Successive Ionization Energies for Selected Elements (kJ/mol)

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

Example 2.7.2: Ranking Ionization Energies

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

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from Al ($Al^{2+} \longrightarrow Al^{3+} + e^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na)$.

Exercise 2.7.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

Variation in Electron Affinities

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

$$X(g) + e^- \longrightarrow X^-(g) \quad EA_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 2.7.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

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

electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

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

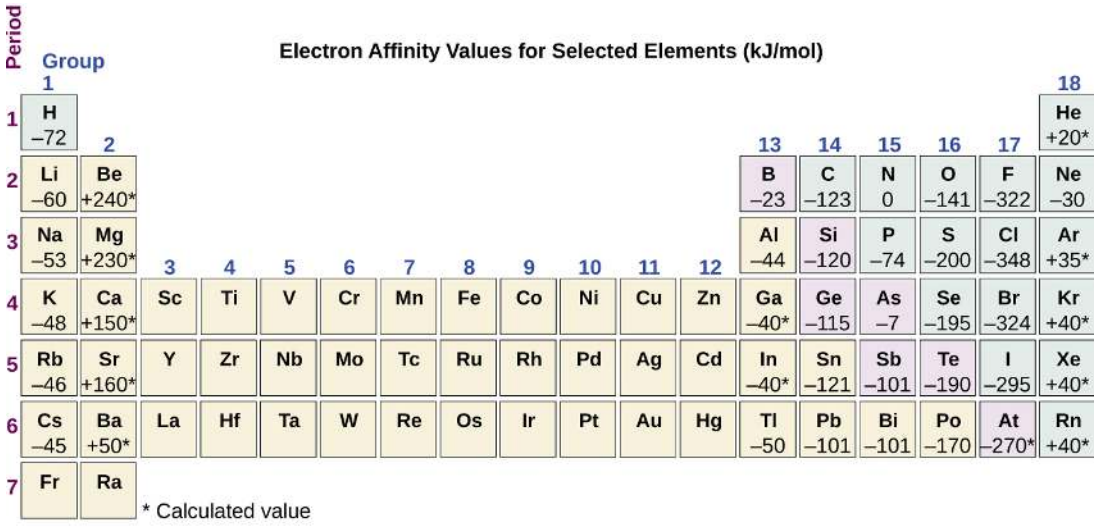


Figure 2.7.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

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

This page titled 2.7: Periodic Trends is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **6.5: Periodic Variations in Element Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.8: Electronegativity

Learning Objectives

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

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 2.8.1 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

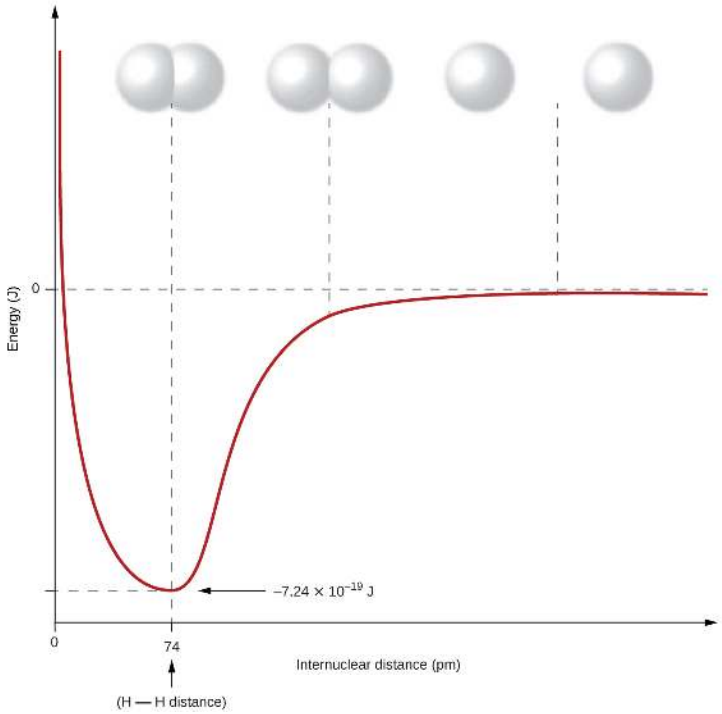


Figure 2.8.1: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)} \quad \Delta H = 436\,\mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$\mathrm{2\,H\,(g)} \longrightarrow \mathrm{H_2\,(g)} \quad \Delta H = -436\,\mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl + Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 2.8.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is

much larger than it is around H. Compare this to Figure 2.8.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 2.8.2.

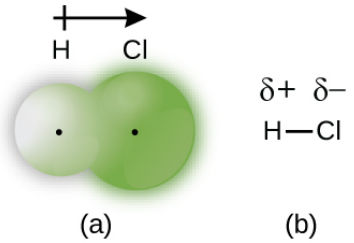


Figure 2.8.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 2.8.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 2.8.4). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

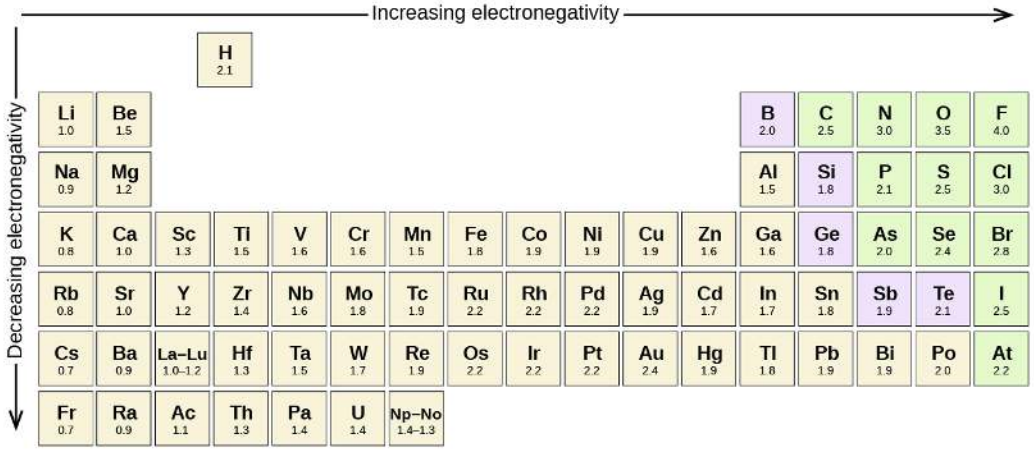


Figure 2.8.3: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless

quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure 2.8.4, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

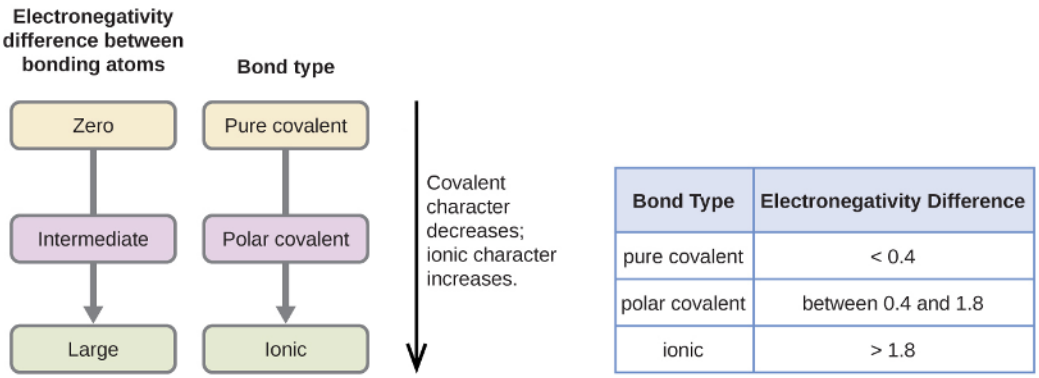


Figure 2.8.4: Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 2.8.5 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 2.8.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 2.8.5. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that

are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, and are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and as well as covalent between the nitrogen and oxygen atoms in

Example 2.8.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 2.8.3, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 2.8.1 shows these bonds in order of increasing polarity.

Table 2.8.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	
S–H	0.4	
C–N	0.5	
N–H	0.9	
C–O	1.0	
O–H	1.4	

Exercise 2.8.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 2.8.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	
Si–C	0.7	
Si–O	1.7	

This page titled 2.8: Electronegativity is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **7.2: Covalent Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.9: Electron-Dot Structures

Learning Objectives

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

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 2.9.1: shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na·
magnesium	$[Ne]3s^2$	·Mg·
aluminum	$[Ne]3s^23p^1$	·Al·
silicon	$[Ne]3s^23p^2$	·Si·
phosphorus	$[Ne]3s^23p^3$	·P·
sulfur	$[Ne]3s^23p^4$	:S·
chlorine	$[Ne]3s^23p^5$	:Cl·
argon	$[Ne]3s^23p^6$	:Ar:

Figure 2.9.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Figure 2.9.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

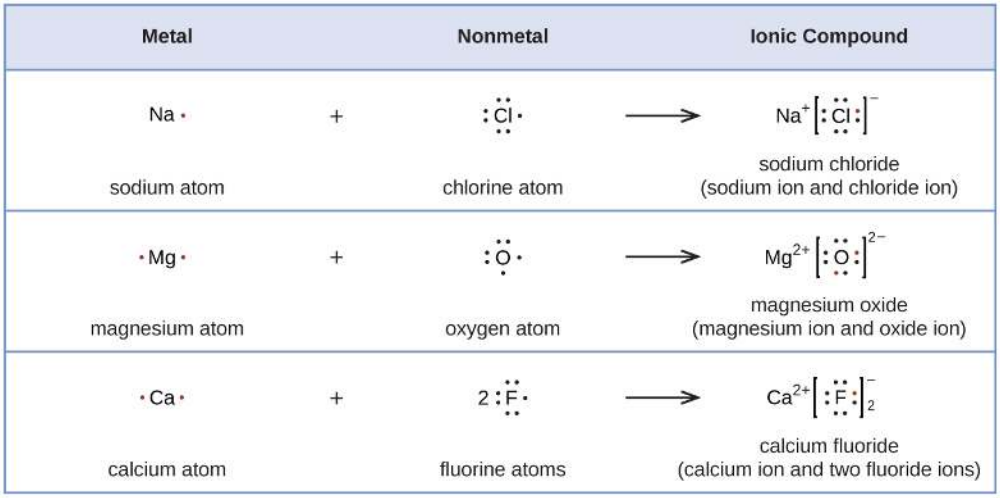
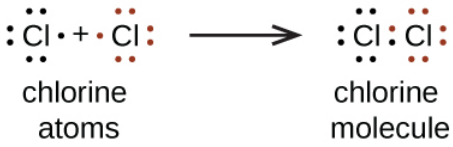


Figure 2.9.2: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

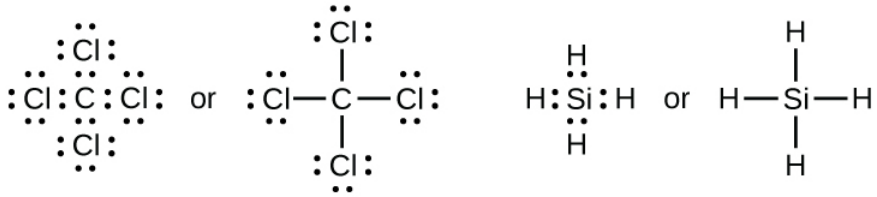


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

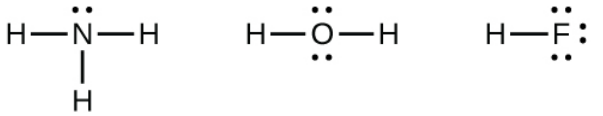
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



carbon tetrachloride silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

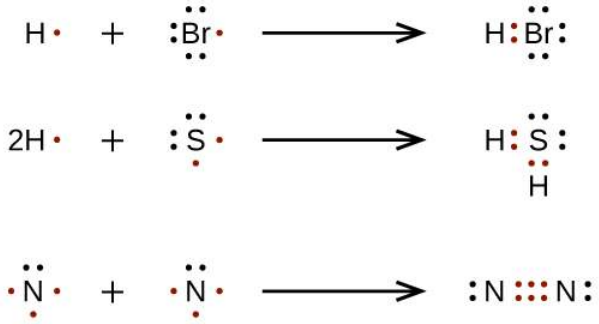
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here.

Writing Lewis Structures

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{array}{rr} & SiH_4 \\ \text{Si: 4 valence electrons/atom} \times & \text{1 atom} = 4 \\ + \quad \text{H : 1 valence electron/atom} \times & \text{4 atoms} = 4 \\ \hline & \text{total valence electrons} = 8 \end{array}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{array}{rr} & CHO_2^- \\ \text{C: 4 valence electrons/atom} \times & \text{1 atom} = 4 \\ \text{H: 1 valence electron/atom} \times & \text{1 atoms} = 1 \\ \text{O: 6 valence electron/atom} \times & \text{2 atoms} = 12 \\ + & \text{1 electron} = 1 \\ \hline & \text{total valence electrons} = 18 \end{array}$$

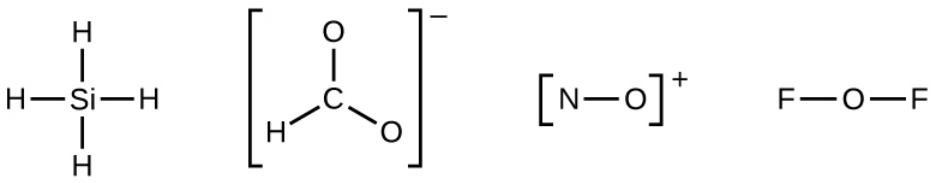
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{array}{r} \mathrm{NO^+} \\ \text{N: 5 valence electrons/atom} \times \text{ 1 atom } = 5 \\ \text{O: 6 valence electron/atom} \times \text{ 1 atoms} = 6 \\ + \quad \text{e: -1 electron (positive charge)} \times \text{ 1 electron} = -1 \\ \hline \text{total valence electrons} = 10 \end{array}$$

- Since $\mathrm{OF_2}$ is a neutral molecule, we simply add the number of valence electrons:

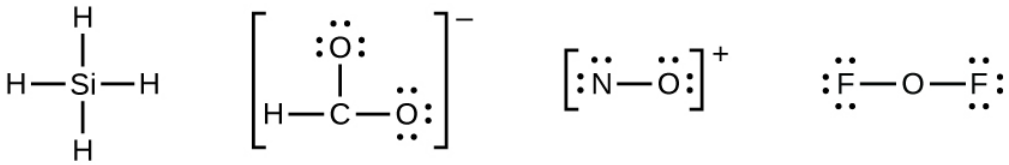
$$\begin{array}{r} \mathrm{OF_2} \\ \text{O: 6 valence electrons/atom} \times \text{ 1 atom } = 6 \\ + \quad \text{F: 7 valence electron/atom} \times \text{ 2 atoms} = 14 \\ \hline \text{total valence electrons} = 20 \end{array}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)

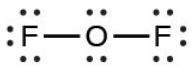


When several arrangements of atoms are possible, as for $\mathrm{CHO_2^-}$, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In $\mathrm{CHO_2^-}$, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $\mathrm{POCl_3}$, S in $\mathrm{SO_2}$, and Cl in $\mathrm{ClO_4^-}$. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

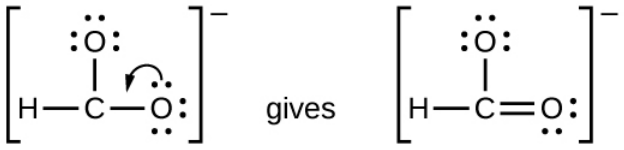
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on $\mathrm{SiH_4}$, so it is unchanged:



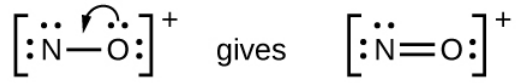
4. Place all remaining electrons on the central atom.
   - For $\mathrm{SiH_4}$, $\mathrm{CHO_2^-}$, and $\mathrm{NO^+}$, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For $\mathrm{OF_2}$, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



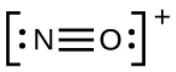
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - $\mathrm{SiH_4}$: Si already has an octet, so nothing needs to be done.
   - $\mathrm{CHO\ 2^-}$: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 2.9.1: Writing Lewis Structures

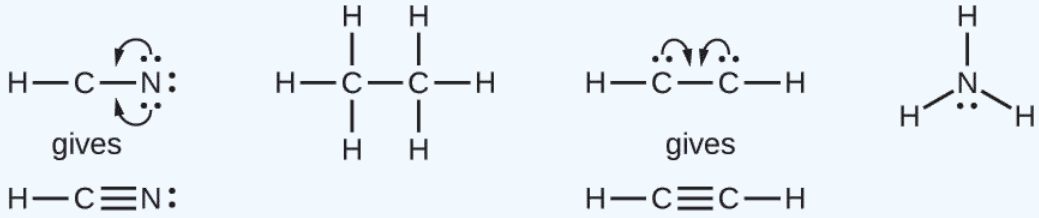
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

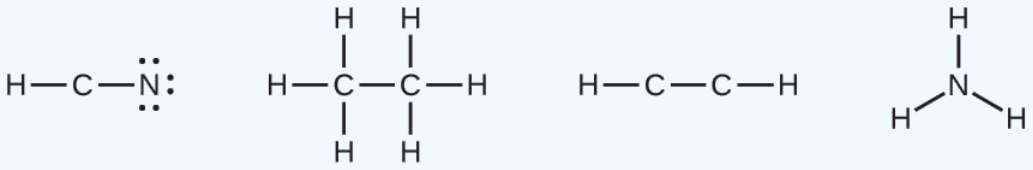
Step 1. *Calculate the number of valence electrons.*

HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
NH_3: (5 × 1) + (3 × 1) = 8

Step 2 *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom:

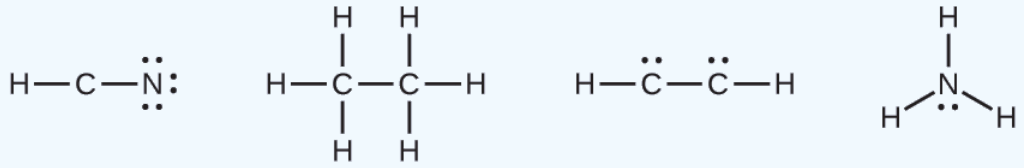


Step 3. *Where needed, distribute electrons to the terminal atoms:*



HCN: six electrons placed on N
H_3CCH_3: no electrons remain
HCCH: no terminal atoms capable of accepting electrons
NH_3: no terminal atoms capable of accepting electrons

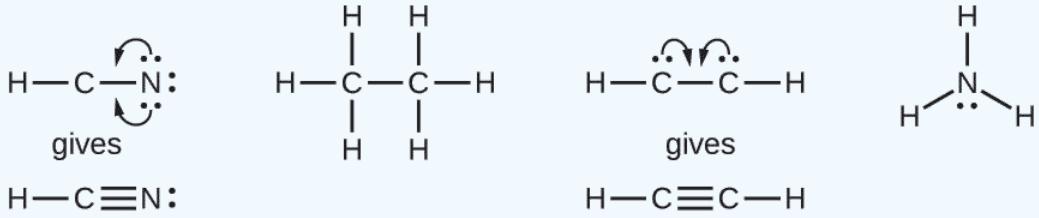
Step 4. *Where needed, place remaining electrons on the central atom:*



HCN: no electrons remain
H_3CCH_3: no electrons remain
HCCH: four electrons placed on carbon
NH_3: two electrons placed on nitrogen

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

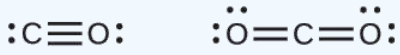
HCN: form two more C–N bonds
H_3CCH_3: all atoms have the correct number of electrons
HCCH: form a triple bond between the two carbon atoms
NH_3: all atoms have the correct number of electrons



? Exercise 2.9.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times, . Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steelmaking process, and diamonds have a unique place in both culture and industry. With all this usage came significant study, particularly with the emergence of organic chemistry. And even with all the known forms and functions of the element, scientists began to uncover the potential for even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu—they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 2.9.3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

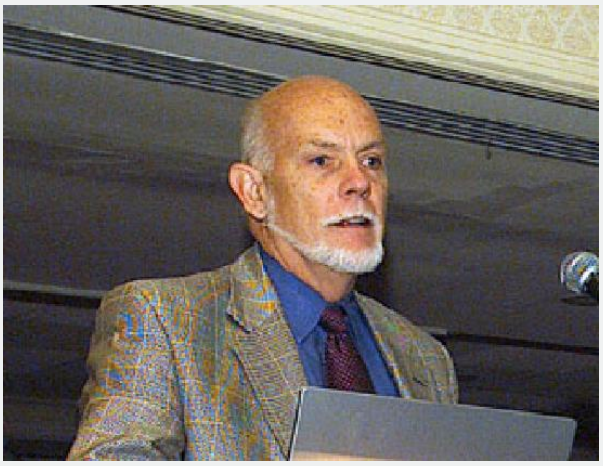


Figure 2.9.3: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

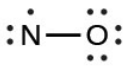
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

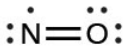
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

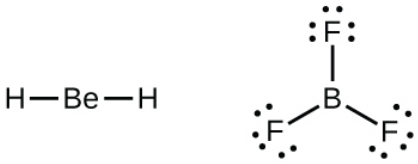


4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

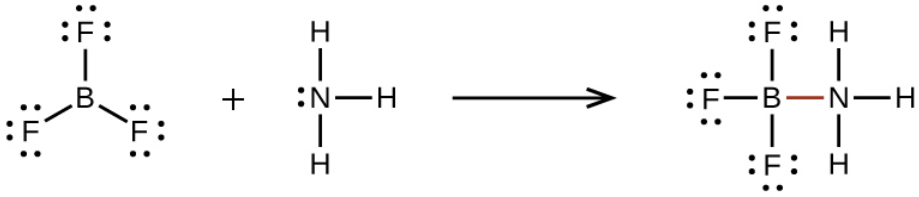


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure 2.9.4: shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

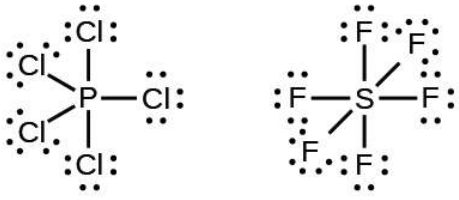
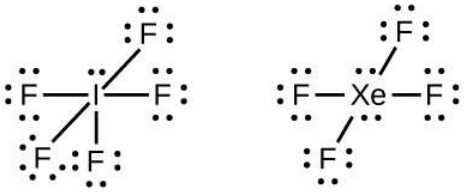


Figure 2.9.4: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 2.9.2: Writing Lewis Structures - Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

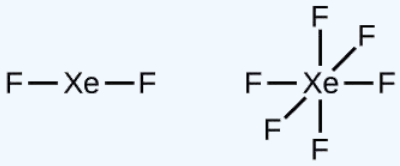
Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

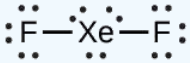
XeF_2: $8 + (2 \times 7) = 22$
XeF_6: $8 + (6 \times 7) = 50$

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

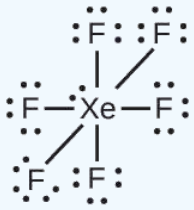


Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



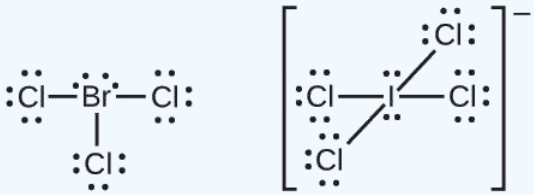
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 2.9.2: Interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer



This page titled 2.9: Electron-Dot Structures is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **7.3: Lewis Symbols and Structures** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.10: Formal Charges and Resonance

Learning Objectives

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

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

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

Thus, we calculate formal charge as follows:

$$\text{formal charge } = \#\text{ valence shell electrons (free atom) } - \#\text{ lone pair electrons } - \frac{1}{2}\#\text{ bonding electrons}$$

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

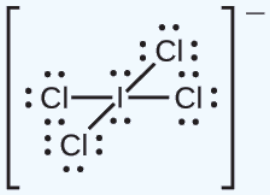
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 2.10.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion

Solution

Step 1. *We divide the bonding electron pairs equally for all I–Cl bonds:*



Step 2. *We assign lone pairs of electrons to their atoms*. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom:*

I: 7 – 8 = –1
Cl: 7 – 7 = 0

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

Exercise 2.10.1

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



Answer

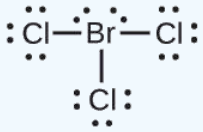
C −1, O +1

Example 2.10.2: Calculating Formal Charge from Lewis Structures

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

Solution

Step 1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



Step 2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge:

Br: 7 – 7 = 0
Cl: 7 – 7 = 0

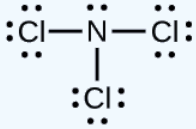
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 2.10.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0

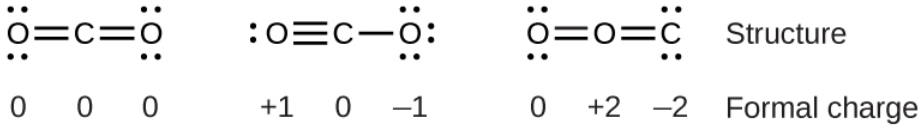


Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

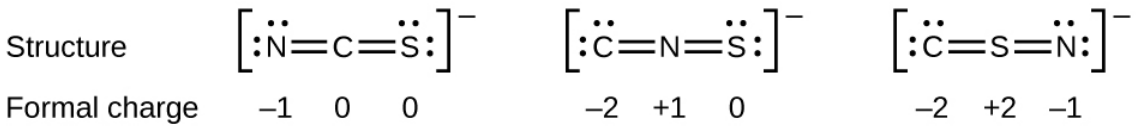
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

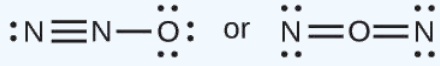
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: NCS^-, CNS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

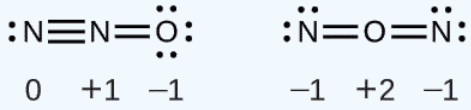
Example 2.10.3: Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the more likely structure for nitrous oxide?

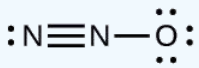


Solution

Determining formal charge yields the following:



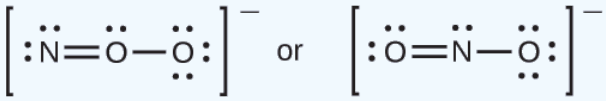
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), there is no formal charge with a magnitude greater than one (Guideline 2), the negative formal charge is on the more electronegative element (Guideline 4), and the less electronegative atom is in the center position.

Exercise 2.10.3

Which is the most likely molecular structure for the nitrite ion?



Answer

ONO^-

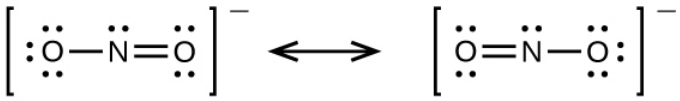
Resonance

Notice that the more likely structure for the nitrite anion in Example 2.10.3 may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:



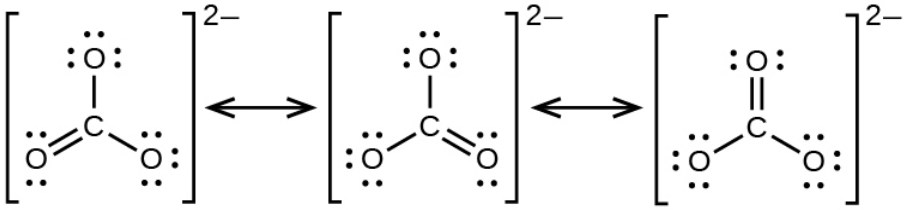
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Link to Learning

Use this online quiz to practice your skills in drawing resonance structures and estimating formal charges.

This page titled 2.10: Formal Charges and Resonance is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

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

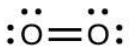
2.11: Molecular Orbitals

Learning Objectives

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

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

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



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

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 2.11.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

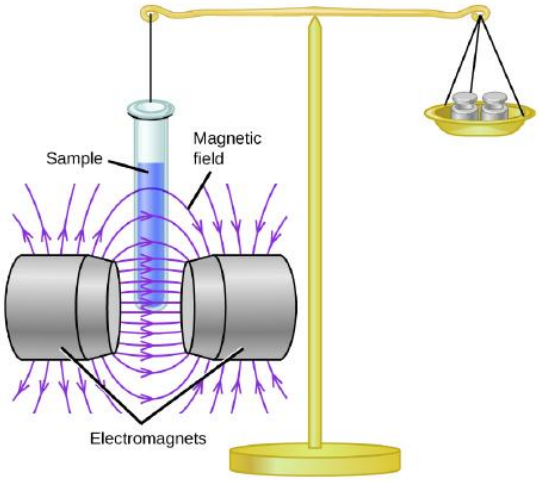


Figure 2.11.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

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

Link to Learning

Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more.

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 2.11.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table 2.11.1: Comparison of Bonding Theories

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

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

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

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals** (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure 2.11.2). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

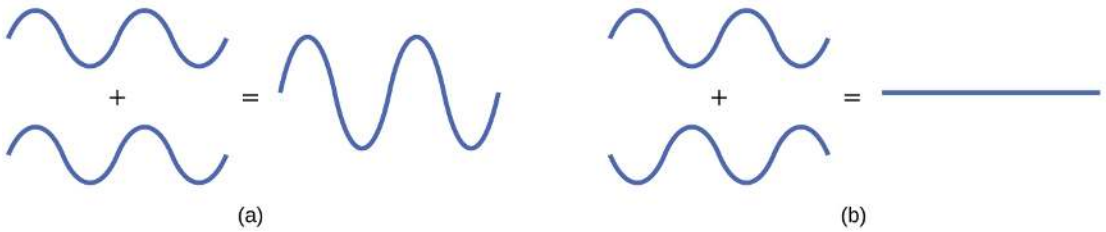


Figure 2.11.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure 2.11.3. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

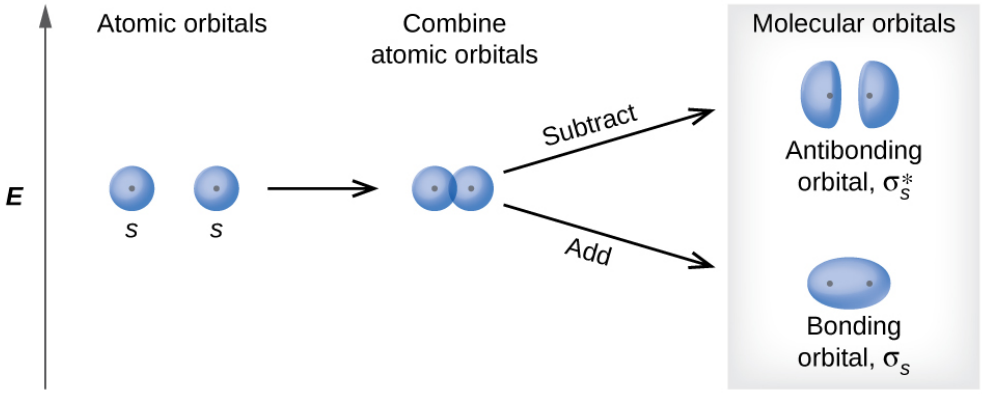


Figure 2.11.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two *s* atomic orbitals. The dots (·) indicate the locations of nuclei.

Link to Learning

You can watch animations visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 2.11.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

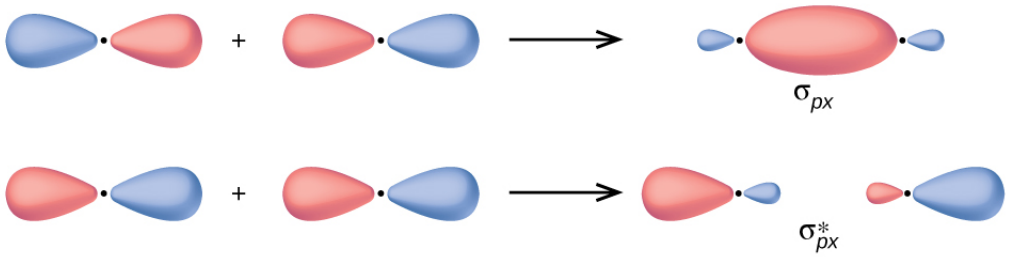


Figure 2.11.4: Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^*.

The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular orbital**, as shown in Figure 2.11.5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

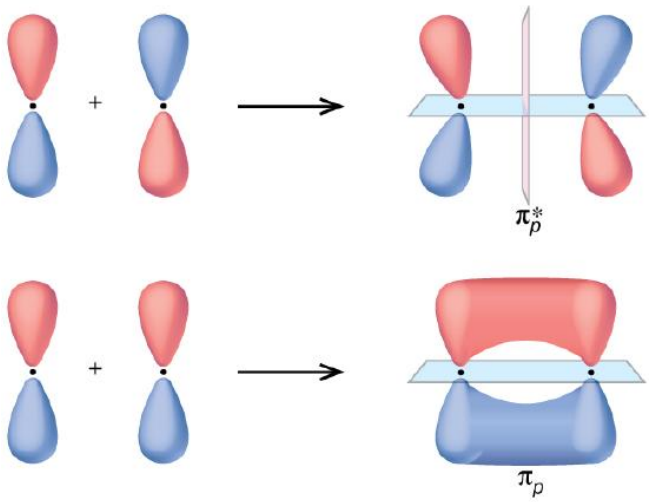
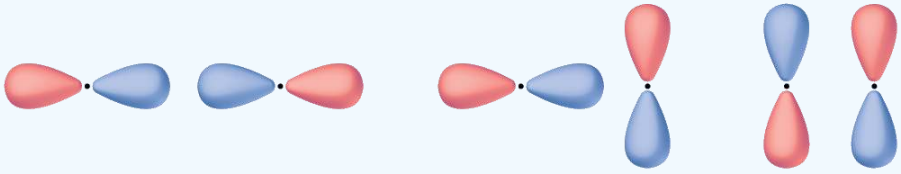


Figure 2.11.5: Side-by-side overlap of each two *p* orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

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

Example 2.11.1: Molecular Orbitals

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



$3p_x$ and $3p_x$ (a) $3p_x$ and $3p_y$ (b) $3p_y$ and $3p_y$ (c)

Solution

a. is an in-phase combination, resulting in a π_{3p} orbital

b. will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.

c. is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Exercise 2.11.1

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



Answer

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



Portrait of a Chemist: Walter Kohn: Nobel Laureate

Walter Kohn (Figure 2.11.6) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the physics of semiconductors.

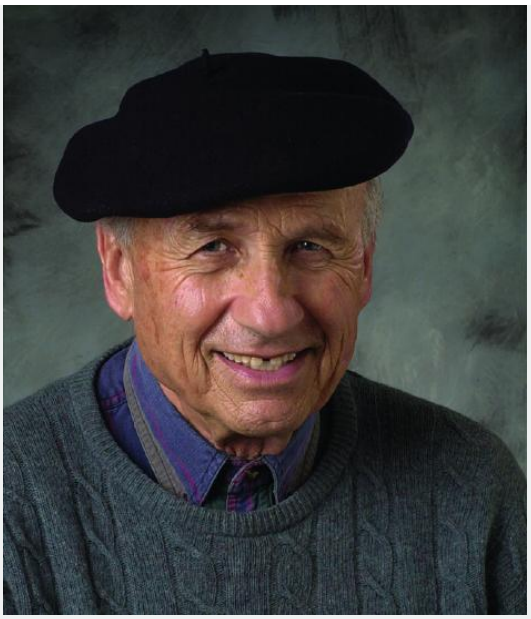


Figure 2.11.6: Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II he was part of the Kindertransport program that rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Dr. Kohn passed away in 2016 at the age of 93.

How Sciences Interconnect: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (see Figure 2.11.7). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

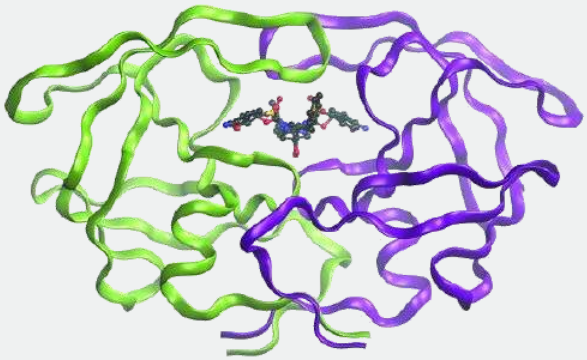


Figure 2.11.7: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 2.11.8). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 2.11.8). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

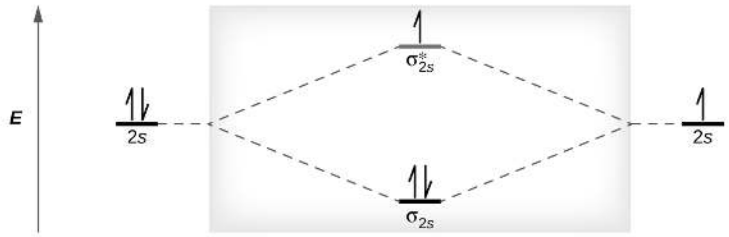


Figure 2.11.8: This is the molecular orbital diagram for the homonuclear diatomic showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

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

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

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

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

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases (Table 8.1). If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

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

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ1s bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 2.11.9) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

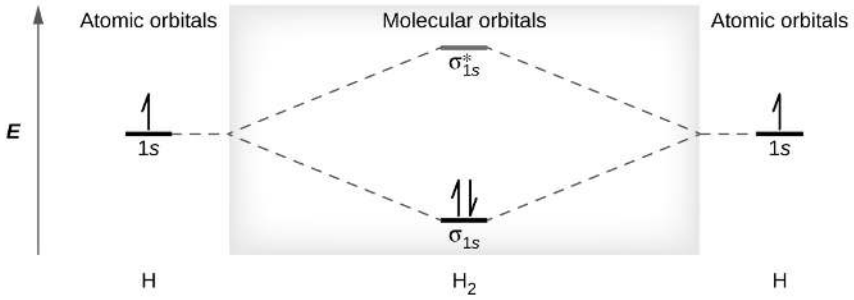


Figure 2.11.9: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

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

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

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

A helium atom has two electrons, both of which are in its 1*s* orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as

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

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

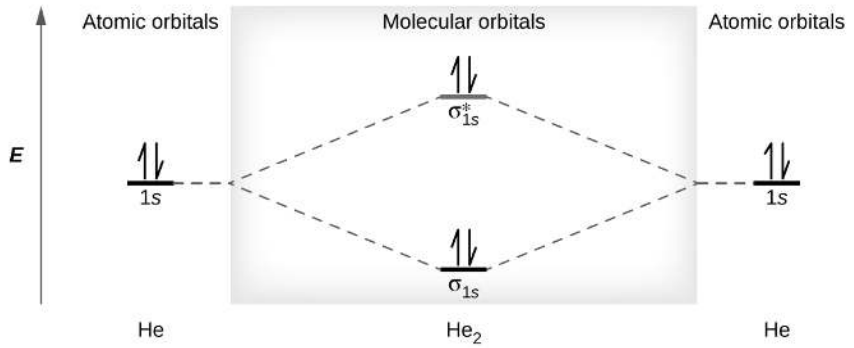


Figure 2.11.10: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 2.11.2).

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

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 2.11.11. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

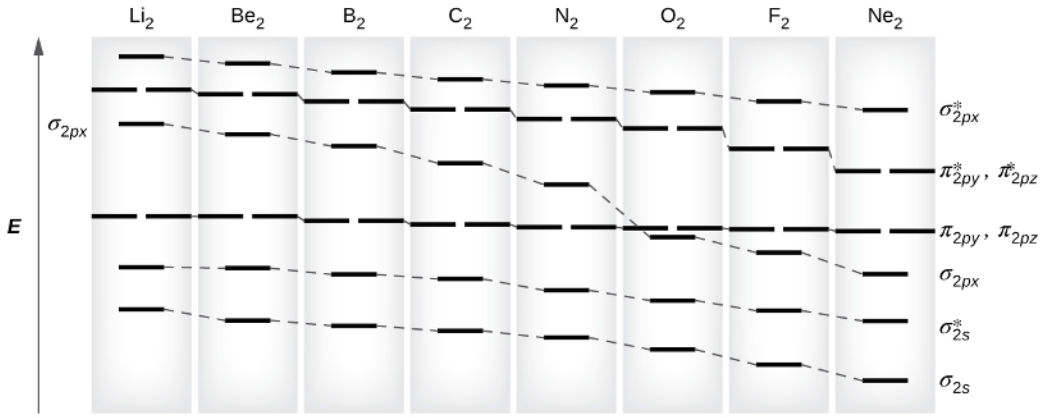


Figure 2.11.11: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 2.11.12). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

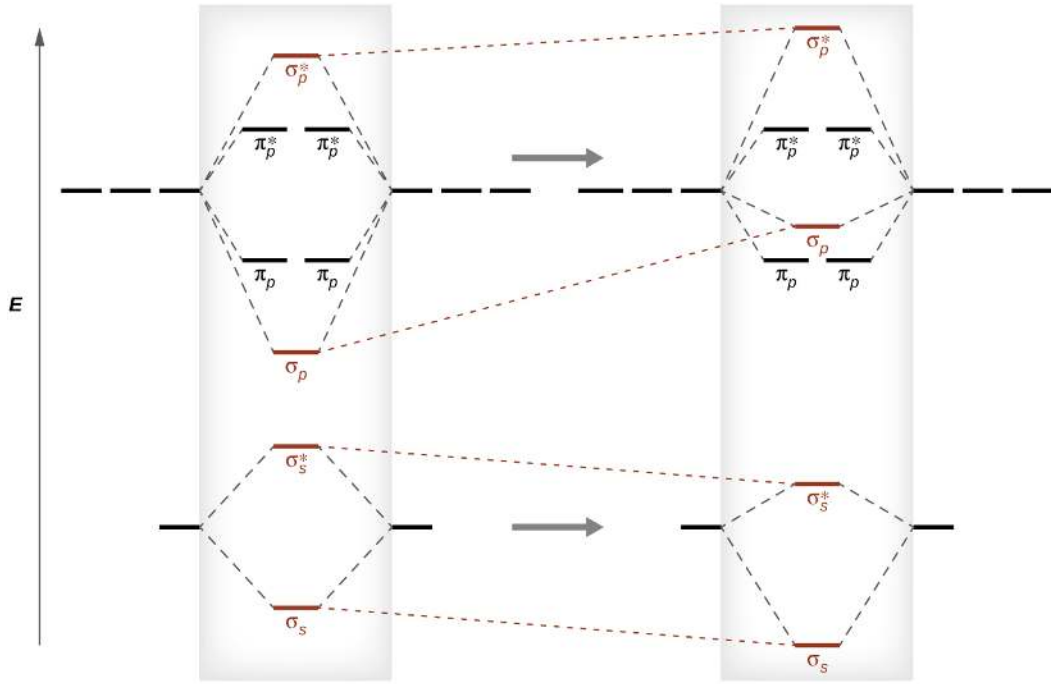


Figure 2.11.12: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the π_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

s-p mixing occurs when the *s* and *p* orbitals have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne_2 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 2.11.11. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure 2.11.11: , we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table 2.11.2, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

Table 2.11.2: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

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

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 2.11.2 with a bond order greater than zero are also known.

The O2 molecule has enough electrons to half fill the $\left(\pi^*_{2py}, \pi^*_{2pz}\right)$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 8.40). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

How Sciences Interconnect: Band Theory

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (see Figure 2.11.3). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When *N* valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, *N*/2 (filled) bonding orbitals and *N*/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure 2.11.13 shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

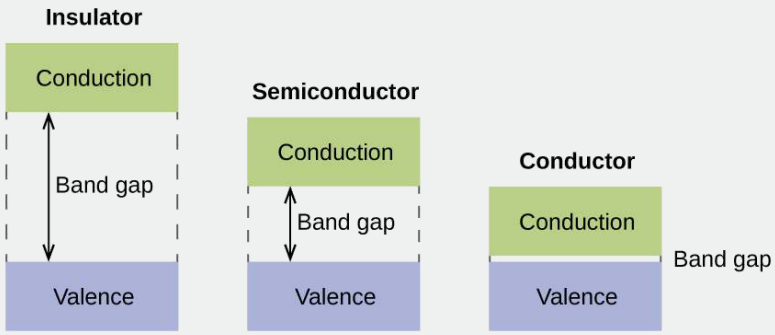


Figure 2.11.13: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

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

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

Example 2.11.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

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

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 2.11.11. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 2.11.14.

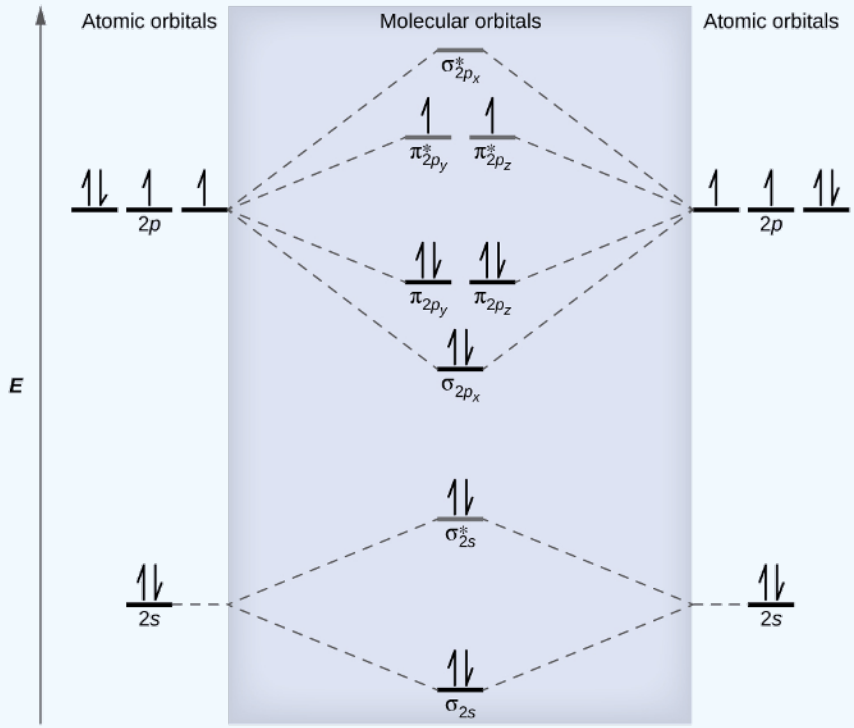


Figure 2.11.14: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

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

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

Exercise 2.11.2

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

Answer

N_2 has a bond order of 3 and is diamagnetic.

Example 2.11.3: Ion Predictions with MO Diagrams

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

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is $(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2py}, \pi_{2pz})^4$. Adding two more electrons to generate the C_2^{2-} anion will give a valence

electron configuration of $(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2py}, \pi_{2pz})^4 (\sigma_{2px})^2$. Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

? Exercise 2.11.3

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

Answer

two, paramagnetic

Link to Learning

Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine. See three-dimensional drawings of the molecular orbitals for C_6H_6.

This page titled 2.11: Molecular Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **8.4: Molecular Orbital Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

CHAPTER OVERVIEW

3: Acid-Base Chemistry

3.1: Acid-Base Theories

3.2: Brønsted-Lowry Model

3.3: Acidity of Binary Hydrides

3.4: Acidity of Oxoacids

3.5: Acidity of Metal Cations

This page titled 3: Acid-Base Chemistry is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

3.1: Acid-Base Theories

There are three primary theories of acid-base chemistry that are often taught together: Arrhenius theory, Brønsted-Lowry theory, and Lewis acid-base theory. Each theory is introduced below.

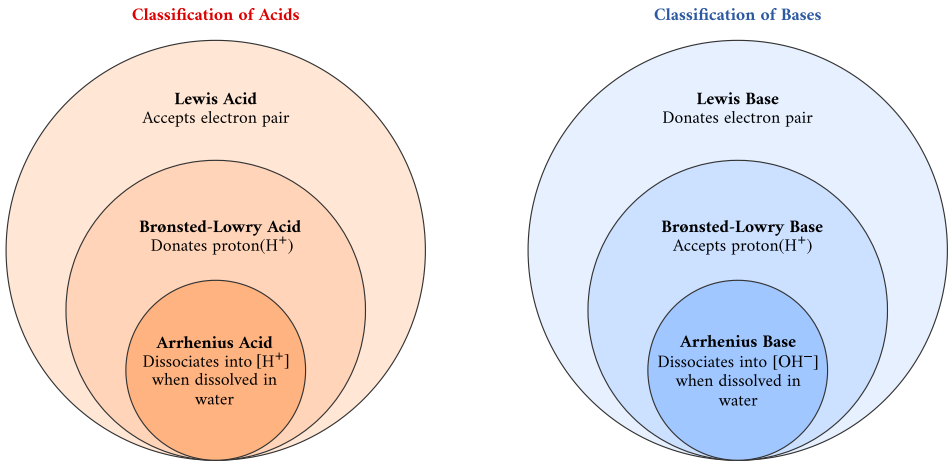


Figure 3.1.1: Hierarchal definitions of acids and bases via the three primary theories. These theories are designed to be "superset" of the previous classification. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Arrhenius Definition of Acids and Bases

The Swedish chemist Svante Arrhenius attributed the properties of acidity to hydrogen ions (H^+) in 1884. An Arrhenius acid is a substance that, when added to water, increases the concentration of H^+ ions in the water. Note that chemists often write $H^+(aq)$ and refer to the hydrogen ion when describing acid-base reactions, but the free hydrogen nucleus does not exist alone in water. It exists in a hydrated form which for simplicity is often written as the hydronium (hydroxonium) ion, H_3O^+. Thus, an Arrhenius acid can also be described as a substance that increases the concentration of hydronium ions when added to water. This definition stems from the equilibrium dissociation (self-ionization) of water into hydronium and hydroxide (OH^-) ions:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

with K_w defined as $[H^+][OH^-]$.

The value of K_w varies with temperature, as shown in the table below where at 25 °C K_w is approximately 1.0×10^{-14}, i.e. $pK_w = 14$.

Water temperature	K_w / 10^{-14}	pK_w
0 °C	0.112	14.95
25 °C	1.023	13.99
50 °C	5.495	13.26
75 °C	19.95	12.70
100 °C	56.23	12.25

In pure water the majority of molecules are H_2O, but the molecules are constantly dissociating and re-associating, and at any time a small number of the molecules (about 1 in 10^7) are hydronium and an equal number are hydroxide. Because the numbers are equal, pure water is neutral (not acidic or basic) and has an electrical conductivity of 5.5 microSiemen, µS/m. For comparison, sea water's conductivity is about one million times higher, 5 S/m (due to the dissolved salt).

Proton vs. Hydron

Although the term proton is often used for H^+, this should really be reserved for H (protium) not D (deuterium) or T (tritium). The more general term, hydron covers all isotopes of hydrogen.

An Arrhenius base, on the other hand, is a substance which increases the concentration of hydroxide ions when dissolved in water, hence decreasing the concentration of hydronium ions.

Upshot

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

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

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

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

The definition is expressed in terms of an equilibrium expression:

$$\text{acid} + \text{base} \rightleftharpoons \text{conjugate base} + \text{conjugate acid}.$$

With an acid, HA, the equation can be written symbolically as:

$$HA + B \rightleftharpoons A^- + HB^+$$

The double harpoons sign, $\rightleftharpoons$, is used because the reaction can occur in both forward and backward directions. The acid, HA, can lose a hydron to become its conjugate base, A^-. The base, B, can accept a hydron to become its conjugate acid, HB^+. Most acid-base reactions are fast so that the components of the reaction are usually in dynamic equilibrium with each other.

Brønsted-Lowry Definition of Acids and Bases

While the Arrhenius concept is useful for describing many reactions, it has limitations. In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently recognized that acid-base reactions involve the transfer of a hydron. A Brønsted-Lowry acid (or simply Brønsted acid) is a species that donates a hydron to a Brønsted-Lowry base. The Brønsted-Lowry acid-base theory has several advantages over the Arrhenius theory. Consider the following reactions of acetic acid (CH_3COOH):

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4{}^+$$

Both theories easily describe the first reaction: CH_3COOH acts as an Arrhenius acid because it acts as a source of H_3O^+ when dissolved in water, and it acts as a Brønsted acid by donating a hydron to water. In the second example CH_3COOH undergoes the same transformation, in this case donating a hydron to ammonia (NH_3), but it cannot be described using the Arrhenius definition of an acid because the reaction does not produce hydronium ions.

Upshot

To qualify as an Brønsted-Lowry acid, the chemical must either cause, directly or otherwise:

- donate a proton.

Conversely, to qualify as an Brønsted-Lowry base, the chemical must either cause, directly or otherwise:

- accept a proton.

Lewis Definition of Acids and Bases

A third concept was proposed in 1923 by Gilbert N. Lewis which includes reactions with acid-base characteristics that do not involve a hydron transfer. A Lewis acid is a species that reacts with a Lewis base to form a Lewis adduct. The Lewis acid accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Brønsted acid-base reactions involve hydron

transfer reactions while Lewis acid-base reactions involve electron pair transfers. All Brønsted acids are Lewis acids, but not all Lewis acids are Brønsted acids.

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

In the first example BF_3 is a Lewis acid since it accepts an electron pair from the fluoride ion. This reaction cannot be described in terms of the Brønsted theory because there is no hydron transfer. The second reaction can be described using either theory. A hydron is transferred from an unspecified Brønsted acid to ammonia, a Brønsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion.

Upshot

To qualify as an Lewis acid, the chemical must

- accept an electron pair

Conversely, to qualify as an Lewis base, the chemical must:

- donate an electron pair

Other Acid-Base Definitions

Lux-Flood acid-base definition

This acid-base theory was a revival of the oxygen theory of acids and bases, proposed by German chemist Hermann Lux in 1939 and further improved by Håkon Flood circa 1947. It is still used in modern geochemistry and for the electrochemistry of molten salts. This definition describes an acid as an oxide ion (O^{2-}) acceptor and a base as an oxide ion donor. For example:

$$MgO\ (\text{base}) + CO_2\ (\text{acid}) \rightleftharpoons MgCO_3$$

$$CaO\ (\text{base}) + SiO_2\ (\text{acid}) \rightleftharpoons CaSiO_3$$

$$NO_3^-\ (\text{base}) + S_2O_7^{2-}\ (\text{acid}) \rightleftharpoons NO_2^+ + 2\,SO_4^{2-}$$

Usanovich acid-base definition

Mikhail Usanovich developed a general theory that does not restrict acidity to hydrogen-containing compounds, and his approach, published in 1938, was even more general than the Lewis theory. Usanovich's theory can be summarized as defining an acid as anything that *accepts negative species, anions or electrons* or *donates positive ones, cations*, and a base as the reverse. This definition could even be applied to the concept of redox reactions (oxidation-reduction) as a special case of acid-base reactions. Some examples of Usanovich acid-base reactions include:

- species exchanged: anion O^{2-}

$$Na_2O\ (\text{base}) + SO_3\ (\text{acid}) \longrightarrow 2\,Na^+ + SO_4^{2-}$$

- species exchanged: anion S^{2-}

$$3\,(NH_4)_2S\ (\text{base}) + Sb_2S_5\ (\text{acid}) \longrightarrow 6\,NH_4^+ + 2\,SbS_4^{3-}$$

- species exchanged: electron

$$2\,Na\ (\text{base}) + Cl_2\ (\text{acid}) \longrightarrow 2\,Na^+ + 2\,Cl^-$$

A comparison of the above definitions of Acids and Bases shows that the Usanovich concept encompasses all of the others but some feel that because of this it is too general to be useful.

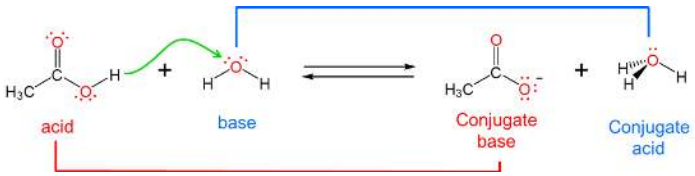
This page titled 3.1: Acid-Base Theories is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **7.1A: Acid-Base Theories and Concepts** by Stephen M. Contakes is licensed CC BY-NC 4.0.

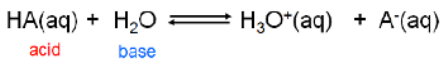
3.2: Brønsted-Lowry Model

The Brønsted-Lowry acid-base concept

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

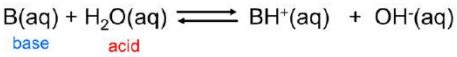


Because the Brønsted-Lowry concept is concerned with H^+ ion transfer rather than the creation of a particular chemical species, it is able to handle a diverse array of acid-base concepts. In fact, from the viewpoint of the Brønsted-Lowry concept, Arrhenius acids and bases are just a special case involving 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^+:



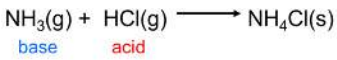
(3.2.1)

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.

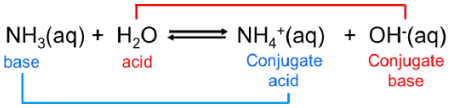
Becasue the Brønsted-Lowry concept can handle any sort of hydrogen ion transfer it readily accommodates many reactions that Arrhenius theory cannot, including those that take place outside of water, such as the reaction between gaseous hydrochloric acid and ammonia:



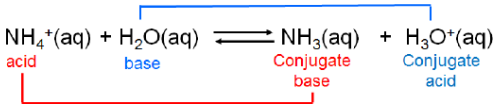
The classification of acids as strong or weak usually refers to their ability to donate or abstract hydrogen ions to or from water to give H_3O^+ and OH^-, respectively, *i.e.*, their Arrhenius acidity and basicity. However, acids and bases may be classified as strong and weak under the Brønsted-Lowry 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:

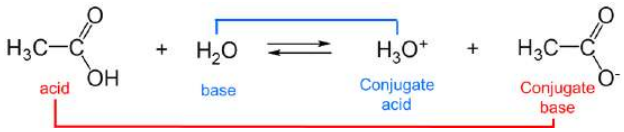


The ammonium ion is itself a weak acid that can undergo dissociation:

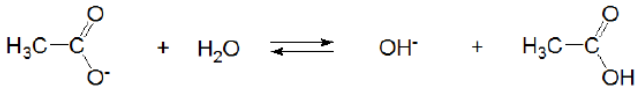


In this case ammonia and ammonium ion are acid-base conjugates. In general acids and bases that differ by a *single ionizable hydrogen ion* are said to be conjugates of one another.

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:



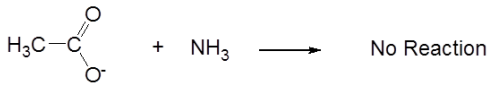
and acetic acid's conjugate base, acetate, acts as a weak Brønsted base.



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



while its conjugate base, acetate, is neutral.



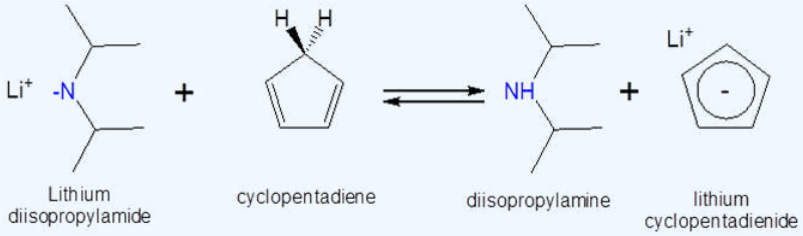
The reciprocal relationship between the strengths of acids and their conjugate bases has several consequences:

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 3.2.1

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



Solution:

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

This page titled 3.2: Brønsted-Lowry Model is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **6.3.1: Brønsted-Lowry Concept** by Stephen M. Contakes is licensed CC BY 4.0.

3.3: Acidity of Binary Hydrides

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

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

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

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

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

For this reason the binary nonmetal hydrides are termed acidic hydrides. Nevertheless not all are equally acidic. The dilute aqueous acid ionization constants for these hydrides are given in Figure 3.3.1. As can be seen from the constants in Figure 3.3.2, the ability of the hydrides to transfer a hydrogen to water increases across a period and down a group.

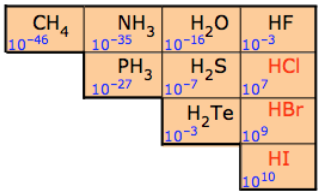


Figure 3.3.1: The acid ionization constants of nonmetal hydrides increase across a period and down a group. (CC BY-NC 3.0; Stephen Lower via Chem1)

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

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

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

2. Going down a group, the acid strength increases because the bond strength decreases as a function of increasing size of the nonmetal, and this has a larger effect than the electronegativity. In fact HF is a weak acid because it is so small that the hydrogen-fluorine bond is so strong that it is difficult to break. Remember, the weaker the bond, the stronger the acid strength. This is further illustrated in Table 3.3.1, where the weakest bond has produced the strongest acid.

Table 3.3.1 Acid strength as function of bond energy

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

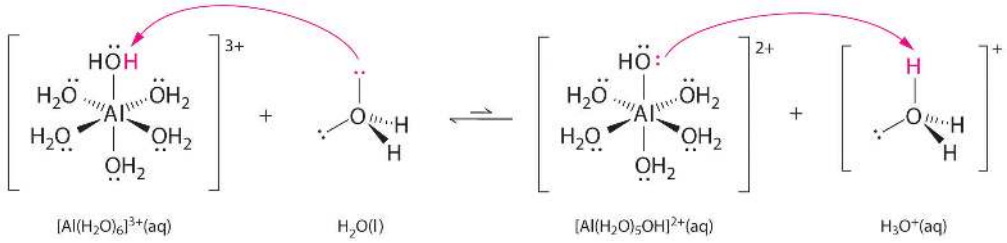
This page titled 3.3: Acidity of Binary Hydrides is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **6.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength** by Stephen M. Contakes is licensed CC BY 4.0.

3.5: Acidity of Metal Cations

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

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



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

Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the O–H bonds, as shown in Figure 3.5.5*b*. With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose an H^+ ion. This is shown schematically in Figure 3.5.1.

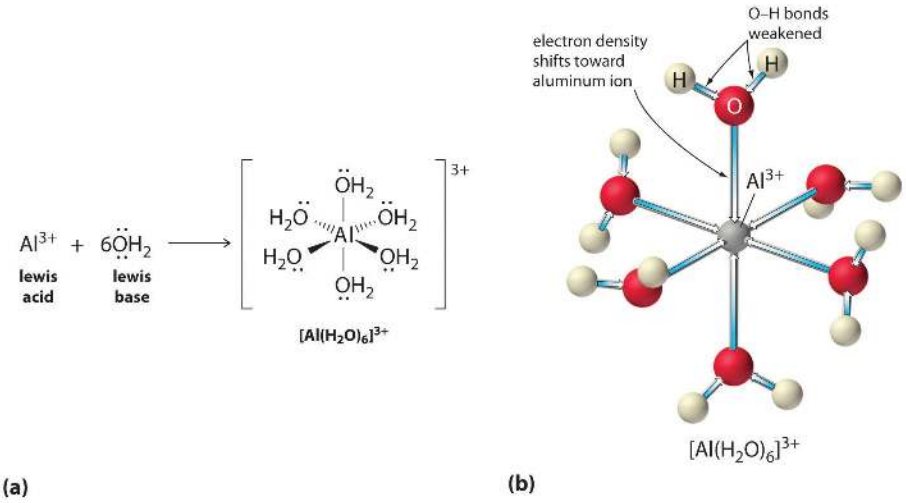


Figure 3.5.1: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton. (CC BY-NC-SA 3.0; anonymous)

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

The magnitude of this effect depends on the following factors, of which the first two are generally considered the most important (Figure 3.5.2):

The charge on the metal ion

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

The radius of the metal ion

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

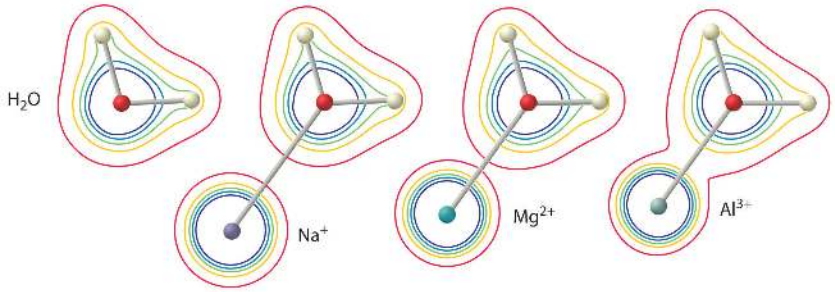


Figure 3.5.2: The effect of the charge and radius of a metal ion on the acidity of a coordinated water molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^{+}, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases. (CC BY-NC-SA 3.0; anonymous)

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

$$[\mathrm{Al(H_2O)_6}]^{3+}(\mathrm{aq}) \rightleftharpoons [\mathrm{Al(H_2O)_5(OH)}]^{2+}(\mathrm{aq}) + \mathrm{H^+}(\mathrm{aq}) \tag{3.5.1}$$

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

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

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

where Z is the charge on the metal ion and r its radius. As can be seen from figure 3.5.3, in general the acidity of metal ions increases with $\frac{Z^2}{r}$). Nevertheless a number of ions have considerably lower pK_a values than predicted from this correlation, suggesting that the acidity of metal cations cannot be predicted using a simple electrostatic model alone.

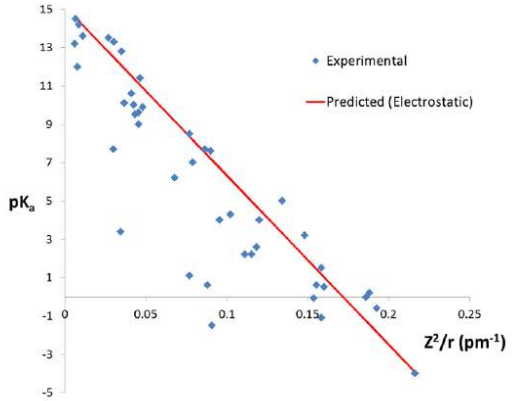


Figure 3.5.3: The pK_a of metal ions (♦) as a function of $\frac{Z^2}{r}$ for 43 metal ions. Drawn using radii listed in reference 1.

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

Electronegativity

All other things being equal, more electronegative elements are better able to withdraw electron density from a bound water ligand and consequently better at enhancing the ability of that water molecule to lose a hydrogen ion. The electrostatic model of ion

acidity can be extended to account for electronegativity effects but only needs to be done so for metals with Pauling electronegativities greater than 1.5. The empirical relationship that has been proposed to account for the effect of electronegativity is:

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

where r is the ion radius in pm and χ is its Pauling electronegativity. As can be seen from figure 3.5.4, the electronegativity term accounts for some of the deviations in metal ion acidity predicted from charge and size effects alone.

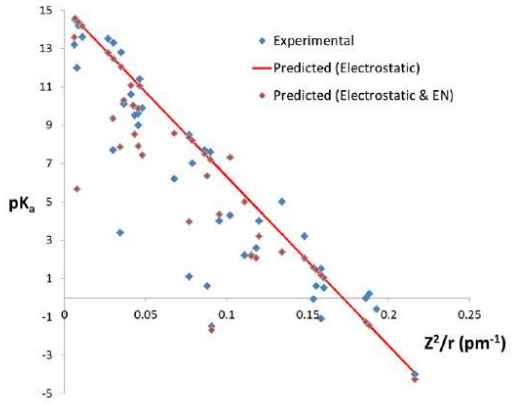


Figure 3.5.4: Comparison between the experimental pK_a values (♦) for 43 metal ions and those predicted empirically accounting for size and charge effects (-) and accounting for size, charge, and electronegativity effects (♦). Drawn using radii listed in reference 1.

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

Hardness and Softness

Cation hardness or softness is assessed according to Pearson's Hard-Soft Acid Base Principle (HSABP). In general, soft cations are more acidic than hard cations of the same charge and radius, as may be seen from the examples in Table 3.5.1. The greater than expected acidity of softer cations is thought to reflect the importance of covalent contributions to the metal-water bond.

Table 3.5.1: Comparison of the pK_a values at 25°C of hard and soft cations with approximately the same radius and charge. Based on Gutmann[2] as reported by Burgess.[3]

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

Ligand field effects

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

References

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

This page titled 3.5: Acidity of Metal Cations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **6.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water** by Stephen M. Contakes is licensed CC BY 4.0.

CHAPTER OVERVIEW

4: Redox Reactivity

4.1: Redox Reactions
4.2: Balancing Redox Reactions
4.3: Electrochemical Potentials
4.4: Pourbaix Diagrams
4.5: Electrochemical Corrosion

This page titled 4: Redox Reactivity is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

4.1: Redox Reactions

Skills to Develop

- To identify a chemical reaction as an oxidation-reduction reaction.

When zinc metal is submerged into a quantity of aqueous HCl, the following reaction occurs (Figure 4.1.1):

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl\ 2\,(aq)} \tag{4.1.1}$$

This is one example of what is sometimes called a *single replacement reaction* because Zn replaces H in combination with Cl.



***Figure** 4.1.1**:** Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas.*

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \longrightarrow H_2\,(g) + Zn^{2+}\,(aq) + 2\,Cl^-\,(aq)} \tag{4.1.2}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the reducing agent, and the species being reduced is called the oxidizing agent.

> *Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.*

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)} \tag{4.1.3}$$

zinc atoms are oxidized to Zn^{2+}. The half reaction for the oxidation reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-} \tag{4.1.4}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance:

the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced reduction half reaction is as follows:

$$2\,H^+ + 2\,e^- \longrightarrow H_2 \tag{4.1.5}$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$\begin{aligned} &Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ &\cancel{2H^+ + 2e^-} \rightarrow H_2 \\ \hline &Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{aligned}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel. The following example demonstrates this process.

Example 4.1.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products.

SOLUTION

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^+ + Al \longrightarrow Ag + Al^{3+} \tag{4.1.6}$$

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

$$Ag^+ + e^- \longrightarrow Ag \tag{4.1.7}$$

Aluminum is oxidized, losing three electrons to change from Al to Al^{3+}:

$$Al \longrightarrow Al^{3+} + 3\,e^- \tag{4.1.8}$$

To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:

$$\begin{aligned} &3\left(Ag^+ + e^- \rightarrow Ag\right) \\ &Al \rightarrow Al^{3+} + 3e^- \\ \hline &3Ag^+ + Al \rightarrow 3Ag + Al^{3+} \end{aligned}$$

Now the equation is balanced, not only in terms of elements but also in terms of charge.

Exercise 4.1.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products.

> *Potassium has been used as a reducing agent to obtain various metals in their elemental form.*

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathrm{Cd\,(s) + 2\,NiOOH\,(s) + 2\,H_2O(\ell) \longrightarrow Cd(OH)_2\,(s) + 2\,Ni(OH)\ 2\,(s)} \tag{4.1.9}$$

The cadmium is oxidized, while the nickel atoms in NiOOH are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathrm{2\,Li\,(s) + I_2\,(s) \longrightarrow 2\,LiI\,(s)} \tag{4.1.10}$$

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.



Figure 4.1.1: *A small button battery like this is used to power a watch, pacemaker, or calculator. Image used with permission from Gerhard H Wrodnigg (via Wikipedia)*

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of oxidation was "adding oxygen," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for reduction: if a molecule loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde ($CH3CHO$) molecule takes on an oxygen atom to become acetic acid ($\mathrm{CH_3COOH}$).

$$\mathrm{2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH} \tag{4.1.11}$$

Thus, acetaldehyde is being oxidized.

Similarly, oxidation and reduction can be defined in terms of the gain or loss of hydrogen atoms. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH \tag{4.1.12}$$

Example 4.1.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \rightarrow NH_3$
b. $CH_3CH_2OHCH_3 \rightarrow CH_3COCH_3$
c. $HCHO \rightarrow HCOOH$

SOLUTION

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Exercise 4.1.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \rightarrow CO_2 + H_2O$
b. $NO_2 \rightarrow N_2$
c. $CH_2{=}CH_2 \rightarrow CH_3CH_3$

Summary

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

Concept Review Exercises

1. Give two different definitions for oxidation and reduction.
2. Give an example of each definition of oxidation and reduction.

Answers

1. Oxidation is the loss of electrons or the addition of oxygen; reduction is the gain of electrons or the addition of hydrogen.
2. $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation); $C_2H_4 + H_2 \rightarrow C_2H_6$ (reduction) (answers will vary)

Exercises

1. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.
   a. $NaOH + HCl \rightarrow H_2O + NaCl$
   b. $3Mg + 2AlCl_3 \rightarrow 2Al + 3MgCl_2$
   c. $H_2O_2 + H_2 \rightarrow 2H_2O$
   d. $KCl + AgNO_3 \rightarrow AgCl + KNO_3$
2. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.
   a. $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
   b. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
   c. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
   d. $2K + 2H_2O \rightarrow 2KOH + H_2$

3. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.

   a. $Ca(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
   b. $I^-(aq) + Br_2(\ell) \rightarrow Br^-(aq) + I_2(s)$

4. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.

   a. $Fe(s) + Sn^{4+}(aq) \rightarrow Fe^{3+}(aq) + Sn^{2+}(aq)$
   b. $Pb(s) + Pb^{4+}(aq) \rightarrow Pb^{2+}(aq)$ (Hint: both half reactions will start with the same reactant.)

Answers

1. a. no
   b. yes; oxidizing agent: $AlCl_3$; reducing agent: Mg
   c. yes; oxidizing agent: H_2O_2; reducing agent: H_2
   d. no

3. a. $Ca \rightarrow Ca^{2+} + 2e^-$

   $2H^+ + 2e^- \rightarrow H_2$

   Combined: $Ca + 2H^+ \rightarrow Ca^{2+} + H_2$

   b. $Br_2 + 2e^- \rightarrow 2Br^-$

   $2I^- \rightarrow I_2 + 2e^-$

   Combined: $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

This page titled 4.1: Redox Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

4.2: Balancing Redox Reactions

In studying redox chemistry, it is important to begin by learning to balance electrochemical reactions. Simple redox reactions (for example, $H_2 + I_2 \rightarrow 2\ HI$) can be balanced by inspection, but for more complex reactions it is helpful to have a foolproof, systematic method. The **ion-electron method** allows one to balance redox reactions regardless of their complexity. We illustrate this method with two examples.

Example 1:
I^- is oxidized to **IO_3^-** by **MnO_4^-**, which is reduced to **Mn^{2+}**.

How can this reaction be balanced? In the ion-electron method we follow a series of four steps:

Step 1A: Write out the (unbalanced) reaction and identify the elements that are undergoing redox.

$\mathbf{Mn}O_4^- + \mathbf{I}^- \rightarrow \mathbf{I}O_3^- + \mathbf{Mn}^{2+}$ (The elements undergoing redox are **Mn** and **I**)

Step 1B: Separate the reaction into two **half reactions**, balancing the element undergoing redox in each.

$\mathbf{Mn}O_4^- \rightarrow \mathbf{Mn}^{2+}$
$\mathbf{I}^- \rightarrow \mathbf{I}O_3^-$

Step 2A: Balance the **oxygen** atoms by adding water to one side of each half reaction.

$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
$3H_2O + I^- \rightarrow IO_3^-$

Step 2B: Balance the **hydrogen** atoms by adding H^+ ions.

$8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

The left side has a net charge of **+7** and the right side has a net charge of **+2**

$3H_2O + I^- \rightarrow IO_3^- + 6H^+$

The left side has a net charge of **-1** and the right side has a net charge of **+5**

Step 2C: Balance the overall charge by adding **electrons**

$8H^+ + 5e^- + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

The left side has a charge of **+2** while the right side has a charge of **+2**. They are balanced.

$3H_2O + I^- \rightarrow IO_3^- + 6H^+ + 6e^-$

The left side has a charge of **-1** while the right side has a charge of **-1**. They are balanced.
Note: We did not need to explicitly determine the oxidation states of Mn or I to arrive at the correct number of electrons in each half reaction.

Step 3: Combine the half reactions so that there are equal numbers of electrons on the left and right sides

6 $(8H^+ + 5e^- + MnO_4^- \rightarrow Mn^{2+} + 4H_2O)$
5 $(3H_2O + I^- \rightarrow IO_3^- + 6H^+ + 6e^-)$

$48H^+ + 30e^- + 15H_2O + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + 24H_2O + 30e^- + 30H^+$
Cancel the **H^+**, **electrons**, and **water**:
~~$48H^+$~~ + ~~$30e^-$~~ + ~~$15H_2O$~~ + $6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+}$ + ~~$24H_2O$~~ + ~~$30e^-$~~ + ~~$30H^+$~~

The overall balanced reaction is therefore:
$\mathbf{18H^+ + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + 9H_2O}$

Check your work by making sure that all **elements** and **charges** are balanced.

Step 4: If the reaction occurs under basic conditions, we add OH^- to each side to cancel H^+
$\mathbf{18H^+} + \mathbf{18OH^-} + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + \mathbf{9H_2O} + \mathbf{18OH^-}$

The $\mathbf{18H^+} + \mathbf{18OH^-}$ will become $\mathbf{18H_2O}$ so the overall balanced reaction is:

$\mathbf{9H_2O + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + 18OH^-}$

Again, it is a good idea to check and make sure that all of the elements are balanced, and that the charge is the same on both sides. If this is not the case, you need to find the error in one of the earlier steps.

Example 2:
Redox reaction of $S_2O_3^{2-}$ and H_2O_2
$\mathbf{S_2O_3^{2-}} + \mathbf{H_2O_2} \rightarrow \mathbf{S_4O_6^{2-}} + \mathbf{H_2O}$

Which elements are undergoing redox? **S** and **O**

Step 1: Write out half reactions, balancing the element undergoing redox

$\mathbf{2S_2O_3^{2-} \rightarrow S_4O_6^{2-}}$
$\mathbf{H_2O_2 \rightarrow 2H_2O}$

Step 2A: Balance oxygen (already balanced)

Step 2B: Balance hydrogen:

$\mathbf{2S_2O_3^{2-} \rightarrow S_4O_6^{2-}}$
$\mathbf{H_2O_2 + 2H^+ \rightarrow 2H_2O}$

Step 2C: Balance charge by adding electrons:

$\mathbf{2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-}$
$\mathbf{H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O}$

Step 3: Combine the half reactions so that there are equal numbers of electrons on the left and right sides (already equal)
Overall balanced reaction:

$\mathbf{2S_2O_3^{2-} + H_2O_2 + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O}$

Note that again, we did not need to know the formal oxidation states of S or O in the reactants and products in order to balance the reaction. In this case, assigning the oxidation states would be rather complex, because $S_2O_3^{2-}$ and $S_4O_6^{2-}$ both contain sulfur in more than one oxidation state.

This page titled 4.2: Balancing Redox Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **4.2: Balancing Redox Reactions** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

4.3: Electrochemical Potentials

In electrochemical cells, or in redox reactions that happen in solution, the thermodynamic driving force can be measured as the **cell potential**. Chemical reactions are spontaneous in the direction of -ΔG, which is also the direction in which the cell potential (defined as $E_{cathode}$ - E_{anode}) is positive. A cell operating in the **spontaneous** direction (for example, a battery that is discharging) is called a **galvanic cell**. A cell that is being driven in the **non-spontaneous** direction is called an **electrolytic cell**. For example, let us consider the reaction of hydrogen and oxygen to make water:

$$2\,H_{2\,(g)} + O_{2\,(g)} = 2\,H_2O_{(l)} \tag{4.3.1}$$

Thermodynamically, this reaction is spontaneous in the direction shown and has an overall standard free energy change (ΔG°) of -237 kJ per mole of water produced.

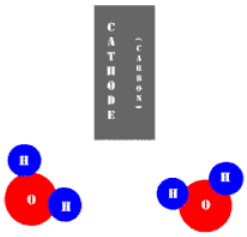
When this reaction occurs electrochemically in the spontaneous direction (e.g., in a hydrogen-air fuel cell), the two half cell reactions that occur are:

Anode: $H_{2\,(g)} \longrightarrow 2\,H^+{}_{(aq)} + 2\,e^-$

Cathode: $O_{2\,(g)} + 4\,H^+{}_{(aq)} + 4\,e^- \longrightarrow 2\,H_2O_{(l)}$

Here the anode is the negative electrode and the cathode is the positive electrode; under conditions of very low current density (where there are minimal resistive losses and kinetic overpotentials), the potential difference we would measure between the two electrodes would be 1.229 V.

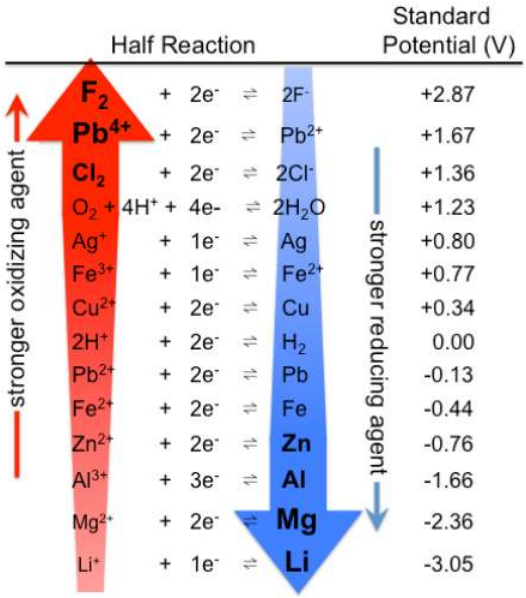
In an **electrolytic cell**, this reaction is run in reverse. That is, we put in electrical energy to split water into hydrogen and oxygen molecules. In this case, the half reactions (and their standard potentials) reverse. O_2(g) bubbles form at the anode and H_2(g) is formed at the cathode. Now the **anode** is the **positive** electrode and the **cathode** is **negative**. Electrons are extracted from the substance at the anode (water) and pumped into the solution at the cathode to make hydrogen. An animation of the cathode half reaction is shown below.



In both galvanic and electrolytic cells, **oxidation** occurs at the **anode** and **reduction** occurs at the **cathode**.

Half-cell potentials

As noted above, the equilibrium voltage of an electrochemical cell is proportional to the free energy change of the reaction. Because electrochemical reactions can be broken up into two half-reactions, it follows that the potentials of half reactions (like free energies) can be added and subtracted to give an overall value for the reaction. If we take the **standard hydrogen electrode** as our reference, i.e., if we assign it a value of zero volts, we can measure all the other half cells against it and thus obtain the voltage of each one. This allows us to rank redox couples according to their **standard reduction potentials** (or more simply their **standard potentials**), as shown in the table below.



Note that when we construct an electrochemical cell and calculate the voltage, we simply take the difference between the half cell potentials and do not worry about the number of electrons in the reaction. For example, for the displacement reaction in which silver ions are reduced by copper metal, the reaction is:

$2\,Ag^{+}{}_{(aq)} + Cu_{(s)} = 2\,Ag_{(s)} + Cu^{2+}{}_{(aq)}$

The two half-cell reactions are:

$Ag^{+}_{(aq)} + e^{-} = Ag_{(s)} \quad +0.80V$

$Cu^{2+}_{(aq)} + 2e^{-} = Cu_{(s)} \quad +0.34V$

and the standard potential $E^{o} = +0.80 - 0.34V = +0.46V$

The reason we don't need to multiply the Ag potential by 2 is that E^{o} is a measure of the free energy change **per electron**. Dividing the free energy change by the number of electrons (see below) makes E^{o} an **intensive property** (like pressure, temperature, etc.).

Relationship between E and ΔG. For systems that are in equilibrium, $\Delta G^{o} = -nFE^{o}_{cell}$, where *n* is number of moles of electrons per mole of products and *F* is the Faraday constant, ~96485 C/mol. Here the ^{o} symbol indicates that the substances involved in the reaction are in their standard states. For example, for the water electrolysis reaction, the standard states would be pure liquid water, H^{+} at 1M concentration (or more precisely, at unit activity), and O_2 and H_2(g) at 1 atmosphere pressure.

More generally (at any concentration or pressure), $\Delta G = -nFE$, where

$$E = E^{o} - \frac{RT}{nF} * lnQ \tag{4.3.2}$$

,

or at 298 K

$$E = E^{o} - \frac{0.0592}{n} * \log Q \tag{4.3.3}$$

where Q is the concentration ratio of products over reactants, raised to the powers of their coefficients in the reaction. This equation (in either form) is called the Nernst equation. The second term in the equation, when multiplied by -nF, is RT*lnQ. This is the free energy difference between ΔG and ΔG°. We can think of this as an entropic term that takes into account the positive entropy change of dilution, or the negative entropy change of concentrating a reactant or product, relative to its standard state.

Using the Nernst equation

Example 1:

For the half reaction $2\,H^+ + 2\,e^- = H_2$, $E°_{1/2}$ = 0.000 V (by definition)

What is $E_{1/2}$ at pH 5 and P_{H_2} = 1 atm?
$pH = -\log[H^+] = 5$, so [H^+] = 10^{-5} M

$$E = E^o - \frac{0.0592}{2} * \log\frac{P_{H2}}{(H^+)^2} = E^o - \frac{0.0592}{2} * \log\,(10^5)^2 = E^o - \frac{0.0592}{2}(10) \qquad (4.3.4)$$
$$= 0.000 - 0.296 = -0.296V$$

Example 2:

What is the potential of a fuel cell (a galvanic H_2/O_2 cell) operating at pH 5?

Overall reaction: $2\,H_{2\,(g)} + O_{2\,(g)} = 2\,H_2O_{(l)}$

In this reaction, H_2 is oxidized to H^+ and O_2 is reduced to H_2O. According to our convention, we write out and balance both half-cell reactions as reductions. For convenience, we do this in acid. (It is left as an exercise to the interested reader to try to work the problem in base)

Half cell reactions:

$2\,H_{2\,(g)} = 4\,H^+ + 4\,e^-$

$O_{2\,(g)} + 4\,H^+{}_{(aq)} + 4\,e^- = 2\,H_2O_{(l)}$



Toyota fuel cell hybrid bus. The bus runs on electrical energy obtained directly from the H_2/O_2 reaction. Individual fuel cells are connected in series to make a power train that charges a battery pack and drives an electric motor. Although the standard potential of the reaction is 1.23 V, because of kinetic overpotentials each fuel cell in the power train operates at a voltage of about 0.70 V. Despite this energy loss, the fuel cell system is still about twice as efficient as a combustion engine performing the same reaction.

To solve this problem we need to find the difference between the H_2/ H^+ and O_2/H_2O half cell potentials at pH 5.

$2\,H^+ + 2\,e^- \longrightarrow H_2$ $E°_{1/2}$ = 0.000 V

Like all standard potentials, this is written as a reduction. We need to reverse it and change the sign of E^o since H_2 is being oxidized:

$H_2 \longrightarrow 2\,H^+ + 2\,e^-$ $E°_{1/2}$ = -0.000 V

and add the standard potential of the substance being reduced at the cathode:

$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$ $E°_{1/2}$ = +1.229 V

The difference between the two standard half cell potentials is +1.229 - 0.000 = +1.229 V

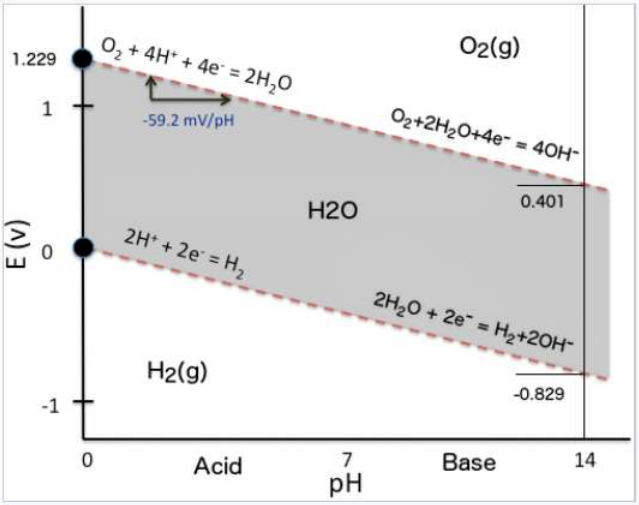
$E°_{cell}$ = +1.229 Volts

We now use the Nernst equation to account for the fact that H^+ is not in its standard state:

$$E_{cell} = E^o - \frac{0.0592}{4} * log\frac{[H^+]^4}{P_{O2}P_{H2}^2[H^+]^4} = E^o - \frac{0.0592}{4} * log(1) = E^o = +1.229V \tag{4.3.5}$$

Note that the value of E_{cell} **does not change** with pH since **both couples shift -59.2 mV/pH** according to the Nernst equation. This is the consequence of the fact that the number of electrons equals the number of protons in each of the half cell reactions. Another way to rationalize this result is to remember that the overall reaction ($2H_2$ + O_2 = $2H_2O$) does not involve H^+ as a reactant or product, so ΔG and E should be independent of pH.

We can plot the shift in the H_2/H^+ and O_2/H_2O half-cell potentials with pH on a potential-pH diagram (also called a Pourbaix diagram) as shown below. The pH-dependent potentials of the H_2 and O_2 couples are shown as dotted lines. Notice that the potential difference between them is always 1.23 V. The dark circles represent the standard potentials.



Pourbaix diagram for water.

Pourbaix diagrams are essentially electrochemical **phase diagrams**, which plot regions of thermodynamic stability for redox-active substances. As in other kinds of phase diagrams, the lines represent conditions under which two phases coexist in equilibrium. The shaded area in the water Pourbaix diagram represents the conditions of potential and pH where liquid water is stable relative to hydrogen or oxygen. Outside the shaded region, water is thermodynamically unstable and is reduced to H_2(g) or oxidized to O_2(g). Although these processes are spontaneous in the thermodynamic sense (for example, water is unstable in the presence of Pb^{4+}, Cl_2, Fe, Zn, or Al), they are kinetically slow and require catalysis to proceed.

This page titled 4.3: Electrochemical Potentials is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **4.3: Electrochemical Potentials** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

4.4: Pourbaix Diagrams

Pourbaix Diagrams plot electrochemical stability for different redox states of an element as a function of pH.[3] As noted above, these diagrams are essentially phase diagrams that map the conditions of potential and pH (most typically in aqueous solutions) where different redox species are stable. We saw a simple example of such a diagram in section 4.2 for H_2O. Typically, the water redox reactions are plotted as dotted lines on these more complicated diagrams for other elements.

The lines in Pourbaix diagrams represent redox and acid-base reactions, and are the parts of the diagram where two species can exist in equilibrium. For example, in the Pourbaix diagram for Fe below, the horizontal line between the Fe^{3+} and Fe^{2+} regions represents the reaction $Fe^{3+}{}_{(aq)} + e^- = Fe^{2+}{}_{(aq)}$, which has a standard potential of +0.77 V. While we could use standard potentials for all these lines, in practice Pourbaix diagrams are usually plotted for lower ion concentrations (often 1 mM) that are more relevant to corrosion and electrochemical experiments.

Example: Iron Pourbaix diagram

Areas in the Pourbaix diagram mark regions where a single species (Fe^{2+}(aq), Fe_3O_4(s), etc.) is stable. More stable species tend to occupy larger areas.

Lines mark places where two species exist in equilibrium.

- **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent
- **Pure acid-base** reactions are **vertical** lines - these do not depend on potential
- Reactions that are **both** acid-base and redox have a slope of -0.0592 V/pH x # H^+/# e^-)

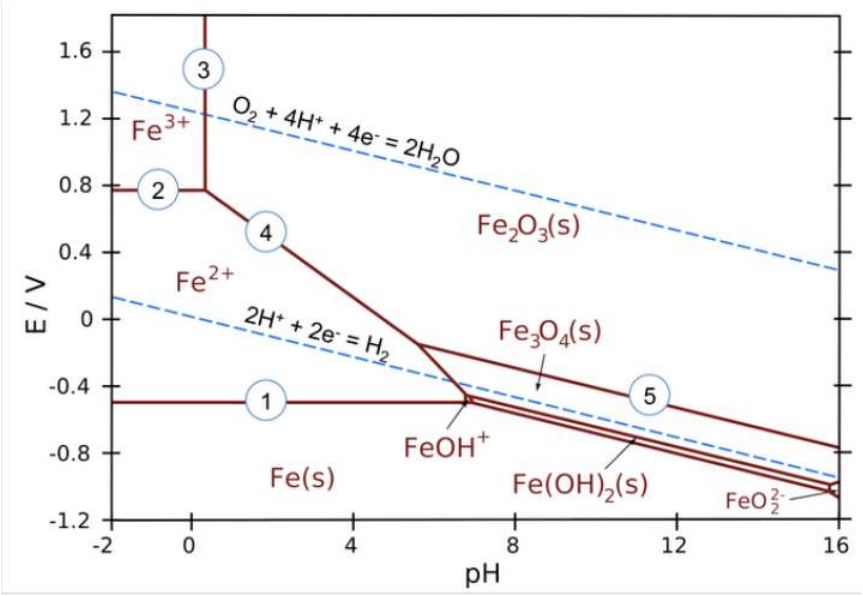


Figure 4.4.1: Pourbaix diagram for iron at ionic concentrations of 1.0 mM. (CC BY-SA 3.0 Unported; Metallos via Wikipedia)

Examples of equilibria in the iron Pourbaix diagram (numbered on the plot):

1. $Fe^{2+} + 2\,e^- \longrightarrow Fe_{(s)}$ (pure redox reaction - no pH dependence)
2. $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (pure redox reaction - no pH dependence)
3. $2\,Fe^{3+} + 3\,H_2O \longrightarrow Fe_2O_{3\,(s)} + 6\,H^+$ (pure acid-base, no redox)
4. $2\,Fe^{2+} + 3\,H_2O \longrightarrow Fe_2O_{3\,(s)} + 6\,H^+ + 2\,e^-$ (slope = -59.2 x 6/2 = -178 mV/pH)
5. $2\,Fe_3O_{4\,(s)} + H_2O \longrightarrow 2\,H^+ + 2\,e^-$ (slope = -59.2 x 2/2 = -59.2 mV/pH)

The water redox lines have special significance on a Pourbaix diagram for an element such as iron. Recall that liquid water is stable *only* in the region between the dotted lines. Below the H_2 line, water is unstable relative to hydrogen gas, and above the O_2 line, water is unstable with respect to oxygen. For active metals such as Fe, the region where the pure element is stable is typically below the H_2 line. This means that iron metal is unstable in contact with water, undergoing reactions:

$Fe_{(s)} + 2\,H^+ \longrightarrow Fe^{2+}{}_{(aq)} + H_2$ (in acid)

$fe_{(s)} + 2\,H_2O \longrightarrow Fe(OH)_{2\,(s)} + H_2$ (in base)

Iron (and most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O_2 line in the Pourbaix diagram. Here the spontaneous reactions are:

$4\,Fe_{(s)} + 3\,O_2 + 12\,H^+ \longrightarrow 4\,Fe^{3+} + 6\,H_2O$ (in acid)

\(\ce{4Fe_{(s)} + 3O2 -> 2Fe2O3_{(s)} (in base)

Corrosion and passivation. It certainly sounds bad for our friend Fe: unstable in water, no matter what the pH or potential. Given enough time, it will all turn into rust. But iron (and other active metals) can corrode, or can be stabilized against corrosion, depending on the conditions. Because our civilization is dependent on the use of active metals such as Fe, Al, Zn, Ti, Cr... for practically everything, it is important to understand this, and we can do so by referring to the Pourbaix diagram.

The **corrosion** of iron (and other active metals such as Al) is indeed rapid in parts of the Pourbaix diagram where the element is oxidized to a soluble, ionic product such as Fe^{3+}(aq) or Al^{3+}(aq). However, solids such as Fe_2O_3, and especially Al_2O_3, form a protective coating on the metal that greatly impedes the corrosion reaction. This phenomenon is called **passivation.**

Draw a vertical line through the iron Pourbaix diagram at the pH of tap water (about 6) and you will discover something interesting: at slightly acidic pH, iron is quite unstable with respect to corrosion by the reaction:

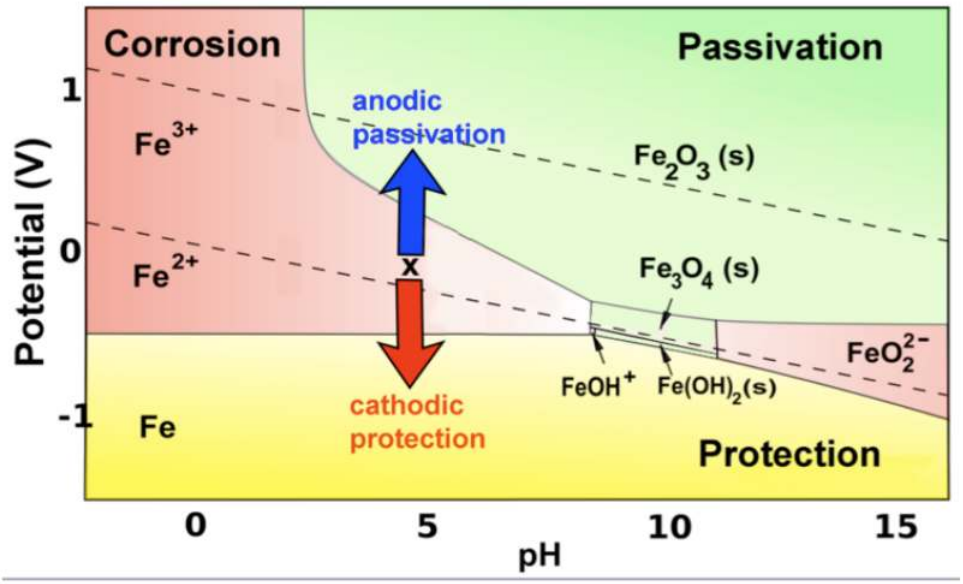
$$Fe_{(s)} + 2\,H^+ \longrightarrow Fe^{2+}{}_{(aq)} + H_2 \tag{4.4.1}$$

but *only in water that contains relatively little oxygen*, i.e., in solutions where the potential is near the H_2 line. Saturating the water with air or oxygen moves the system closer to the O_2 line, where the most stable species is Fe_2O_3 and the corrosion reaction is:

$$4\,Fe_{(s)} + 3\,O_2 \longrightarrow 2\,Fe_2O_{3\,(s)} \tag{4.4.2}$$

This oxidation reaction is orders of magnitude slower because the oxide that is formed *passivates* the surface. Therefore iron corrodes much more slowly in oxygenated solutions.

More generally, iron (and other active metals) are passivated whenever they oxidize to produce a solid product, and corrode whenever the product is ionic and soluble. This behavior can be summed up on the color-coded Pourbaix diagram below. The red and green regions represent conditions under which oxidation of iron produces soluble and insoluble products, respectively.



In the yellow part of the diagram, an active metal such as iron can be **protected** by a second mechanism, which is to bias it so that its potential is below the oxidation potential of the metal. This **cathodic protection** strategy is most frequently carried out by connecting a more active metal such as Mg or Zn to the iron or steel object (e.g., the hull of a ship, or an underground gas pipeline) that is being protected. The active metal (which must be higher than Fe in the activity series) is also in contact with the solution and slowly corrodes, so it must eventually be replaced. In some cases a battery or DC power supply - the anode of which oxidizes water to oxygen in the solution - is used instead to apply a negative bias.



The white patches visible on the ship's hull are zinc block sacrificial anodes.

Another common mode of corrosion of iron and carbon steel is **differential aeration.** In this case, part of the iron object - e.g., the base of a bridge, or the drill in an oil rig - is under water or in an anoxic environment such as mud or soil. The potential of the solution is close to the H_2 line in the Pourbaix diagram, where Fe can corrode to Fe^{2+} (aq). Another part of the iron object is in the air, or near the surface where water is well oxygenated. At that surface oxygen can be reduced to water, $O_2 + 4H^+ + 4e^- = 2\ H_2O$. The conductive iron object completes the circuit, carrying electrons from the anode (where Fe is oxidized) to the cathode (where O_2 is reduced). Corrosion by differential aeration can be rapid because soluble ions are produced, and the reaction has a driving force of over 1 V. Iron or carbon steel that is subjected to frequent weathering, such as the cast iron bridge and lamppost shown below, is corroded on the surface by differential aeration.



Rusty cast iron bridge and lamppost, North Ayrshire, Scotland

Differential aeration is involved in the formation of a rust ring around wet areas of cast iron, e.g., an iron frying pan left partially submerged in water for a day or more. (You may have seen this mechanism of corrosion in action when you did not get to the dirty dishes right away). Under the water, Fe is oxidized to soluble Fe^{2+}, and at the water line O_2 is reduced to H_2O. As Fe^{2+} ions diffuse towards the water surface, they encounter oxygen molecules and are oxidized to Fe^{3+}. However Fe^{3+} is insoluble at neutral pH and deposits as rust, typically just below the water line, forming the rust ring.

This page titled 4.4: Pourbaix Diagrams is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **4.6: Pourbaix Diagrams** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

4.5: Electrochemical Corrosion

Learning Objectives

Make sure you thoroughly understand the following essential ideas. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Electrochemical corrosion of metals occurs when electrons from atoms at the surface of the metal are transferred to a suitable electron acceptor or *depolarizer*. Water must be present to serve as a medium for the transport of ions.
- The most common depolarizers are oxygen, acids, and the cations of less active metals.
- Because the electrons flow through the metallic object itself, the anodic and cathodic regions (the two halves of the electrochemical cell) can be at widely separated locations.
- Anodic regions tend to develop at locations where the metal is stressed or is protected from oxygen.
- Contact with a different kind of metal, either direct or indirect, can lead to corrosion of the more active one.
- Corrosion of steel can be inhibited by *galvanizing*, that is, by coating it with zinc, a more active metal whose dissolution leaves a negative charge on the metal which inhibits the further dissolution of Fe^{2+}.
- *Cathodic protection* using an external voltage source is widely used to protect underground structures such as tanks, pipelines and piers. The source can be a sacrificial anode of zinc or aluminum, or a line-operated or photovoltaic power supply.

Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^{+} + e^{-}$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a *depolarizer.*

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes. The economic aspects of corrosion are far greater than most people realize; the estimated cost of corrosion in the U.S. alone was $276 billion per year. Of this, about $121 billion was spent to control corrosion, leaving the difference of $155 billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer the largest economic impact, with motor vehicles and transportation being a close second.

Corrosion Cells and Reactions

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions (Figure 4.5.1). The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.

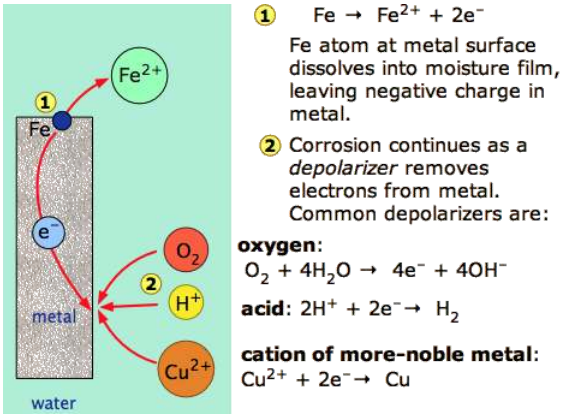


Figure 4.5.1: Corrosion is a two-step process. Figure 4.5.1: Electrochemical corrosion of iron. Corrosion often begins at a location (1) where the metal is under stress (at a bend or weld) or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.) The metal ions dissolve in the moisture film and the electrons migrate to another location (2) where they are taken up by a *depolarizer*. Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as *rust*. (CC BY 3.0 Unported; Stephen Lower)

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like

$$\mathrm{Fe\,(s)\ \rightarrow Fe^{2+}\,(aq) + 2\,e^-} \tag{4.5.1}$$

and the cathodic steps may invove the reduction of oxygen gas

$$\mathrm{O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-} \tag{4.5.2}$$

or the reduction of protons

$$\mathrm{H^+ + e^- \rightarrow \tfrac{1}{2}\,H_2\,(g)} \tag{4.5.3}$$

or the reduction of a metal ion

$$\mathrm{M^{2+} + 2\,e^- \rightarrow M\,(s)} \tag{4.5.4}$$

where M is a metal.

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

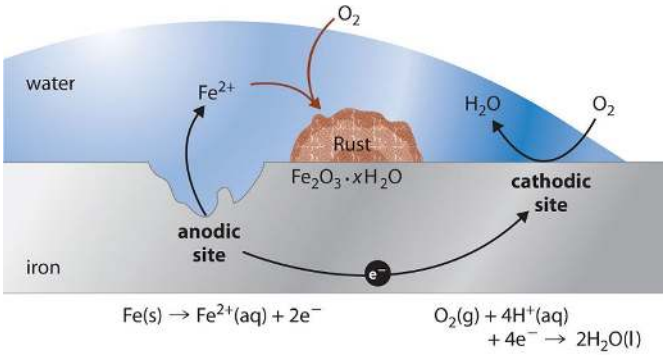


Figure 4.5.2: Schematic diagram of corrosion cells on iron. (CC BY-NSA-NC; Anonymous by request)

If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this "protected" region will often be the site at which corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.

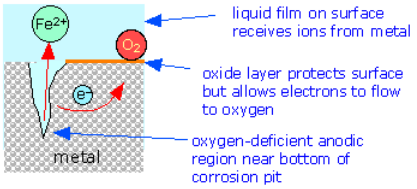


Figure 4.5.3: Pitting corrosion Most metals are covered with a thin oxide film which inhibits anodic dissolution. When corrosion does occur, it sometimes hollows out a narrow hole or pit in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal. (CC BY 3.0 Unported; Stephen Lower)

In contrast to anodic sites, which tend to be localized to specific regions of the surface, the cathodic part of the process can occur almost anywhere. Because metallic oxides are usually semiconductors, most oxide coatings do not inhibit the flow of electrons to the surface, so almost any region that is exposed to O_2 or to some other electron acceptor can act as a cathode. The tendency of oxygen-deprived locations to become anodic is the cause of many commonly-observed patterns of corrosion.

Anyone who has owned an older car has seen corrosion occur at joints between body parts and under paint films. You will also have noticed that once corrosion starts, it tends to feed on itself. One reason for this is that one of the products of the O_2 reduction reaction is hydroxide ion. The high pH produced in these cathodic regions tends to destroy the protective oxide film, and may even soften or weaken paint films, so that these sites can become anodic. The greater supply of electrons promotes more intense cathodic action, which spawns even more anodic sites, and so on.



Figure 4.5.4: Rusted out car. Severely rusted floorboards of 1990 Chrysler New Yorker. Car was damaged to the point where it became unsafe to drive. Under the rusting section between the two holes were the two brake lines (Public Domain; Bige1977 via Wikipedia).

A very common cause of corrosion is having two dissimilar metals in contact, as might occur near a fastener or at a weld joint. Moisture collects at the junction point, acting as an electrolyte and forming a cell in which the two metals serve as electrodes. Moisture and conductive salts on the outside surfaces provide an external conductive path, effectively short-circuiting the cell and producing very rapid corrosion; this is why cars rust out so quickly in places where salt is placed on roads to melt ice.

Dissimilar-metal corrosion can occur even if the two metals are not initially in direct contact. For example, in homes where copper tubing is used for plumbing, there is always a small amount of dissolved Cu^{2+} in the water. When this water encounters steel piping or a chrome-plated bathroom sink drain, the more-noble copper will plate out on the other metal, producing a new metals-in-contact corrosion cell. In the case of chrome bathroom sink fittings, this leads to the formation of Cr^{3+} salts which precipitate as greenish stains.

Control of Corrosion

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads. A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction to take place:

$$M \longrightarrow M^{2+} + 2e^{-}. \tag{4.5.5}$$

Protection Method 1: Sacrificial Coatings

One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing.The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.

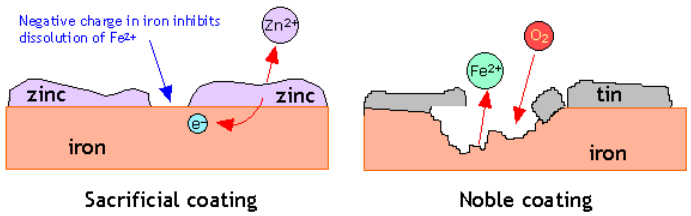


Figure 4.5.5: Sacrificial Coatings (CC BY 3.0 Unported; Stephen Lower)

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

Protection Method 2: Cathodic Protection

A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as *cathodic protection*. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a piece of zinc or aluminum buried in the ground nearby, as is shown in the illustration of the buried propane storage tank below.

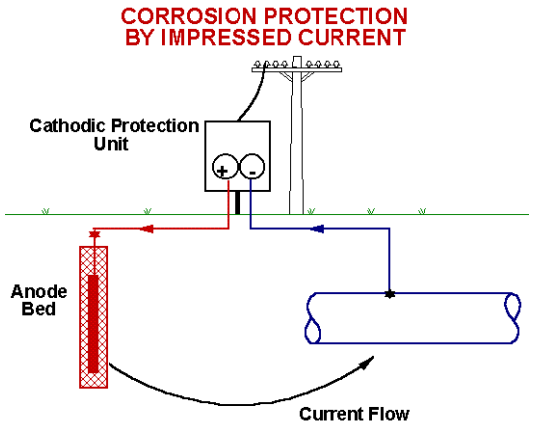


Figure 4.5.6: Cathodic Protection (CC BY 3.0 Unported; Stephen Lower)

This page titled 4.5: Electrochemical Corrosion is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **16.8: Electrochemical Corrosion** by Stephen Lower is licensed CC BY 3.0. Original source: http://www.chem1.com/acad/webtext/virtualtextbook.html.

CHAPTER OVERVIEW

5: Electrochemistry

5.1: Electrolysis

5.2: Cyclic Voltammetry

5.3: CV Electrodes

This page titled 5: Electrochemistry is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

5.1: Electrolysis

Skills to Develop

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In electrolytic cells, electrical energy causes nonspontaneous reactions to occur in a process known as electrolysis. The charging electric barttery shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile. The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure 5.1.1. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode: } 2\,\text{Cl}^-(l) \longrightarrow \text{Cl}_2(g) + 2\,\text{e}^- \quad E^\circ_{\text{Cl}_2/\text{Cl}^-} = +1.3\ \text{V} \tag{5.1.1}$$

$$\text{cathode: } \text{Na}^+(l) + \text{e}^- \longrightarrow \text{Na}(l) \quad E^\circ_{\text{Na}^+/\text{Na}} = -2.7\ \text{V} \tag{5.1.2}$$

$$\text{overall: } 2\,\text{Na}^+(l) + 2\,\text{Cl}^-(l) \longrightarrow 2\,\text{Na}(l) + \text{Cl}_2(g) \quad E^\circ_{\text{cell}} = -4.0\ \text{V} \tag{5.1.3}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

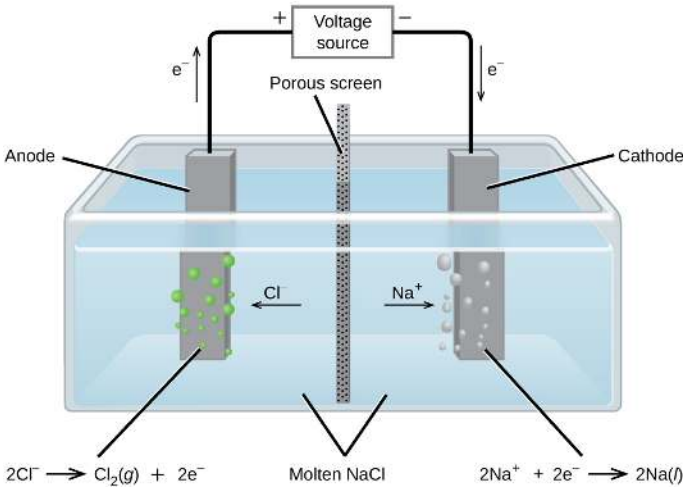


Figure 5.1.1***:*** *Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.*

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure 5.1.2). The reactions are

$$\text{anode: } 2\,\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\,\text{H}^+(aq) + 4\,\text{e}^- \quad E^\circ_{\text{anode}} = +1.229\ \text{V} \tag{5.1.4}$$

$$\text{cathode: } 2\,\text{H}^+(aq) + 2\,\text{e}^- \longrightarrow \text{H}_2(g) \quad E^\circ_{\text{cathode}} = 0\ \text{V} \tag{5.1.5}$$

$$\text{overall: } 2\,\text{H}_2\text{O}(l) \longrightarrow 2\,\text{H}_2(g) + \text{O}_2(g) \quad E^\circ_{\text{cell}} = -1.229\ \text{V} \tag{5.1.6}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

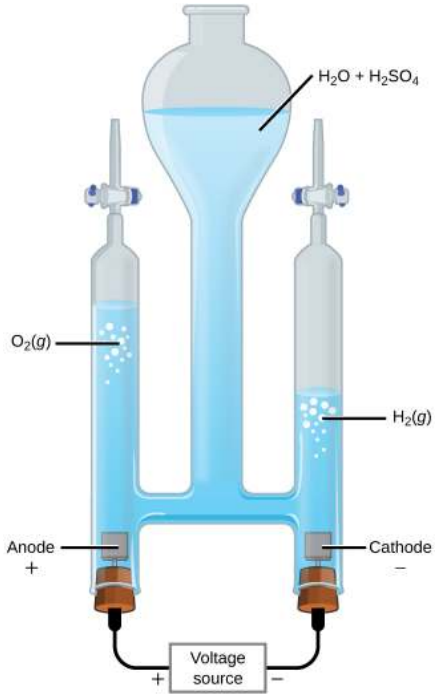


Figure 5.1.2***:*** *Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.*

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i) } 2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{\text{anode}} = +1.35827\ \text{V} \tag{5.1.7}$$
$$\text{(ii) } 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{\text{anode}} = +1.229\ \text{V} \tag{5.1.8}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The overpotential is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii) } 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{\text{cathode}} = 0\ \text{V} \tag{5.1.9}$$
$$\text{(iv) } 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \quad E^\circ_{\text{cathode}} = -0.8277\ \text{V} \tag{5.1.10}$$
$$\text{(v) } Na^+(aq) + e^- \longrightarrow Na(s) \quad E^\circ_{\text{cathode}} = -2.71\ \text{V} \tag{5.1.11}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only 1×10^{-7} *M*. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$\text{overall: } 2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq) \quad E^\circ_{\text{cell}} = -2.186\ \text{V} \tag{5.1.12}$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure 5.1.3).

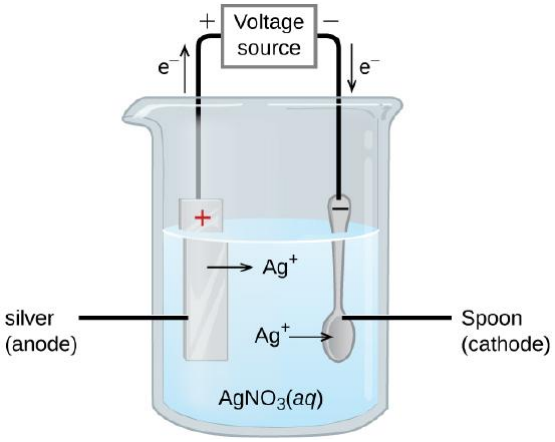


Figure 5.1.3*: The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.*

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\text{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{e^-} \tag{5.1.13}$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\text{cathode: } \mathrm{Ag^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Ag}(s) \tag{5.1.14}$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second ($1\ \text{A} = 1\ \frac{\text{C}}{\text{s}}$). The total charge ($Q$, in coulombs) is given by

$$Q = I \times t = n \times F \tag{5.1.15}$$

where

- t is the time in seconds,
- n the number of moles of electrons, and
- F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 5.1.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} \tag{5.1.16}$$

$$= \frac{\frac{10.23\ \text{C}}{\text{s}} \times 1\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{60\ \text{s}}{\text{min}}}{96,485\ \text{C/mol e}^-} = \frac{36,830\ \text{C}}{96,485\ \text{C/mol e}^-} = 0.3817\ \text{mol e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } \text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s) \tag{5.1.17}$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817\ \text{mol e}^- \times \frac{1\ \text{mol Ag}}{1\ \text{mol e}^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 41.19\ \text{g Ag} \tag{5.1.18}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Exercise 5.1.1

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer

$\text{Al}^{3+}(aq) + 3\,\text{e}^- \longrightarrow \text{Al}(s)$; 7.77 mol Al = 210.0 g Al.

Example 5.1.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume} = \left(0.010\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}}\right) \times \left(3.3\ \text{m}^2 \times \left(\frac{10,000\ \text{cm}^2}{1\ \text{m}^2}\right)\right) = 33\ \text{cm}^3 \tag{5.1.19}$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass} = \text{volume} \times \text{density} = 33\ \cancel{\text{cm}^3} \times \frac{7.19\ \text{g}}{\cancel{\text{cm}^3}} = 237\ \text{g Cr} \tag{5.1.20}$$

$$\text{mol Cr} = 237\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} = 4.56\ \text{mol Cr} \tag{5.1.21}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\ \text{mol Cr} \times \frac{3\ \text{mol e}^-}{1\ \text{mol Cr}} \times \frac{96485\ \text{C}}{\text{mol e}^-} = 1.32 \times 10^6\ \text{C} \tag{5.1.22}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\ \text{C}}{33.46\ \text{C/s}} = 3.95 \times 10^4\ \text{s} = 11.0\ \text{hr} \tag{5.1.23}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

Exercise 5.1.2

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

231 g Zn required 446 minutes.

Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Glossary

electrolysis
process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell
electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating
depositing a thin layer of one metal on top of a conducting surface

overpotential
difference between the theoretical potential and actual potential in an electrolytic cell; the "extra" voltage required to make some nonspontaneous electrochemical reaction to occur

Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

This page titled 5.1: Electrolysis is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

5.2: Cyclic Voltammetry

This page titled 5.2: Cyclic Voltammetry is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

5.3: CV Electrodes

This page titled 5.3: CV Electrodes is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

CHAPTER OVERVIEW

6: Ionic Compounds

6.1: Unit Cells
6.2: Ionic Radii and Radius Ratios
6.3: Lattice Energy
6.4: Born-Haber Cycles
6.5: Ionic Lattices - Examples
6.5A: Structure - Rock Salt (NaCl)
6.5B: Structure - Caesium Chloride (CsCl)
6.5C: Structure - Fluorite and Antifluorite
6.5D: Structure - Zinc Blende (ZnS)
6.6: Lattice Energy and Solubility
6.7: Solubility Equilibria

This page titled 6: Ionic Compounds is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

6.1: Unit Cells

Introduction

The term "closest packed structures" refers to the most tightly packed or space-efficient composition of crystal structures (lattices). Imagine an atom in a crystal lattice as a sphere. While cubes may easily be stacked to fill up all empty space, unfilled space will always exist in the packing of spheres. To maximize the efficiency of packing and minimize the volume of unfilled space, the spheres must be arranged as close as possible to each other. These arrangements are called **closest packed structures**. The packing of spheres can describe the solid structures of crystals. In a crystal structure, the centers of atoms, ions, or molecules lie on the lattice points. Atoms are assumed to be spherical to explain the bonding and structures of metallic crystals. These spherical particles can be packed into different arrangements. In closest packed structures, the arrangement of the spheres are densely packed in order to take up the greatest amount of space possible.

Close-Packing of Identical Spheres

Crystals are of course three-dimensional objects, but we will begin by exploring the properties of arrays in two-dimensional space. This will make it easier to develop some of the basic ideas without the added complication of getting you to visualize in 3-D — something that often requires a bit of practice. Suppose you have a dozen or so marbles. How can you arrange them in a single compact layer on a table top? Obviously, they must be in contact with each other in order to minimize the area they cover. It turns out that there are two efficient ways of achieving this:



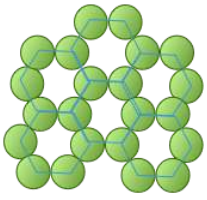
The essential difference here is that any marble within the interior of the square-packed array is in contact with four other marbles, while this number rises to six in the hexagonal-packed arrangement. It should also be apparent that the latter scheme covers a smaller area (contains less empty space) and is therefore a more efficient packing arrangement. If you are good at geometry, you can show that square packing covers 78 percent of the area, while hexagonal packing yields 91 percent coverage.

If we go from the world of marbles to that of atoms, which kind of packing would the atoms of a given element prefer?



If the atoms are identical and are bound together mainly by dispersion forces which are completely non-directional, they will favor a structure in which as many atoms can be in direct contact as possible. This will, of course, be the hexagonal arrangement.

Directed chemical bonds between atoms have a major effect on the packing. The version of hexagonal packing shown at the right occurs in the form of carbon known as *graphite* which forms 2-dimensional sheets. Each carbon atom within a sheet is bonded to three other carbon atoms. The result is just the basic hexagonal structure with some atoms missing.



The coordination number of 3 reflects the sp^2-hybridization of carbon in graphite, resulting in plane-trigonal bonding and thus the sheet structure. Adjacent sheets are bound by weak dispersion forces, allowing the sheets to slip over one another and giving rise to the lubricating and flaking properties of graphite.

Types of Holes From Close-Packing of Spheres

When a single layer of spheres is arranged into the shape of a hexagon, gaps are left uncovered. The hole formed between three spheres is called a **trigonal hole** because it resembles a triangle. In Figure 6.1.1, two out of the the six trigonal holes have been highlighted green.

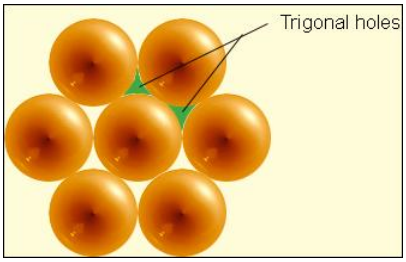


Figure 6.1.1: Trigonal holes (green) between close packed spheres in a single layer

Once the first layer of spheres is laid down, a second layer may be placed on top of it. The second layer of spheres may be placed to cover the trigonal holes from the first layer. Holes now exist between the first layer (the orange spheres) and the second (the lime spheres), but this time the holes are different (Figure 6.1.2). The triangular-shaped hole created over a orange sphere from the first layer is known as a **tetrahedral hole** because the surrounding spheres are in a tetrahedral arrangement. A hole from the second layer that also falls directly over a hole in the first layer is called an **octahedral hole** because the surrounding spheres are in an octahedral arrangement.

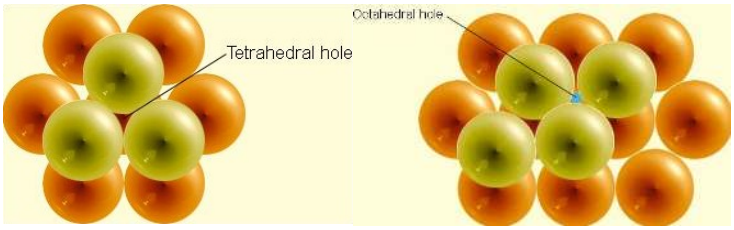


Figure 6.1.2: Illustrations of tetrahedral (left) and octahedral (right) holes formed between two close packed layers

Close Packed Crystal Structures

Hexagonal Close-Packed (hcp)

In a hexagonal close-packed structure, the third layer has the same arrangement of spheres as the first layer and covers all the tetrahedral holes. Since the structure repeats itself after every two layers, the stacking for hcp may be described as "a-b-a-b-a-b." The atoms in a hexagonal close-packed structure efficiently occupy 74% of space while 26% is empty space.

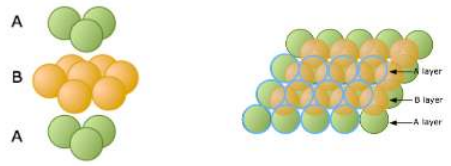


Figure 6.1.3: Side and top views of the layers in the hexagonal close-packed (hpc) structure.

Cubic Close-Packed (ccp)

The arrangement in a cubic closest packing also efficiently fills up 74% of space. Similar to hexagonal closest packing, the second layer of spheres is placed on to of half of the depressions of the first layer. The third layer is completely different than that first two layers and is stacked in the depressions of the second layer, thus covering all of the octahedral holes. The spheres in the third layer are not in line with those in layer A, and the structure does not repeat until a fourth layer is added. The fourth layer is the same as the first layer, so the arrangement of layers is "a-b-c-a-b-c."

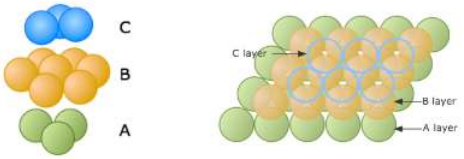


Figure 6.1.4: Side and top views of the layers in cubic close-packed (ccp) structure.

Coordination Number and Number of Atoms Per Unit Cell

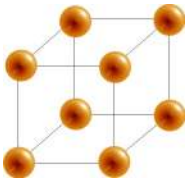
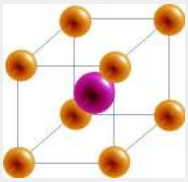
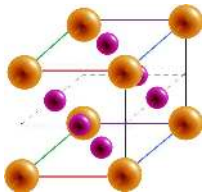
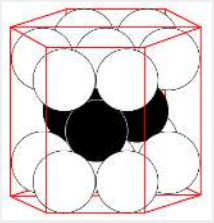
A unit cell is the smallest representation of an entire crystal. All crystal lattices are built of repeating unit cells. In a unit cell, an atom's coordination number is the number of atoms it is touching.

- The simple cubic has a sphere at each corner of a cube. Each sphere has a coordination number of 6 and there is 1 atom per unit cell.
- The body-centered cubic (bcc) has a sphere at each corner of a cube and one in the center. Each sphere has a coordination number 8 and there are 2 atoms per unit cell.
- The cubic closest packed, also called face-centered cubic (fcc) has has a sphere at each corner and each face of a cube. Each sphere has a coordination number of 12 and there are 4 atoms per unit cell.
- The hexagonal closest packed has spheres arranged in hexagons with one in the center. each sphere has a coordination number of 12 and there are 6 atoms per unit cell.

Atoms Per Unit Cell

The amount that an atom contributes to a unit cell depends on its position in the unit cell

- Each corner atom contributes $\frac{1}{8}$ to the unit cell in the cubic cells and $\frac{1}{6}$ to the unit cell in hcp
- Each edge atom contributes $\frac{1}{4}$ to the unit cell
- Each face atom contributes $\frac{1}{2}$ to the unit cell
- Each center atom contributes 1 to the unit cell

Unit Cell	Coordination Number	# of Atoms Per Unit Cell	% space
Simple Cubic 	**6**	**1**	**52%**
Body-Centered Cubic 	**8**	**2**	**68%**
Face-centered Cubic 	**12**	**4**	**74.04%**
Hexagonal Closest Packed 	**12**	**6**	**74.04%**

Inorganic Crystals

Many common inorganic crystals have structures that are related to cubic close packed (face-centered cubic) or hexagonal close packed sphere packings. One component of the material will pack in one of the arrangements above. The remaining component(s) will fill some or all of the holes between the layers. An interstitial atom filling a tetrahedral hole is coordinated to four packing atoms, and an atom filling an octahedral hole is coordinated to six packing atoms. In both the hexagonal close packed and cubic close packed lattices, there is one octahedral hole and two tetrahedral holes per packing atom.

Are Anions or Cations Better Packing Atoms?

We might expect that anions, which are often larger than cations, would be better suited to the positions of packing atoms. While this is often true, there are many examples of structures in which cations are the packing atoms, and others in which the distinction is arbitrary. The NaCl structure is a good example of the latter.

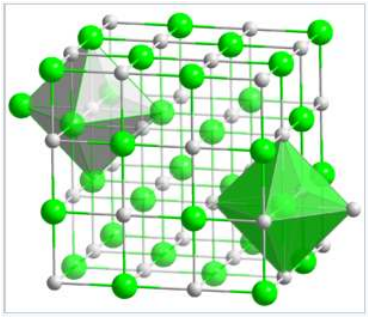


Figure 6.1.5: Crystal structure of NaCl. Both the Na^+ (grey) and Cl^- (green) ions are octahedrally coordinated.

In the rock salt or NaCl structure, shown in Figure 6.1.5, the green spheres are the Cl^- ions and the gray spheres are the Na^+ ions. The packing atoms (Na^+) are in a face centered cubic arrangement. The octahedral holes in a face-centered cubic lattice can be found at the edges and in the center of the unit cell, and they are filled by the chloride ions. Alternatively the structure can be described as the Cl^- ions in a fcc arrangement with the Na^+ ions occupying the octrahedral holes. Another way of stating this is that the structure consists of **two interpenetrating fcc lattices**, which are related to each other by a translation of half the unit cell along any of the three Cartesian axes. Thus the distinction between packing and interstitial atoms in this case is arbitrary.

NaCl is interesting in that it is a three-dimensional checkerboard, and thus there are no NaCl "molecules" that exist in the structure. When this structure was originally solved (in 1913 by using X-ray diffraction) by W. L. Bragg, his interpretation met resistance by chemists who thought that precise integer stoichiometries were a consequence of the valency of atoms in molecules. The German chemist Pfeiffer noted in 1915 that ‘the ordinary notion of valency didn’t seem to apply’, and fourteen years later, the influential chemist Armstrong still found Bragg’s proposed structure of sodium chloride ‘more than repugnant to the common sense, not chemical cricket’! Nevertheless, Bragg and his father, W. H. Bragg, persevered and used the then-new technique of X-ray diffraction to determine the structures of a number of other compounds, including diamond, zincblende, calcium fluoride, and other alkali halides. These experiments gave chemists their first real look at the atomic structure of solids, and laid the groundwork for X-ray diffraction experiments that later elucidated the structures of DNA, proteins, and many other compounds. For their work on X-ray diffraction the Braggs received the Nobel prize in Physics in 1915.

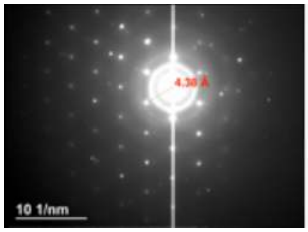


Figure 6.1.6: X-ray difffraction pattern for a NaCl crystal. The lattice dimensions and positions of atoms in crystals such as NaCl are inferred from diffraction patterns.

Since each type of atom in the NaCl structure forms a face-centered cubic lattice, there are four Na and four Cl atoms per NaCl unit cell. It is because of this ratio that NaCl has a 1:1 stoichiometry. The shaded green and gray octahedra in the NaCl lattice (Figure 6.1.5) show that the Na^+ ions are coordinated to six Cl^- ions, and vice versa.

Other materials with the NaCl structure

- Alkali Halides (except CsCl, CsBr, and CsI)
- Transition Metal Monoxides (TiO, VO,..., NiO)
- Alkali Earth Oxides and Sulfides (MgO, CaO, BaS... except BeO and MgTe)
- Carbides and Nitrides (TiC, TiN, ZrC, NbC) -these are very stable refractory, interstitial alloys (metallic)

Other Unit Cell Types

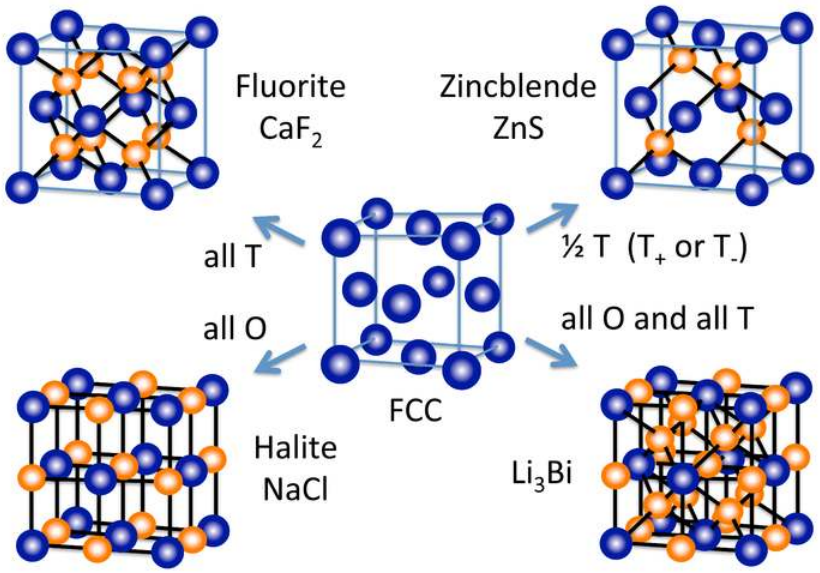


Figure 6.1.7: Illustration of how different unit cell types are formed by filling holes in the fcc lattice

A number of other inorganic crystal structures are formed (at least conceptually) by filling octahedral and/or tetrahedral holes in close-packed lattices. Figure 6.1.7 shows some of the most common structures (fluorite, NaCl, and zincblende) as well as a rather rare one (Li_3Bi) that derive from the fcc lattice. From the hcp lattice, we can make the NiAs and wurzite structures, which are the hexagonal relatives of NaCl and zincblende, respectively.

An alternative and very convenient way to represent inorganic crystal structures (especially complex structures such as Li_3Bi) is to draw the unit cell in slices along one of the unit cell axes. This kind of representation is shown at the left for the fcc lattice and the NaCl structure. Since all atoms in these structures have z-coordinates of either 0 or 1/2, only those sections need to be drawn in order to describe the contents of the unit cell. It is a useful exercise to draw some of the fcc compound structures (above) in sections.

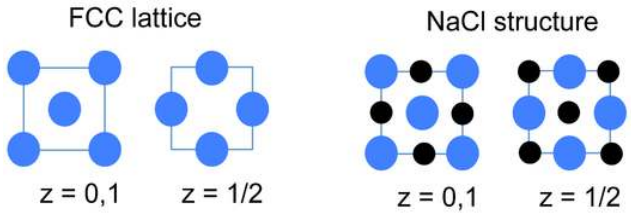


Figure 6.1.8: Alternative representation of the fcc lattice (left) and the NaCl structure (right). The z = 0,1 represent the bottom and top faces of the unit cell. The z = $\frac{1}{2}$ represents a slice through the center of the unit cell

Fluorite

In ccp and hcp lattices, there are two tetrahedral holes per packing atom. A stoichiometry of either M_2X or MX_2 gives a structure that fills all tetrahedral sites, while an MX structure fills only half of the sites. An example of an MX_2 structure is fluorite, CaF_2, whose structure is shown in the figure at the left. The packing atom in fluorite is Ca^{2+} and the structure is composed of three interpenetrating fcc lattices. It should be noted that the Ca^{2+} ion (gray spheres) as a packing atom defies our "rule" that anions are larger than cations and therefore must be the packing atoms. The fluorite structure is common for ionic MX_2 (MgF_2, ZrO_2, etc.) and M_2X compounds (Li_2O). In contrast, the hcp relative of the fluorite structure is quite rare because of unfavorable close contacts between like-charged ions.

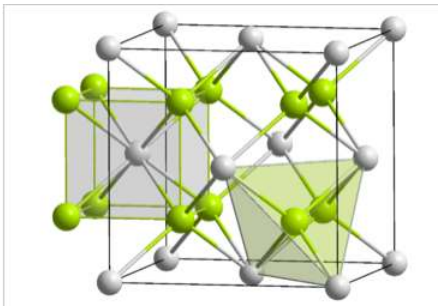


Figure 6.1.9: The fluorite (CaF_2) crystal structure showing the coordination environments of the Ca (grey) and F (green) atoms

In terms of geometry, Ca^{2+} is in cubic coordination with eight F^- neighbors, and the fluoride ions are tetrahedrally coordinated by four Ca^{2+} ions. The 8:4 coordination geometry is consistent with the 1:2 Ca:F stoichiometry; in all crystal structures the ratio of the coordination numbers is the inverse of the stoichiometric ratio. Looking more closely at the tetrahedral sites in fluorite, we see that they fall into two distinct groups: T_+ and T_-. If a tetrahedron is oriented with a vertex pointing upwards along the stacking axis, the site is T_+. Likewise, a tetrahedron with a vertex oriented downward is T_-. The alternation of T_+ and T_- sites allows for efficient packing of ions in the structure.

Zincblende and wurtzite

Tetrahedrally bonded compounds with a 1:1 stoichiometry (MX compounds) have only half of the tetrahedral sites (either the T_+ or T_- sites) filled. In this case, both the M and the X atoms are tetrahedrally coordinated. The zincblende and wurtzite structures of ZnS are 1:1 tetrahedral structures based on fcc and hcp lattices, respectively. Both structures are favored by p-block compounds that follow the octet rule, and these compounds are usually semiconductors or insulators. The zincblende structure, Figure 6.1.10, can be thought of as two interpenetrating fcc lattices, one of anions and one of cations, offset from each other by a translation of 1/4 along the body diagonal of the unit cell. Examples of compounds with the zincblende structure include CuCl, CuI, ZnSe, HgS, BeS, CdTe, AlP, GaP, SnSb, CSi, and diamond. Using ZnS as a representative of zincblende, the coordination of both Zn and S atoms is tetrahedral.

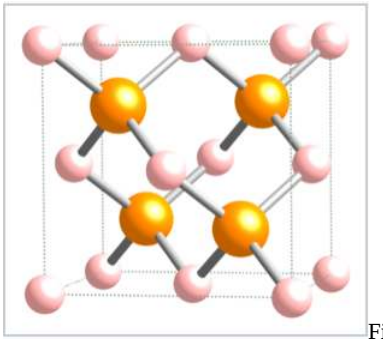


Figure 6.1.10: The zincblende structure of ZnS. The Zn^{2+} ions are in pink and the S^{2-} ions are in orange.

The wurtzite structure is a close relative of zincblende, based on filling half the tetrahedral holes in the hcp lattice. Like zincblende, wurtzite contains planes of fused six-membered rings in the chair conformation. Unlike zincblende, however, the rings joining these planes contain non-planar, six-membered rings. The structure aligns the anions so that they are directly above the cations in the structure, a less favorable situation sterically but a more favorable one in terms of electrostatics. As a result, the wurtzite structure tends to favor more polar or ionic compounds (e.g., ZnO, $NH_4^+F^-$) than the zincblende structure. As with zincblende, both ions are in tetrahedral (4:4) coordination and there are typically eight valence electrons in the MX compound. Examples of compounds with this structure include: BeO, ZnO, MnS, CdSe, MgTe, AlN, and NH_4F.

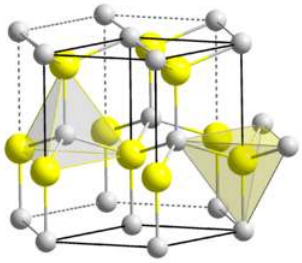


Figure 6.1.11: The wurtzite structure of ZnS with the tetrahedral coordination of anion and cation highlighted. The Zn^{2+} ions are in grey and the S^{2-} ions are in yellow. (Public domain; Solid State via Wikimedia Commons)

An interesting consequence of the layer stacking in the wurtzite structure is that the crystals are polar. When cleaved along the c-axis (the stacking axis), crystals of ZnO, ZnS, and GaN have one negatively charged face and an opposite positively charged face. An applied electric field interacts with the crystal dipole, resulting in compression or elongation of the lattice along this direction. For this reason crystals of compounds in the wurtzite structure are typically piezoelectric (increasing the pressure on the material generates a voltage in the material).

Some compounds are diamorphic and can have either the zincblende or wurtzite structure. Examples of these compounds that have intermediate polarities include CdS and ZnS. SiO_2 exists in polymorphs (crystobalite and tridymite) that resemble zincblende and wurtzite with O atoms midway between each of the Si atoms. The zincblende and wurtzite structures have efficient packing arrangements for tetrahedrally bonded networks and are commonly found in compounds that have tetrahedral bonding. Water, for example, has a tetrahedral hydrogen bonding network and is wurtzite-type. The undistorted wurtzite and zincblende structures are typically found for AX compounds with eight valence electrons, which follow the octet rule. AX compounds with nine or ten electrons such as GaSe and GaAs crystallize in distorted variants of the wurtzite structure. In GaSe, the extra electrons form lone pairs and this creates layers in the structure, as can be seen in the figure below. To the right of GaSe, the structures of As, Sb, and SbAs show an ever further breakdown of the structure into layers as more valence electrons are added.

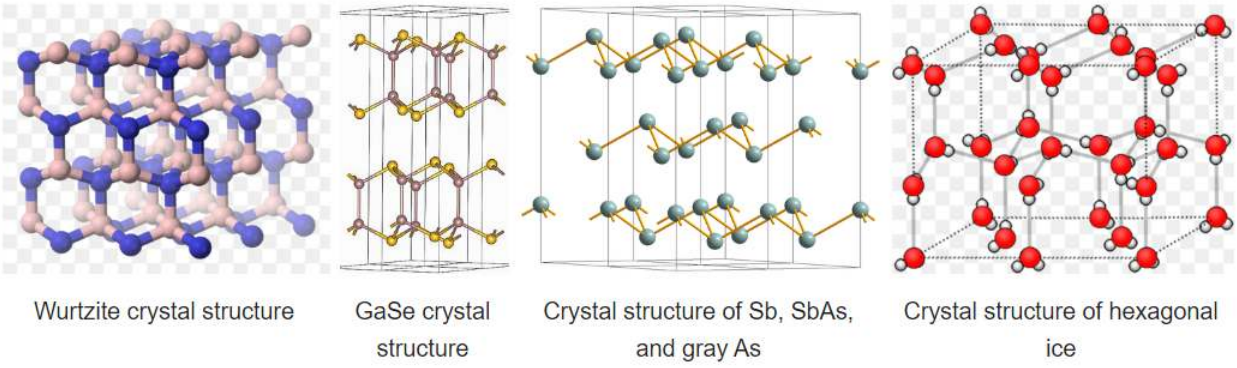


Figure 6.1.12: Different variations of the wurtzite crystal structure (Copyright; author via source)

Hexagonal ice is the most stable polymorph of ice, which is obtained upon freezing at 1 atmosphere pressure. This polymorph (ice-I) has a hcp wurtzite-type structure. Looking at the structure shown at the right, we see that there are irregular arrangements of the O-H---O bonds. In the structure, hydrogen bonding enforces the tetrahedral coordination of each water molecule, resulting in a relatively open structure that is less dense than liquid water. For this reason, ice floats in water.

References

1. Conway, J. H. and Sloane, N. J. A. *Sphere Packings, Lattices, and Groups, 2nd ed.* New York: Springer-Verlag, 1993.
2. Krishna, P. and Verma, A. R. Closed Packed Structures, Chester, UK: International Union of Crystallography, 1981.
3. Petrucci, Ralph H., William S. Harwood, F. Geoffrey Herring, and Jeffry D. Madura. "Crystal Structures" General Chemistry: Principles & Modern Applications, ninth Edition. New Jersey: Pearson Education, Inc., 2007. 501-508.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Brittanie Harbick, Laura Suh, Jenny Fong

This page titled 6.1: Unit Cells is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

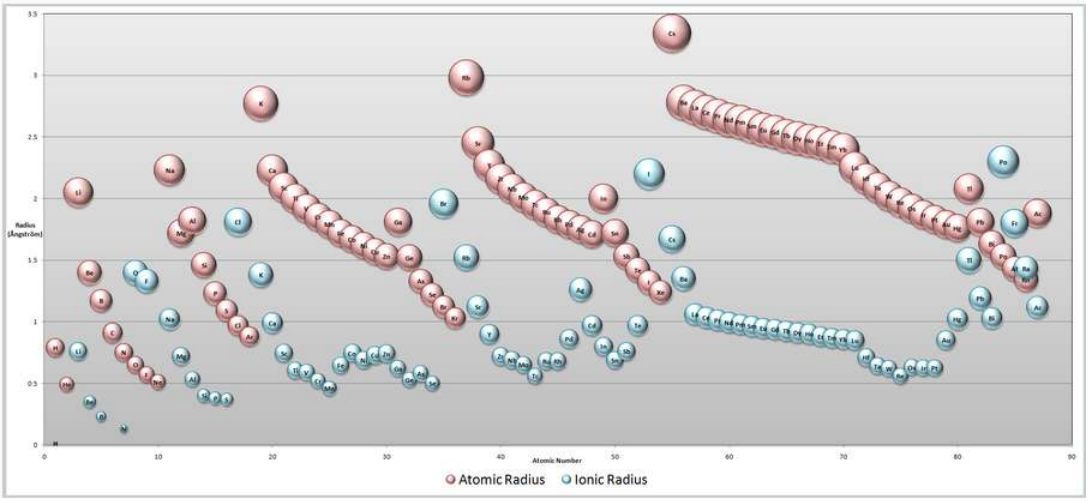
- **5.1: Crystal Structures and Unit Cells** is licensed CC BY-NC-SA 4.0.
- **7.8: Cubic Lattices and Close Packing** by Stephen Lower is licensed CC BY 3.0. Original source: http://www.chem1.com/acad/webtext/virtualtextbook.html.
- **8.2: Close-packing and Interstitial Sites** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.
- **8.4: Tetrahedral Structures** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

6.2: Ionic Radii and Radius Ratios

Atoms in crystals are held together by electrostatic forces, van der Waals interactions, and covalent bonding. It follows that arrangements of atoms that can maximize the strength of these attractive interactions should be most favorable and lead to the most commonly observed crystal structures.

Radius ratio rules

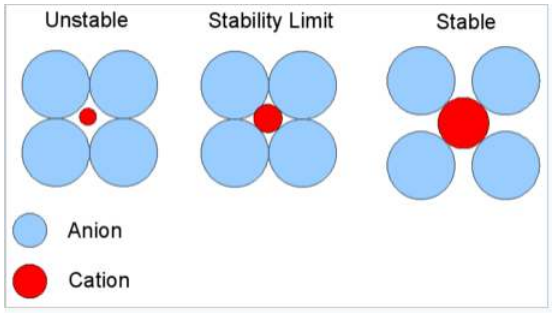
Early crystallographers had trouble solving the structures of inorganic solids using X-ray diffraction because some of the mathematical tools for analyzing the data had not yet been developed. Once a trial structure was proposed, it was relatively easy to calculate the diffraction pattern, but it was difficult to go the other way (from the diffraction pattern to the structure) if nothing was known *a priori* about the arrangement of atoms in the unit cell. It was (and still is!) important to develop some guidelines for guessing the coordination numbers and bonding geometries of atoms in crystals. The first such rules were proposed by Linus Pauling, who considered how one might pack together oppositely charged spheres of different radii. Pauling proposed from geometric considerations that the quality of the "fit" depended on the **radius ratio** of the anion and the cation.



Atomic and Ionic Radii. Note that cations are always smaller than the neutral atom (pink) of the same element, whereas anions are larger. Going from left to right across any row of the periodic table, neutral atoms and cations contract in size because of increasing nuclear charge. (click for larger image)

The basic idea of radius ratio rules is illustrated at the right. We consider that the anion is the packing atom in the crystal and the smaller cation fills interstitial sites ("holes"). Cations will find arrangements in which they can contact the largest number of anions. If the cation can touch all of its nearest neighbor anions, as shown at the right for a small cation in contact with larger anions, then the fit is good. If the cation is too small for a given site, that coordination number will be unstable and it will prefer a

lower coordination structure. The table below gives the ranges of cation/anion radius ratios that give the best fit for a given coordination geometry.



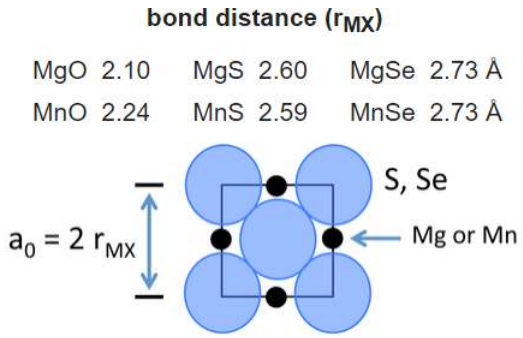
Critical Radius Ratio. This diagram is for coordination number six: 4 anions in the plane are shown, 1 is above the plane and 1 is below. The stability limit is at $r_C/r_A = 0.414$

Coordination number	Geometry	$\rho = r_{cation}/r_{anion}$
2	linear	0 - 0.155
3	triangular	0.155 - 0.225
4	tetrahedral	0.225 - 0.414
4	square planar	0.414 - 0.732
6	octahedral	0.414 - 0.732
8	cubic	0.732 - 1.0
12	cuboctahedral	1.0

There are unfortunately several challenges with using this idea to predict crystal structures:

- We don't know the radii of individual ions
- Atoms in crystals are not really ions - there is a varying degree of covalency depending electronegativity differences
- Bond distances (and therefore ionic radii) depend on bond strength and coordination number (remember Pauling's rule D(n) = D(1) - 0.6 log n)
- Ionic radii depend on oxidation state (higher charge => smaller cation size, larger anion size)

We can build up a table of ionic radii by assuming that the bond length is the sum of the radii ($r_+ + r_-$) if the ions are in contact in the crystal. Consider for example the compounds MgX and MnX, where X = O, S, Se. All of these compounds crystallize in the NaCl structure:



For the two larger anions (S^{2-} and Se^{2-}), the unit cell dimensions are the same for both cations. This suggests that the anions are in contact in these structures. From geometric considerations, the anion radius in this case is given by:

Extra close brace or missing open brace

and thus the radii of the S^{2-} and Se^{2-} ions are 1.84 and 1.93 Å, respectively. Once the sizes of these anions are fixed, we can obtain a self-consistent set of cation and anion radii from the lattice constants of many MX compounds.

How well does this model work? Let's consider the structures of tetravalent metal oxides (MO_2), using Pauling radii and the predictions of the radius ratio model:

Oxide MO_2	Radius ratio	Predicted coord. no.	Observed coord no. (structure)
CO_2	~0.1	2	2 (linear molecule)
SiO_2	0.32	4	4 (various tetrahedral structures)
GeO_2	0.43	4	4 (silica-like structures)
"	0.54	6	6 (rutile)
TiO_2	0.59	6	6 (rutile)
ZrO_2	0.68	6	7 (baddleyite)
"	0.77	8	8 (fluorite)
ThO_2	0.95	8	8 (fluorite)

Note that cations have different radii depending on their coordination numbers, and thus different radius ratios are calculated for Ge^{4+} with coordination numbers 4 and 6, and for Zr^{4+} with coordination numbers 6 and 8.

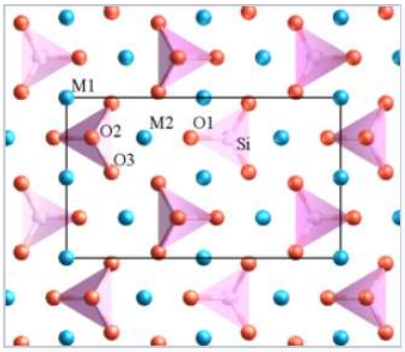
For this series of oxides, the model appears to work quite well. The correct coordination number is predicted in all cases, and borderline cases such as GeO_2 and ZrO_2 are found in structures with different coordination numbers. The model also correctly predicts the structures of BeF_2 (SiO_2 type), MgF_2 (rutile), and CaF_2 (fluorite).

What about the alkali halides NaCl, KBr, LiI, CsF, etc.? All of them have the NaCl structure except for CsCl, CsBr, and CsI, which have the CsCl (8-8) structure. In this case the radius ratio model fails rather badly. The Li^+ salts LiBr and LiI are predicted to have tetrahedral structures, and KF is predicted to have an 8-8 structure like CsCl. We can try adjusting the radii (e.g., making the cations larger and anions smaller), but the best we can do with the alkali halides is predict about half of their structures correctly. Since the alkali halides are clearly ionic compounds, this failure suggests that there is something very wrong with the radius ratio model, and its success with MO_2 compounds was coincidental.

In addition to the radius ratio rule, Linus Pauling developed other useful rules that are helpful in rationalizing and also predicting the structures of inorganic compounds. Pauling's rules[1] state that:

- Stable structures are **locally electroneutral**. For example, in the structure of the double perovskite Sr_2FeMoO_6, MO_6 (M = Fe^{2+}, Mo^{6+}) octahedra share all their vertices, and Sr^{2+} ions fill the cubooctahedral cavities that are flanked by eight MO_6 octahedra.[2] Each O^{2-} ion is coordinated to one Fe^{2+} and one Mo^{6+} ion in order to achieve local electroneutrality, and thus the FeO_6 and MoO_6 octahedra alternate in the structure.
- **Cation-cation repulsion** should be minimized. Anion polyhedra can share vertices (as in the perovskite structure) without any energetic penalty. Shared polyhedral edges, and especially shared faces, cause cation-cation repulsion and should be avoided. For example, in rutile, the most stable polymorph of TiO_2, the TiO_6 octahedra share vertices and two opposite edges, forming ribbons in the structure. In anatase TiO_2, each octahedron shares four edges so the anatase polymorph is less thermodynamically stable.

- **Highly charged cations** in anion polyhedra tend not to share edges or even vertices, especially when the coordination number is low. For example, in orthosilicates such as olivine (M_2SiO_4), there are isolated SiO_4^{4-} tetrahedra.



Structure of olivine. M (Mg or Fe) = blue spheres, Si = pink tetrahedra, O = red spheres.

As we will soon see, all of Pauling's rules are justified on the basis of lattice energy considerations. In ionic compounds, the arrangement of atoms that maximizes anion-cation interactions while minimizing cation-cation and anion-anion contacts is energetically the best.

This page titled 6.2: Ionic Radii and Radius Ratios is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **9.1: Ionic Radii and Radius Ratios** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

6.3: Lattice Energy

Lattice Energy

Many ionic compounds have simple structures. Because the forces holding the atoms together are primarily electrostatic, we can calculate the cohesive energy of the crystal lattice with good accuracy. Interesting questions to ask about these lattice energy calculations are:

- How accurate are lattice energy calculations?
- What do they teach us about the chemical bonds in ionic crystals?
- Can we use lattice energies to predict properties such as solubility, stability, and reactivity?
- Can we use lattice energies to predict the crystal structures of ionic compounds?

Let's start by looking at the forces that hold ionic lattices together. There are mainly two kinds of force that determine the energy of an ionic bond.

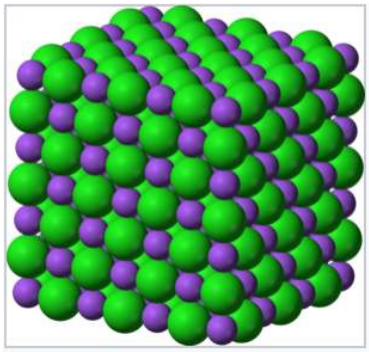


Figure 6.3.1: The NaCl crystal structure is the archetype for calculating lattice energies and computing enthalpies of formation from Born-Haber cycles.

Electrostatic force

Electrostatic force is the attraction and repulsion between ions described by Coulomb's Law. Two ions with charges z_+ and z_-, separated by a distance r, experience a force F:

$$\mathbf{F} = -\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r^2} \tag{6.3.1}$$

where

$e = 1.6022\times10^{-19}$ C

$4\,\pi\,\varepsilon_0 = 1.112\times10^{-10}$ C²/(J m)

This force is attractive for ions of opposite charge and repulsive for ions of the same charge.

Closed-shell repulsion

When electrons in the core shells of one ion overlap with those of another ion, there is a repulsive force due to the Pauli exclusion principle. A third electron cannot enter an orbital that already contains two electrons. This force is short range, and is typically modeled as falling off exponentially or with a high power of the distance r between atoms. For example, in the Born approximation, B is a constant and ρ is a number with units of length, which is usually empirically determined from compressibility data. A typical value of ρ is 0.345 Å.

$$\mathbf{E}_{repulsion} = Bexp(\frac{-r}{\rho}) \tag{6.3.2}$$

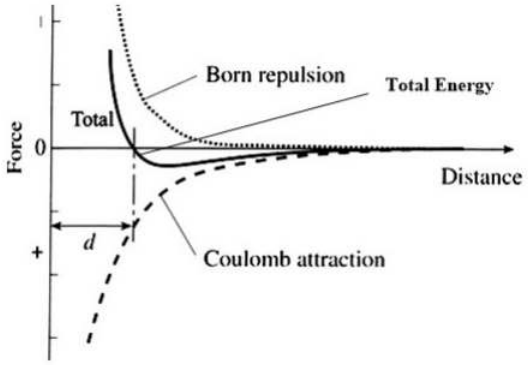


Figure 6.3.2: Total energy of an ionic bond (solid) determined by the combination of Coulombic attraction (dashed) and Born (closed-shell) repulsion (dotted).

The energy of the ionic bond between two atoms is then calculated as the combination of net electrostatic and the closed-shell repulsion energies, as shown in Figure 6.3.2. Note that for the moment we are ignoring the attractive van der Waals forces between ions. For a pair of ions, the equilibrium distance between ions is determined by the minimum in the total energy curve.

Madelung Constant

We can use the above equations to calculate the lattice energy of a crystal by summing up the interactions between all pairs of ions. Because the closed-shell repulsion force is short range, this term is typically calculated only for interactions between neighboring ions. However, the Coulomb force is long range, and must be calculated over the entire crystal. This problem was first solved in 1918 by Erwin Madelung, a German physicist.

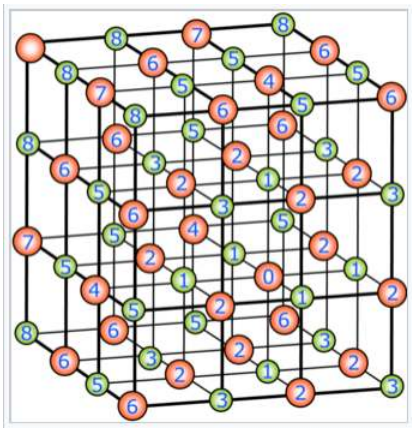


Figure 6.3.3: The Madelung constant is calculated by summing up electrostatic interactions with ion labeled 0 in the expanding spheres method. Each number designates the order in which it is summed. For example, ions labeled 1 represent the six nearest neighbors (attractive interaction), ions labeled 2 are the 12 next nearest neighbors (repulsive interaction) and so on.

Consider an ion in the NaCl structure labeled "0" in Figure 6.3.3. We can see that the nearest neighbor interactions (+ -) with ions labeled "1" are attractive, the next nearest neighbor interactions (- - and + +) are repulsive, and so on. In the NaCl structure, counting from the ion in the center of the unit cell, there are 6 nearest neighbors (on the faces of the cube), 12 next nearest neighbors (on the edges of the cube), 8 in the next shell (at the vertices of the cube), and so on. Their distances from ion "0" increase progressively: r_o, $\sqrt{2}\ r_o$, $\sqrt{3}\ r_o$, and so on, where r_o is the nearest neighbor distance.

We can now write the electrostatic energy at ion "0" as:

$$\mathbf{E}_{elec} = -6\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r_o} + 12\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{\sqrt{2}r_o} - 8\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{\sqrt{3}r_o} + ... \tag{6.3.3}$$

Factoring out constants and the nearest-neighbor bond distance r_o we obtain:

$$\mathbf{E}_{elec} = \frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r_o}(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + ...) \tag{6.3.4}$$

Where the sum in parentheses, which is unitless, slowly converges to a value of A = 1.74756. Generalizing this formula for any three-dimensional ionic crystal we get a function:

$$\mathbf{E}_{elec} = \frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r_o}NA \tag{6.3.5}$$

where N is Avogadro's number (because we are calculating energy per mole of ions) and A is called the *Madelung constant*. The **Madelung constant** depends only on the geometrical arrangement of the ions and so it varies between different types of crystal structures, but within a given structure type it does not change. Thus MgO and NaCl have the same Madelung constant because they both have the NaCl structure.

Table 6.3.1: Madelung Constants

Compound	*Crystal Lattice*	*M*	*A : C*	*Type*
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244	6 : 3	
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132	4 : 4	Wurtzite
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
$bSiO_2$	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Born–Landé Equation

There are other factors to consider for the evaluation of lattice energy and the treatment by Max Born and Alfred Lande led to the formula for the evaluation of lattice energy for a mole of **crystalline solid**. The Born–Landé equation (Equation 6.3.6) is a means of calculating the lattice energy of a crystalline ionic compound and derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term

$$U = \frac{N_A M Z^2 e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{6.3.6}$$

where

- N_A is Avogadro constant;
- M is the Madelung constant for the lattice
- z^+ is the charge number of cation
- z^- is the charge number of anion
- e is elementary charge, 1.6022×10^{-19} C
- ε_0 is the permittivity of free space
- r_0 is the distance to closest ion
- n is the **Born exponent** that is typically between 5 and 12 and is determined experimentally. n is a number related to the electronic configurations of the ions involved (Table 6.3.3).

Table 6.3.2: n values for select solids

Atom/Molecule	*n*
He	5
Ne	7
Ar	9
Kr	10
Xe	12
LiF	5.9
LiCl	8.0
LiBr	8.7
NaCl	9.1
NaBr	9.5

Example 6.3.1: NaCl

Estimate the lattice energy for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by

$$U_{NaCl} = \frac{(6.022 \times 10^{23}/mol)(1.74756)(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12}C^2/m)(282 \times 10^{-12}\ m)}\left(1 - \frac{1}{9.1}\right)$$
$$= -756\,kJ/mol$$

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Hable cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.



Figure 6.3.4: Lithium fluoride (shown here as a large single crystal in a beaker of water) is the only alkali halide that is not freely soluble in water. The lattice energy of LiF is the most negative of the alkali fluorides because Li^+ and F^- are both small ions and lattice energy is proportional to $1/r_0$.

This page titled 6.3: Lattice Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

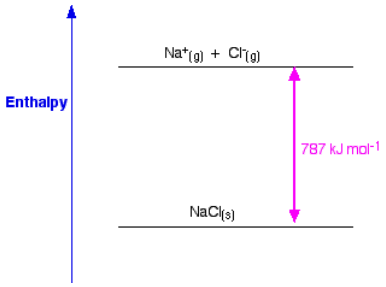
- **5.2: Energetics of Ionic Solids- Lattice Energy** is licensed CC BY-NC-SA 4.0.
- **9.3: Energetics of Crystalline Solids- The Ionic Model** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.
- **6.13E: Madelung Constants** is licensed CC BY-NC-SA 4.0.

6.4: Born-Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

Factors affecting Lattice Enthalpy

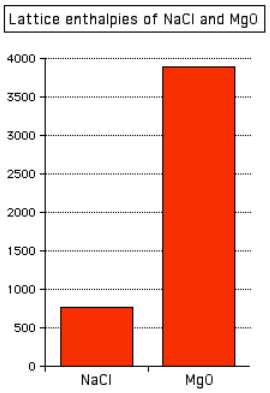
The two main factors affecting lattice enthalpy are

- The charges on the ions and

- The ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

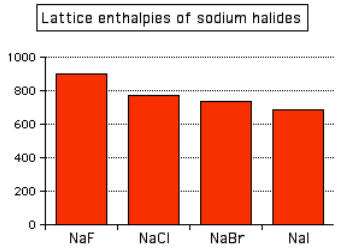


You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

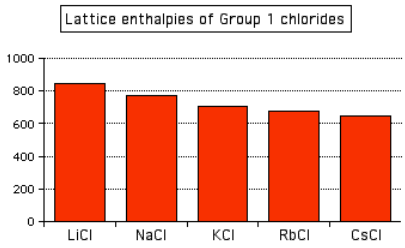
The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:



Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart shows the lattice enthalpies of the Group 1 chlorides.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

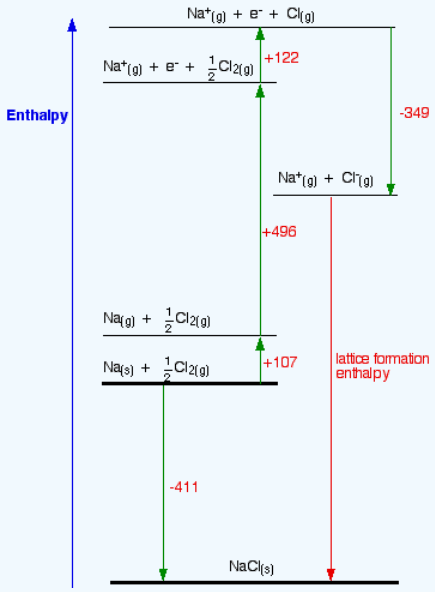
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\,kJ\,mol^{-1}$$

Notice particularly that the "mol^{-1}" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

Example 6.4.1: Born-Haber Cycle for NaCl

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

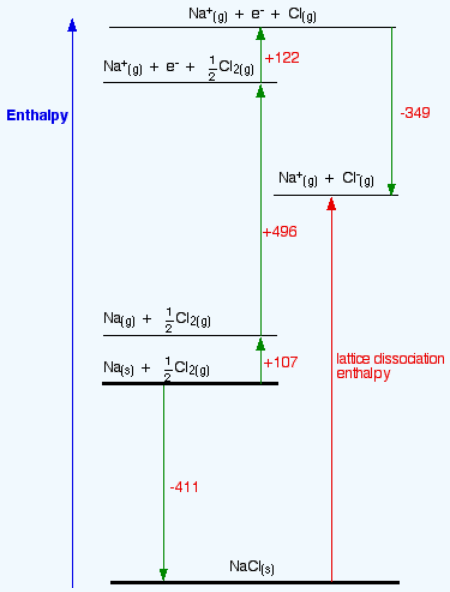
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

Theoretical Estimates of Lattice Energies

Let's assume that a compound is fully ionic. Let's also assume that the ions are point charges - in other words that the charge is concentrated at the center of the ion. By doing physics-style calculations, it is possible to calculate a theoretical value for what you would expect the lattice energy to be. Calculations of this sort end up with values of *lattice energy*, and not *lattice enthalpy*. If you know how to do it, you can then fairly easily convert between the two.

There are several different equations, of various degrees of complication, for calculating lattice energy in this way. There are two possibilities:

- There is reasonable agreement between the experimental value (calculated from a Born-Haber cycle) and the theoretical value. Sodium chloride is a case like this - the theoretical and experimental values agree to within a few percent. That means that for sodium chloride, the assumptions about the solid being ionic are fairly good.
- The experimental and theoretical values do not agree. A commonly quoted example of this is silver chloride, AgCl. Depending on where you get your data from, the theoretical value for lattice enthalpy for AgCl is anywhere from about 50 to 150 kJ mol^{-1} less than the value that comes from a Born-Haber cycle. In other words, treating the AgCl as 100% ionic underestimates its lattice enthalpy by quite a lot.

The explanation is that silver chloride actually has a significant amount of covalent bonding between the silver and the chlorine, because there is not enough electronegativity difference between the two to allow for complete transfer of an electron from the silver to the chlorine. Comparing experimental (Born-Haber cycle) and theoretical values for lattice enthalpy is a good way of judging how purely ionic a crystal is.

Example 6.4.2: Born-Haber Cycle for $MgCl_2$

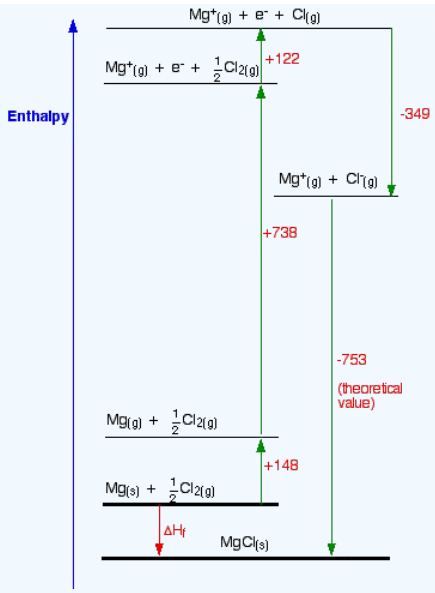
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine.

Let's look at this in terms of Born-Haber cycles of and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$\mathrm{Mg\,(s)} + \tfrac{1}{2}\,\mathrm{Cl_2\,(g)} \rightarrow \mathrm{MgCl\,(s)}$$



Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

2. The Born-Haber cycle for $MgCl_2$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg\,(s) + Cl_2\,(g) \ \rightarrow MgCl_2\,(s)}$$

So how does that change the numbers in the Born-Haber cycle?

- You need to add in the second ionization energy of magnesium, because you are making a 2+ ion.
- You need to multiply the atomization enthalpy of chlorine by 2, because you need 2 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 2, because you are making 2 moles of chloride ions.
- You obviously need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
atomization enthalpy of Cl (x 2)	+244
electron affinity of Cl (x 2)	-698
lattice enthalpy	-2526
calculated ΔH_f	-643

You can see that much more energy is released when you make $MgCl_2$ than when you make MgCl. Why is that? You need to put in more energy to ionize the magnesium to give a 2+ ion, but a lot more energy is released as lattice enthalpy. That is because there are stronger ionic attractions between 1- ions and 2+ ions than between the 1- and 1+ ions in MgCl. So what about $MgCl_3$? The lattice energy here would be even greater.

3. The Born-Haber cycle for $MgCl_3$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg\,(s)} + \tfrac{3}{2}\,\mathrm{Cl_2\,(g)} \rightarrow \mathrm{MgCl_3\,(s)}$$

So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a 3+ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.
- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of $MgCl_3$ to form!

Look carefully at the reason for this. The lattice enthalpy is the **highest** for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium.

Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so

much more energy is needed to remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

Magnesium chloride is $MgCl_2$ because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 6.4: Born-Haber Cycles is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **Lattice Enthalpies and Born Haber Cycles** by Jim Clark is licensed CC BY-NC 4.0.

SECTION OVERVIEW

6.5: Ionic Lattices - Examples

Topic hierarchy

6.5A: Structure - Rock Salt (NaCl)

6.5B: Structure - Caesium Chloride (CsCl)

6.5C: Structure - Fluorite and Antifluorite

6.5D: Structure - Zinc Blende (ZnS)

This page titled 6.5: Ionic Lattices - Examples is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

6.5A: Structure - Rock Salt (NaCl)

Rock salt also known as NaCl is an ionic compound. It occurs naturally as white cubic crystals. The structure of NaCl is formed by repeating the unit cell. It has an organized structure and has a 1:1 ratio of Na:Cl.

Introduction

Rock salt (NaCl) is an ionic compound that occurs naturally as white crystals. It is extracted from the mineral form halite or evaporation of seawater. The structure of NaCl is formed by repeating the face centered cubic unit cell. It has 1:1 stoichiometry ratio of Na:Cl with a molar mass of 58.4 g/mol. Compounds with the sodium chloride structure include alikali halides and metal oxides and transition-metal compounds. An important role to many important applications is structure and dynamics of water. Some applications include crystallization of proteins and conformational behavior of peptides and nucleic acids.

Structure

Figure $6.5A.1$ shows how the Na^+ and Cl^- ions occupy the space. The smaller ions are the Na^+ with has an atomic radius of 102 pm, and the larger ions are the Cl^- with an atomic radium of 181 pm. Since NaCl are one to one ratio as a compound, the coordination numbers of Na and Cl are equal. The larger green ions represent Cl^- and the smaller purple ions represent Na^+. However, the structure of this molecule allows their positions to be switched since the coordination numbers are equivalent.

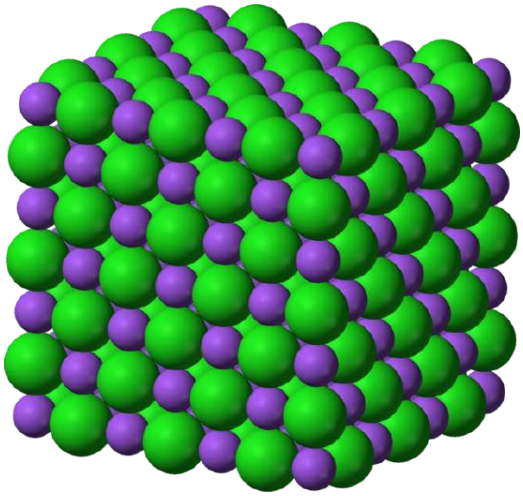


Figure $6.5A.1$: The crystal structure of sodium chloride, NaCl, a typical ionic compound. The smaller purple spheres represent sodium cations, $\mathrm{Na^+}$, and the larger green spheres represent chloride anions, $\mathrm{Cl^-}$. (Public Domain; Benjah-bmm27 via Wikipedia)

A Unit Cell

The unit cell of NaCl consists of $\mathrm{Na^+}$ ions and $\mathrm{Cl^-}$ ions. There are four types of site: unique central position, face site, edge sites and corner site, which are used to determine the number of Na^+ ions and Cl^- ions in the unit cell of NaCl. When counting the number of ions, a corner site would be shared by 7 other unit cells. Therefore, 1 corner would be 1/8 of an ion. A similar occurrence happens with the face site and the edge sites. For a face site, it is shared by 1 other unit cell and for an edge site, the ion is shared by 3 other unit cells. NaCl is a face centered cubic unit cell which has four cations and four anions. This can be shown by counting the number of ions and multiplying them in relation to their position.

- $\mathrm{Na^+}$:

$$1_{center} + 12_{edge} \times \frac{1}{4} = 4 \,\text{sodium ions total per cell}$$

- $\mathrm{Cl^-}$:

$$4_{face} \times \frac{1}{2} + 8_{corner} \times \frac{1}{8} = 4 \,\text{chloride ions total per cell}$$

Each ion in this lattice has six of the other kind of ion as its nearest neighbors, and twelve of the same kind of ions as its second nearest neighbors. There are many ionic compounds that assume this structure including all other halides of Na, Li, K and Rb. CsF, AgF, AgCl, BaO, CoO, and SrS are also among many that will form similar structures to NaCl.

Outside Links

- Video about structure of NaCl: http://www.youtube.com/watch?v=csfOBynrF8E
- Unit Cell. http://www.case.edu/artsci/chem/chim...ids/xtal1.html

References

1. Gao, H.X., L.-M. Peng, and J.M Zuo. "Lattice dynamics and Debye-Waller factors of some compounds with the sodium chloride structure." *Acta Crystallographica: Section A (Wiley-Blackwell)* 55.6 (1999): 1014. *Academic Search Complete*. EBSCO. Web.
2. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print.
3. Jun Soo, Kim, and Yethiraj Arun. "A Diffusive Anomaly of Water in Aqueous Sodium Chloride Solutions at Low Temperatures." *Journal of Physical Chemistry B* 112.6 (2008): 1729-1735. *Academic Search Complete*. EBSCO. Web.

Contributors and Attributions

- Michael Ford

This page titled 6.5A: Structure - Rock Salt (NaCl) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **6.11A: Structure - Rock Salt (NaCl)** is licensed CC BY-NC-SA 4.0.

6.5B: Structure - Caesium Chloride (CsCl)

This page is going to discuss the structure of the molecule cesium chloride ($CsCl$), which is a white hydroscopic solid with a mass of 168.36 g/mol. Cesium Chloride is a type of unit cell that is commonly mistaken as Body-Centered Cubic. This misconception is easy to make, since there is a center atom in the unit cell, but CsCl is really a **non-closed packed structure** type.

Introduction

CsCl has a boiling point of 1303 degrees Celsius, a melting point of 646 degrees Celsius, and is very soluble in water. For the most part this molecule is stable, but is not compatible with strong oxidizing agents and strong acids. Although it is not hazardous, one should not prolong their exposure to CsCl. CsCl is an ionic compound that can be prepared by the reaction:

$$Cs_2CO_3 + 2\,HCl \longrightarrow 2\,CsCl + H_2O + CO_2 \tag{6.5B.1}$$

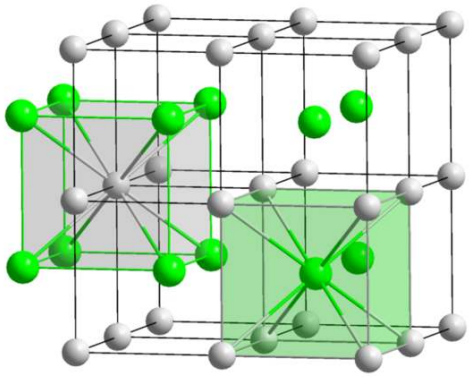


Figure $6.5B.1$: $CsCl$ Coordination Cubes. (Public Domain; Solid State via Wikipedia)

CsCl crystallize in a primitive cubic lattice which means the cubic unit cell has nodes only at its corners. The structure of CsCl can be seen as two interpenetrating cubes, one of Cs^+ and one of Cl^-. The ions are not touching one another. Touching would cause repulsion between the anion and cation. Some may mistake the structure type of CsCl with NaCl, but really the two are different. CsCl is more stable than NaCl, for it produces a more stable crystal and more energy is released.

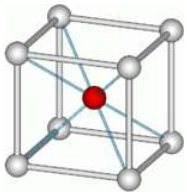


Figure $6.5B.2$: Unit Cell of CsCl (en.Wikipedia.org/wiki/Caesium_chloride

Anions and cations have similar sizes. Each Cs^+ is surrounded by 8 Cl^- at the corners of its cube and each Cl^- is also surrounded by 8 Cs^+ at the corners of its cube. The cations are located at the center of the anions cube and the anions are located at the center of the cations cube. There is one atom in CsCl. To determine this, the following equation is given:

8 Corners of a given atom x 1/8 of the given atom's unit cell = 1 atom

Applications

Cesium chloride is used in centrifugation, a process that uses the centrifugal force to separate mixtures based on their molecular density. It is also used in the preparation of electrically conducting glasses. Radioactive CsCl is used in some types of radiation therapy for cancer patients, although it is blamed for some deaths.

References

1. Carter, C. Barry., and M. Grant. Norton. "Binary Compounds." *Ceramic Materials Science and Engineering*. New York, NY: Springer, 2007. pg87-88
2. Quéré, Yves. "Stable Structure of Halides." *Physics of Materials*. Amsterdam: Gordon and Breach Science, 1998.

Contributors and Attributions

- Ana Popovich

This page titled 6.5B: Structure - Caesium Chloride (CsCl) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **6.11B: Structure - Caesium Chloride (CsCl)** is licensed CC BY-NC-SA 4.0.

6.5C: Structure - Fluorite and Antifluorite

Fluorite

Calcium Fluoride is a solid and forms a cube like structure that is centralized around the calcium molecules. The crystal lattice structure that Calcium Fluoride is also known as the fluorite structure (Figure $6.5C.1$) where the Ca^{2+} ions are eight-coordinate, being centered in a cube of eight F^- ions. Each F^- is coordinated to four Ca^{2+} in the shape of a tetrahedron.

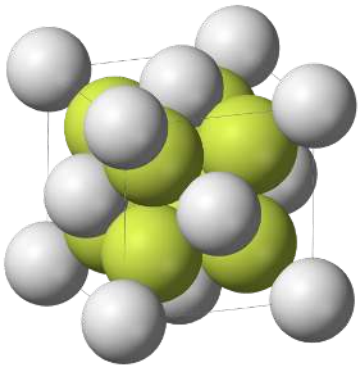


Figure $6.5C.1$: Fluorite unit cell. (Public Domain; Benjah-bmm27 via Wikipedia)

When Calcium Fluoride is in a single molecule it forms a Quasilinear structure. Quasilinear means the molecule resonates between a linear shape and a bent shape.Calcium Fluoride is a polyatomic molecule that contains one calcium molecule and two fluoride molecules. Calcium Fluoride is a quasilinear molecule the bonds are created from the single electrons of calcium and the single electron from fluoride. CaF_2 has its electrons contained with in the 3d orbitals and are able to move between d_{yz} and d_z^2 squared. The molecule in linear when they are in the d_z^2 orbitals the molecule is also the most stable in this shape. When the electrons are in the d_{yz} orbitals the molecule becomes bent. The molecule resonates between these two shapes making it quasilinear.

Antifluorite

Antifluorite is a mineral with a crystal structure identical with that of fluorite but with the positions of the cations and anions reversed (Figure $6.5C.2$).

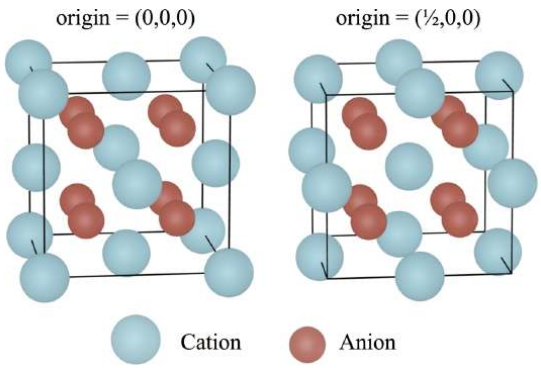


Figure $6.5C.2$: Unit cell of the fluorite structure, from two equivalent perspectives. In the antifluorite structure, the blue positions are taken by the anion, the red positions by the cation. (CC BY-SA 4.0; Paburr via source)

The same crystal structure is found in numerous ionic compounds with formula AB2, such as ceria (CeO2), zirconia (cubic ZrO2), uranium dioxide (UO2). In the corresponding anti-structure, called the antifluorite structure, anions and cations are swapped, such as beryllium carbide (Be2C) or lithium oxide (Li2O), potassium sulfate (K2SO4).

Contributors and Attributions

- en.Wikipedia.org/wiki/Anti-structure

This page titled 6.5C: Structure - Fluorite and Antifluorite is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **6.11C: Structure - Fluorite (CaF_2)** is licensed CC BY-NC-SA 4.0.
- **6.11D: Structure - Antifluorite** is licensed CC BY-NC-SA 4.0.

6.5D: Structure - Zinc Blende (ZnS)

ZnS has a unique structure type compared to other molecules, having different types of unique structures. ZnS can have a zinc blende structure which is a "diamond-type network" and at a different temperature, ZnS can become the wurtzite structure type which has a hexagonal type symmetry. Structure-wise, the zinc blende structure is more thermodynamically favored, however, because of the wurtzite structures slow construction, both forms of ZnS can be found.

Summary: Zinc blend is a compound that comes in two forms: sphalerite and wurtzite. These are characterized by a 1:1 stoichiometric ratio of Zinc to Sulfur. It maintains a tetrahedral arrangement in both forms.

Introduction

Zinc sulfide (ZnS) is a unique compound that forms two types of crystalline structures. These two polymorphs are wurtzite and zincblende (also known as sphalerite). Wurtzite has a hexagonal structure, while zincblende is cubic. It is characterized by single bonds between each atom and maintenance of a 1:1 zinc to sulfur ratio.

sphalerite:

Site	Zn	S
Central	4	0
Face	0	6(1/2) = 3
Corner	0	8(1/8) = 1
Total	4	4

Since the number of atoms in a single unit cell of Zn and S is the same, it is consistent with the formula ZnS.

The ionic radius for Zn^{2+} is 74pm and for S^{2-} is 190pm. Therefore the ratio between cationic and anionic radii in zinc blend is 0.39 (74pm/190 pm) .This suggests a tetrahedral ion arrangement and four nearest neighbors from standard crystal structure prediction tables. Therefore, four sulfur atoms surround each zinc atom and four zinc atoms surround each sulfur atom.$_2$ The coordination number, the number of of electron pairs donated to a metal by its ligands, for both zinc an sulfur is four.[1,2] The difference between wurtzite and zincblende lies in the different arrangements of layers of ions.[2]

Zincblende (Sphalerite)

Zincblende is characterized as a **cubic closet packing** (ccp), also known as face-centered cubic, structure.[1,4] This crystal lattice structure is shown in Figures 1 & 2 below.

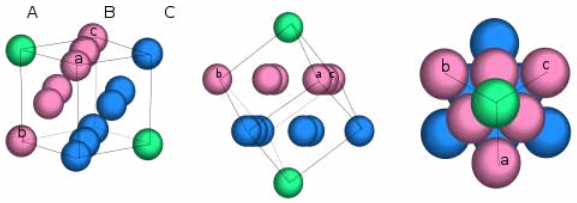


Fig. 1. A break down of cubic closest packing. (Author: Maghémite Date: May 5, 2008. Licensed under the Creative Commons Attribution-Share Alike 3.0 Unported, 2.5 Generic, 2.0 Generic and 1.0 Generic license.)

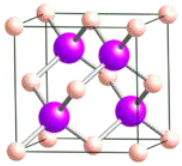


Fig. 2. A representation of ccp structure. (from Public Domain)

Notice how only half of the tetrahedral sites are occupied.

Thermal stability

Density tends to decrease as temperature increases. In this case, since ccp structures are more dense than hcp structures, so a conversion from sphalerite to wurtzite occurs naturally over time at a rate similar to that of diamond to graphite. The sphalerite structure is favored at 298k by 13kJ/mol, but at 1296K the transition to wurtzite occurs.[3]

Wurtzite

Wurtzite has a hexagonal closest packing structure (hcp), which is characterized by 12 ions in the corners of each unit that create a hexagonal prism (seen in Fig. 3).[2] As discussed previously, zincblende slowly transforms to wurtzite due to thermodynamic stability.

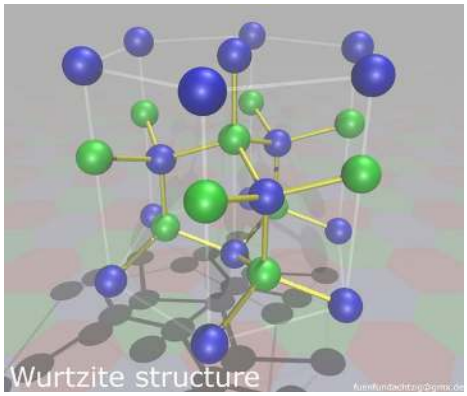


Fig 3. HCP structure of wurtzite. (Creator: Alexander Mann Date: 01/14/2006 Licensed under the Creative Commons Attribution-Share Alike 2.0 Germany license)

Calculating density of a crystal structure

Density = Mass of unit cell / volume of unit cell.

where:

Mass of unit cell = Number of atoms in a unit cell x the mass of each atom

volume of unit cell = $a^3 \times 10^{-30}$

Contributors and Attributions

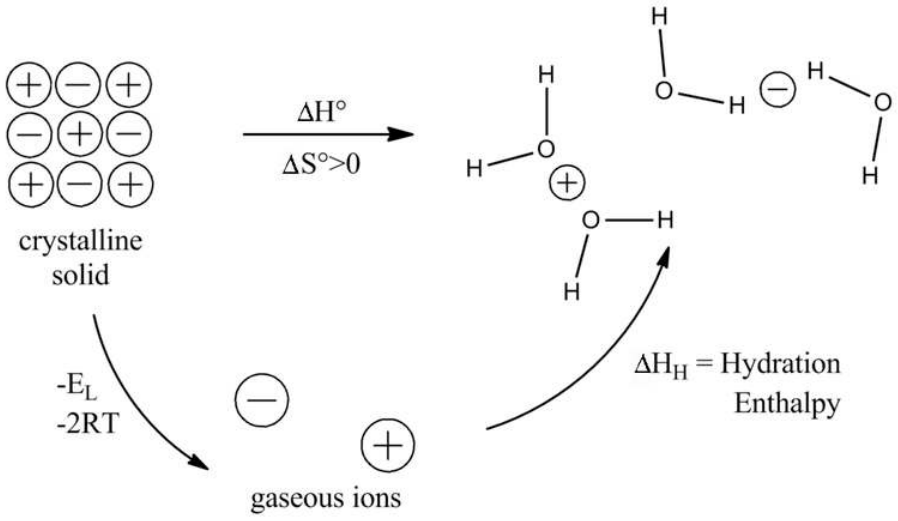
- Emma Mele, UC Davis Animal Biology

This page titled 6.5D: Structure - Zinc Blende (ZnS) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **6.11E: Structure - Zinc Blende (ZnS)** is licensed CC BY-NC-SA 4.0.

6.6: Lattice Energy and Solubility

Lattice energies can also help predict compound solubilities. Let's consider a Born-Haber cycle for dissolving a salt in water. We can imagine this as the sum of two processes: (1) the vaporization of the salt to produce gaseous ions, characterized by the lattice enthalpy, and (2) the hydration of those ions to produce the solution. The enthalpy change for the overall process is the sum of those two steps. We know that the entropy change for dissolution of a solid is positive, so the solubility depends on the enthalpy change for the overall process.



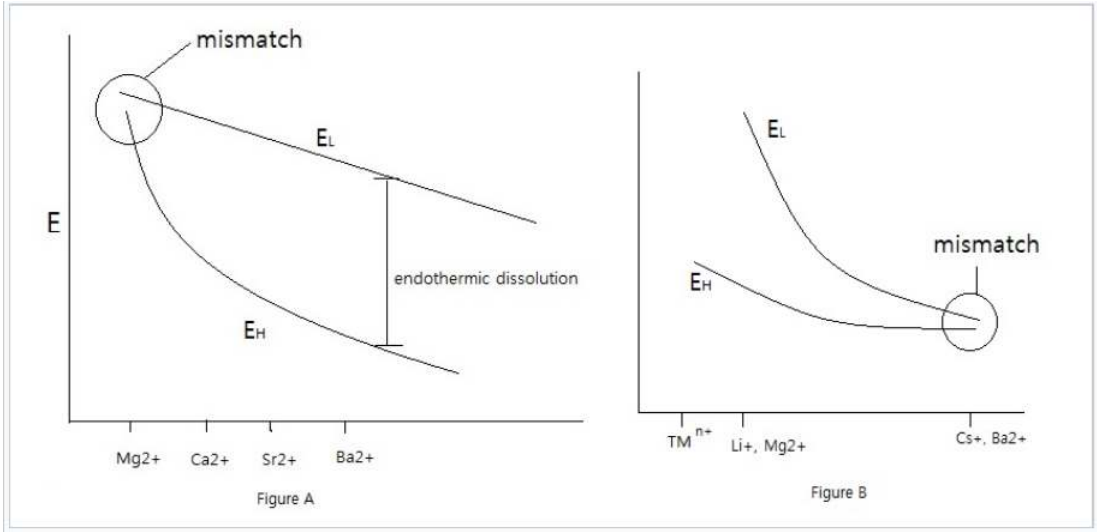
Here we need to consider the trends in both the lattice energy E_L and the hydration energy E_H. The lattice energy depends on the sum of the anion and cation radii ($r_+ + r_-$), whereas the hydration energy has separate anion and cation terms. Generally the solvation of small ions (typically cations) dominates the hydration energy because of the $1/r^2$ dependence.

$$E_L \alpha \frac{1}{r_+ + r_-} \tag{6.6.1}$$

$$E_H \alpha \frac{1}{r_+^2} + \frac{1}{r_-^2} \tag{6.6.2}$$

For salts that contain large anions, E_L doesn't change much as r_+ changes. That is because the anion dominates the $r_+ + r_-$ term in the denominator of the formula for E_L. On the other hand, E_H changes substantially with r_+, especially for small cations.

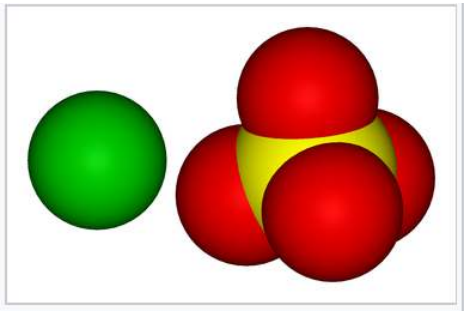
As a result, sulfate salts of small divalent cations, such as $MgSO_4$ (epsom salts), are soluble, whereas the lower hydration energy of Ba^{2+} in $BaSO_4$ makes that salt insoluble ($K_{sp} = 10^{-10}$).



Left: E_L diagram for sulfate salts. The large SO_4^{2-} ion is size-mismatched to small cations such as Mg^{2+}, which have large hydration energies, resulting soluble salts. With larger cations such as Ba^{2+}, which have lower E_H, the lattice energy exceeds the solvation enthalpy and the salts are insoluble.. Right: In the case of small anions such as F^- and OH^-, the lattice energy dominates with small cations such as transition metal ions (TM^{n+}), Mg^{2+}, and Li^+. Anion-cation size mismatch occurs with larger cations, such as Cs^+ and Ba^{2+}, which make soluble fluoride salts.

For small anions, E_L is more sensitive to r_+, whereas E_H does not depend on r_+ as strongly. For fluorides and hydroxides, LiF is slightly soluble whereas CsF is very soluble, and $Mg(OH)_2$ is insoluble whereas $Ba(OH)_2$ is very soluble.

Putting both trends together, we see that **low solubility** is most often encountered when the **anion and cation match well in their sizes**, especially when one or both are **multiply charged**.



Space-filling models showing the van der Waals surfaces of Ba^{2+} and SO_4^{2-}. The similarity in size of the two ions contributes to the low solubility of $BaSO_4$ in water.

Combining all our conclusions about solubility, we note the following trends:

1) Increasing **size mismatch** between the anion and cation leads to greater solubility, so CsF and LiI are the most soluble alkali halides.

2) Increasing **covalency** leads to lower solubility in the salts (due to larger E_L. For example, AgF, AgCl, AgBr, and AgI exhibit progressively lower solubility because of increasing covalency.

$$AgF > AgCl > AgBr > AgI$$

3) Increasing the **charge on the anion** lowers the solubility because the increase in E_L is large relative to the increase in E_H.

4) Small, polyvalent cations (having large E_H) make **soluble salts with large, univalent anions** such as I^-, NO_3^-, ClO_4^-, PF_6^-, and acetate.

Examples: Salts of transition metal and lanthanide ions

- Ln^{3+}: Nitrate salts are soluble, but oxides and hydroxides are insoluble.
- Fe^{3+}: Perchlorate is soluble, but sulfate is insoluble.

5) Multiple charged anions such as O^{2-}, S^{2-}, PO_4^{3-}, and SO_4^{2-} make insoluble salts with most M^{2+}, M^{3+}, and M^{4+} metals.

This page titled 6.6: Lattice Energy and Solubility is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

- **9.12: Lattice Energies and Solubility** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.
- **5.4: Lattice Energy and Solubility** is licensed CC BY-SA 4.0.

6.7: Solubility Equilibria

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{6.7.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2}{[\mathrm{Ca}_3(\mathrm{PO}_4)_2]} \tag{6.7.2}$$

$$[\mathrm{Ca}_3(\mathrm{PO}_4)_2]K = K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2 \tag{6.7.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 6.7.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 6.7.2 and 6.7.3, changes in pH can affect the solubility of a compound as discussed later.

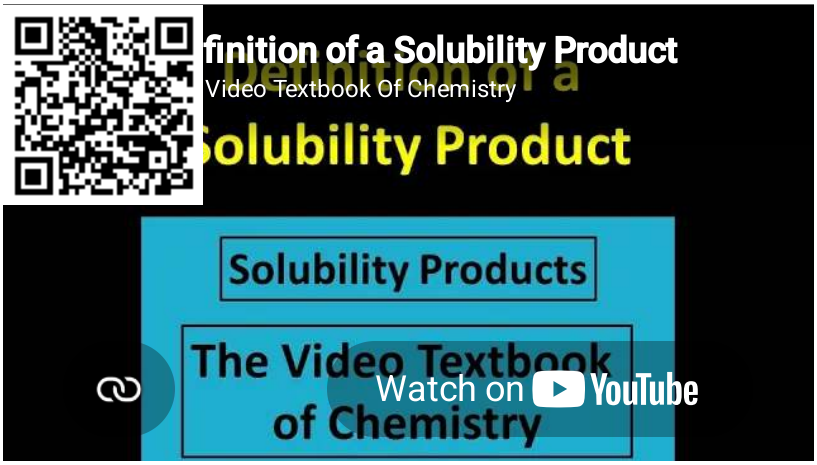
> *As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table 6.7.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2 \cdot 3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates				$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		
Chlorides				Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}		**Sulfates**		
Chromates				Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
Fluorides				**Sulfides**		
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
Hydroxides				PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				

*These contain the Hg_2^{2+} ion.

https://chem.libretexts.org/@go/page/537267



Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 6.7.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)\cdot H_2O$, also written as $CaC_2O_4\cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.

B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l) \quad K_{sp} = [Ca^{2+}][ox^{2-}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine [Ca^{2+}] and [ox^{2-}] at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 6.7.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calcite its K_{sp}.

Answer

4.5×10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 6.7.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 6.7.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.

B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 6.7.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \quad (6.7.4)$$
$$2.07 \times 10^{-33} = 108x^5 \quad (6.7.5)$$
$$1.92 \times 10^{-35} = x^5 \quad (6.7.6)$$
$$1.14 \times 10^{-7}\ \text{M} = x \quad (6.7.7)$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

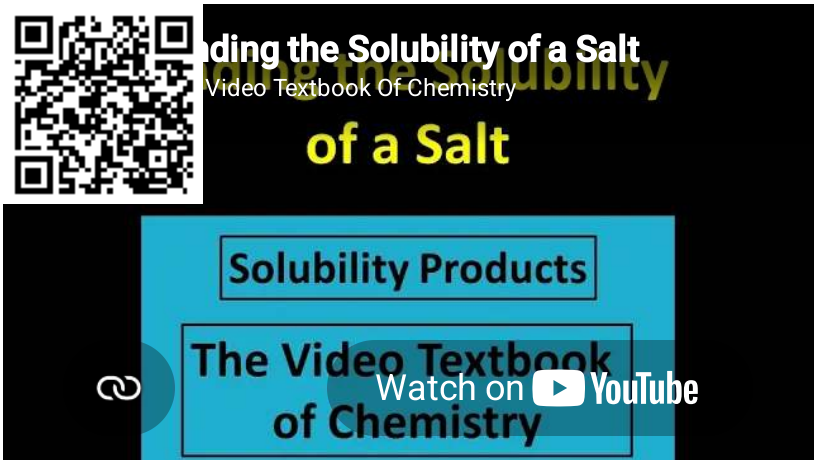
? Exercise 6.7.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg



Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

> *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure 6.7.1, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.

- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

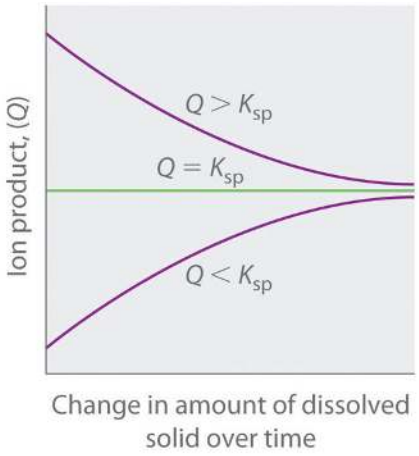


Figure 6.7.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 6.7.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.

B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).

C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

? Exercise 6.7.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)



Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of

$Ca_3(PO_4)_2$ in water contains 3 × (1.14 × 10^{-7} M) = 3.42 × 10^{-7} M Ca^{2+} and 2 × (1.14 × 10^{-7} M) = 2.28 × 10^{-7} M PO_4^{3-}, according to the stoichiometry shown in Equation 6.7.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 6.7.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *The common ion effect usually **decreases** the solubility of a sparingly soluble salt.*

Example 6.7.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again +3x, and the change in $[PO_4^{3-}]$ is +2x. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	Ca3(PO4)2	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	+3x	+2x
final	pure solid	0.20 + 3x	2x

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that x << 0.20. Thus (0.20 + 3x) M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ \text{M} \end{aligned}$$

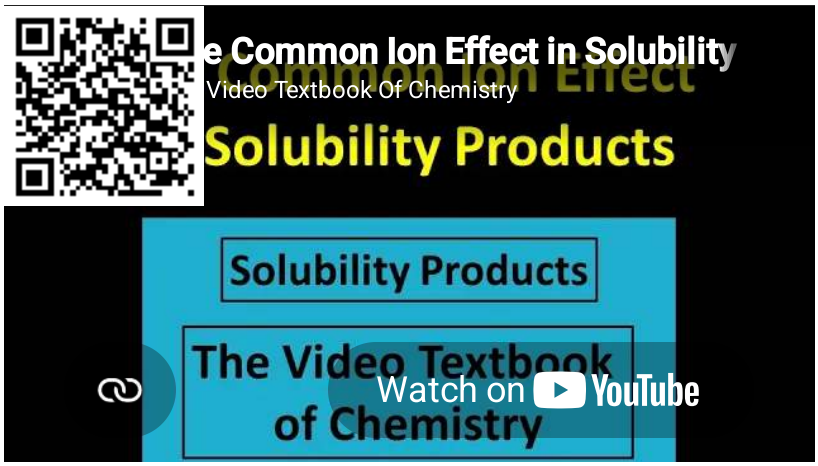
This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 6.7.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 6.7.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45 × 10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

This page titled 6.7: Solubility Equilibria is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **17.4: Solubility Equilibria** is licensed CC BY-NC-SA 3.0.

CHAPTER OVERVIEW

7: Coordination Compounds

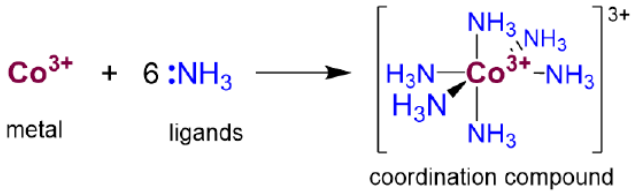
7.1: Coordination Compounds
7.2: Lewis Acids and Bases
7.3: Nomenclature and Ligands
7.4: Structures
7.5: Isomerism
7.6: Complex-Ion Equilibria
7.7: Hard-Soft Acid-Base Theory

This page titled 7: Coordination Compounds is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

7.1: Coordination Compounds

What is a coordination compound?

Coordination compounds consist of one or more **metals** bound to one or more Lewis base **ligands**. For example, hexammineruthenium (3+) ion is a coordination complex in which six ammonia ligands coordinate a Co^{3+} ion, as shown in Scheme 7.1.1.



Scheme 7.1.1: Formation of hexammineruthenium(3+) ion from Co^{3+} and NH_3. (CC BY 4.0; Stephen Contakes)

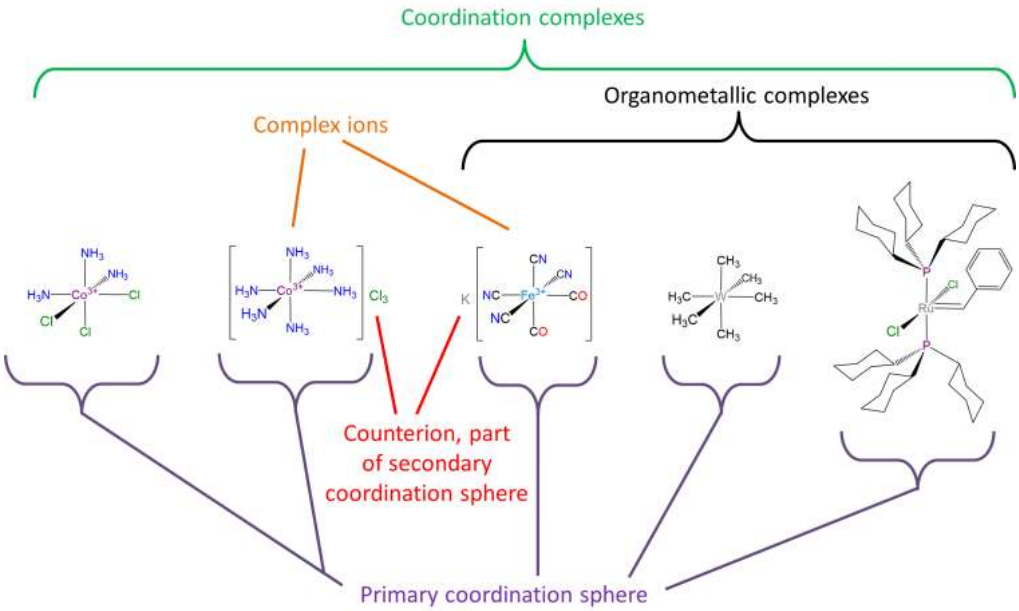
Such complexes are called coordination complexes because the ligand-metal bond may be thought of as a **coordinate covalent bond** in which both of the bonding electrons come from the ligand, which is then said to **coordinate** the metal. This coordinate covalent model is a very useful formalism for understanding the basic features of coordination chemistry, although it does not always accurately reflect the actual details of the bonding in every coordination complex. Nevertheless, even in those cases where the simple coordinate covalent bond model breaks down, the coordinate covalent bond concept supplies the language sophisticated models employ to describe the more complex bonding involved.

Additional important terms

Some of the common widely used terms that follow from the coordinate covalent model of bonding in coordination complexes include:

- Coordination compounds are also called **coordination complexes**, **metal complexes**, or just **complexes**. The term **complex** refers to coordination compounds' composite nature, in that they may be thought of as comprising multiple ligand and metal ion parts that can be restored by breaking the coordinate covalent bonds holding the complex together. This is in contrast to inorganic or organic molecules which are more commonly thought about as whole molecules held together by the sharing of electrons contributed by all the atoms.
- Coordination complexes that are ions are called **complex ions.**
- Ligands bound to the coordination complex are said to reside in the **primary** or **inner coordination sphere**. These bound ligands are not readily exchangeable, in contrast to nearby counterions and solvent molecules, which are said to reside in the **secondary** or **outer coordination sphere**.
- The portion of the complex contributing the electron pairs is said to be the **donor** and the portion which receives them the **acceptor**. In conventional coordination compounds the ligand is the donor and the metal the acceptor. In these cases it would be equally convenient to refer to the ligand donor as the Lewis base and the metal acceptor as the Lewis acid. However, in more complex bonding scenarios there may be multiple electron pair donation and acceptance interactions taking place between each pair of atoms and donor-acceptor language will be more convenient.
- The number of ligand sites donating lone pairs to the central atom is referred to as the **coordination number**. For most complexes this will just be equal to the number of ligand atoms bound to the metal. In simple complexes it is just equal to the number of ligands. For instance, the cobalt in Scheme 7.1.1 has a coordination number of six.
- Although technically compounds with metal-carbon bonds are coordination complexes, the term coordination complex is sometimes used to refer to complexes which do not possess metal-carbon bonds in their primary coordination sphere. Complexes which possess metal-carbon bonds are called **organometallic compounds** instead. The use of the terms organometallic and coordination to distinguish organometallic compounds from other types of coordination compounds is often convenient since many organometallic ligands engage in more than simple σ donor-acceptor coordinate covalent bond formation with the metal center. However, this is true of some wholly inorganic ligands too, so it should always be kept in mind that organometallic compounds are just a type of coordination compound and that inorganic ligands can in principle be tuned to interact with a metal center in much the same way an organic ligand does.

A summary of some of the concepts and terms used to describe coordination compounds is given in Scheme 7.1.2.



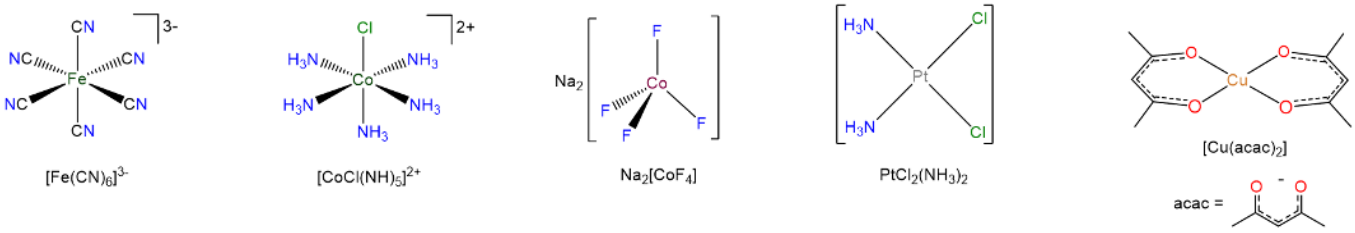
Scheme 7.1.2: Some terms used to describe coordination compounds. (CC BY 4.0; Stephen Contakes)

The formulae of coordination complexes

The way the formulae of coordination complexes are written reflects the fact that it is often convenient to think of coordination compounds as a composite of metals and ligands. When writing the formula of a complex

- the atoms of a ligand are not added to those of the rest of the compound. Instead, the ligand atoms are kept together, if necessary by enclosing the ligand formula in parentheses or giving an abbreviation for the ligand.
- For complex ions the metal and ligands are enclosed in square brackets. Sometimes this is also done for neutral coordination compounds as well. In either case the brackets enclose those parts of the compound which comprise the primary coordination sphere; anything else is in the secondary coordination sphere outside.

A careful perusal of the examples in Scheme 7.1.3 should make the important features of this system clear.



Scheme 7.1.3: Formulae of coordination compounds and complex ions. (CC BY 4.0; Stephen Contakes)

This page titled 7.1: Coordination Compounds is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.1: Prelude to Coordination Chemistry I - Structure and Isomers** by Stephen M. Contakes is licensed CC BY 4.0.

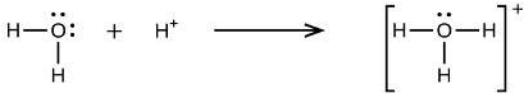
7.2: Lewis Acids and Bases

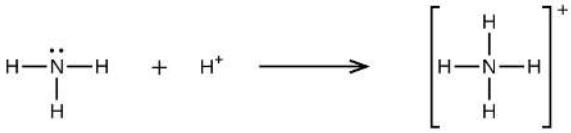
Skills to Develop

- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

A coordinate covalent bond (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



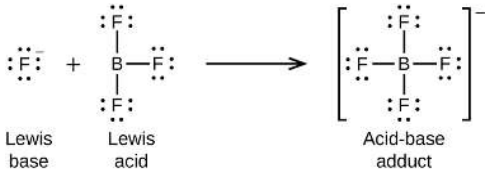


Definition: Lewis Acids and Bases

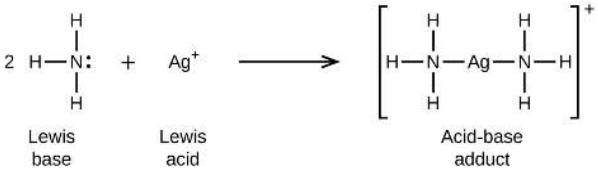
- A Lewis acid is any species (molecule or ion) that can *accept* a pair of electrons, and a Lewis base is any species (molecule or ion) that can *donate* a pair of electrons.

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid. A **Lewis acid-base adduct**, a compound that contains a coordinate covalent bond between the Lewis acid and the Lewis base, is formed. The following equations illustrate the general application of the Lewis concept.

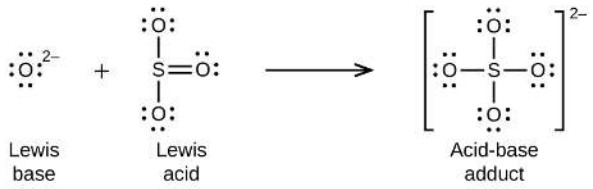
The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



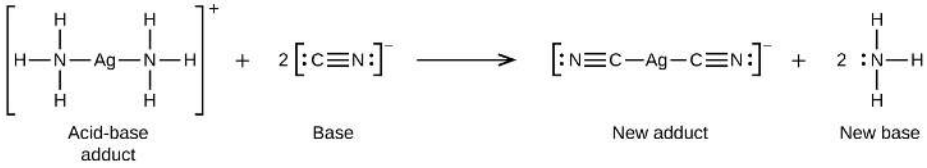
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:

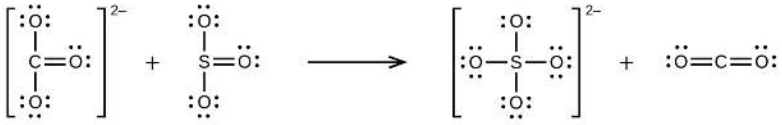


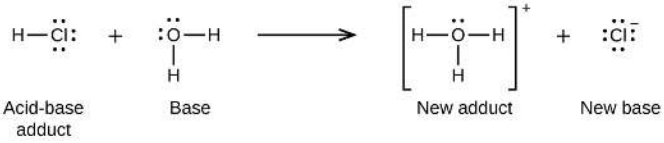
Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:



Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:

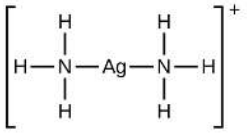






The last displacement reaction shows how the reaction of a Brønsted-Lowry acid with a base fits into the Lewis concept. A Brønsted-Lowry acid such as HCl is an acid-base adduct according to the Lewis concept, and proton transfer occurs because a more stable acid-base adduct is formed. Thus, although the definitions of acids and bases in the two theories are quite different, the theories overlap considerably.

Many slightly soluble ionic solids dissolve when the concentration of the metal ion in solution is decreased through the formation of complex (polyatomic) ions in a Lewis acid-base reaction. For example, silver chloride dissolves in a solution of ammonia because the silver ion reacts with ammonia to form the complex ion $\mathrm{Ag(NH_3)_2{}^+}$. The Lewis structure of the $\mathrm{Ag(NH_3)_2{}^+}$ ion is:



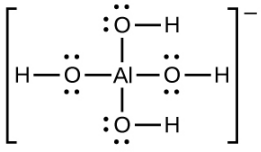
The equations for the dissolution of AgCl in a solution of NH_3 are:

$$\mathrm{AgCl}(s) \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \tag{7.2.1}$$

$$\mathrm{Ag^+}(aq) + 2\,\mathrm{NH_3}(aq) \longrightarrow \mathrm{Ag(NH_3)_2{}^+}(aq) \tag{7.2.2}$$

$$\text{Net: } \mathrm{AgCl}(s) + 2\,\mathrm{NH_3}(aq) \longrightarrow \mathrm{Ag(NH_3)_2{}^+}(aq) + \mathrm{Cl^-}(aq) \tag{7.2.3}$$

Aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $\mathrm{Al(OH)_4{}^-}$. The Lewis structure of the $\mathrm{Al(OH)_4{}^-}$ ion is:



The equations for the dissolution are:

$$\mathrm{Al(OH)_3}(s) \longrightarrow \mathrm{Al^{3+}}(aq) + 3\,\mathrm{OH^-}(aq) \tag{7.2.4}$$

$$\mathrm{Al^{3+}}(aq) + 4\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Al(OH)_4^-}(aq) \tag{7.2.5}$$

$$\text{Net: } \mathrm{Al(OH)_3}(s) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{Al(OH)_4^-}(aq) \tag{7.2.6}$$

Mercury(II) sulfide dissolves in a solution of sodium sulfide because HgS reacts with the S^{2-} ion:

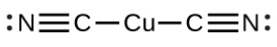
$$\mathrm{HgS}(s) \longrightarrow \mathrm{Hg^{2+}}(aq) + \mathrm{S^{2-}}(aq) \tag{7.2.7}$$

$$\mathrm{Hg^{2+}}(aq) + 2\,\mathrm{S^{2-}}(aq) \longrightarrow \mathrm{HgS_2^{2-}}(aq) \tag{7.2.8}$$

$$\text{Net: } \mathrm{HgS}(s) + \mathrm{S^{2-}}(aq) \longrightarrow \mathrm{HgS_2^{2-}}(aq) \tag{7.2.9}$$

A complex ion consists of a central atom, typically a transition metal cation, surrounded by ions, or molecules called ligands. These ligands can be neutral molecules like H_2O or NH_3, or ions such as CN^- or OH^-. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. The ligands aggregate themselves around the central atom, creating a new ion with a charge equal to the sum of the charges and, most often, a transitional metal ion. This more complex arrangement is why the resulting ion is called a *complex ion*. The complex ion formed in these reactions cannot be predicted; it must be determined experimentally. The types of bonds formed in complex ions are called coordinate covalent bonds, as electrons from the ligands are being shared with the central atom. Because of this, complex ions are sometimes referred to as coordination complexes. This will be studied further in upcoming chapters.

The equilibrium constant for the reaction of the components of a complex ion to form the complex ion in solution is called a formation constant (K_f) (sometimes called a stability constant). For example, the complex ion $\mathrm{Cu(CN)_2^-}$ is shown here:



It forms by the reaction:

$$\mathrm{Cu^+}(aq) + 2\,\mathrm{CN^-}(aq) \rightleftharpoons \mathrm{Cu(CN)_2^-}(aq) \tag{7.2.10}$$

At equilibrium:

$$K_f = Q = \frac{[Cu(CN)2-]}{[Cu+][CN-]^2} \tag{7.2.11}$$

The inverse of the formation constant is the dissociation constant (K_d), the equilibrium constant for the *decomposition* of a complex ion into its components in solution. We will work with dissociation constants further in the exercises for this section. Table E4 and Table 7.2.1 are tables of formation constants. In general, the larger the formation constant, the more stable the complex; however, as in the case of K_{sp} values, the stoichiometry of the compound must be considered.

Table 7.2.1*: Common Complex Ions by Decreasing Formation Constants*

Substance	K_f at 25 °C
$[\mathrm{Cd(CN)_4}]^{2-}$	3×10^{18}
$\mathrm{Ag(NH_3)_2^+}$	1.7×10^{7}
$[\mathrm{AlF_6}]^{3-}$	7×10^{19}

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[Ag^+] = 1.3 \times 10^{-5}\ M$):

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \tag{7.2.12}$$

However, if NH_3 is present in the water, the complex ion, $\mathrm{Ag(NH_3)_2^+}$, can form according to the equation:

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq) \tag{7.2.13}$$

with

$$K_f = \frac{[Ag(NH3)2+]}{[Ag+][NH3]^2} = 1.7 \times 10^7 \tag{7.2.14}$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form $Ag(NH_3)_2{}^+$. As a consequence, the concentration of silver ions, [Ag^+], is reduced, and the reaction quotient for the dissolution of silver chloride, [Ag^+][Cl^-], falls below the solubility product of AgCl:

$$Q = [Ag^+][Cl^-] < K_{sp} \tag{7.2.15}$$

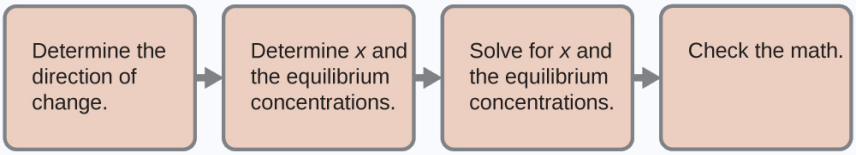
More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

Example 7.2.1: Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 *M* with respect to $Ag(NH_3)_2{}^+$.

Solution

We use the familiar path to solve this problem:



1. *Determine the direction of change.* The complex ion $Ag(NH_3)_2{}^+$ is in equilibrium with its components, as represented by the equation:

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq) \tag{7.2.16}$$

   We write the equilibrium as a formation reaction because Table E4 lists formation constants for complex ions. Before equilibrium, the reaction quotient is larger than the equilibrium constant (K_f = 1.7 \times 10^7\), and $Q = \frac{0.10}{0 \times 0} = \infty$ (it is infinitely large), so the reaction shifts to the left to reach equilibrium.

2. *Determine* x *and equilibrium concentrations.* We let the change in concentration of Ag^+ be *x*. Dissociation of 1 mol of $Ag(NH_3)_2{}^+$ gives 1 mol of Ag^+ and 2 mol of NH_3, so the change in [NH_3] is 2*x* and that of $Ag(NH_3)_2{}^+$ is –*x*. In summary:

	Ag^+ +	$2NH_3$ ⇌	$Ag(NH_3)_2{}^+$
Initial concentration (*M*)	0	0	0.10
Change (*M*)	*x*	2*x*	−*x*
Equilibrium concentration (*M*)	0 + *x*	0 + 2*x*	0.10 − *x*

3. *Solve for x and the equilibrium concentrations.* At equilibrium:

$$K_f = \frac{[Ag(NH3)2+]}{[Ag+][NH3]^2} \tag{7.2.17}$$

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2} \tag{7.2.18}$$

   Both *Q* and K_f are much larger than 1, so let us assume that the changes in concentrations needed to reach equilibrium are small. Thus 0.10 – *x* is approximated as 0.10:

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2} \tag{7.2.19}$$

$$x^3 = \frac{0.10}{4(1.7 \times 10^7)} = 1.5 \times 10^{-9} \tag{7.2.20}$$

$$x = \sqrt[3]{1.5 \times 10^{-9}} = 1.1 \times 10^{-3} \tag{7.2.21}$$

Because only 1.1% of the $Ag(NH_3)_2^+$ dissociates into Ag^+ and NH_3, the assumption that x is small is justified.

Now we determine the equilibrium concentrations:

$$[Ag^+] = 0 + x = 1.1 \times 10^{-3}\ M \tag{7.2.22}$$

$$[NH_3] = 0 + 2x = 2.2 \times 10^{-3}\ M \tag{7.2.23}$$

$$[Ag(NH_3)_2^+] = 0.10 - x = 0.10 - 0.0011 = 0.099 \tag{7.2.24}$$

The concentration of free silver ion in the solution is 0.0011 *M*.

4. *Check the work.* The value of Q calculated using the equilibrium concentrations is equal to K_f within the error associated with the significant figures in the calculation.

Exercise 7.2.1

Calculate the silver ion concentration, $[Ag^+]$, of a solution prepared by dissolving 1.00 g of $AgNO_3$ and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because $Q < K_f$, assume the reaction goes to completion then calculate the $[Ag^+]$ produced by dissociation of the complex.)

Answer:

$2.5\times 10^{-22}\ M$

Summary

G.N. Lewis proposed a definition for acids and bases that relies on an atom's or molecule's ability to accept or donate electron pairs. A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts. In a complex ion, we have a central atom, often consisting of a transition metal cation, which acts as a Lewis acid, and several neutral molecules or ions surrounding them called ligands that act as Lewis bases. Complex ions form by sharing electron pairs to form coordinate covalent bonds. The equilibrium reaction that occurs when forming a complex ion has an equilibrium constant associated with it called a formation constant, K_f. This is often referred to as a stability constant, as it represents the stability of the complex ion. Formation of complex ions in solution can have a profound effect on the solubility of a transition metal compound.

Glossary

complex ion
ion consisting of a transition metal central atom and surrounding molecules or ions called ligands

coordinate covalent bond
(also, dative bond) bond formed when one atom provides both electrons in a shared pair

dissociation constant
(K_d) equilibrium constant for the decomposition of a complex ion into its components in solution

formation constant
(K_f) (also, stability constant) equilibrium constant for the formation of a complex ion from its components in solution

Lewis acid
any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct
compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis base
any species that can donate a pair of electrons and form a coordinate covalent bond

ligand
molecule or ion that surrounds a transition metal and forms a complex ion; ligands act as Lewis bases

Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

This page titled 7.2: Lewis Acids and Bases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

7.3: Nomenclature and Ligands

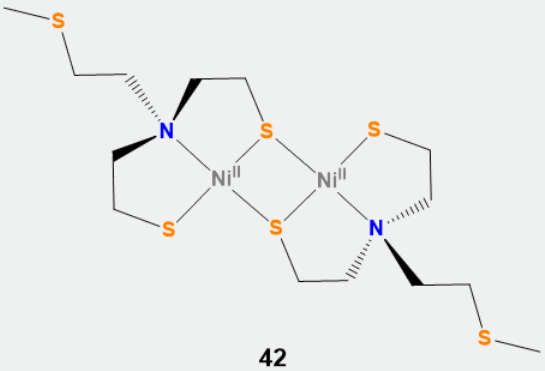
Systems of nomenclature and formulae are intended as tools, to be employed insofar as they are useful

There are well-established rules for both naming and writing the formulae of coordination compounds. The purpose of these rules is to facilitate clear and precise communication among chemists. As with all such rules, some are more burdensome than others to employ, and some serve more crucial roles in the communication process while others are more peripheral - and all are poorly used in the service of pedantic tyranny, especially when used against those who are otherwise doing good work. For this reason, you are urged to approach the rules in a spirit of generosity towards others in

- naming and writing formulas as reasonably accurately as you can so that ligands and metals are where readers expect them and thus can understand what you mean more easily.
- being gracious towards the many professional inorganic chemists who adhere loosely to some of the rules you are about to learn.
- recognizing that in cases when a structure is particularly complex and a picture may make be particularly useful, you should supply one (See the note below).

Note 7.3.1: Sometimes the most helpful name to give a compound is 42.

Even though the IUPAC nomenclature rules permit specification of even the most complex structures, it is often much easier and more effective to supply a numbered structure that can be referred to instead of the IUPAC name. Consider bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. Which is easier, to expect readers and hearers to work out the structure from that name or to just refer them to compound **42** in Scheme 7.3.1?



42

Scheme 7.3.1. Structure of bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. The authors of the synthesis of this compound in Inorganic syntheses1 may have had to figure out an IUPAC name for this compound but if you have this scheme in your paper and your instructor is OK with it you can just call it **42**

Coordination Complexes are named as the ligand derivatives of a metal

A variety of systems have been used for naming coordination compounds since the development of the discipline in the time of Alfred Werner. In this section the most common approaches as they are currently used by practicing chemists will be described. Those who need a more thorough and accurate acquaintance with the full IUPAC nomenclature rules are encouraged to consult the IUPAC brief guide to inorganic nomenclature followed by complete guidelines, commonly known as the IUPAC red book. If those are still not enough a careful read of note 7.3.1 is suggested.

The systems for naming coordination compounds used at present are additive, meaning that they consider coordination compounds as comprising a central metal to which are added ligands. To specify the structure and bonding in this metal-ligand complex then involves:

1. when there are several different ways of attaching the metal and ligands, specifying the structural or stereoisomer
2. systematically listing the ligands in a way that, as necessary, conveys information about how they are linked to the metal and their stereochemistry

3. providing the identity of the metal and its oxidation state, or if the oxidation state is unclear, at least the overall charge on the complex
4. specifying any counterions present

Since the stereochemistry of coordination compounds forms the subject of the next section, in this section it will be addressed by simply giving the prefixes that designate stereochemistry as if they were self-evident. Do not worry about these for now. They will make sense after you have learned more about stereochemistry in the next section. At that time, you can go back over the examples in that section to solidify your understanding of how to name coordination compounds.

However, in order to name coordination compounds accurately you will need to learn how to think about and name ligands first.

Ligands

Ligands are classified based on whether they bind to the metal center through a single site on the ligand or whether they bind at multiple sites. Ligands that bind through only a single site are called **monodentate** from the Latin word for tooth; in contrast, those which bind through multiple sites are called **chelating** after the Greek $\chi\alpha\lambda\epsilon$ for "claw". These relationships are summarized in Figure 7.3.1.

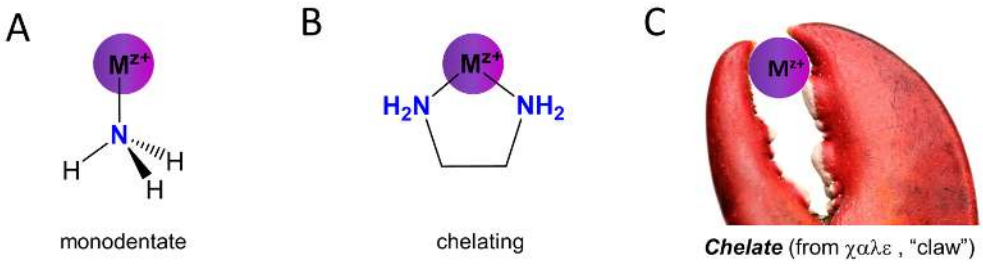
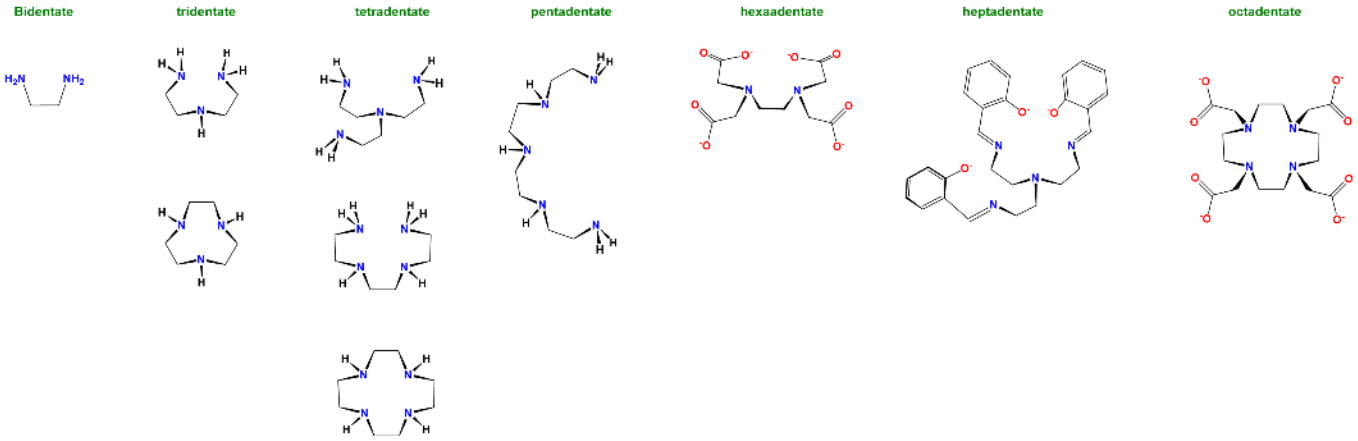


Figure 7.3.1. (A) Ammonia is a monodentate ligand while (B) ethylene diamine is a chelating ligand owing to its capacity to bind metals via its two amine functional groups. (C) Chelating ligands act like a lobster claw in attaching to the metal via multiple sites. The lobster claw image is adapted from https://www.clipart.email/download/1127636.html. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Following naturally from the classification of non-chelating ligands as monodentate, chelating ligands are further classified according to the number of sites which they can use to bind a metal center. This number of binding sites is called the denticity and ligands are referred to as monodentate (non- chelating), bidentate, tridentate, etc., based on the number of sites available. Ligands with two binding sites have a denticity of two and are said to be bidentate; those with three are tridentate, four tetradentate, and so on. To illustrate this classification system examples of chelating ligands classified according to denticity are given in Scheme 7.3.I.

Scheme 7.3.I**.** A selection of chelating ligands classified according to denticity.

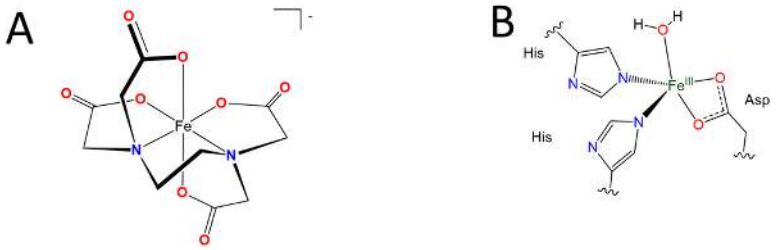


Scheme 7.3.IIA. Because only one oxygen per carboxylate *typically* binds, only one is counted when assigning a ligand's denticity. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

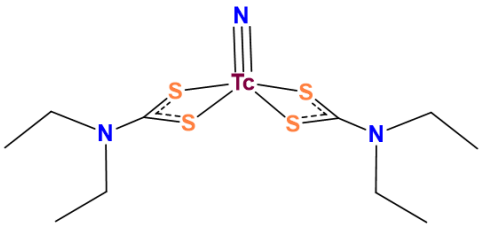
Although only one carboxylate oxygen *usually* binds to a metal, it is still possible to bind for both oxygens to bind to a single metal. As shown in Scheme 7.3.IIB, complexes in which both carboxylates bind to a metal are known, and in fact are common in the

active sites of some enzymes. It is just that the binding of both oxygens gives a strained four-membered ring that is usually unstable.

Scheme 7.3.**II.** (A) Only one oxygen per carboxylate counts towards the denticity of EDTA since on binding the other oxygen generally points away from the metal center, as in the structure of $Fe(EDTA)^-$. (B) In some enzyme active sites both oxygens of a carboxylic acid (aspartate or Asp in this example) bind to a metal. The aspartate carboxylic acid group is bidentate while the EDTA carboxlic acid groups in A are monodentate. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.



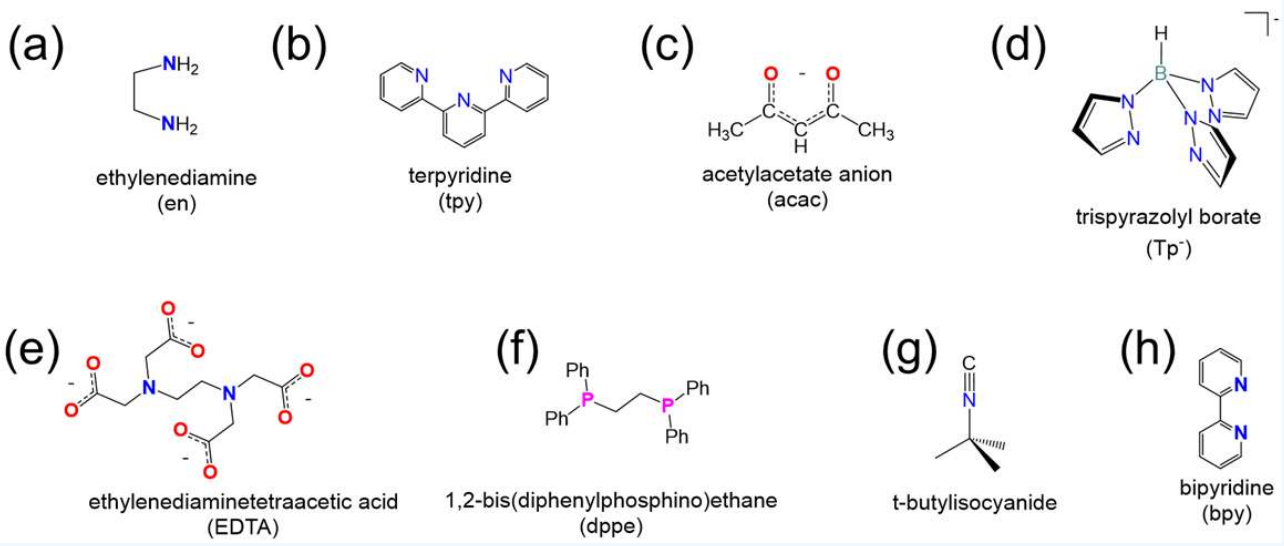
Scheme 7.3.**III.** As in this complex, dithiocarbamates commonly bind metals through both sulfur atoms. Consequently, dithiocarbamates are classified as bidentate. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.



Because of these factors it is technically more correct to say that carboxylates *usually act as* monodentate ligands and dithiocarbamates bidentate ones than it is to say that carboxylates *are* monodentate ligands and dithiocarbamates bidentate ones. So in other words the ligand classifications presented here just represent common binding modes.

? Exercise 7.3.1

Determine the denticity of each ligand in the list below and classify them as monodentate, tridentate, etc.



Answer

(a) bidentate

(b) tridentate

(c) bidentate

(d) tridentate (only the lower N on each ring has a lone pair that can be used to bind the metal)

(e) hexadentate (remember that each carboxylate only counts as one point of attachment)

(f) bidentate

(g) monodentate (through the lone pair on the isocyanide C)

(h) bidentate

This experimentally-based classification of dithiocarbamates as bidentate and carboxylates as monodentate can be confusing to a beginner. Fortunately, such experimentally based classifications are embedded in the lists of common monodentate ligands as given in Table 7.3.1 and common chelating ligands in Table 7.3.2.

A perusal of the ligands in Table 7.3.1 reveals that several can bind to a metal in multiple ways. For example, thiocyanate, SCN^- can bind metals through its S or N atoms. Such ligands are called **ambidentate ligands**. In naming an ambidentate ligand, the atom through which it attaches to the metal is commonly specified after the ligand name using the italicized element symbol or, more formally, a κ followed by the italicized element symbol. An example is given in Scheme 7.3.I.[2]

Scheme 7.3.I. Two possible binding modes of nitrite acting as a ligand.[3]

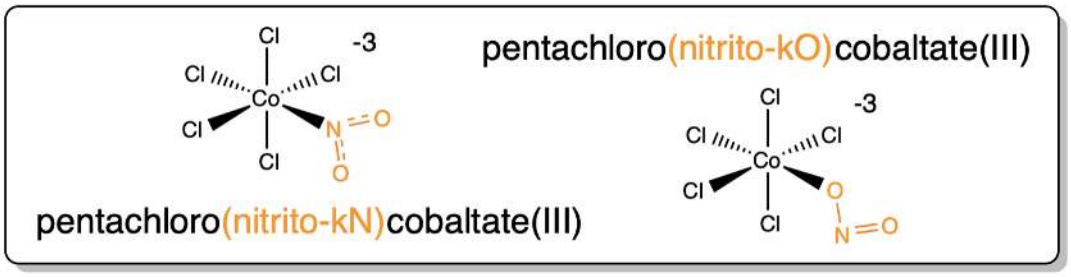
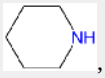
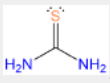
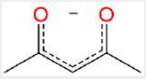
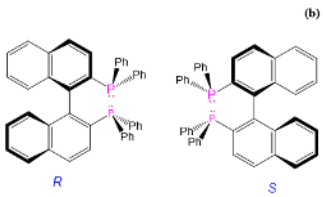
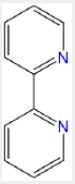
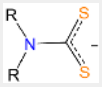
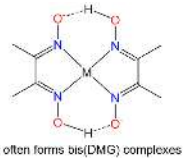
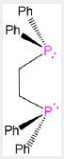
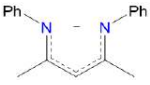


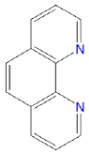
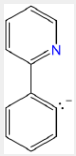
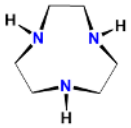
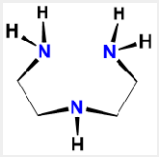
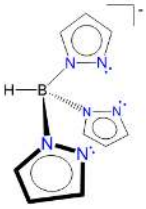
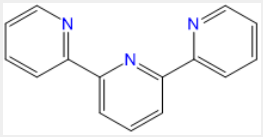
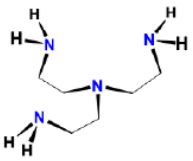
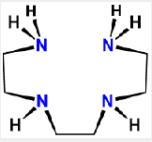
Table 7.3.1. Common monodentate ligands. Most chemists still prefer common names over the IUPAC ones.

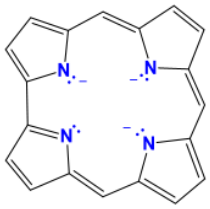
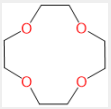
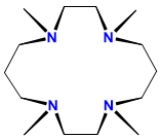
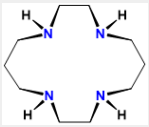
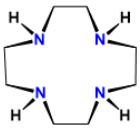
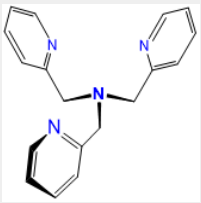
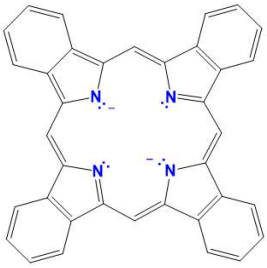
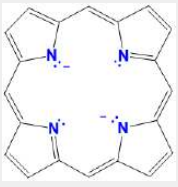
Ligand	Common name	IUPAC name
H^- (H ligands are always considered anions for naming purposes)	hydrido	hydrido
F^-	fluoro	fluorido
Cl^-	chloro	chlorido
Br^-	bromo	bromido
I^-	iodo	iodido
CN^-, as M-CN	cyano	cyanido or cyanido-κC or cyanido-*C*
CN^-, as M-NC	isocyano	isocyanido or cyanido-κN or cyanido-*N*
CH_3NC	methylisocyanide	methylisocyanide
N_3^-	azido	azido
SCN^-, *e.g.* thiocyanate as M-SCN	thiocyanato	thiocyanato-κS or thiocyanato-*S*
NCS^-, *e.g.* thiocyanate as M-NCS	isothiocyanato	thiocyanato-κN or thiocyanato-*N*
$CH_3CO_2^-$	acetato	ethanoato
N^{3-}	nitrido	nitrido
NH^{2-}	imido	azanediido
NH_2^-	amido	azanido
NH_3	ammine	ammine
RNH_2, R_2NH, R_3N	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)
 , piperidine, abbreviated pip	piperidine	piperidine
 , pyridine, abbreviated py	pyridine	pyridine
CH_3CN, acetonitrile, abbreviated MeCN	acetonitrile	acetonitrile
P^{3-}	phosphido	phosphido
PH_3	phosphine	phosphane
PR_3	trialkylphosphine (*e.g.* trimethylphosphine for Me_3P)	trialkylphosphane (*e.g.* trimethylphosphane for Me_3P)
PAr_3	triarylphosphine (*e.g.* triphenylphosphine for Ph_3P)	triarylphosphine (*e.g.* triphenylphosphane for Ph_3P)
 , dimethylsulfoxide or DMSO or dmso	dimethylsulfoxide (sometimes called dimethylsulfoxo but this usage is rare and violates the nomenclature rules for neutral ligands)	(methanesulfinyl)methane or dimethyl(oxido)sulfur
 , thiourea or tu	thiourea	thiourea

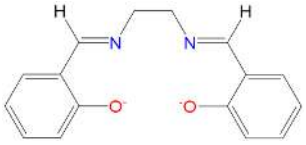
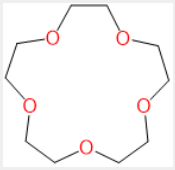
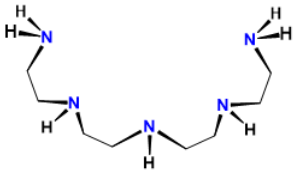
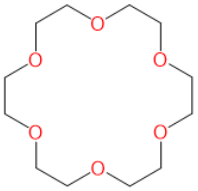
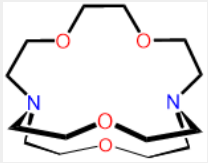
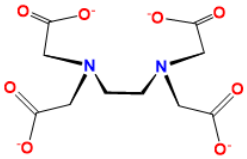
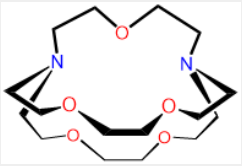
Ligand	Common name	IUPAC name
O^{2-}	oxo	oxido
OH^-	hydroxo	hydroxido
H_2O	aqua	aqua
S^{2-}	sulfo	sulfo
HS^-	hydrosulfido	hydrosulfido
RS^-	alkanethiolate (*e.g.* ethanthiolate for EtS^-)	thioalkanoate
H_2S	hydrogen sulfide	hydrogen sulfide
R_2S	alkylsulfanylalkane (*e.g.* ethylsulfanylethane for Et_2S)	dialkyl sulfide
O_2	dioxygen	dioxygen
O_2^-, superoxide	superoxido	dioxido(1-) or superoxido
O_2^{2-}, peroxide	peroxido	dioxido(2-) or peroxido
N_2	dinitrogen	dinitrogen
NO (are always considered neutral for naming purposes)	nitrosyl	nitrosyl
CO	carbonyl	carbonyl
CS	thiocarbonyl	thiocarbonyl
SO, as M-SO	sulfino	sulfur monoxide-κS or sulfur monoxide-*S*
NO_2, as M-NO_2	nitryl	nitrogen dioxide-κN or nitrogen dioxide-*N*
CO_3^{2-}	carbonato	carbonato
NO_2^-, as M-NO_2	nitro or nitrito-*N*	nitrito-κN or nitrito-*N*
NO_2^-, as M-ONO	nitrito or nitrito-*O*	nitrito-κO or nitrito-*O*
NO_3^-	nitrato	nitrato
SO_3^{2-}	sulfito	sulfito
SO_4^{2-}	sulfato	sulfato
$S_2O_3^{2-}$, as M-S-SO_2-O^-	thiosulfato-*S*	thiosulfato-κS or thiosulfato-*S*
$S_2O_3^{2-}$, as M-O-SO_2-S^-	thiosulfato-*O*	thiosulfato-κO or thiosulfato-*O*

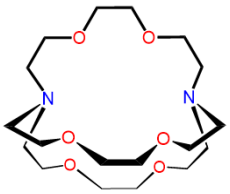
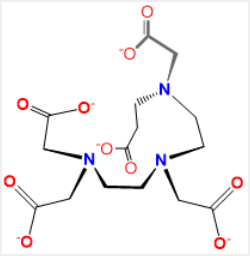
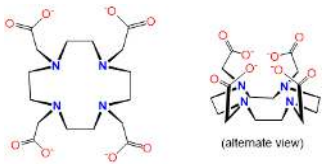
Table 7.3.2. Common chelating ligands organized by denticity. Most chemists use the common names and abbreviations to describe these ligands.

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
bidentate ligands			
acetylacetonato	2,4-pentanediono	acac	
R-BINAP and *S*-BINAP	*R*- or *S*-2,2'-bis(diphenylphosphino)-1,1'-binapthyl	BINAP	
2,2'-bipyridine	2,2'-bipyridine	bpy or bipy	
cyclooctadiene	1,5-cyclooctadiene	COD	 (binding to the metal occurs through the alkene π cloud)
dialkyldithiocarbamato	dialkylcarbamodithiolato	$R_2NCS_2^-$ or dtc	
dimethylgloximato	butanedienedioxime	Hdmg or DMG	 
diphenylphosphinoethane or 1,2-(diphenylphosphino)ethane	Ethane-1,2-diylbis(diphenylphosphane)	dppe	
ethylenediamine	Ethane-1,2-diamine	en	
ethylenedithiolato	Ethane-1,2-dithiolato	$C_2H_2S_2^{2-}$	
nacnac	*N*,*N*'-diphenyl-2,4-pentanediiminato	nacnac	
oxalato	oxalato	ox	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
1,10-phenanthroline or *o*-phenanthroline	1,10-phenanthroline	phen or *o*-phen	
phenylpyridinato	2-phenylpyridinato-C^2,*N* or 2-phenylpyridinato-κC^2,*N*	ppy	
tridentate ligands			
triazacyclononane	1,4,7-triazacyclononane	tacn	
diethylenetriamine	1,4,7-triazaheptane	dien	
pyrazoylborato (scorpionate)	hydrotris(pyrazo-1-yl)borato	Tp	
terpyridine or 2,2';6',2"-terpyridine	1^2,2^2:2^6,3^2-terpyridine or 2,6-bis(2-pyridyl)pyridine, tripyridyl, 2,2′:6′,2″-terpyridine	tpy or terpy	
tetradentate ligands			
β, β', β"-triaminotriethylamine	β, β', β"-tris(2-aminoethyl)amine	tren	
triethylenetetramine	1,4,7,10-tetraazadecane	trien	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
corroles	variable and generally not used	cor or Cor	
12-crown-4	1,4,7,10-tetraoxacyclododecane	12-crown-4	
tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC or cyclam	
cyclam	1,4,8,11-tetraazacyclotetradecane	cyclam	
cyclen	1,4,7,10-tetraazacyclododecane	cyclen	
tris(2-pyridylmethyl)amine	1-pyridin-2-yl-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine	tpa or TPA	
phthalocyanines	variable and generally not used	variable, usually a modified Pc	
porphyrins	variable and generally not used	variable, usually a modified por, Por, or P (e.g. TPP = tetraphenylporphyrin)	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
salen	2,2'-ethylenebis(nitrilomethylidene) diphenoxido	salen	
pentadentate ligands			
15-crown-5	1,4,7,10,13-Pentaoxacyclopentadecane	15-crown-5	
tetraethylenepentamine	1,4,7,10,13-pentaazatridecane	tepa or TEPA	
hexadentate ligands			
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane	18-crown-6	
2,1,1-cryptand	4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]icosane	2,1,1-crypt or [2.1.1]-cryptand kryptofix 211 and variations thereof	
ethylenediaminetetraaceto	2,2′,2″,2‴-(Ethane-1,2-diyldinitrilo)tetraaceto	EDTA, edta, Y^{4-}	
heptadentate ligands			
2,2,1-cryptand	4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]icosane	2,2,1-crypt or [2.2.1]-cryptand kryptofix 221 and variations thereof	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
octadentate ligands			
2,2,2-cryptand	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan	2,2,2-crypt or [2.2.2]-cryptand kryptofix 222 and variations thereof	
pentetato acid or diethylenetriaminepentaacetato or DTPA	2-[bis[2-[bis(carboxylatomethyl)amino]ethyl]amino]acetato	DTPA	
DOTA or tetraxetan	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid	Dota, DOTA	

Rules for Naming Coordination Compounds

As explained above, the name of a coordination compound communicates

- as appropriate, information about isomerism
- systematically listing the ligands in a way that as necessary conveys information about their oxidation state and how they are linked to the metal
- the identity of the metal and its oxidation state
- any counterions present

Before going into these rules it is worth pointing out a few things.

1. It is easiest to learn these rules by starting with one or two of the rules, learning how to apply them, and then adding additional rules one at a time. To that end, instructors who wish to use a more programmed approach may find it convenient to first direct their students to this page which focuses on getting the names of the ligands and metal right, without worrying about isomerism or stereochemistry.

2. The rules also assume some familiarity with common coordination geometries and patterns of isomerism in metal complexes. Thus it might be easiest to learn about common coordination geometries first, followed by common patterns of isomerism in metal complexes before beginning this section. If you decide to dive right in to this section you might find it helpful to know that when applying nomenclature and formula rules most textbooks *assume*

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four are tetrahedral

Like all assumptions these don't always work in real life but they should be good enough to get you through your first inorganic chemistry course.

For the pedants among you, note that the complexes given as examples and in exercises on this page have been selected for pedagogical utility. Although many are well-known compounds, others are hypothetical.

Now on to the rules.

Rule 1: If ions are present, name the cation first, followed by the anion.

Examples:

$K_2[Pt^{II}Cl_4]$ potassium tetrachloroplatinate(2-)

$[Co^{III}(NH_3)_6](NO_3)_3$ hexaamminecobalt(3+) nitrate

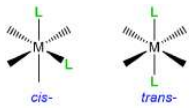
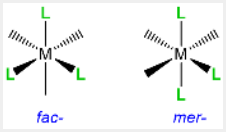
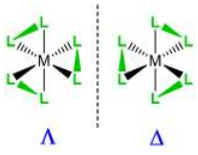
$[Co^{III}(NH_3)_6][Cr^{III}(C_2O_4)_3]$ hexaamminecobalt(3+) tris(oxalato)chromium(3-)

Rule 2: When multiple isomers are possible, designate the particular isomer in italics at the front of the name of each complex

If you have not yet learned about isomerism in coordination compounds skip this rule for now and return to it after you have.

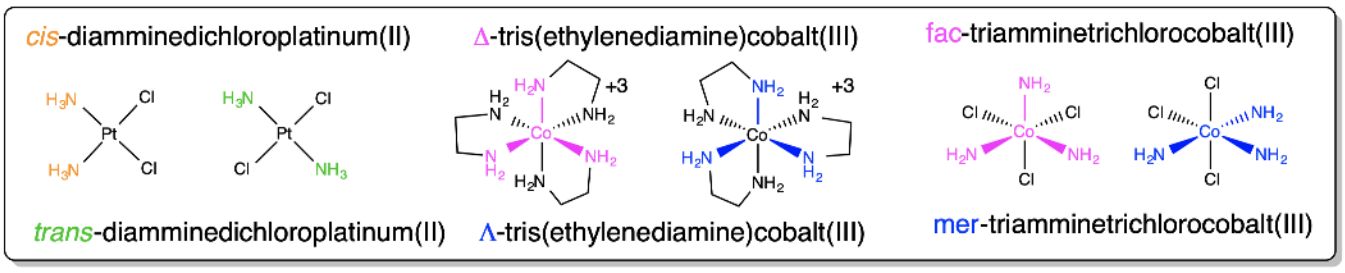
When a complex might exist as one of two stereoisomers, prefixes are commonly used to designate which isomer is present. The most common cases are listed in Table 7.3.3.

Table 7.3.3. Prefixes used to specify isomerism about a metal center when naming and writing coordination compounds' formulae.

Type of isomerism	Graphical reminder	Prefixes
Geometric, *cis-* , *trans-*		*cis-* or *trans-*
Geometric, *fac- /mer-*		*fac-* or *mer-*
Enantiomers, Λ-, Δ-		Λ- or Δ-

Examples of how isomerism about a metal center is designated are given in Scheme 7.3.II.

Scheme 7.3.II**.** Application of nomenclature rules for stereosimerism about a metal.[3]



There are a number of other cases where it might be advisable to specify the stereochemistry of a complex. These cases involve specifying

- the coordination geometry about a metal center (octahedral, trigonal prismatic, tetrahedral, square planar, etc.)

- the geometry cannot be unambigouously described by a single *cis/trans* or *fac/mer* relaionship of ligands

These cases may also be handled by using a designator to specify the coordination geometry and, as necessary, giving the position of ligated atoms in terms of designated numbered positions for that geometry. See the IUPAC red book for details as such cases fall outside the scope of what is normally advisable for an undergraduate course.

Rule 3: Specify the identity, number, and as appropriate, isomerism of the ligands present in alphabetical order by ligand name.

Before specifying the metal, the ligands are written as prefixes of the metal.

In specifying the ligands several rules are followed.

1. The ligands are written in alphabetical order by the ligand name only; symbols are not considered and prefixes do not count in determining alphabetical order.

   Example: In the name of the complex ion $[Co(NH_3)_5Cl]^{2+}$, pentamminechlorocobalt(II), the ammine ligand is named before the chloro ligand because the order is alphabetical by the ligand name by virtue of which ammine comes before chloro.

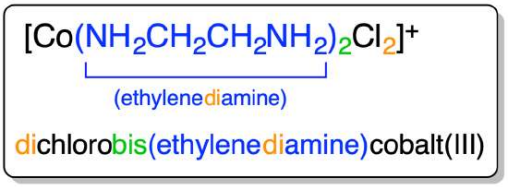
2. Prefixes are used to indicate the number of each ligand present. Specifically, *di-*, *tri-*, *tetra-* , *penta-*, *hexa-*, *etc.* prefixes are used to indicate multiple ligands of the same type EXCEPT when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc. In that case *bis-*,*tris-*, *tetrakis-*, etc. are used instead. These prefix rules are summarized in Table 7.3.3.

Table 7.3.3. Prefixes used to specify the number of a given ligand present.

Number of identical ligands	prefix used when the ligand name is simple	prefix used when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc.
2	di-	bis-
3	tri-	tris-
4	tetra-	tetrakis-
5	penta-	pentakis-
6	hexa-	hexakis-
7	hepta-	heptakis-
8	octa-	octakis-
9	nona-	nonakis-
10	deca-	decakis-

An example of the application of the prefix rule is given in Scheme 7.3.III.

Scheme 7.3.III. Example of the use of prefixes to specify the number of ligands of each type in a complex.[3]



3. Ligand names are based on their charge.

   - Neutral and cationic ligand names are the same as the names of their neutral compounds with two caveats:

     i. names that involve spaces should either be put in parentheses or the spaces should be eliminated (preferred)

     Example: cis-dichlorobis(**dimethyl sulfoxide**)platinum(II) or *cis*-dichlorobis(**dimethylsulfoxide**)platinum(II)

ii. A few ligands are given common names.

- H_2O = aqua
- NH_3 = ammine (notice that there are two n's)
- CO = carbonyl
- CS = thiocarbonyl
- NO = nitrosyl

- For anionic ligands, the vowel at the end of their anion names is changed to an -"o"

  Examples: Cl^- = chloro, NH_2^- = amido, N_3^- = azido

  Caveat: some anionic ligands have common names that may also be used

  Examples:

  I^- = iodo or iodino

  CN^- = cyano or cyanido

  O^{2-} = oxo or oxido

The IUPAC and common names of many ligands are given in Tables 7.3.1. and 7.3.2.

4. When an ambidentate ligand is present, the atom through which it is bound to the metal is indicated by giving either its element symbol or a κ and its element symbol in italics after the ligand name.

   Example:

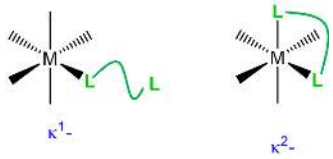
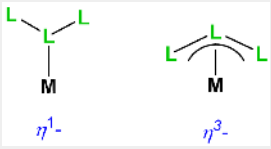
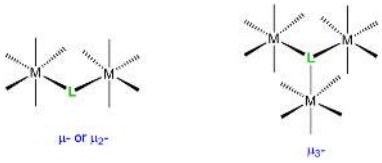
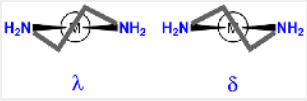
   M-SCN is thiocyanato-*S* or thiocyanato-κ*S*

   M-NCS = thiocyanato-*N or* thiocyanato-κ*N*

   The use of κ and an element symbol to indicate how a ligand and metal are linked is called a **k-term**. More complex k-terms might also involve specifying the atoms by number, though their use is outside the scope of this text.

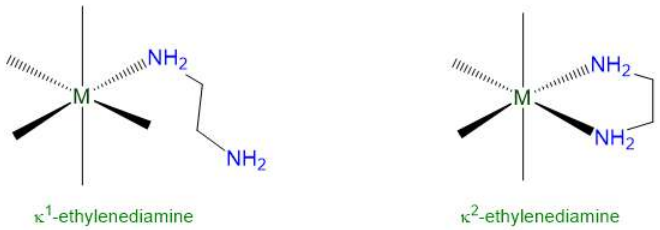
5. As appropriate, additional information about the way a ligand is bound to the metal center and/or its stereochemistry is specified using a prefix. The prefixes to provide linkage and stereochemistry for ligands are given in Table 7.3.4.

Table 7.3.4. Prefixes used to specify ligands' isomerism when naming and writing coordination compounds' formulae. Some of these types of isomerism will be discussed in later pages.

Type of isomerism	Graphical reminder	Prefixes
when a multidentate ligand binds through less than the full number of atoms		κ^n where n is the number of attached atoms; used when the attached atoms are not directly connected by a chemical bond. The metal-ligand bonding usually involves σ-type coordination.
hapticity		η^n where n is the number of attached atoms; used when the coordinated atoms are all connected by bonds. Usually the metal-ligand bonding involves π-type coordination. In speech, η^1=monohapto; η^2=dihapto; η^3=trihapto, etc.
bridging ligands		μ_n where n is the number of atoms bridged. The number n is usually omitted when n =2.
chelating ligand ring twist		λ- or δ-

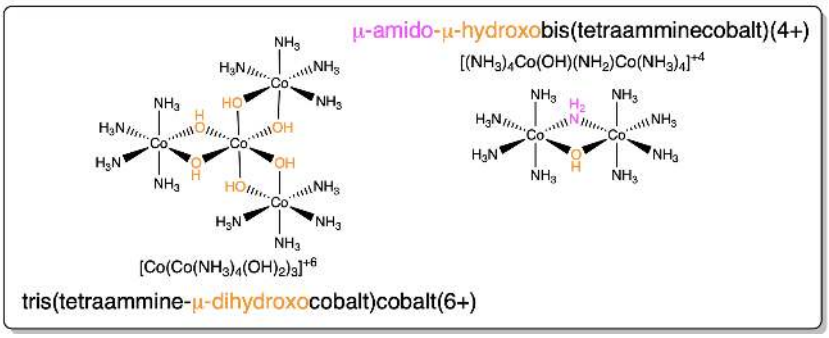
A example showing how the nomenclature rule is applied to a ligand that can have two coordination modes is given in Scheme 7.3.IV.

Scheme 7.3.IV**.** Use of the κ notation to specify the number of attached groups in a multidentate ligand.



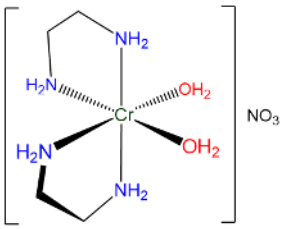
Scheme 7.3.V. The names of the complexes follow the rules described in 9.2.6: multinuclear coordination complexes.

Scheme 7.3.V**.** Use of the μ notation to specify bridging ligands in metal complexes.[3]



6. If desired, parentheses *may* be used to delineate a ligand name to make it easier to identify in the name of the complex. This can be particularly helpful when the entire name contains a lot of information to keep track of. An example is given in Scheme 7.3.VI.

Scheme 7.3.VI**.** When naming the complex shown, *cis*-diaquabis(ethylenediamine)chromium(III) nitrate is easier to read than *cis*-diaquabisethylenediaminechromium(III) nitrate.



Rule 4: Specify the identity of the metal

- In neutral and cationic complexes the metal's name is used directly

  - *e.g.* as in hexammineruthenium(III) for $[Ru(NH_3)_6]^{3+}$

- In anionic complexes, *-ate* replaces *-ium*, *-en*, or *–ese* or adds to the metal name,

  e.g., as in hexachloromanganate(IV) for $MnCl_6^{2-}$

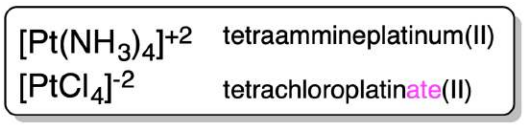
- In anionic complexes of some metals a Latin-derived name is used instead of the element's English name. These names are given in Table 7.3.5.

Table 7.3.5. Latin terms for select metal Ions. Redrawn from this page describing the nomenclature of coordination complexes.

Transition Metal	Latin
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Silver	Argentate
Tin	Stannate

An example of the application of the metal naming rules is given in Scheme \sf{\PageIndex{VII}}\).

Scheme 7.3.VII**.** Example of the application of the metal specification rules to a cationic and an anionic platinum complex.[3]



Rule 5: Specify the oxidation state of the metal.

Two different systems are used to specify the oxidation state of the metal.

1. In the **Stock system** the metal's oxidation state is indicated in Roman numerals after the metal name.

   Examples:

   $[CoCl(NH_3)_5]Cl_2$ = pentamminechlorocobalt(III) chloride

   $[PtBr_2(bpy)]$ = dibromobipyridineplatinium(II)

   $K[Ag(SCN)_2]$ = potassium di-*S*-thiocyanatoargentate(I)

2. In the **Ewing-Bassett system** the charge on the complex is specified in Arabic numerals after the complex name. This provides a way of specifying a complex even when the oxidation state of the metal isn't known and, in cases where it is known, the value

of the metal's oxidation state may be inferred from the complex ion's charge.

$[CoCl(NH_3)_5]Cl_2$ = pentamminechlorocobalt(2+) chloride

$[PtBr_2(bpy)]$ = dibromobipyridineplatinium(0)

$K[Ag(SCN)_2]$ = potassium di-*S*-thiocyanatoargentate(1-)

Summary of rules for naming coordination complexes.

A graphical summary of the **rules for naming complexes** along with a few examples that you can use to review the nomenclature rules is given in Figure 7.3.1. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

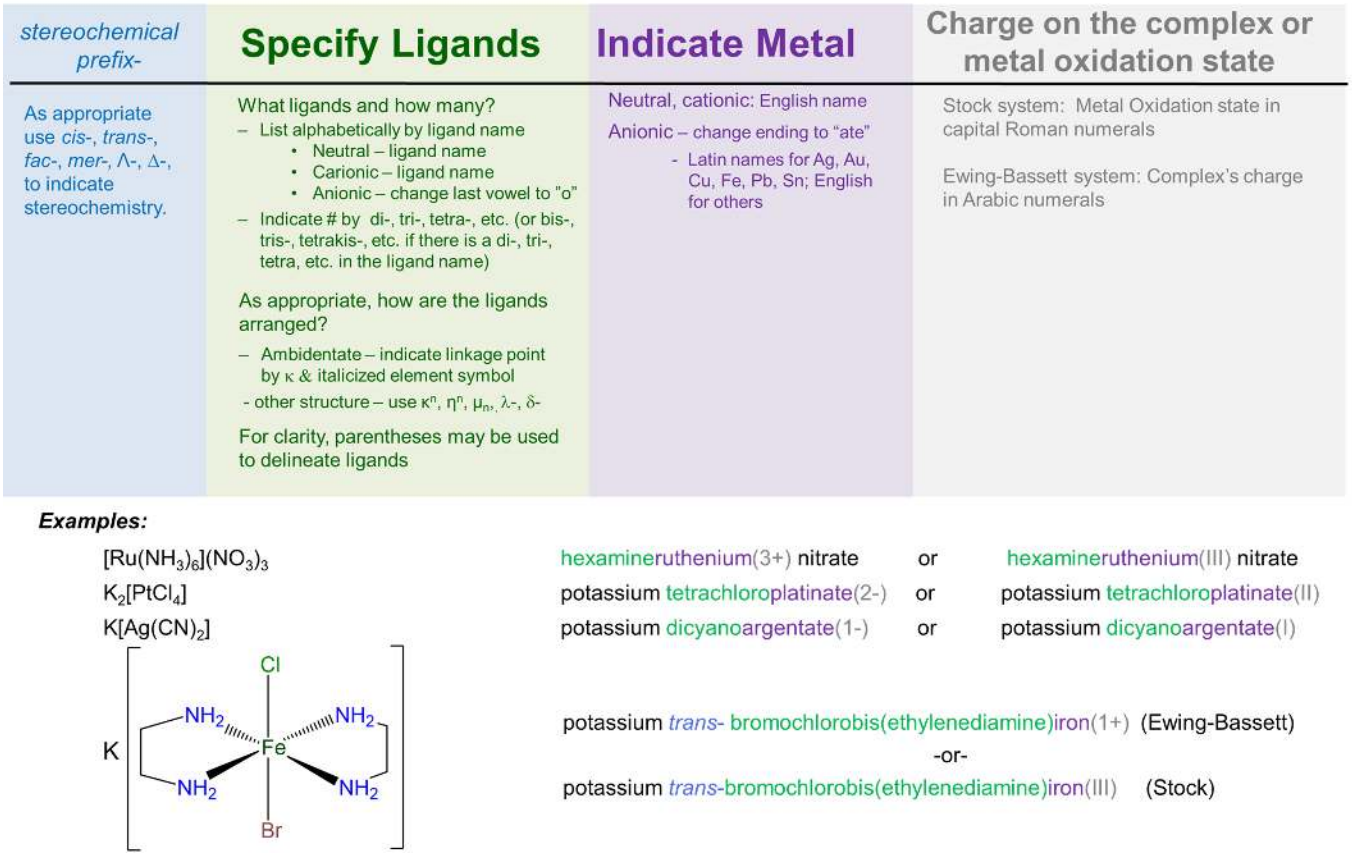


Figure 7.3.1. Summary of nomenclature rules for coordination complexes along with a few examples of their application.

When learning chemical nomenclature, practice makes perfect. The following examples and exercises are provided to give you this practice. Additional examples and exercises on the https://chem.libretexts.org/ site include a set of simple examples with explained solutions, a set of simple exercises with solutions, and a set of more challenging exercises without solutions.

? Exercise 7.3.2. Assigning metal oxidation states in a complex

In order to name a complex in the Stock system it is necessary to assign a formal oxidation state to the metal. For this reason it is important to be able to assign the oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state the ligands can be treated as having an oxidation state equal to their charge - *i.e.*, the charge they possess in the form in which they coordinate the metal, so if they need to lose a proton to bind, don't forget to account for that.

Given the above, assign the oxidation state of the metal in the following real and hypothetical complexes.

a. $K_3[Fe(CN)_6]$

b. $[CoCl(NH_3)_5](NO_3)_2$
c. $K_2[PtCl_4]$
d. [MnCl(por)]
e. $[Ru(bpy)_3]Cl_2$
f. $[PdCl_2(dppe)]$
g. $[Mn(en)_2(SCN)_2]$

Answer for $K_3[Fe(CN)_6]^{3-}$.

This contains $[Fe(CN)_6]^{3-}$; so $O.S._{Fe}$ + 6 x (-1) (for CN^-) = -3 (the complex's charge) so $O.S._{Fe}$ = +3 or Fe^{3+}.

Answer for $[CoCl(NH_3)_5](NO_3)_2$.

This contains $[CoCl(NH_3)_5]^{2+}$; so $O.S._{Co}$ + 1 x (-1) (for Cl^-) + 0 x 5 (for NH_3) = +2 (the complex's charge) so $O.S._{Co}$ = +3 or Co^{3+}.

Answer for $K_2[PtCl_4]$.

This contains $2K^+$ and $[PtCl_4]^{2-}$; so $O.S._{Pt}$ + 4 x (-1) (for Cl^-) = -2 (the complex's charge) so $O.S._{Pt}$ = +2 or Pt^{2+}.

Answer for [MnCl(por)].

$O.S._{Pt}$ + 1 x (-2) (for por; see table 9.2.2) + 1 x (-1) (for Cl^-) = +0 (the complex's charge) so $O.S._{Mn}$ = +3 or Mn^{3+}.

Answer $[Ru(bpy)_3]Cl_2$.

The complex is $[Ru(bpy)3]^{2+}$ so $O.S._{Ru}$ + 0 x 3 (for bpy) = +2 (the complex's charge) so $O.S._{Ru}$ = +2 or Ru^{2+}.

Answer $[PdCl_2(dppe)]$.

$O.S._{Pd}$ + 2 x (-1) (for Cl^-) + 0 x 3 (for dppe) = +0 (the complex's charge) so $O.S._{Pd}$ = +2 or Pd^{2+}.

Answer $[Mn(en)_2(SCN)_2]$.

$O.S._{Mn}$ + (2 x 0) (for en) + 2 x (-1) (for SCN^-) = +0 (the complex's charge) so $O.S._{Mn}$ = +2 or Mn^{2+}.

? Exercise 7.3.3: Simple Nomenclature Problems.

Name the following compounds in both the Stock and Ewing-Bassett systems:

a. $[Ru(NH_3)_6](NO_3)_3$
b. $K_2[PtCl_4]$
c. $K[Ag(CN)_2]$
d. $Cs[CuBrCl_2F]$
e. $[Cu(acac)_2]$

Answer

	Complex	Stock system name	Ewing-Bassett System name
a	$[Ru(NH_3)_6](NO_3)_3$	hexammineruthenium(III) nitrate	hexammineruthenium(3+) nitrate
b	$K_2[PtCl_4]$	potassium tetrachloroplatinate(II)	potassium tetrachloroplatinate(2-)
c	$K[Ag(CN)_2]$	potassium dicyanoargentate(I)	potassium dicyanoargentate(1-)
d	$Cs_2[CuBrCl_2F]$	cesium bromodichlorofluorocuprate(II)	cesium bromodichlorofluorocuprate(2-)
e	$[Cu(acac)_2]$	bis(acetylacetonato)copper(II)	bis(acetylacetonato)copper(0)

? Exercise 7.3.4: More simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems.

a. $Cu(OH)_4^-$
b. $[AuXe_4]^{2+}$
c. $AuCl_4^-$
d. $Fe(CN)_6^{3-}$
e. $K_4[Fe(CN)_6]$
f. *trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)
g. cis-$IrCl_2(CO)(PPh_3)$ (ignore stereochemistry)
h. $IrCl(PPh_3)_3$

Answer

	Compound	Stock System Name	Ewing-Bassett System Name
a	$Cu(OH)_4^-$	tetrahydroxidocuprate(III) or tetrahydroxidocuprate(III)	tetrahydroxidocuprate(1-) or tetrahydroxidocuprate(1-)
b	$[AuXe_4]^{2+}$	tetraxenongold(II)	tetraxenongold(2+)
c	$AuCl_4^-$	tetrachloroaurate(III)	tetrachloroaurate(1-)
d	$Fe(CN)_6^{3-}$	hexacyanoferrate(III) or hexacyanidoferrrate(III)	hexacyanoferrate(3-) or hexacyanidoferrate(3-)
e	$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II) or potassium hexacyanidoferrrate(II)	potassium hexacyanoferrate(4-) or potassium hexacyanidoferrrate(4-)
f	*trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)	bis(ethylenediamine)bisnitrocopper(II) or bis(ethylenediamine)bis(nitrito-κN)copper(II)	bis(ethylenediamine)bisnitrocopper(0) or bis(ethylenediamine)bis(nitrito-κN)copper(0)
g	*cis*-$IrCl_2(CO)(PPh_3)$	*cis*-dichlorocarbonyltriphenylphosphineiridium(I) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(I)	*cis*-dichlorocarbonyltriphenylphosphineiridium(0) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(0)
h	$IrCl(PPh_3)_3$	chlorotris(triphenylphosphine)iridium(I)	chlorotris(triphenylphosphine)iridium(0)

? Exercise 7.3.5: Even more simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

a. $Fe(acac)_3$
b. $K_2[CuBr_4]$
c. ReH_9
d. $[Ag(NH_3)_2]BF_4$
e. $[Ag(NH_3)_2][Ag(CN)_2]$
f. $[Ni(CN)_4]^{2-}$
g. $[Co(N_3)(NH_3)_5]SO_4$
h. $[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)

Sample Answers

	Complex	Stock system name	Ewing-Bassett System name
a	$Fe(acac)_3$	tris(acetoacetato)iron(III)	tris(acetoacetato)iron(0)
b	$Na_2[CuBr_4]$	sodium tetrabromocuprate(II)	sodium tetrabromocuprate(2-)
c	$[Co(NH_3)_6][Co(ox)_3]$	hexamminecobalt(III) tris(oxalato)cobalt(III)	hexamminecobalt(3+) tris(oxalato)cobalt(3-)
d	$[Ag(NH_3)_2]BF_4$	diamminesilver(I) tetrafluoroborate	diamminesilver(1+) tetrafluoroborate
e	$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I) or diamminesilver(I) dicyanidoargentate(I)	diamminesilver(1+) dicyanoargentate(1-) or diamminesilver(1+) dicyanidoargentate(1-)
f	$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) or tetracyanonickelate(II) ion	tetracyanonickelate(2-) or tetracyanonickelate(2-) ion
g	$[Co(N_3)(NH_3)_5]SO_4$	pentammineazidocobalt(III) sulfate	pentammineazidocobalt(2+) sulfate
h	$[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)	ammineaquabromochlorocobalt(III) iodide	ammineaquabromochlorocobalt(1+) iodide

? Exercise 7.3.6: Nomenclature problems, some of which involve consideration of isomerism.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

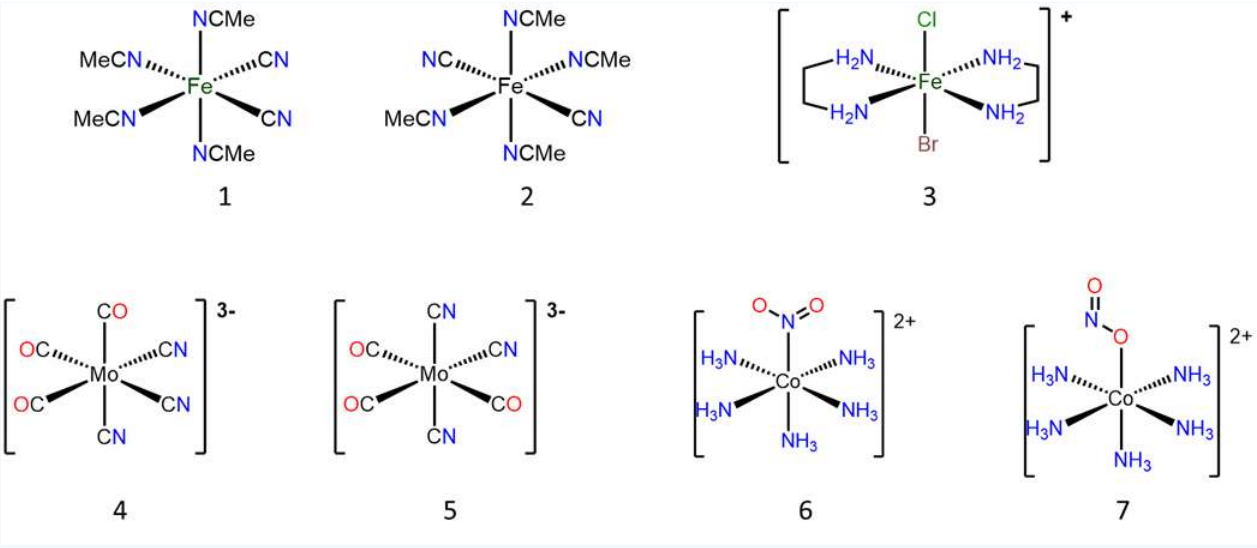
a. *trans*-$[Cu(dppe)_2(NO_2)_2]$ (the N is bound to Cu)
b. $[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN
c. $[Mn(CO)_6]BPh_4$ (BPh_4 = tetraphenylborate)
d. $Rb[AgF_4]$
e. K_2ReH_9
f. K_3CrCl_6
g. $[Ru(H_2O)_6]Cl_2$
h. [*cis*-$Fe(CO)_4I_2$]
i. K_2[*trans*-$Fe(CN)_4(CO)_2$]
j. [*cis*-$MnCl(H_2O)_4(NH_3)](NO_3)$
k. K_3[*fac*-$RuCl_3(PMe_3)_3$]

Answer

	Complex	Stock system name	Ewing-Bassett System name
a	*trans*-$[Cu(dppe)_2(NO_2)_2]$	*trans*-bis(diphenylphosphinoethane)bisnitrocopper(II) or *trans*-bis(diphenylphosphinoethane)bis(nitrito-κN)copper(II)	*trans*-bis(diphenylphosphinoethane)bisnitrocopper(0) or *trans*-bis(diphenylphosphino)ethane bis(nitrito-κN)copper(0)
b	$[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN	bis(ethylenediamine)bisthiocyanatopalladium(II) or bis(ethylenediamine)bis(thiocyanato-*S*)palladium(II) or bis(ethylenediamine)bis(thiocyanato-κS)palladium(II)	bis(ethylenediamine)bisthiocyanatopalladium(0) or bis(ethylenediamine)bis(thiocyanato-*S*)palladium(0) or bis(ethylenediamine)bis(thiocyanato-κS)palladium(0)
c	$[Mn(CO)_6]BPh_4$	hexacarbonylmanganese(I) tetraphenylborate	hexacarbonylmanganese(1+) tetraphenylborate
d	$Rb[AgF_4]$	rubidium tetrafluoroargentate(III)	rubidium tetrafluoroargentate(1-)
e	K_2ReH_9	potassium nonahydridorhenium(VII)	potassium nonahydridorhenium(2-)
f	K_3CrCl_6 or $K_3[CrCl_6]$	potassium hexachlorochromium(III) or potassium hexachloridochromium(III)	potassium hexachlorochromium(3-) or potassium hexachloridochromium(3-)
g	$[Ru(H_2O)_6]Cl_2$	hexaaquaruthenium(II) chloride	hexaaquaruthenium(2+) chloride
h	[*cis*-$Fe(CO)_4I_2$]	*cis*-tetracarbonyldiiodoiron(II)	*cis*-tetracarbonyldiiodoiron(0)
i	K_2[*trans*-$Fe(CN)_4(CO)_2$]	potassium *trans*-dicarbonyltetracyanoferrate(II)	potassium *trans*-dicarbonyltetracyanoferrate(2-)
j	[*cis*-$MnCl(H_2O)_4(NH_3)$] (NO_3)	*cis*-amminetetraaquachloromanganese(0) nitrate	*cis*-amminetetraaquachloromanganese(1+) nitrate
k	K[*fac*-$RuCl_3(PMe_3)_3$]	potassium *fac*-trichlorotris(triphenylphosphine)ruthenium(II)	potassium *fac*-trichlorotris(triphenylphosphine)ruthenium(1-)

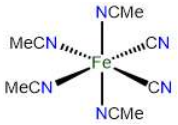
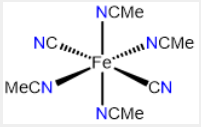
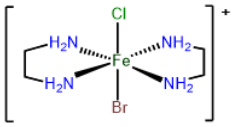
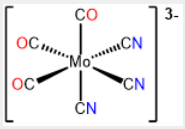
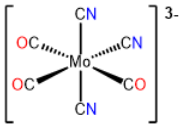
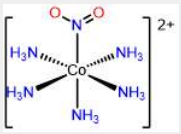
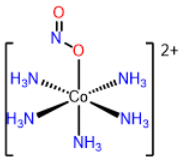
? Exercise 7.3.7

Name the compounds and ions below using both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.



Answer

https://chem.libretexts.org/@go/page/537270

#	Structure	Stock system name	Ewing-Bassett system name
1		*cis*-tetraacetonitriledicyanoiron(II) or *cis*-tetraacetonitriledicyanidoiron(II)	*cis*-tetraacetonitriledicyanoiron(0) or *cis*-tetraacetonitriledicyanidoiron(0)
2		*trans*-tetraacetonitriledicyanoiron(II) or *trans*-tetraacetonitriledicyanidoiron(II)	*trans*-tetraacetonitriledicyanoiron(0) or *trans*-tetraacetonitriledicyanidoiron(0)
3		*trans*-bromochlorobis(ethylenediamine)iron(III) or *trans*-bromidochloridobis(ethylenediamine)iron(III)	*trans*-bromochlorobis(ethylenediamine)iron(1+) or *trans*-bromidochloridobis(ethylenediamine)iron(1+)
4		*fac*-tricarbonyltricyanomolybdate(0) or *fac*-tricarbonyltricyanidomolybdate(0)	*fac*-tricarbonyltricyanomolybdate(3-) or *fac*-tricarbonyltricyanidomolybdate(3-)
5		*mer*-tricarbonyltricyanomolybdate(0) or *mer*-tricarbonyltricyanidomolybdate(0)	*mer*-tricarbonyltricyanomolybdate(3-) or *mer*-tricarbonyltricyanidomolybdate(3-)
6		pentamminenitrito-*N*-cobalt(III), pentamminenitrito-κN-cobalt(III), or pentamminenitrocobalt(III)	pentamminenitrito-*N*-cobalt(2+), pentamminenitrito-κN-cobalt(2+), or pentamminenitrocobalt(2+)
7		pentamminenitrito-*O*-cobalt(2+), pentamminenitrito-κO-cobalt(2+), or pentamminenitritocobalt(2+)	pentamminenitrito-*O*-cobalt(2+), pentamminenitrito-κO-cobalt(2+), or pentamminenitritocobalt(2+)

? Exercise 7.3.8

Draw structural formulae for the following compounds and ions. You may assume that

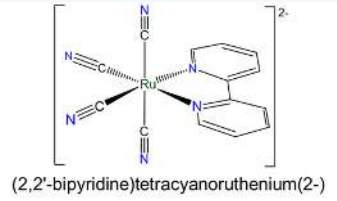
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal

- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

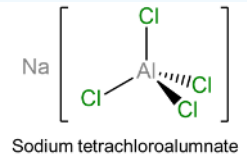
a. (2,2'-bipyridine)tetracyanoruthenium(2-)
b. sodium tetrachloroaluminate (note that since Al is a main group metal with a generally fixed oxidation state no oxidation state is given)
c. pentaamminechlorocobalt(2+) sulfate
d. carbonylhydridotris(triphenylphosphine)rhodium(I) (the ligands in this complex occupy sterically preferred positions)
e. bromotrichlorocobaltate(III)
f. hexaaquacopper(2+) sulfate
g. sodium tris(oxalato)cobalt(III)
h. *fac*-(1,10-phenanthroline)tricarbonylchlororhenium(I)
i. *mer*-triaquatrichlorochromium(III)
j. *trans*-dichlorobis(ethylenediamine)platinum(IV)

Answers

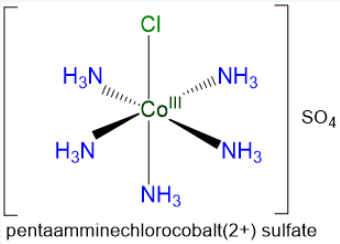
a



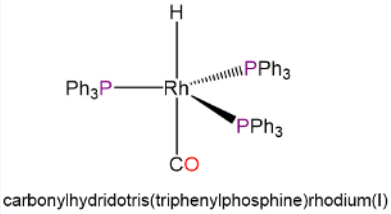
b



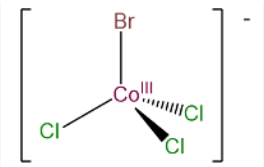
c



d

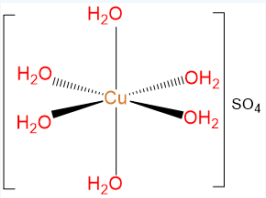


e



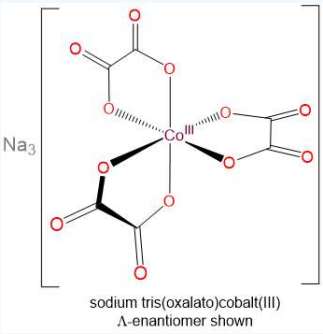
bromotrichlorocobaltate(III)

f



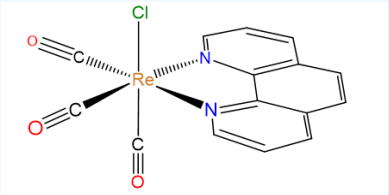
hexaaquacopper(2+) sulfate

g



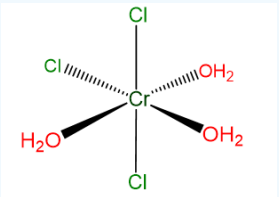
sodium tris(oxalato)cobalt(III)
Λ-enantiomer shown

h



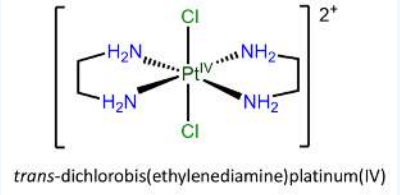
fac-(1,10-phenanthroline)tricarbonylchlororhenium(I)

i



mer-triaquatrichlorochromium(III)

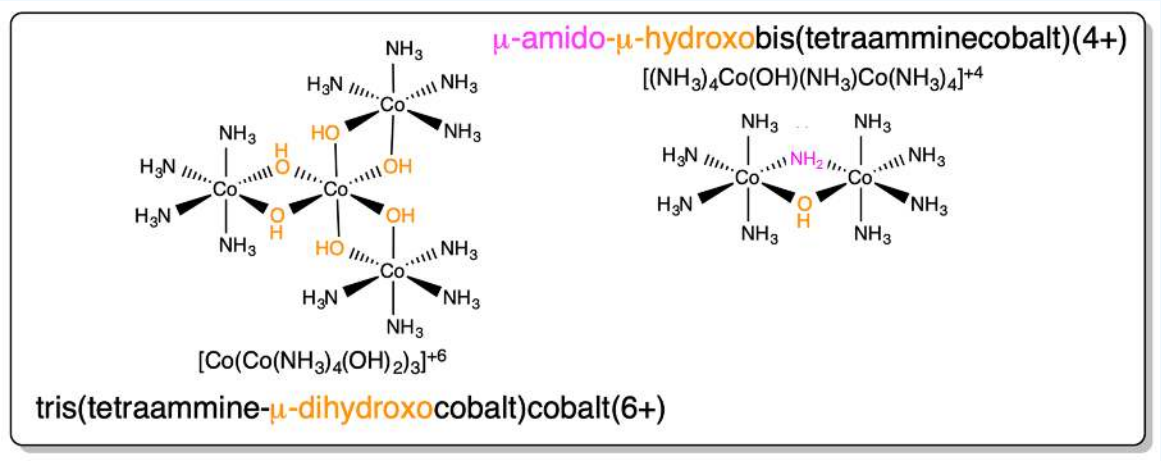
j



trans-dichlorobis(ethylenediamine)platinum(IV)

Exercise 7.3.9.

The name of the structure named tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) in Scheme 7.3.III (reproduced below) is incomplete. Give the complete name of the structure in both the Stock and Ewing-Basset systems.



Answer

Δ-tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) or Δ-tris(tetraammine-μ-dihydroxocobalt(III)cobalt(III)

Note: Rules for Writing the Formulae of Coordination Copounds

Rules for writing the formulae of coordination compounds

As organized predictable formulae can be easier to read and understand than haphazardly written ones, the rules for writing the formulae of coordination compounds have value. To support those who wish to employ them they are given in this section. The rules as given here are adapted from a summary by Robert Lancashire.

The rules for writing the formulae of coordination compounds follow the same convention used to specify their names.

1. If there are multiple ions present list the cations before anions.
2. Enclose all the constituents of each complex ion in square brackets.
3. For each complex ion,
   - Give the **central metal** atom first.
   - Then **ligands** next, listed in alphabetical order, ignoring prefixes according to the first letters in the ligand's symbol as written. This is true regardless of whether the symbol is an element symbol (like C, N, O, etc.) or a symbol for the ligand name (bpy, en, MeCN, etc.). Contrary to widely-circulated myths, the ligand's charge does not matter.[4]
   - The formulae or abbreviations (*e.g.* en) for all polyatomic ligands should be enclosed in ordinary parentheses.
   - As appropriate, use italicized atom symbols to indicate linkage isomerism and prefixes such as *cis*-, *trans*-, *fac*-, *mer*-, Λ-, Δ-, κ^n, η^n , μ_n, λ-, or δ- to indicate stereochemistry.
   - When a ligand is bound to a metal through a particular atom, preferably place that atom closest to the metal - *e.g.*, $[Fe(CN)_6]^{3-}$ not $[Fe(NC)_6]^{3-}$ (Note: this rule is used primarily for ambidentate ligands; although IUPAC recommends that aqua ligands be written as OH_2 when the O would be closest to its coordinated metal, they are still usually written as H_2O).

These rules are graphically summarized in Figure 7.3.2.

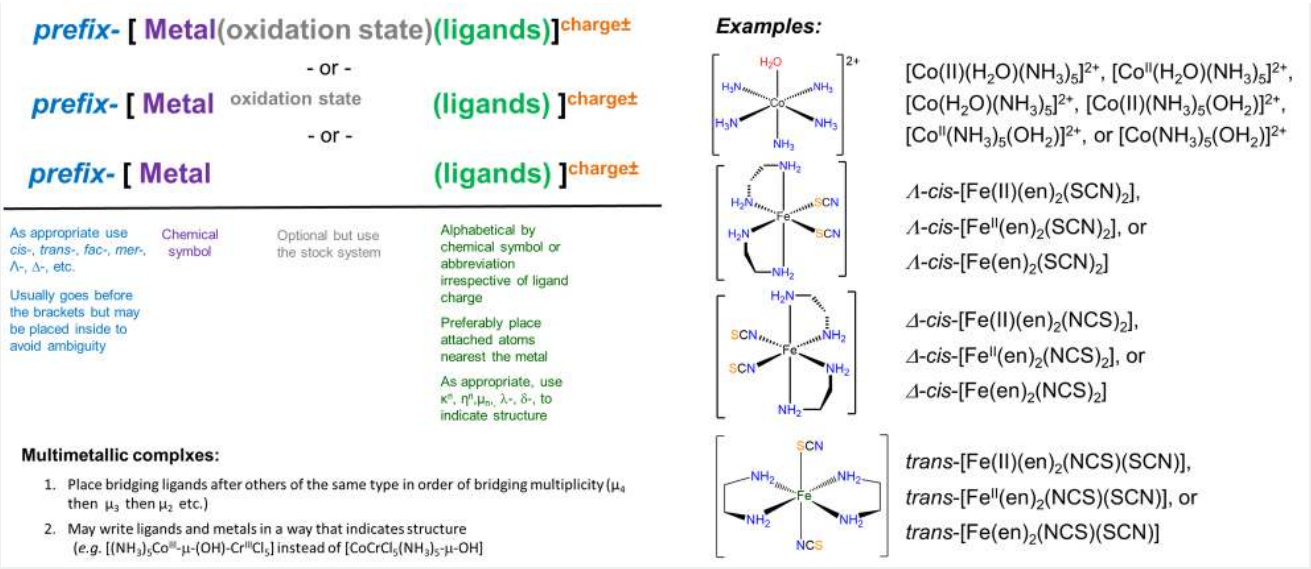
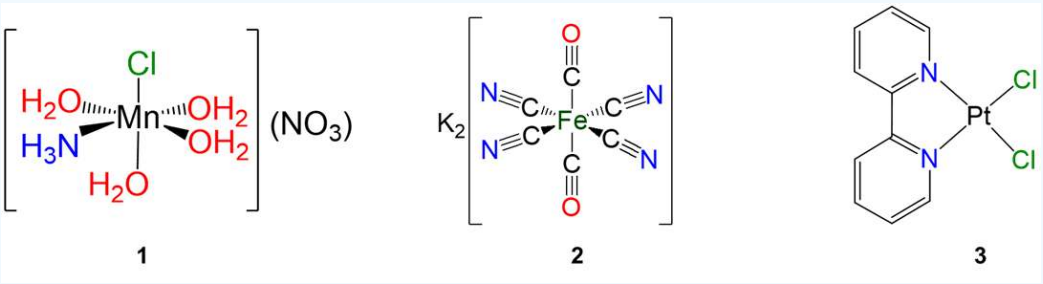


Figure 7.3.2. Summary of the rules for writing the formula of a coordination complexes along with a few examples of their application. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

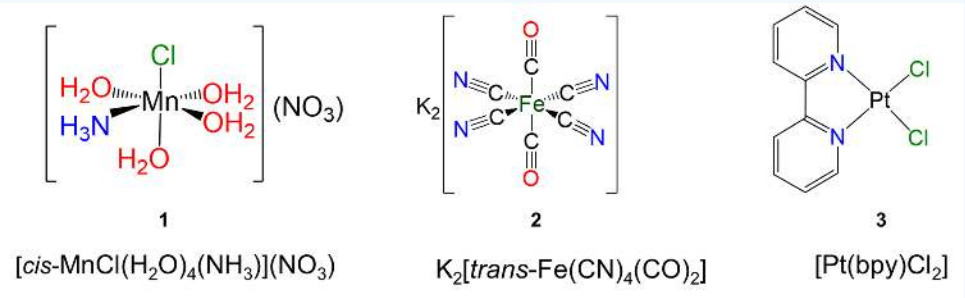
Exercise 7.3.10

Give the formulae of the following complexes.



.

Answer

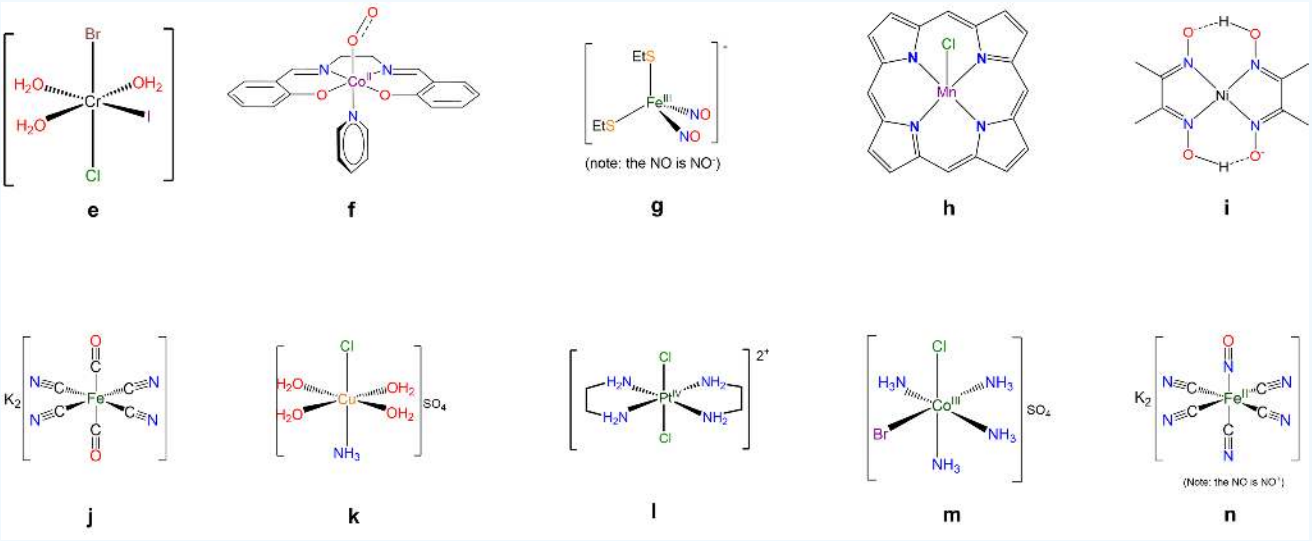


Exercise 7.3.11

Write formulae for each of the following compounds and ions. When multidentate ligands are present use suitable abbreviations.

a. pentaamminechlorocobalt(2+) sulfate
b. Δ-diamminebis(oxalato)manganate(III)
c. *trans*-tetraacetonitriledicyanoiron(II)

d. tricarbonyldichlorobis(triphenylphosphine)molybdenum



Answers

a.

$[CoCl(NH_3)_5](SO_4)$

b.

Δ-$[Mn(NH_3)_2(ox)_2]^-$

c.

trans-$[Fe(CN)_2(NCMe)_4]$

d.

$[MoCl_2(CO)_3(PPh_3)]$ or $MoCl_2(CO)_3(PPh_3)$

e.

mer-$[CrBrCl(H_2O)_3I]$

f.

$[Co(O_2)py(salen)]$

g.

$[Fe(NO)_2(SEt)_2]^-$

h.

$[MnCl(por)]^-$ or $[MnCl(porphyrin)]^-$

i.

$[Ni(DMG)_2]$ or $[Ni(Hdmg)_2]$

j.

potassium *trans*-$[Fe(CN)_2(CO)_4]$

k.

trans-$[CuCl(H_2O)_4(NH_3)]SO_4$

l.

trans-$[PtCl_2(en)_2]^{2+}$

m.

cis-$[CoBrCl(NH_3)_4]SO_4$

n.

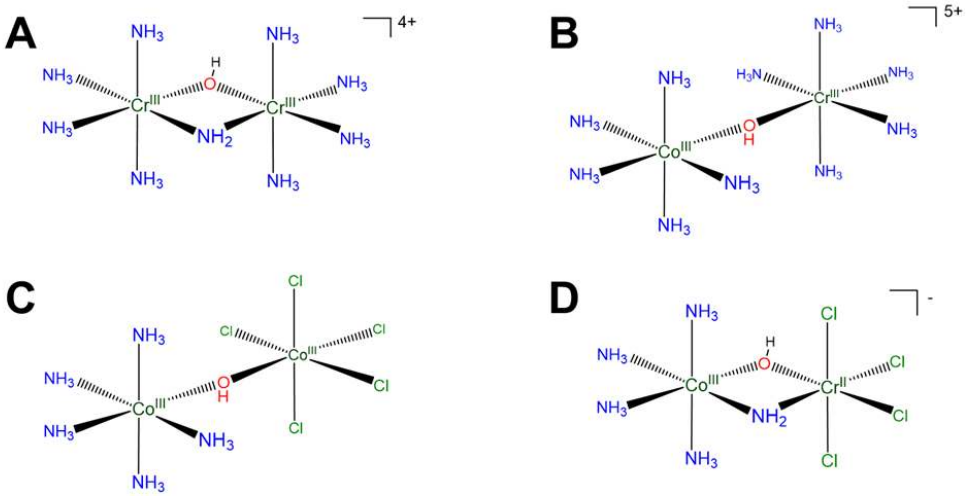
$K_2[Fe(CN)_5NO]$

Multinuclear coordination complexes

Multinuclear coordination complexes contain multiple metals connected by one or more bridging ligands. The structures of bridging complexes can usually be inferred from their μ-tagged ligands in their names and formulae. For the benefit of instructors who wish to have their students name multinuclear complexes, the rules are presented below.

Multinuclear complexes are named differently depending on whether the groups on either side of the bridging ligands are identical or different, as shown in Scheme 7.3.VIII.

Scheme 7.3.VIII. Multinuclear coordination complexes may be named differently depending on whether the groups on either side of the bridging ligands are the same or different. The groups are the same if the metal, ligands, and ligand arrangement are identical. This is true in A but in B the metals differ, in C the ligands differ, and in D both the metal and ligands differ.



Naming multinuclear complexes

Let's look at the rules for naming symmetric and asymmetric multinuclear complexes.

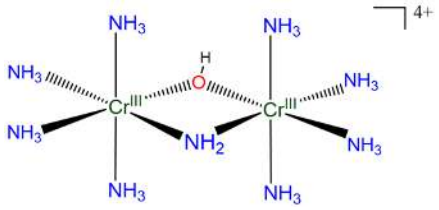
Application of the IUPAC system and variants thereof to symmetric complexes

The IUPAC naming system helpfully avoids the sort of ambiguities and *ad hoc* choices involved in most textbook-level nomenclature systems for multimetallic complexes. Unfortunately, it is correspondingly difficult for beginners to employ. Thus it will only be applied in depth to the case of symmetric complexes. Symmetric complexes are particularly easy to name in the IUPAC system and several of its variants that find common use. In these

1. The ligands are given in alphabetical order. When there are bridging and non-bridging ligands of the same type the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.*, μ_4-, μ_3-, μ_2-), the bridging ligands are specified in decreasing order of bridging multiplicity, *e.g.*, μ_3 -sulfido-di-μ-sulfido.
2. The groups bridged are given afterwards using names that follow the ordinary rules. Generally this involves either
   a. naming all the ligands followed by all the metals, in both cases using prefixes to indicate the number of each, or
   b. naming each group of atoms individually as in the less formal naming system, using prefixes to indicate the number of ligands (this is an unofficial variant of the IUPAC system that some textbook authors seem to prefer).

These two rules are sufficient to describe simple symmetric bridging complexes.

Example: The compound in Scheme 7.3.VIIIA



may be named

[μ-amido-μ-hydroxo-octaamminedichromium(4+)] ion

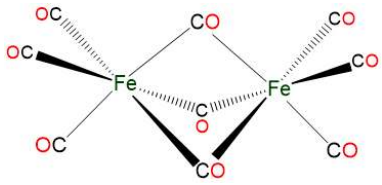
or

[μ-amido-μ-hydroxo-bis(tetraamminechromium(III))] ion

or

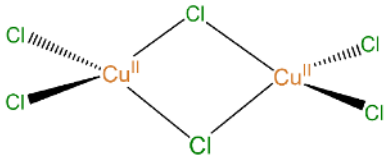
[μ-amido-μ-hydroxo-bis(tetraamminechromium)(4+)] ion

Example: The complex[5]



may be named [tri-μ-carbonyl-bis(tricarbonyliron)(0)], [tri-μ-carbonyl-bis(tricarbonyliron(0))], or [tri-μ-carbonyl-hexacarbonyldiiron)(0)]

Example: The complex



may be named di-μ-chlorido-tetrachloridodicopper(II), di-μ-chlorido-bis(dichlorocopper(II)), or di-μ-chlorido-bis(dichlorocopper)(0)

A note on the application of the IUPAC system and variants thereof to asymmetric complexes

For a symmetrical complex like the $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ considered above it is enough to specify the existence of the two bridging and four terminal chloro ligands; there is no need to number the chloro ligands or to specify exactly which ones are involved in bridging or to clarify that the bridging involves κ^2 coordination of the chloro ligands. In cases where the two metal centers or the chloro ligands differ it is necessary to specify the exact ligands and metals involved and how they are connected.

For example, a more extensive IUPAC name for $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ in which the chloro ligands are individually and more completely specified would read di-μ_2-chlorido-tetrachlorido-1κ^2Cl,2κ^2Cl-dicopper(II).

Even more extensive systems would involve numbering the metals and specifying how they are connected together too. The details of how this is done are typically beyond the level of most undergraduate and graduate courses in inorganic chemistry. Those who want to know the details should consult the red book. In many cases it is sufficient to reserve the use of formal IUPAC names for use in publications and to employ a convenient shorthand naming system for everyday use. An example of one type of system that is sometimes employed is given next.

Unofficial but commonly used methods applicable to complexes in which the groups bridged are identical or different.

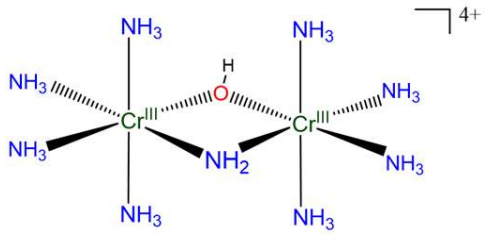
It can be quite complicated to use the IUPAC system to name asymmetric multinuclear coordination complexes. Fortunately it is rarely necessary and there are a variety of simpler somewhat *ad hoc* methods that work well for such cases. Since these methods

are commonly used by textbooks and inorganic instructors it is likely worth your while to learn about their general features. In these methods

1. A multinuclear complex is named as a derivative of one of the metal centers and the other metal centers and their ligands are treated as ligands to the prioritized metal center.
2. Unfortunately, most of the time the choice of which metals are part of the ligands and which one is central is made haphazardly. In other words, there is no agreed upon system for assigning which metal center is the central metal and which should be regarded as part of the ligands around it. One way to be more systematic about the selection of the central and ligand-embedded metals is to assign the central metal as the metal of highest priority in the IUPAC priority rules. In the IUPAC priority rules, the central metal is the highest priority metal alphabetically by name; then if there is a tie the ligands on each tied metal center are ranked alphabetically and the tied metal center with the highest priority (or most highest priority) ligands wins.
3. The metal centers not chosen as the primary metal center and all ligands around them, including those bridging to the winning metal center, are then treated as a single ligand that coordinates the winning metal center.
4. When naming the ligands and the overall complex, again there is much that is haphazard. However, in the best systems each coordination sphere is named using the same rules as for mononuclear complexes - *i.e.*, the ligands are given in alphabetical order, etc.
    - This is true of any metal center-containing ligands.
    - When there is a bridging and non-bridging ligand of the same type, the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.* μ_4-, μ_3-, μ_2-), the ligands are specified in decreasing order of bridging multiplicity, *e.g.* μ_3 -sulfido-di-μ-sulfido.

Let's apply these rules to the examples in Scheme 7.3.VIII.

Compound A:



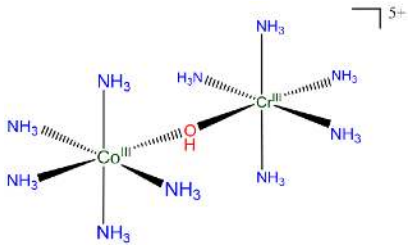
Using hydroxo for the OH^-, it may be named

[(μ-amido-tetraammine-μ-hydroxochromium(III))tetraamminechromium(III)] ion

or

[(μ-amido-tetraammine-μ-hydroxochromium)chromium(4+)] ion

Compound B:



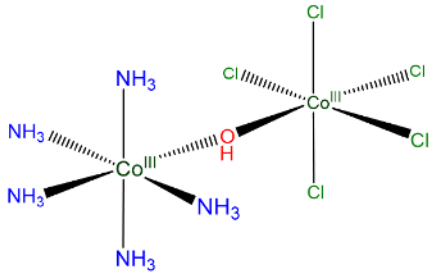
Using hydroxo for the OH^-, it may be named

[(pentaammine-μ-hydroxocobalt(III))tetraamminechromium(III)] ion

or

[(pentaammine-μ-hydroxocobalt)tetraamminechromium(5+)] ion

Compound C:



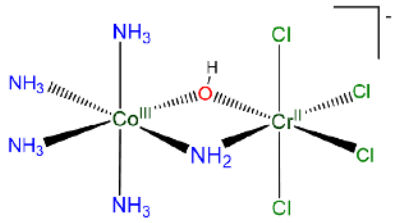
Using hydroxo for OH^-, it may be named

[pentaammine(pentachloro-μ-hydroxocobalt(III))cobalt(III)]

or

[pentaammine(pentachloro-μ-hydroxocobalt)cobalt](0)]

Compound D:



Using hydroxo for OH^- and chloro for Cl^-, it may be named

[pentaammine(pentachloro-μ-hydroxocobalt(III))chromate(III)] ion

or

[(tetrammine-μ-ammine-μ-hydroxocobalt)tetrachlorochromate](1-)] ion

As can be seen from the examples above this system gives serviceable names for multimetallic complexes but those names are not the IUPAC names and so should not be used to describe complexes outside of pedagogical and informal settings.

Writing and interpreting formulae for multinuclear complexes

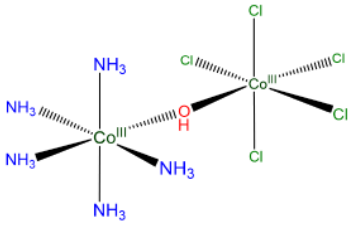
The rules for writing formulae for multinuclear complexes are the same as for mononuclear ones with two added details:

1. Write bridging ligands after nonbridging ligands of the same type. For example, Cu_2Cl_6 should be written as $[Cu_2Cl_4\text{-}(\mu\text{-}Cl)_2]$
2. However, you may ignore that and other rules if you find it helpful to keep groups of metals and ligands together in a way that better conveys how the atoms are connected. Just as the structure of ethane may be more clearly conveyed as H_3CCH_3 instead of CH_3CH_3, the complex $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ may be written as $[(Cl_2Cu)(\mu\text{-}Cl)_2(CuCl_2)]$.

Other Examples:

For dichromate write, $[Cr_2O_6(\mu\text{-}O)]^{2-}$ or $[O_5Cr\text{-}\mu\text{-}O\text{-}CrO_5]^{2-}$

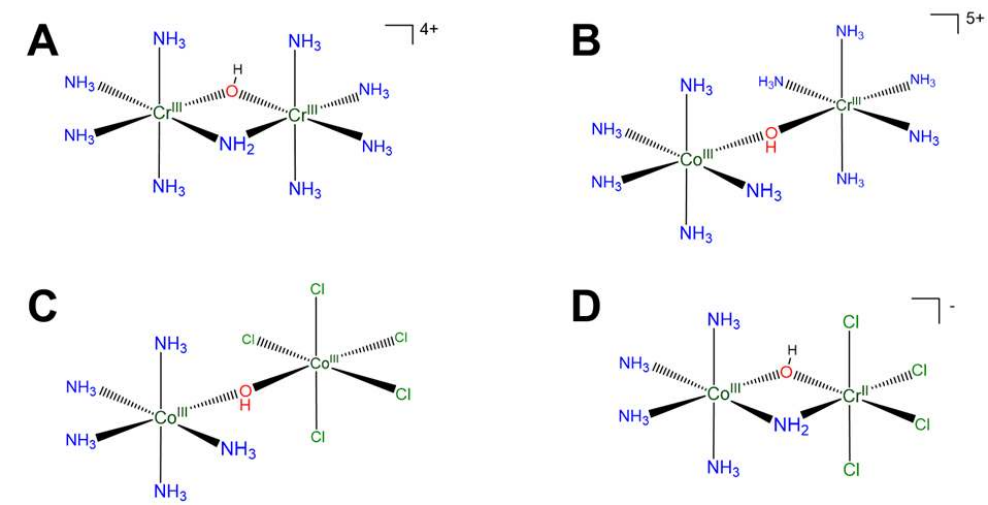
For compound C of Scheme 7.3.VIII.



write $[Co_2Cl_5(NH_3)_5(\mu\text{-}OH)]$ or, even better, $[(H_3N)_5Co(\mu\text{-}OH)CoCl_5]$.

Exercise 7.3.10

Write reasonable formulae for complexes A, B, and D in Scheme 7.3.VIII, which for convenience is reproduced below.



Sample answers for A

$[Cr_2(NH_3)_8\text{-}\mu(NH_2)\text{-}\mu(OH)]^{4+}$ or $[(H_3N)_4Cr^{III}\text{-}\mu(NH_2)\text{-}\mu(OH)\text{-}Cr^{II}(NH_3)_4]$ and variants thereof involving writing the H_3N as NH_3, μ as μ_2, etc.

Sample answers for B

$[CoCr(NH_3)_{10}\text{-}\mu(OH)]^{5+}$ or, better, $[(H_3N)_5Co^{III}\text{-}\mu(OH)\text{-}Cr^{III}(NH_3)_5]^{5+}$

Sample answers for C

This was already done as an example above, $[Co_2Cl_5(NH_3)_5\text{-}\mu(OH)]$ or, better, $[(NH_3)_5Co^{III}\text{-}\mu(OH)\text{-}Co^{III}Cl_5]$ and variants thereof

Sample answers for D

$[CoCrCl_4(NH_3)_4\text{-}\mu(NH_2)\text{-}\mu(OH)]$ or, better, $[(H_3N)_4Co^{III}\text{-}\mu(NH_2)\text{-}\mu(OH)\text{-}Cr^{II}Cl_4]$

References

1. International Union of Pure and Applied Chemistry *Nomenclature of Inorganic Chemistry* Cambridge, UK, 2005.

2. The structure and name is taken from Choudhury, S. B.; Allan, C. B.; Maroney, M.; Wodward, A. D.; Lucas, C. R. *Inorg. Synth.* **1998**, *32*, 98-107.

3. Haas, K. Naming Transition Metal Complexes. https://chem.libretexts.org/Courses/Saint_Mary's_College%2C_Notre_Dame%2C_IN/CHEM_342%3A_Bio-inorganic_Chemistry/Readings/Week_2%3A_Introduction_to_Metal-Ligand_Interactions_and_Biomolecules/2.1_Transition_metal_complexes/2.1.6%3A_Naming_Transition_Metal_Complexes

4. There is a widely-circulated myth that anionic ligands should be named before neutral ones. This myth is false. According to the IUPAC red book (bolding mine):

> IR-2.15.3.4: Ordering ligands in formulae and names in formulae of coordination compounds,
>
> The formulae or abbreviations representing the ligands **are cited in alphabetical order as the general rule**. Bridging ligands are cited immediately after terminal ligands of the same kind, if any, and in increasing order of bridging multiplicity. (See also Sections IR-9.2.3 and IR-9.2.5.)
>
> IR-9.2.3.1 Sequence of symbols within the coordination formula

(i) The central atom symbol(s) is (are) listed first.

(ii) The **ligand symbols (line formulae, abbreviations or acronyms) are then listed in alphabetical order** (see Section IR-4.4.2.2).5 Thus, CH_3CN, MeCN and NCMe would be ordered under C, M and N respectively, and CO precedes Cl because single letter symbols precede two letter symbols. **The placement of the ligand in the list does not depend on the charge of the ligand.**

(iii) More information is conveyed by formulae that show ligands with the donor atom nearest the central atom; this procedure is recommended wherever possible, even for coordinated water.

5. Technically organometallic complexes are named according to slightly different rules but the coordination compound naming system works here. Note that this complex was once thought to possess an Fe-Fe bond, in accordance with the predictions of the 18-electron rule. Consequently, older sources often give an [*Fe-Fe*] after the name to reflect the presence of that bond. However, as the complex is no longer thought to possess an Fe-Fe bond it is omitted here.

Contributors and Attributions

Stephen Contakes, Westmont College, to whom comments, corrections, and criticisms should be addressed.

with some examples taken from Naming Transition Metal Complexes by Kathryn Haas.

Consistent with the policy for original artwork made as part of this project, all unlabeled drawings of chemical structures are by Stephen Contakes and licensed under a Creative Commons Attribution 4.0 International License.

This page titled 7.3: Nomenclature and Ligands is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.3: Nomenclature and Ligands** by Stephen M. Contakes has no license indicated.

7.4: Structures

7.4.1 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:

7.4.1.1 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.

7.4.1.2 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 7.4.1. 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).

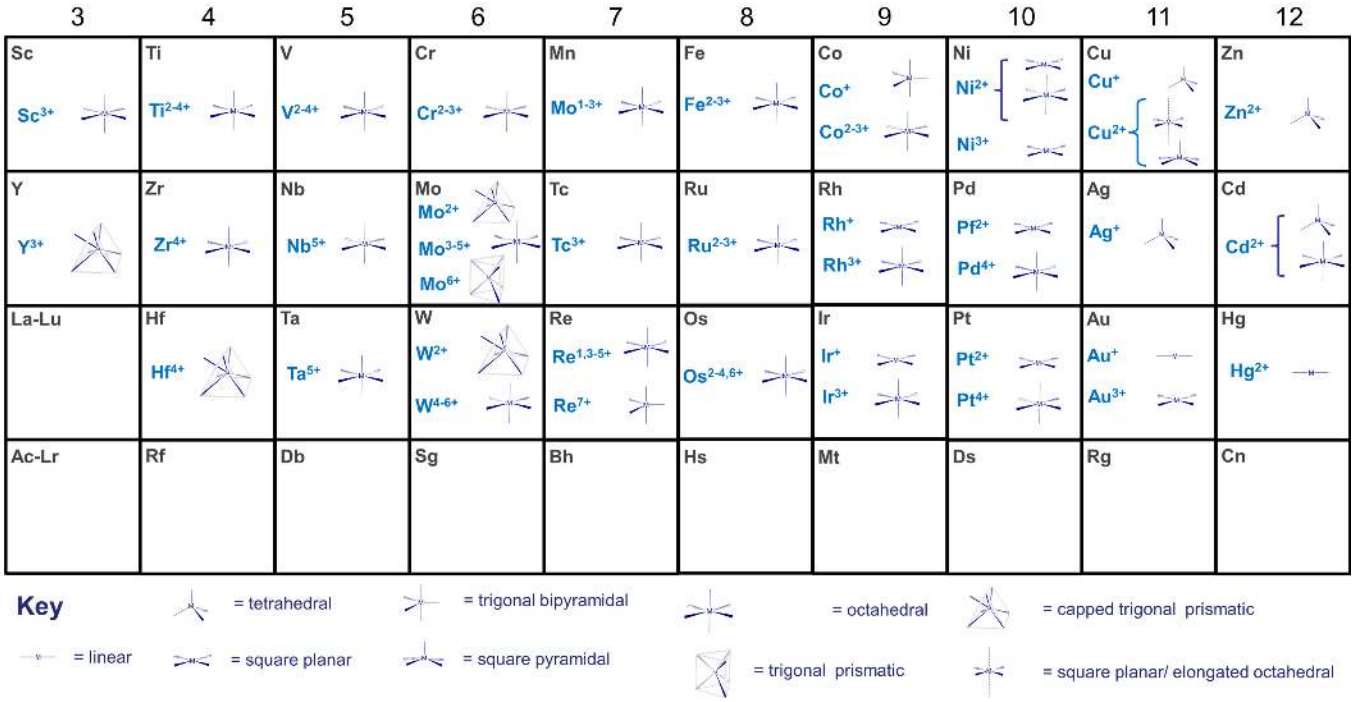


Figure 7.4.1. Preferred coordination geometries of the transition elements. Assignments are as reported in reference 1 except for Cu^{2+}, which is assigned above as square planar/elongated octahedral instead of the square planar assignment given in that work. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.1.3 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 7.4.2. As may be seen from the geometries listed in Figure 7.4.2, 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 7.4.2.

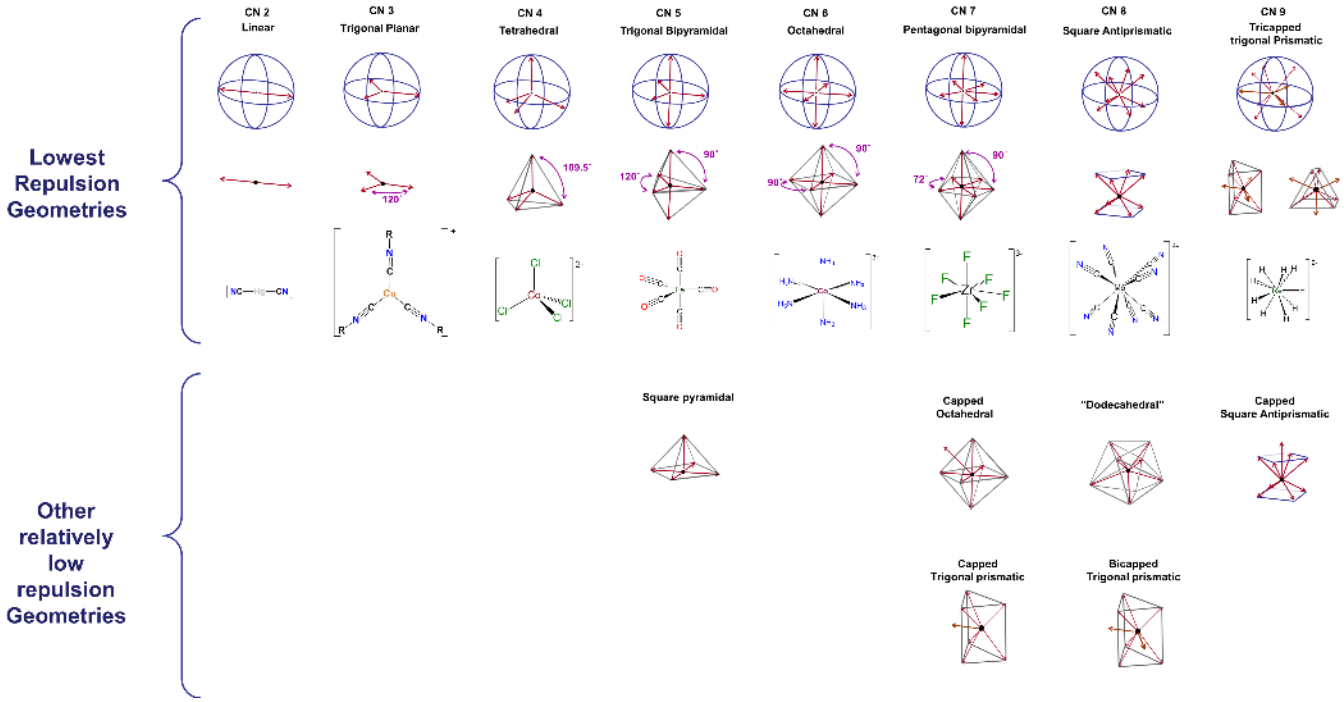


Figure 7.4.2. Coordination geometries predicted by the Kepert model for coordination numbers two through nine along with other coordination geometries similar in energy to the lowest repulsion geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.1.4 d-electron effects

A few coordination geometries are noticeably absent from the Kepert-preferred and Kepert-accessible geometries in Figure 7.4.1. 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 7.4.2 may be extended to that shown in Figure 7.4.3.

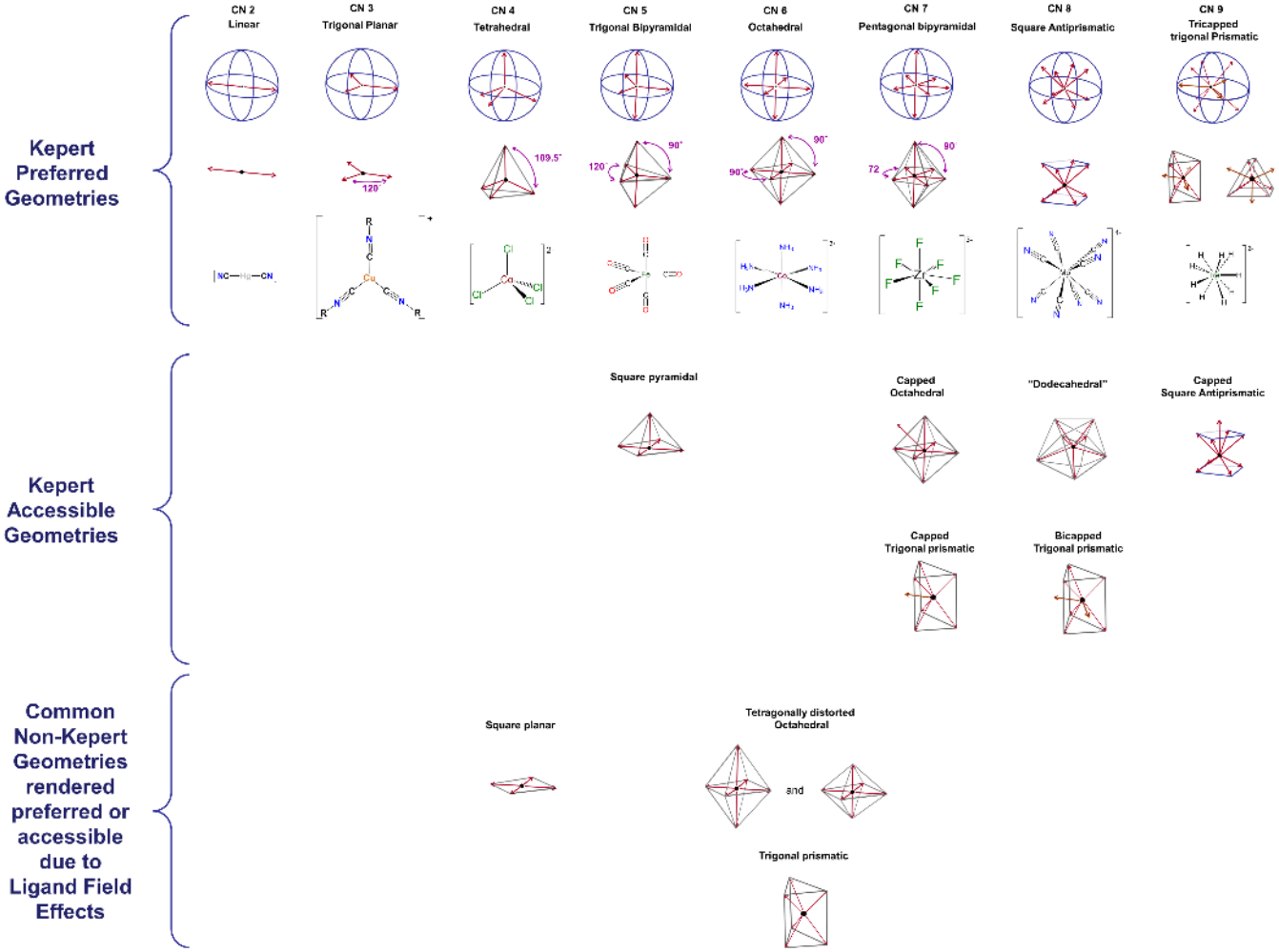


Figure 7.4.3. Coordination geometries accessible for 2-9 coordinate complexes even without constraint by rigid or semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.1.5 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 7.4.4.

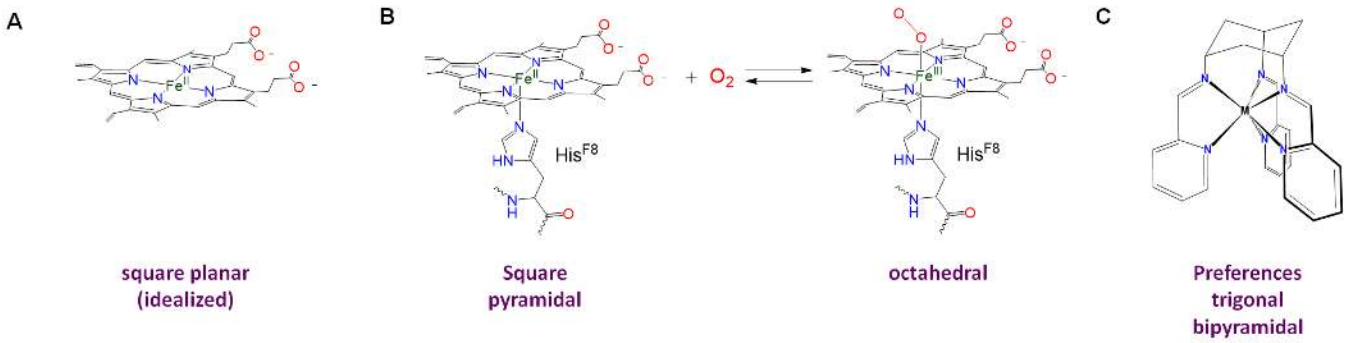


Figure 7.4.4. Examples of rigid/semirigid ligands that can impose their preferred coordination geometry on a metal center. Porphyrins, phyhalocyanines and related macrocycles tend to impose a slightly bent square planar coordination geometry, although (B) many such complexes, including the iron of myoglobin's heme cofactor, coordinate additional ligands to give square planar or octahedral complexes. (C) Synthetic multidentate ligands have been developed to preference trigonal prismatic coordination geometries, including the one shown here. It forms roughly trigonal prismatic complexes with Co^{II} and $Zn^{II,}$ albeit imperfect ones.[3] This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The influence of ligands on coordination geometry is important in living systems, in which proteins and nucleic acids can act as rigid or semirigid ligands. The ability of these ligands to distort the coordination geometries of metal atoms in ways that enable them to perform specific functions is so common that the resulting distorted geometries are termed entactic states. A particularly spectacular case of an entactic state involves the blue copper proteins azurin and plastocyanin, the structure of which is given in Figure 7.4.5.

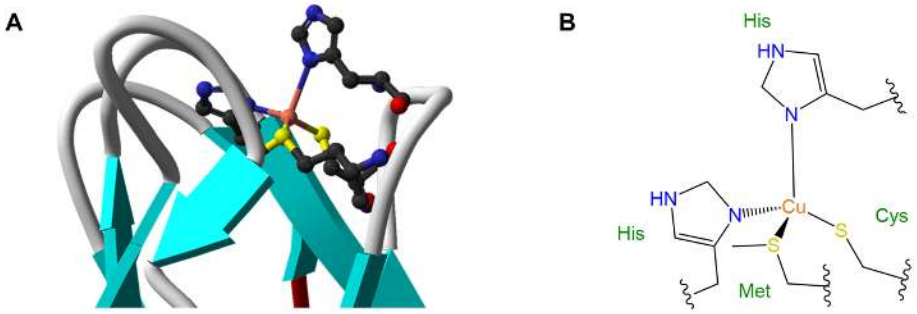


Figure 7.4.5. (A) Structure and (B) schematic of the plastocyanin active site showing the distorted tetrahedral coordination environment that the protein imposes on the copper center (tan), which is most evident from the long vertically oriented Cu-Histidine bond. The image in part A is cropped from 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 7.4.5, 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.

7.4.1.6 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.

7.4.1.7 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 7.4.6A.

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 7.4.6B, 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.

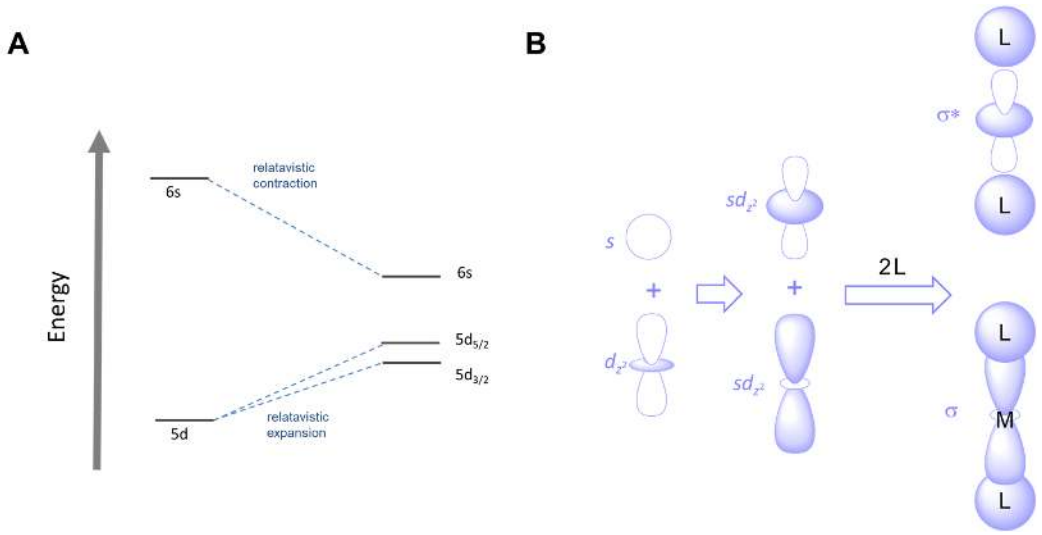


Figure 7.4.6. (A) Gold experiences relativistic expansion and contraction of its 5*d* and 6*s* orbitals, resulting in shifts to their relative energies. (B) This makes mixing of these orbitals more favorable, facilitating the ability of gold to form two-coordinate complexes with strong sigma bonds that involve considerable sd_{z^2} character. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2 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.

7.4.2.1 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 7.4.7.

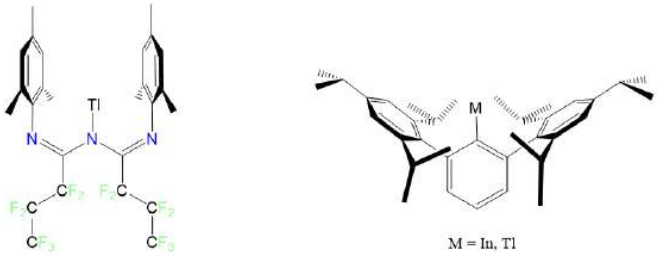
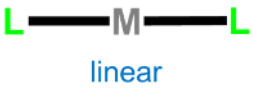


Figure 7.4.7. No monocoordinate transition metal complexes are known, but Tl^{+} and In^{+} form monocoordinate complexes with extremely bulky ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2.2 Coordination Number 2.

A coordination number of 2 is rare outside of ***d*^{10} complexes of the group 11 metals and mercury**, specifically, Cu^+, Ag^+, Au^+, and Hg^{2+}. In accordance with the predictions of the Kepert model these give **linear complexes.**



Among these,

- Cu^+ more commonly gives tetrahedral complexes but can be coaxed to give linear ones. The most prominent example is $[CuCl_2]^-$, which forms when CuCl is treated with concentrated HCl under anerobic conditions.
- Ag^+ also commonly forms tetrahedral or trigonal planar complexes but can give linear ones. The most prominent example is $[Ag(NH_3)_2]^+$, which can be formed by treating silver slats with concentrated aqueous or liquid ammonia.
- Au^+ almost always forms linear complexes, but many of these formally two-coordinate complexes associate as depicted in Figure 7.4.8. 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.

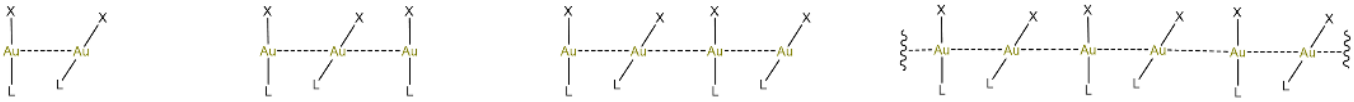


Figure 7.4.8. Many "linear" gold complexes associate side-on to form dimers, trimers, tetramers, and chains. Although in this chapter L is usually taken to represent a generic ligand, in this scheme L represents a neutral ligand that donates two electrons to the metal (py, PR_3, CO, etc.) and X an anionic 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 7.4.9.

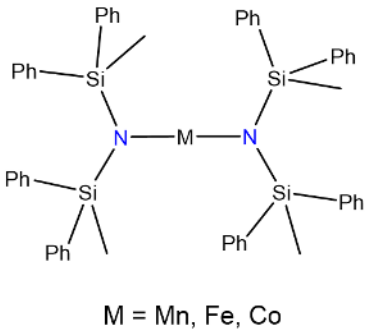
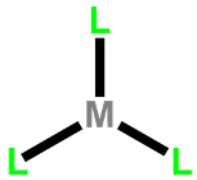


Figure 7.4.9. Two-coordinate complexes form between Mn^{2+}, Fe^{2+}, and Co^{2+} with $N(SiMePh_2)_2$.[6] This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2.3 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

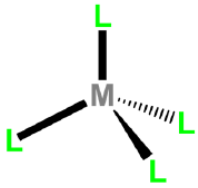
Figure 7.4.10.



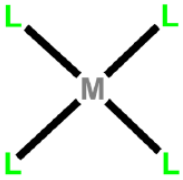
Figure 7.4.10. Three-coordinate complexes prepared using bulky and semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2.4 Coordination Number 4

The two common four-coordinate geometries are tetrahedral and square planar.



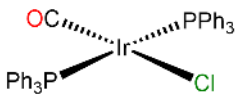
tetrahedral



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

7.4.2.5 Coordination Number 5

The two common coordination geometries for five-coordinate complexes are trigonal bipyramidal and square pyramidal.



Figure 7.4.11.

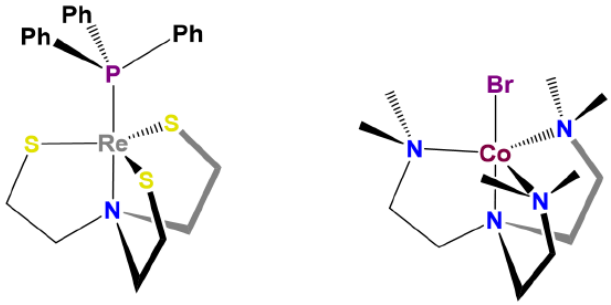


Figure 7.4.11. Some tripodal ligands preference the formation of trigonal bipyramidal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 7.4.4 and for complexes containing oxo and nitrido ligands, examples of which are shown in Figure 7.4.12.

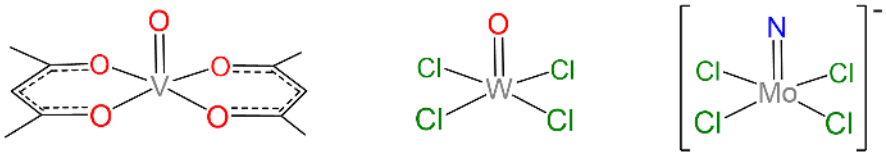


Figure 7.4.12. Some square pyramidal oxo and nitrido complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 7.4.13.

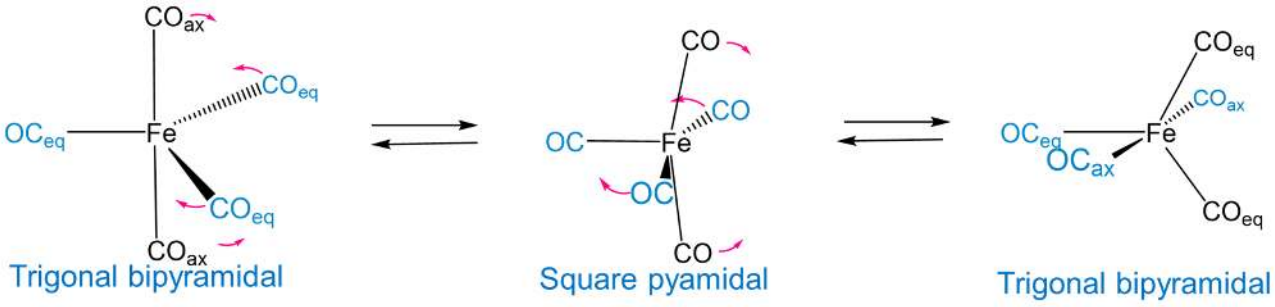


Figure 7.4.13. Fluxionality in pentacarbonyliron(0) involves exchange of axial and equatorial carbonyl ligands via Berry pseudorotation. Interconversion of the axial and equatorial carbonyl groups occurs faster than the NMR timescale at room temperature. As a result the ^{13}C NMR spectrum of $Fe(CO)_5$ 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.

7.4.2.6 Coordination Number 6

The two common coordination geometries for coordination number 8 are octahedral and trigonal prismatic.

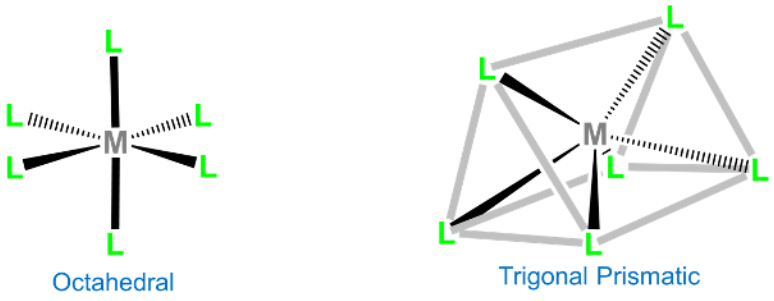


Figure 7.4.14.

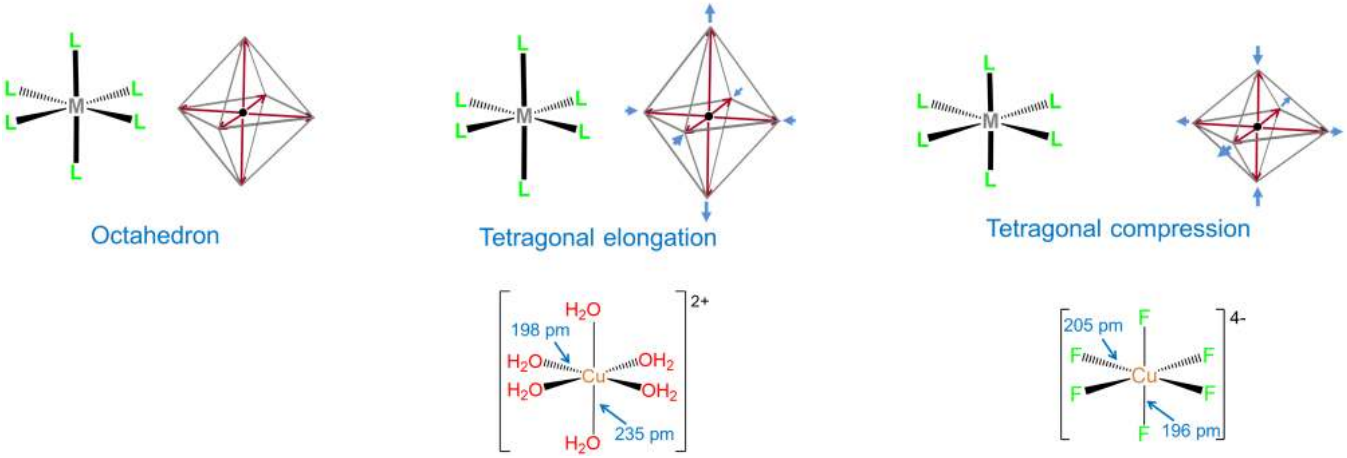


Figure 7.4.14. Tetragonal distortions commonly occur for d^4, d^7 , and d^9 octahedral complexes. The most common type involves axial elongation in which the octahedron is stretched along a single *trans*-L-M-L axis, but axial compressions in which the octahedron is compressed along such an axis instead 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 7.4.15. As may be seen in Figure 7.4.15, 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.

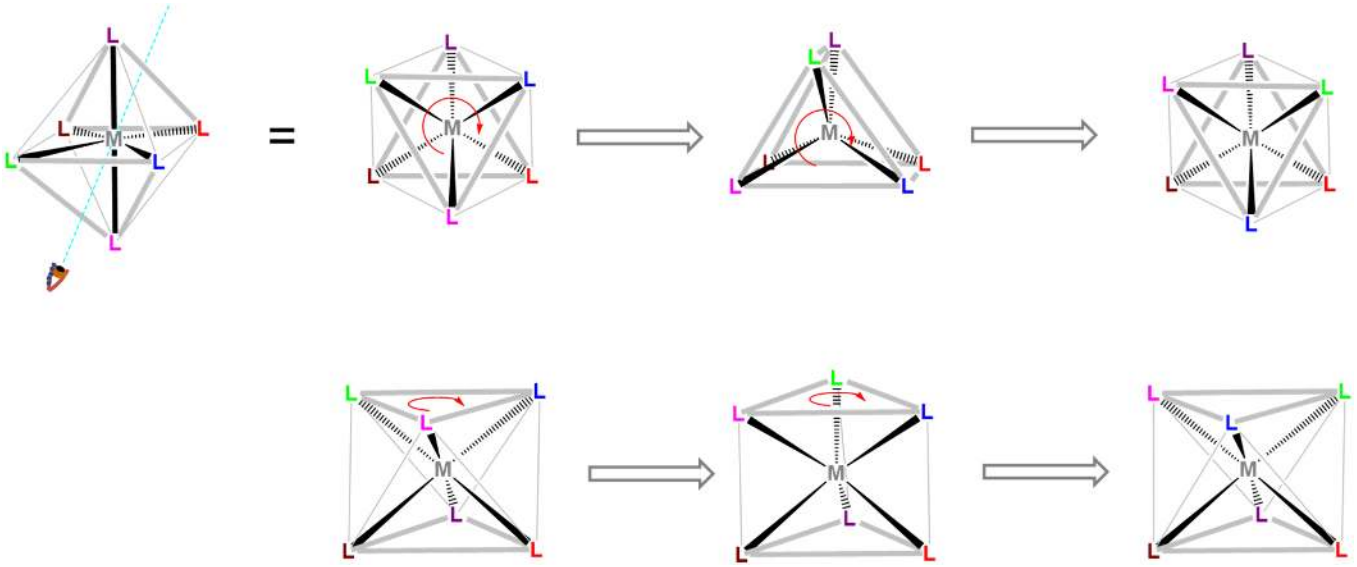


Figure 7.4.15. Since an octahedron is a trigonal antiprism, a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is 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 7.4.16. Semirigid ligands like that shown in Figure 7.4.4C 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.

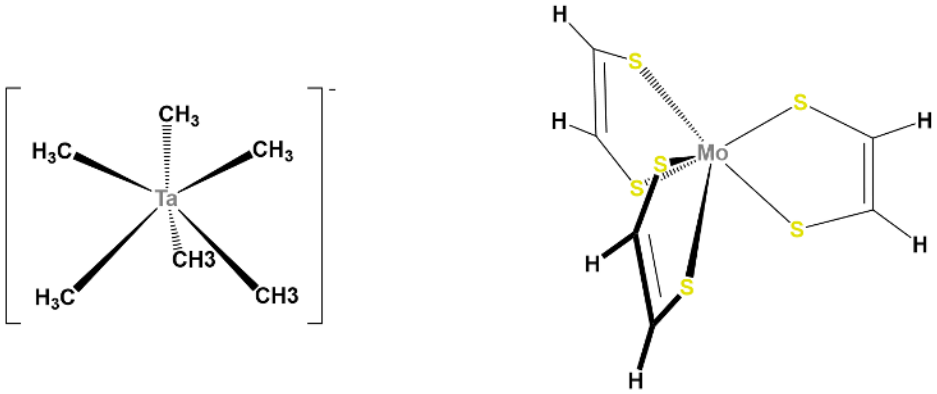
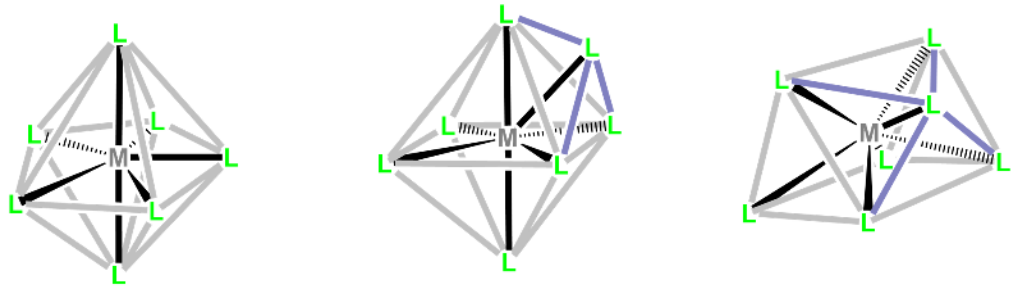


Figure 7.4.16. The complexes $[Ta(CH_3)_6]^-$ and $[Mo(S_2C_2H_2)_3]$ adopt a trigonal prismatic geometry. Trigonal prismatic coordination is common for d^0 and d^1 complexes with alkyl and dithiolene ligands. It is also typical for the dithiolene ligands to coordinate along the rectangular edges of the trigonal prism instead of the triangular ones. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2.7 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 7.4.17.

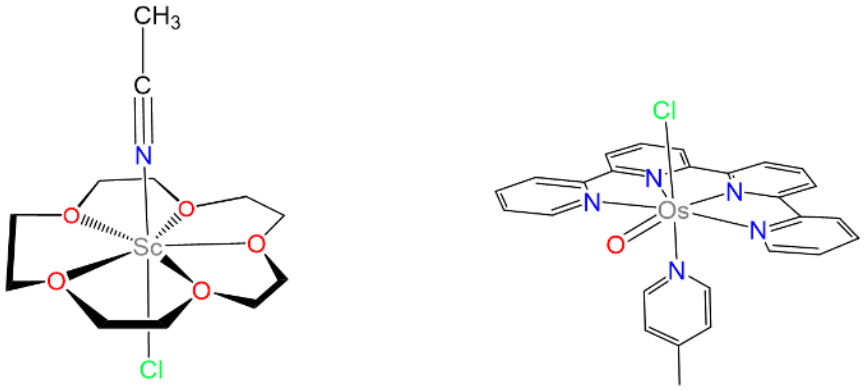


Figure 7.4.17. Seven-coordinate complexes containing ligands that encourage the formation of seven-coordinate geometries. Note that while in $[NbOF_6]^{3-}$ and $[UO_2F_5]^{3-}$ the oxo ligands occupy axial positions, the Osmium complex shown possesses an oxo ligand in an equatorial position. This is 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 7.4.18.

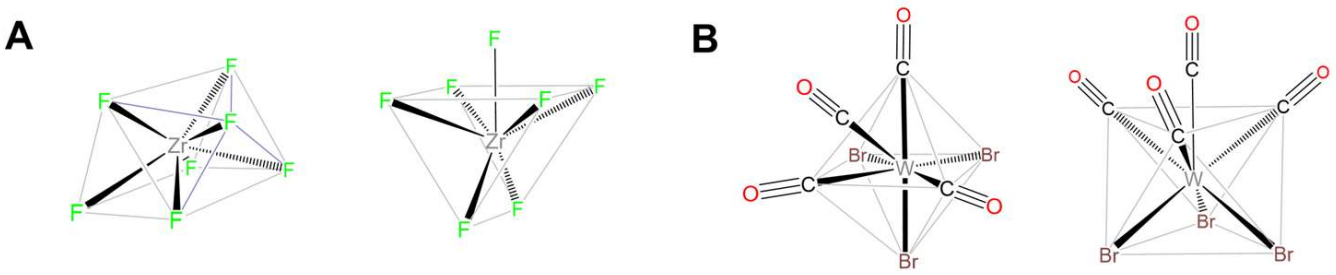


Figure 7.4.18. Examples of complexes that adopt monocapped triconal prismatic and monocapped octahedral geometries.(A) Two views of the structure of (A) capped trigonalprismatic $[ZrF_7]^{3-}$ and (B) capped octahedral $[WBr_3(CO)_4]$. This work by Stephen Contakes is licensed under a Creative Commons 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 7.4.19).

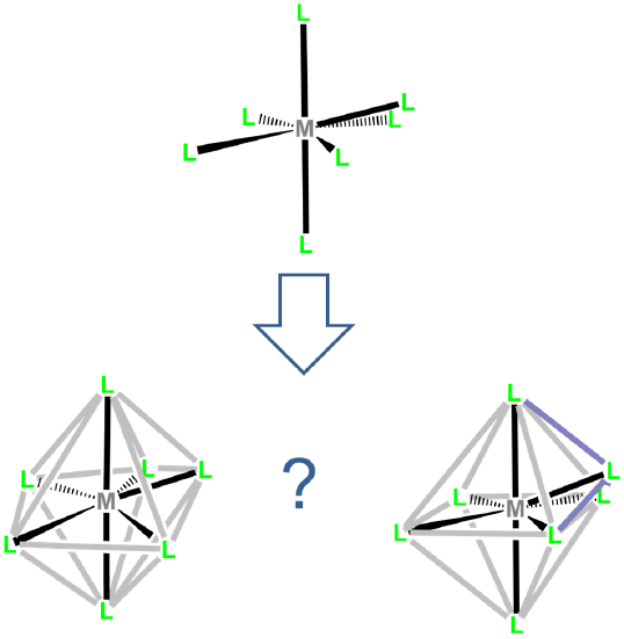


Figure 7.4.19. Many seven-coordinate structures are distorted and can be difficult to classify. For example, how should the geometry of this complex be described - as distorted trigonal bipyramidal or distorted monocapped octahedral? This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2.8 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 $Na_3[UF_8]$.

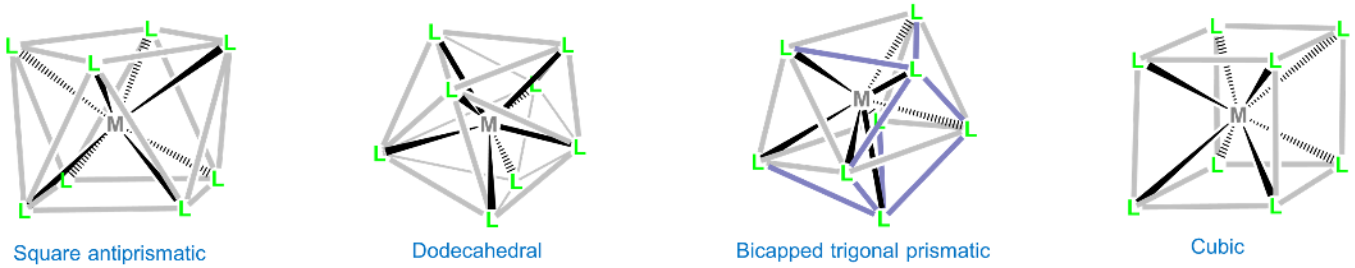


Figure 7.4.20. The square antiprism may be made by twisting one face of a cube relative to another, and the dodecahedron by folding opposing faces towards one another.

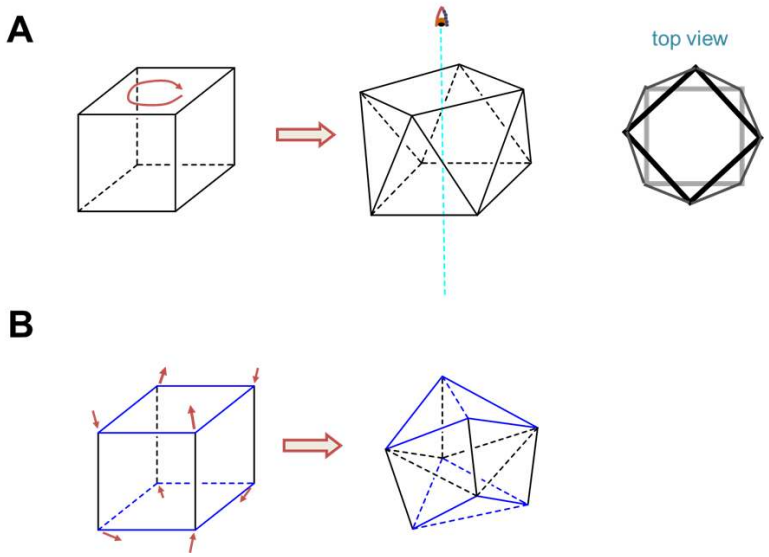


Figure 7.4.20. The (A) square antiprismatic and (B) dodecahedral coordination geometries are distorted cubic geometries. (A) The square antiprismatic coordination geometry is just a cubic coordination geometry in which one face has been rotated 45° relative to its opposite (and for which the distance 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 7.4.21.

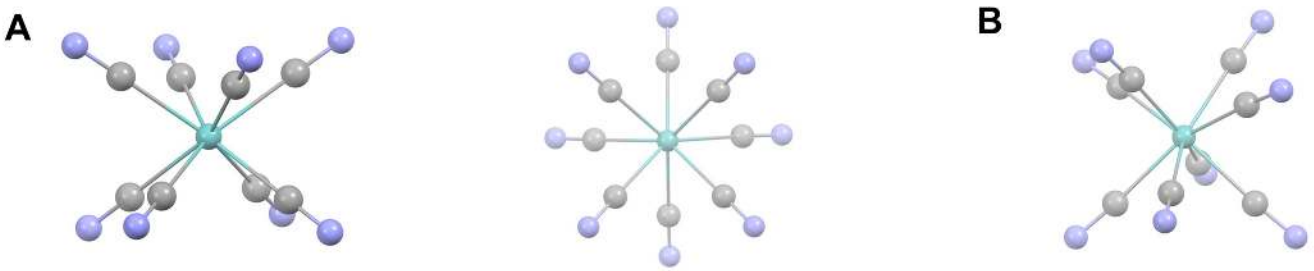


Figure 7.4.21: Structures reported for (A) square antiprismatic $[Mo(CN)_8]^{3-}$ as a solid 4,4'-Diazenediyldipyridinium salt and (B) dodecahedral $[Mo(CN)_8]^{4-}$ as a solid tetra-n-butylammonium salt.

7.4.2.9 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 $[ReH_9]^{2-}$.

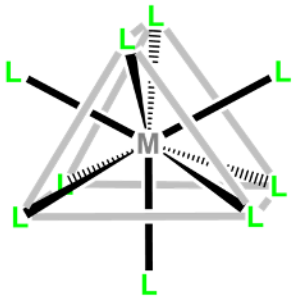


Figure 7.4.22.

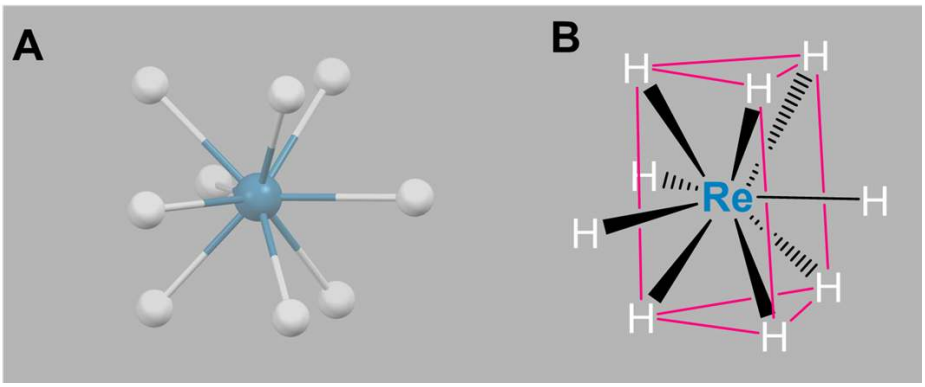


Figure 7.4.22. (A) Structure of $[ReH_9]^{2-}$ in $K_2[ReH_9]$ and (B) schematic showing how the structure maps onto a tricapped trigonal pyramidal coordination geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

7.4.2.10 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 7.4.23, $[Hf(BH_4)_4]$ 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.

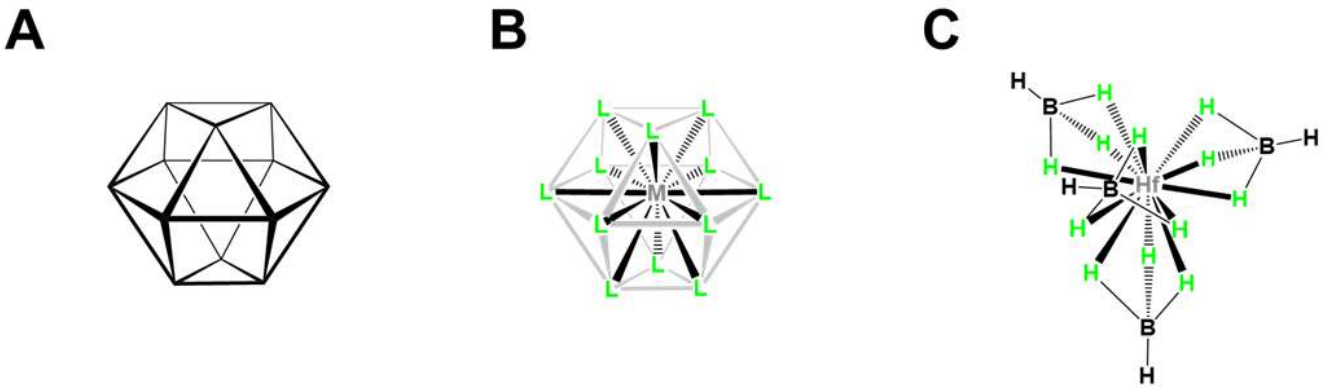


Figure 7.4.23. The anticubooctahedral coordination geometry is observed for $[Hf(BH_4)_4]$. (A) An anticubooctahedron consists of a hexagonal ring capped with antiparallel triangles above and below the ring. (B) Idealized anticubooctahedral complex. (C) Structure of $[Hf(BH_4)_4]$. This work by Stephen 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 7.4.24. The nitrates in the structure bind the Ce center in bidentate fashion in an octahedral array.

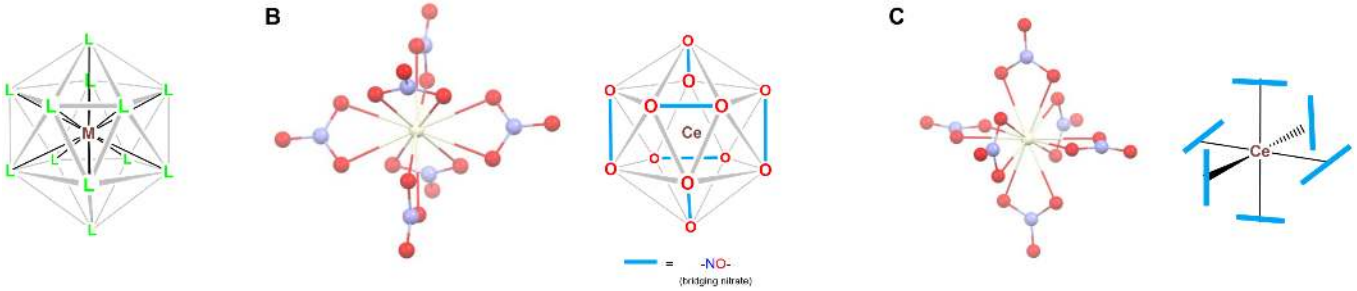


Figure 7.4.24. Coordination geometry of $[Ce(NO_3)_6]^{2-}$ in $[Mg(H_2O)_6][Ce(NO_3)_6]\cdot H_2O$. (A) Idealized icosahedral coordination. (B) View of the structure of $[Ce(NO_3)_6]^{2-}$ showing how it maps onto the icosahedral coordination geometry. (C) The structure may also be thought of as comprising 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 7.4.25. 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.

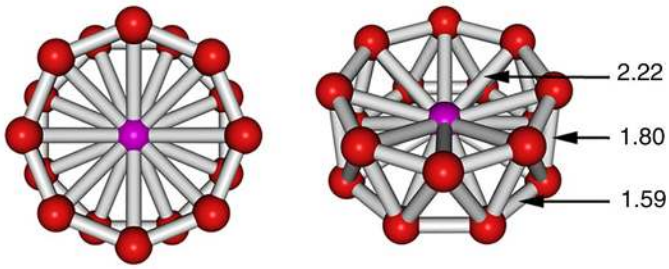


Figure 2A from Popov, I., Jian, T., Lopez, G. *et al.* Cobalt-centered boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015). https://doi.org/10.1038/ncomms9654, which is is licensed in that publication under a Creative Commons Attribution 4.0 International License.

7.4.3 References

1. Dudev, M.; Wang, J.; Dudev, T.; Lim, C., Factors Governing the Metal Coordination Number in Metal Complexes from Cambridge Structural Database Analyses. *The Journal of Physical Chemistry B* **2006**, *110(4)*, 1889-1895.
2. Kuppuraj, G.; Dudev, M.; Lim, C., Factors Governing Metal−Ligand Distances and Coordination Geometries of Metal Complexes. *The Journal of Physical Chemistry B* 2009, 113 (9), 2952-2960.
3. Cremades, E.; Echeverría, J.; Alvarez, S., The Trigonal Prism in Coordination Chemistry. *Chemistry – A European Journal* 2010, 16 (34), 10380-10396.
4. Xiong, X.-G.; Wang, Y.-L.; Xu, C.-Q.; Qiu, Y.-H.; Wang, L.-S.; Li, J., On the gold–ligand covalency in linear $[AuX_2]^-$ complexes. *Dalton Transactions* 2015, 44 (12), 5535-5546.
5. Concepción Gimeno, M. The Chemistry of Gold in Laguna, Antonio (ed.) *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications*. Wiley, 2008.
6. Andersen, R. A.; Faegri, K.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W. P.; Rypdal, K., Synthesis of bis[bis(trimethylsilyl)amido]iron(II). Structure and bonding in M[N(SiMe3)2]2 (M = manganese, iron, cobalt): two-coordinate transition-metal amides. *Inorganic Chemistry* 1988, 27 (10), 1782-1786.
7. Persson, I., Hydrated metal ions in aqueous solution: How regular are their structures? Pure and Applied Chemistry 2010, 82*(10)*, 1901.

8. Aramburu, J. A.; García-Fernández, P.; García-Lastra, J. M.; Moreno, M., Jahn–Teller and Non-Jahn–Teller Systems Involving CuF_6^{4-} Units: Role of the Internal Electric Field in Ba2ZnF6:Cu2+ and Other Insulating Systems. *The Journal of Physical Chemistry C* 2017, *121(9)*, 5215-5224.
9. Brown, M. D.; Levason, W.; Murray, D. C.; Popham, M. C.; Reid, G.; Webster, M., Primary and secondary coordination of crown ethers to scandium(iii). Synthesis, properties and structures of the reaction products of ScCl3(thf)3, ScCl3·6H2O and Sc(NO3)3·5H2O with crown ethers. Dalton Transactions 2003, (5), 857-865.
10. Liu, Y.; Ng, S.-M.; Lam, W. W. Y.; Yiu, S.-M.; Lau, T.-C., A Highly Reactive Seven-Coordinate Osmium(V) Oxo Complex: [OsV(O)(qpy)(pic)Cl]2+. Angewandte Chemie International Edition 2016, 55 (1), 288-291.
11. Popov, I., Jian, T., Lopez, G. *et al.* Cobalt-centred boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015). https://doi.org/10.1038/ncomms9654
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.
15. Zalkin, A.; Forrester, J.D.; Templeton, D.H. Crystal structure of cerium magnesium nitrate hydrate *Journal of Chemical Physics*, **1963**, *39*, 2881-2891.
16. Daly, S. R.; Piccoli, P. M. B.; Schultz, A. J.; Todorova, T. K.; Gagliardi, L.; Girolami, G. S., Synthesis and Properties of a Fifteen-Coordinate Complex: The Thorium Aminodiboranate [Th(H3BNMe2BH3)4]. Angewandte Chemie International Edition 2010, 49 (19), 3379-3381.
17. Popov, I., Jian, T., Lopez, G., Boldyrev, A. I.; Wang, L-S. Cobalt-centred boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015).

This page titled 7.4: Structures is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.5: Coordination Numbers and Structures** by Stephen M. Contakes is licensed CC BY 4.0.

7.5: Isomerism

Metal complexes present a rich, interesting, and diverse structural chemistry. Major points of variation in the structural chemistry of metal complexes include

1. **coordination number** and **coordination geometry**, which involve differences in how many ligands surround a central metal and their overall geometric arrangement. Examples of the latter include the tetrahedral and square planar geometries commonly observed for four-coordinate metal centers. Tetrahedral, square planar, and octahedral coordination serve as a backdrop to the discussion of isomerism on this page. Readers who are unfamiliar with these structures might consider reading the section on coordination geometries before this one.
2. **structural iosmerism** involves differences in how potential ligand atoms are bound to metals in a complex. Possibilities for structural isomerism include
   - linkage or ambidentate isomerism
   - hydrate/solvate isomerism
   - ionization isomerism
   - coordination isomerism.

   Of these, linkage isomerism should always be considered when working with ambidentate ligands. As classifications, the last three forms of structural isomerism are mainly of academic interest since they represent permutations of ordinary structure patterns for solvates, salts, and coordination complexes, respectively.
3. **stereochemistry**, which includes
   - which coordination geometry is adopted for a metal with a given set of ligands in a particular oxidation state. For instance, $[Ni^{II}Cl_4]^{2-}$ is tetrahedral while $[Pt^{II}Cl_4]^{2-}$ is square planar. Since this geometry is usually fixed by the metal and ligands it is typically not a source of stereoisomeric varierty.
   - metal-centric stereoisomerism involving possible variations in where ligands are located relative to one another around the metal. The possibilities depend on the coordination number, geometry, and number of different types of ligands. For instance, square planar complexes can exhibit *cis-/trans-* isomerism while tetrahedral ones cannot. Tetrahedral complexes with four different ligands exhibit *R* and *S* chirality but complexes of that type are relatively rare. The more common cases include *cis* and *trans* isomerism in square planar complexes and *cis* & *trans-*, *mer* & *fac-*, and Λ & Δ isomerism in octahedral ones, although some multidentate ligands present additional possibilities for stereochemical variation
   - Stereoisomerism centered on the ligands bound to a metal center. Possibilities include
     - stereoisomerism inherent to a ligand. This would include cases where the ligand itself is chiral or, as in the case of amines, exists as a rapidly interconverting mixture of isomers. Thus this sort of stereoisomerism is an extension of the isomerism encountered in ordinary organic and other main group compounds. The main new issues introduced by binding of such ligands to a metal center involve the creation of new possibilities for diastereoisomerism based on the stereochemistry of the metal center and the freezing out of stereocenter inversion on binding to a metal. The latter is particularly important for amines, which as free amines racemize rapidly by nitrogen inversion.
     - or conformational isomerism involving five-membered **chelate rings** created when a multidentate ligand binds to a metal. This isomerism is often called chelate ring twist since individual rings can exhibit one of two conformations depending on how they twist on binding.

A summary of these forms of isomerism is given in Figure 7.5.1.

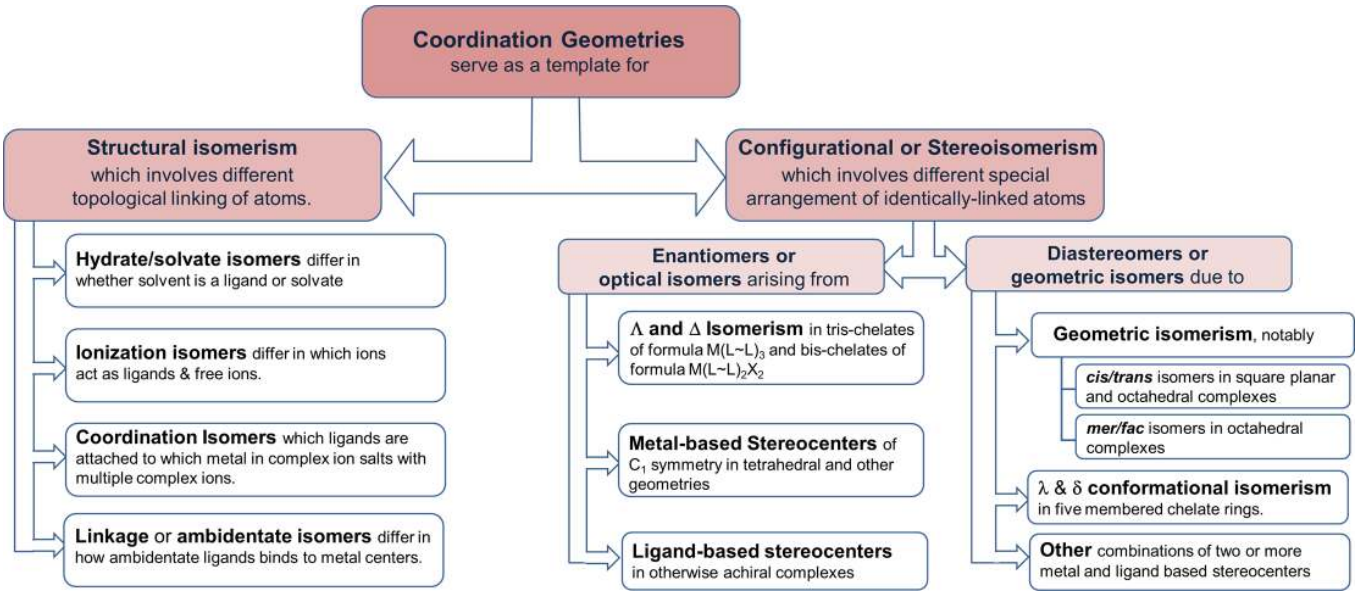


Figure 7.5.1. Relationship among the common types of isomerism in metal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Structural isomers

Structural isomerism involves different topological linkages of atoms. Differences in atomic linkages distinctive to coordination chemistry involve the linkages between metals and ligands. The main variations are:

1. Hydrate/solvate isomerism

Solvate isomers differ in terms of whether a molecule acts as a ligand or whether it acts as a solvate by occupying a lattice site in the crystal. Among solvate isomers, the case in which water is the ligand or solvate is the best known. The resulting isomers are called **hydrate isomers** after the term for water acting as a solvate, hydrate. A well-known example that illustrates how solvate isomerism works is the series $[CrCl_x(H_2O)_{6-x}]Cl_{3-x}{\cdot}xH_2O$, for which x = 0-2. The structures of the complex ions involved in this series are shown in Figure 7.5.2.[1]

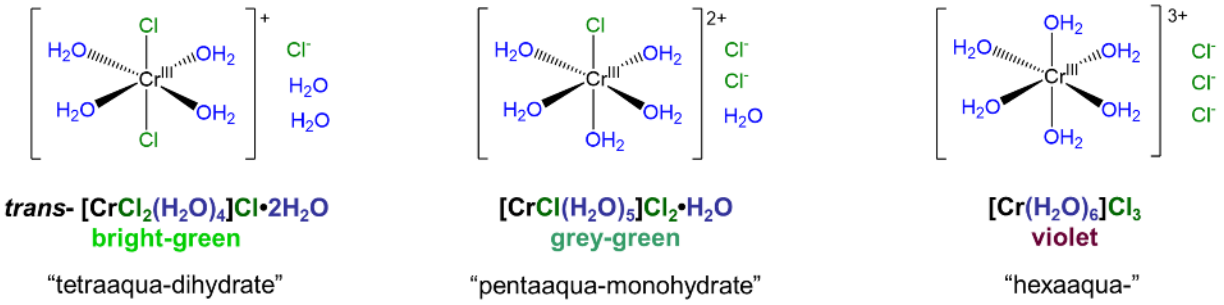


Figure 7.5.2. Complexes of the hydrate isomer series $[CrCl_x(H_2O)_{6-x}]Cl_{3-x}{\cdot}xH_2O$ (x = 0-2). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen from the compounds in Figure 7.5.2, hydrate isomers differ both in terms of whether water acts as a ligand or hydrate *and* in terms of whether a potential counterion acts as a counterion or ligand. Thus, in *trans*-$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ two chlorides act as chloro ligands and four waters as aqua ligands while in $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$ five water molecules act as aqua ligands while only one chloride acts as a chloro ligand. In this way, solvate isomers simply represent cases in which two or more of the possible permutations for metal ligand binding among a set of solvent and counterion molecules are stable.

2. Ionization isomerism

In **ionization isomerism** there are two or more potential ions that can act as ligands. The ionization isomers differ in terms of which of these ions act as counterions and which act as ligands. Consider, for instance, the complexes shown in Figure 7.5.3. These complexes differ in terms of whether the chloride or sulfate acts as a ligand, with the other acting as a counterion.

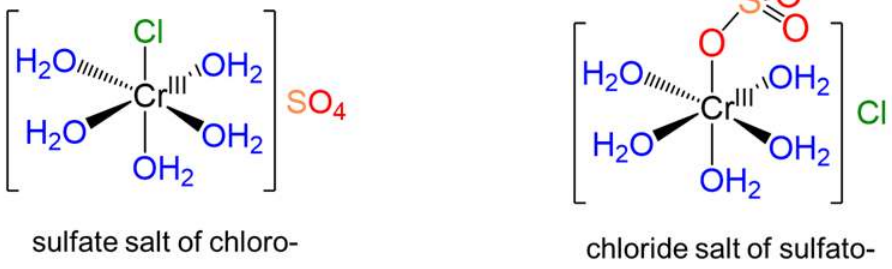


Figure 7.5.3. Ionization isomers comprising a pentaaquachromium(III) fragment and the anions chloride and sulfate. As with all ionization isomers, the isomers differ in terms of which anion acts as a ligand and which a counterion. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

3. Coordination isomerism

Coordination isomers exist in compounds containing two or more complexes, each of which possesses a different set of ligands that can in principle be swapped with a ligand of the other complex. An example involves $[Co^{III}(NH_3)_6][Cr^{III}(ox)_3]$, depicted in Figure 7.5.4A.[1] Coordination isomers of this complex involve swapping the ammine ligands around the Co^{3+} center for oxalato ligands surrounding the Cr^{3+} center. For instance, swapping all the ammine and oxalato ligands between the metal centers gives the coordination isomer $[Cr^{III}(NH_3)_6][Co^{III}(ox)_3]$ shown in Figure 7.5.4B.

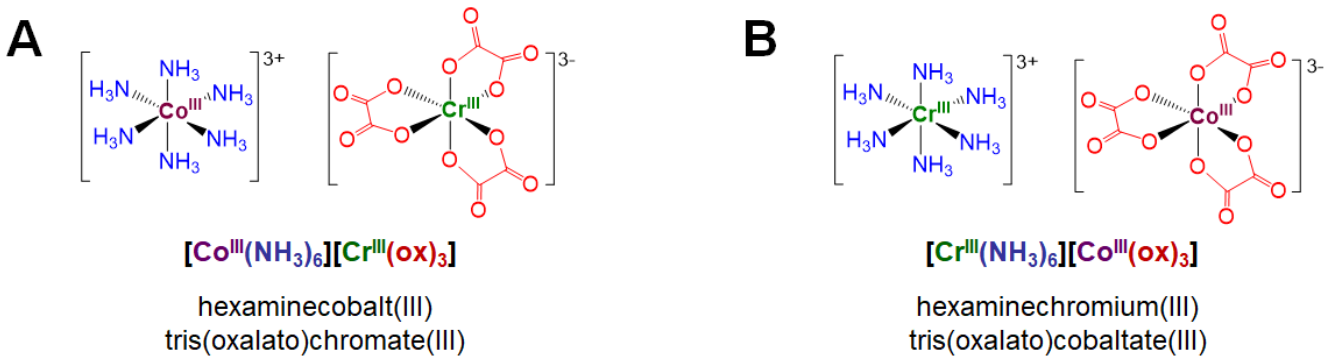
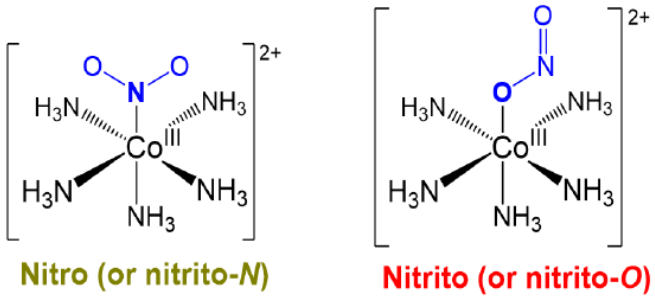


Figure 7.5.4. Two coordination isomers comprising a Co^{3+} ,Cr^{3+}, six NH_3. and three oxalato ligands. The isomers differ in terms of which ligand type is bound to which metal. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As classifications, hydrate/solvate, ionization, and coordination isomerism represent permutations of ordinary structure patterns for solvates, salts, and coordination complexes, respectively. As a result these forms of isomerism are rarely used as independent conceptual frameworks when thinking and talking about the structure of coordination compounds. Not so the final type of structural isomerism, linkage isomerism. That is because linkage isomerism has to do with the special *capacity* of ambidentate ligands to bind metals in multiple ways.

4. Linkage or ambidentate isomerism

Linkage or ambidentate isomers differ in how one or more ambidentate ligands bind to metal centers in a complex. The classic example dating from the work of Jørgensen and Werner is given in Scheme 7.5.I.



Scheme 7.5.I. Linkage isomers of penaamminenitritocobalt(III) ion. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Just as alkenes exist as *E* and *Z* isomers, compounds possessing ambidentate ligands exist as one among the possible linkage isomers. As such, when working with ambidentate ligands the particular linkage isomer formed should be determined experimentally and considered when interpreting the complex's chemical and physical behavior.

The main ambidentate ligands which give rise to linkage isomerism are

- cyanide, CN^-
- thiocyanate, SCN^-, and the O and Se analogues, OCN^- and $SeCN^-$
- nitrite, NO_2^-
- sulfite, SO_3^-
- nitrosyl, NO

Although ambidentate ligands can bind metals in multiple ways, most exhibit a preferred binding mode (*i.e.*, prefer to bind metal centers in one of the possible ways). For instance, cyanide almost always binds through its carbon atom and thiocyanate almost always binds through its nitrogen (μ-*N*). However, the other binding mode can sometimes be formed kinetically or by using conditions that particularly favor its formation. Thus thiocyanate forms M-SCN^- linkages in the presence of exceptionally soft metal centers or in hard polar solvents (in which Lewis acid groups can stablize the terminal nitrogen of a bound thiocyanate ligand).

Ambidentate ligands are of significant research interest because many don't just bind to metal centers in two ways; the linkage isomers sometimes have significantly different physical properties. In addition, the possibility of two binding modes introduces the possibility of exploiting linkage isomerism to take advantage of some of these ligands:

a. different structural chemistry in different coordination modes. In mononuclear complexes the coordination mode influences which side of the ligand faces away from the complex and might be susceptible to stabilization by interaction with solvent. Additionally, the orientation of the ligand relative to the metal center might differ between one coordination mode and another. For instance, as predicted from the minor contributor to its resonance structure, thiocyanate binds nonlinearly via its S atom and linearly via its N (Figure 7.5.5). Because of this the apparent steric bulk of the ligand around the metal center might differ between forms.

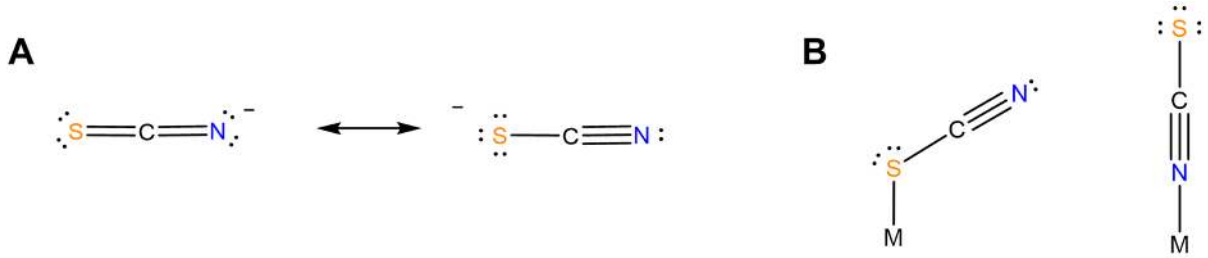


Figure 7.5.5. Thiocyanate generally prefers to bind metals nonlinearly but in some cases forms linear M-SCN bonds. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

b. bind two different metal centers at the same time, linking them together. Perhaps the best-known examples involve thiocyanate and cyanide. The latter forms linkages of the type M-C≡N-M'. In the dye Prussian blue these take the form Fe^{II}-C≡N-Fe^{III}. An example from the author's graduate research involved tetrahedral clusters containing four metal atoms linked by six cyano ligands, as shown in Figure 7.5.6.

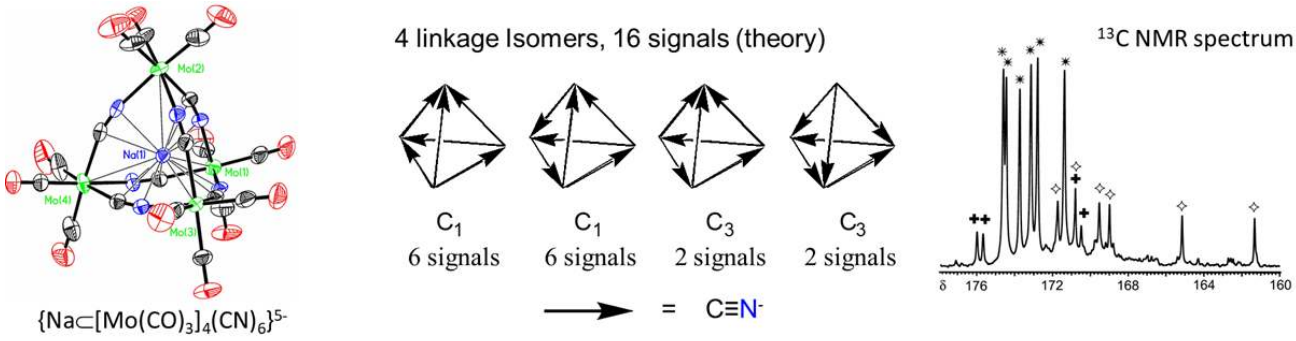


Figure 7.5.6. (A) Structure of $\{Na@[Mo(CO)_3]_4(CN)_6\}$ showing the linking of four Mo centers by six CN ligands. Thermal ellipsoids for the C atoms are shown in black; those of the N atoms in blue. (B) The complex exists as a mixture of four linkage isomers in which the bridging CN^- ligands are oriented in different ways, as may be seen from the presence of the expected sixteen signals in its ^{13}C NMR spectrum. Based on work reported in reference 2.

c. can be induced to change from one binding mode to another in response to a stimulus. The classic example involves the light-driven transformation of the thermodynamically more stable yellow nitro complex of pentamminecobalt(III), $[Co(NH_3)_5NO_2]^{2+}$ to the less stable red *O*-nitrito complex, $[Co(NH_3)_5ONO]^{2+}$. Less stable cyanometallate coordination networks like those in the red $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ transform into the more stable green $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ form on heating, as shown in Figure 7.5.7.[3]

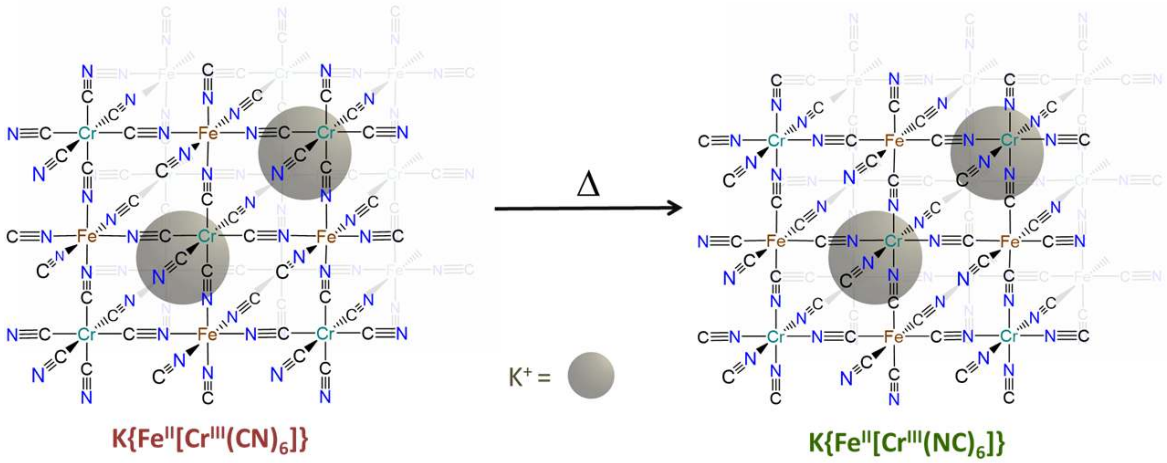


Figure 7.5.7. Thermally-induced transformation of one $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ into its more stable green linkage isomer $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ involves "flipping" the cyano ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

? Exercise 7.5.1: Bridging ambidentate ligands and the Hard-Soft Acid- Base Principle.

The hard-soft acid-base principle helps explain the preference of bridging ambidentate ligands for particular binding modes. How might the greater stability of the green $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ over red $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ be explained in terms of the hard and soft acid-base concept?

Answer

The greater stability of $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ over $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ reflects the greater stability of the Fe^{II}-CN-Cr^{III} linkages in the former over the Fe^{II}-NC-Cr^{III} linkages in the latter. This is consistent with the preference for hard-hard and soft-soft Lewis acid-base interactions of the Hard-Soft Acid-Base Principle.

The Fe^{II}-CN-Cr^{III} linkages are more stable because they possess bonds between

- the softer Lewis acid (Fe^{II}) and Lewis base (the C end of CN^-)
- the harder Lewis acid (Cr^{III}) and Lewis base (the N end of CN^-)

In contrast, the Fe^{II}-NC-Cr^{III} linkages in the less stable linkage isomer involve bonds between

- the softer base (the C end of CN^-) and harder acid (Cr^{III})
- the harder base (the N end of CN^-) and softer acid (Fe^{II})

Stereoisomerism

Optical Isomerism/Chirality

Molecules of D_n, C_n, or C_1 symmetry with only proper rotation axes (including $E = C_1$) are chiral and exhibit optical isomerism. As described in Figure 7.5.1, the main sources of such optical isomerism in coordination chemistry are:

1. Chirality inherent to an organic or main group ligand.

   This type of isomerism is just an extension of the sort described in undergraduate organic texts and consequently does not merit separate discussion here, other than to note that some forms of optical isomerism which are of little importance in organic chemistry lead to optical activity in coordination compounds. In particular, the nitrogen inversion process which serves to rapidly racemize chiral amines is frozen out on formation of a metal-ligand bond. Because of this chiral amine, ligands bound to a metal form non-interconvertible *R* and *S* enantiomers, as shown in Figure 7.5.8.

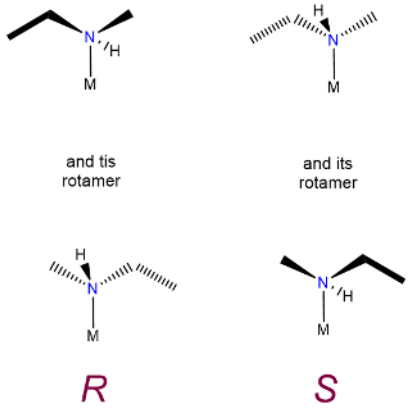


Figure 7.5.8. Two views of *R* and *S* enantiomers formed when the chiral amine ethylmethylamine binds a metal that are commonly used to represent chiral amines in complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2. Chirality arising from the symmetry of ligands about a metal center.

   The two common situations through which such chirality arises involve:

   i. Chirality at a tetrahedral metal center surrounded by four different ligand attachment points.

      Such cases are often referred to as MABCD or Mabcd where M stands for the metal and a, b, c, and d the four different ligand attachment points. An example of such a complex is given in Figure 7.5.9A. The chirality of such complexes is analogous to the chirality arising from a tetrahedral carbon stereocenter. There are two caveats, though. First, it is not enough to have a four-coordinate complex; the metal must possess tetrahedral symmetry since, as shown in Figure 7.5.9B, square planar M complexes with four different ligands are identical to their mirror images. Second, such chirality is most easily realized using macrocyclic ligands like proteins. Metal ligand bonds involving sterically unhindered monodentate complexes like that in the example of Figure 7.5.9A are in general weaker and more flexible than analogous carbon-carbon bonds. Consequently, in such cases it is likely that the enantiomers would interconvert through a fluxional process, making their resolution difficult if not impossible.

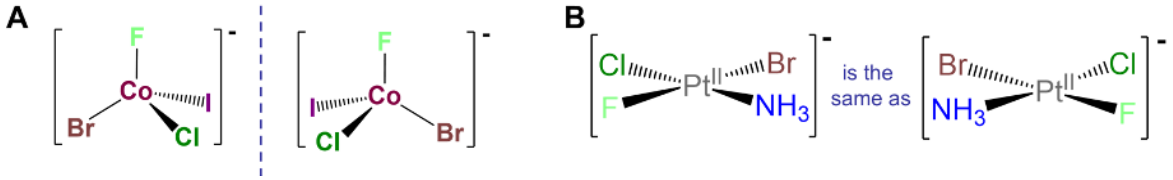


Figure 7.5.9. (A) In principle tetrahedral metal centers surrounded by four different ligands (Mabcd) exhibit chirality analogous to the chirality of tetrahedral carbon stereocenters; (B) in contrast, square planar Macbd complexes like $[PtBrClF(NH_3)]^-$ are not chiral since they are the same as their mirror images. (It is easiest to see this by either working out its point group (C_s) or by rotating the left $[PtBrClF(NH_3)]^-$ structure clockwise 180 degrees to give its mirror image. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

ii. Λ and Δ isomerism at octahedral metal centers surrounded by two or three chelating ligands.

Specifically,

a. Octahedral tris-chelates of formula $M(L\sim L)_3$ exhibit D_3 symmetry.
b. cis-octahedral bis-chelates of formula $M(L\sim L)_2XY$ exhibit C_2 or C_1 symmetry: C_2 if X = Y and C_1 if $X \neq Y$.

As shown in Figure 7.5.10A, octahedral tris-chelates like $[V(ox)_3]^{3-}$ are chiral and can exist as nonsuperimposable Λ and Δ enantiomers. The chirality of these tris-chelates is analogous to that of pinwheels. As shown in Figure 7.5.10B, when looking directly at the head of any individual pinwheel from above, the blades will be angled from back to front going around the pinwheel in either the clockwise or counterclockwise direction. As shown in Figure 7.5.10C, the case for which the blades are angled in the clockwise direction is analogous to the Λ enantiomer and the case when they are angled in the counterclockwise direction the Δ.

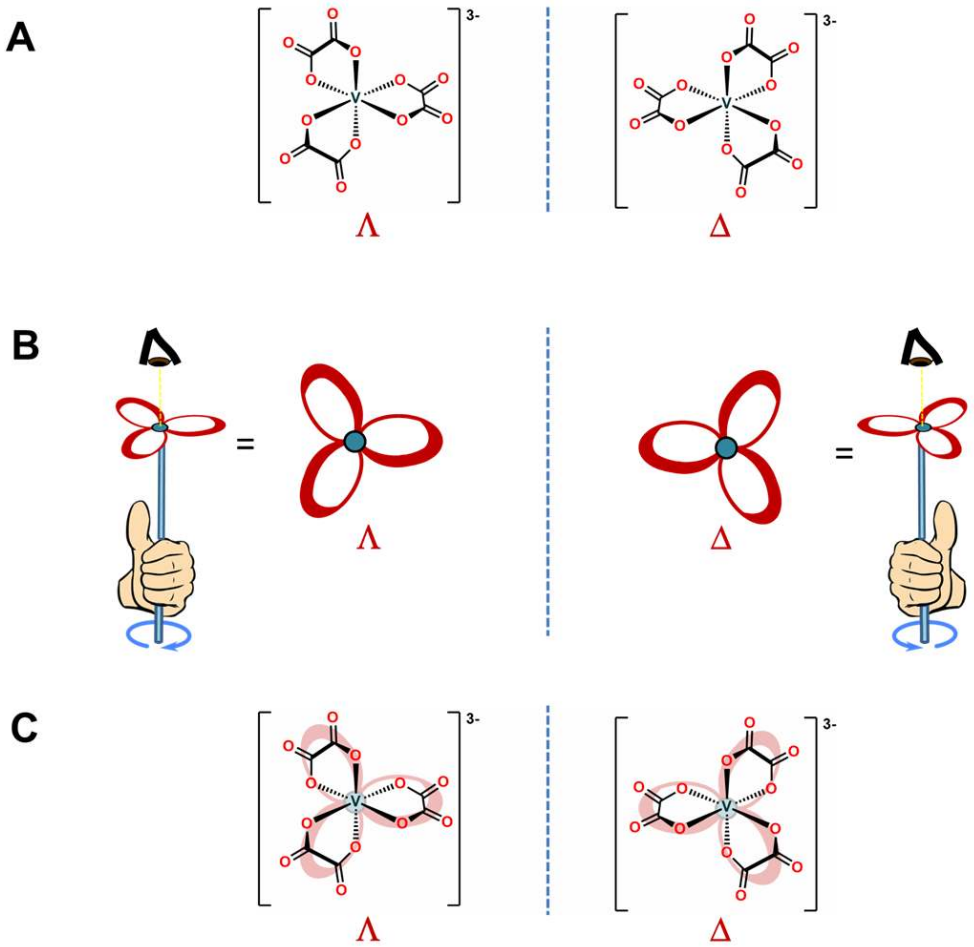


Figure 7.5.10. (A) Octahedral tris-chelates like $[V(ox)_3]^{3-}$ are chiral and can exist as Λ and Δ enantiomers. (B) The chirality in these systems is analogous to that of a pinwheel, with the Λ enantiomer exhibiting the symmetry of a left-handed pinwheel and the Δ enantiomer that of a right handed one. (C) The pinwheel-like nature of Λ and Δ enantiomers is easiest to see by overlaying the structures of $[V(ox)_3]^{3-}$ from A with the pinwheel structures of B. One way to recognize Λ and Δ enantiomers is to draw them in these projections. If a left hand is curled around the Λ enantiomer with the thumb facing up the curl of the fingers will flow from the back of each ligand towards the front. The same will be true if the right hand is curled around the Δ enantiomer. Credits: Although the image is largely an original drawing, the hand images used in part B are adapted from an image by SVGguru / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0). Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The Λ and Δ chirality in octahedral bis-chelates is analogous to that in the tris-chelates except this time the third chelating ligand is replaced by an arbitrary pair of ligands. This lowers the symmetry of the complex to either C_2 or C_1, as shown for the C_2 complex $[CoCl_2(en)_2]^+$ in Figure 7.5.11A. In either case the result is that such complexes exist as Λ and Δ enantiomers analogous to those in the metal tris-chelates, as shown in Figure 7.5.11B.

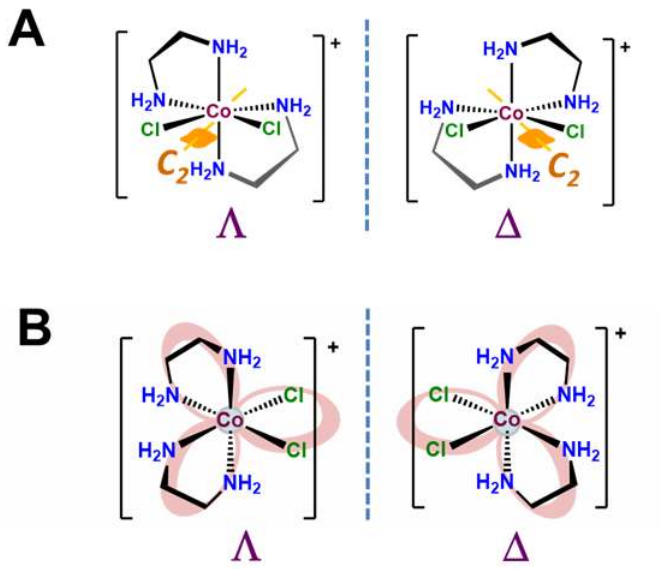


Figure 7.5.9C. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Octahedral complexes containing ligands with denticities of four or more also exhibit Λ and Δ chirality; it is just that in such cases the bound ligand defines multiple rings within the complex that can be defined as existing in either Λ or Δ orientations relative to each other. The procedure for making these assignments is beyond the scope of most introductory inorganic courses but the result is that such complexes are designated as ΛΛ, ΔΔ, ΔΛ, ΔΔΔ, etc., depending on the number of relationships involving the rings defined by the bound ligand. Interested readers should consult reference 4 for more details.

Circular dichroism may be used to characterize optically active metal complexes.

At the present the most definitive way to determine the absolute configuration of an optically active coordination compound is to determine its 3D molecular structure using single crystal X-ray crystallography.[5] However, as that is not always possible or convenient, the optical activity of coordination complexes is also commonly studied using circular dichroism (CD) spectroscopy. CD spectroscopy is used because, unlike most chiral organics, optically active coordination complexes possess low-energy electronic transitions that occur in the far UV and visible range. This means that it is often convenient to use the ability of a complex to refract and absorb different circular polarizations of light to derive information about both the configuration of an optically active complex and its electronic structure. The focus of this section will be to explain how the determination of absolute configuration by circular dichroism and optical rotatory dispersion work, as well as the relationship of these techniques to the more ordinary sort of polarimetry used to measure optical rotation in organic systems. Only brief notes will be made about the instrumental and electronic structure applications of these techniques since the electronic spectra of metal complexes will be discussed in Chapter 11: Coordination Chemistry III - Electronic Spectra and the instrumental aspects of CD are well-treated elsewhere.

Both polarimetry and circular dichroism spectroscopy are grounded in the recognition that plane polarized light is equivalent to a superposition of left and right circularly polarized light, as shown in Figure 7.5.12.

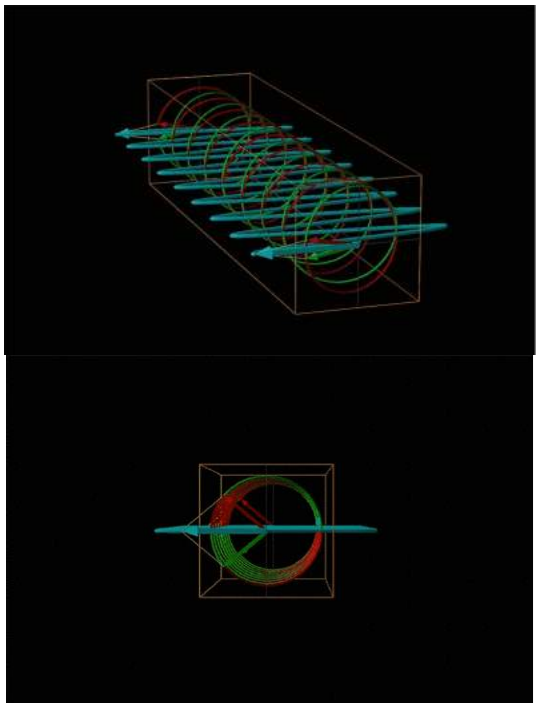


Figure 7.5.12. Angled and front view of plane polarized light (light blue) as the vector sum of left circularly polarized light (red) and right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

When plane polarized light passes through a chiral medium, its left and right circularly polarized components move at different rates (*i.e.*, have different indices of refraction). This causes the plane of polarization to rotate in the direction of the faster component according to the relationship

$$\alpha = \frac{n_l - n_r}{\lambda}$$

where α is the angle of rotation, λ the light's wavelength, and n_l and n_r the refractive indices experienced by left and right circularly polarized light.

An example of such a rotation is shown in Figure 7.5.13.

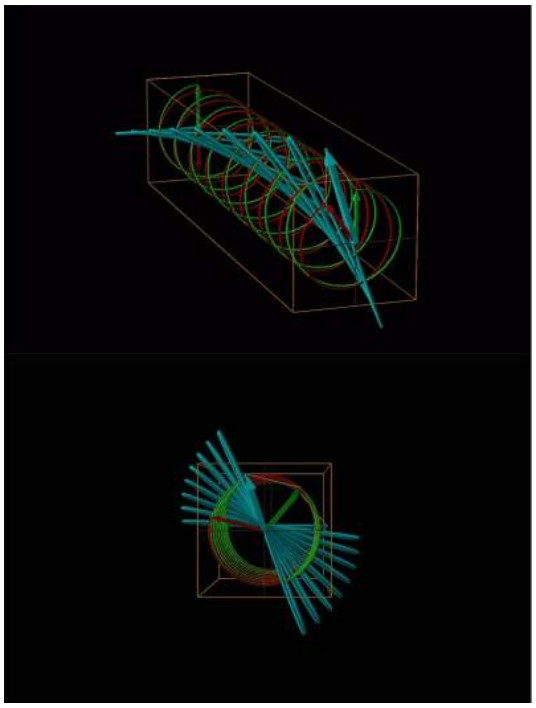


Figure 7.5.13. Angled and front view of plane polarized light (light blue) as it passes through a medium (represented by the orange box) in which left circularly polarized light (red) experiences a higher refractive index (and so moves slower) than right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim) with a refractive index of 1.05 for left circularly polarized light and 1.00 for right circularly polarized light. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Chemists typically call this rotation of light by a chiral medium optical rotation. In organic chemistry it is common to measure the optical rotation at the sodium D wavelength of 589.29 nm, a much longer wavelength than most organics are able to absorb. Because of this the optical rotations commonly measured by organic chemists are largely independent of absorption and mainly serve as a characteristic physical property similar to melting points or are used to establish the purity of a mixture of enantiomers. The sort of spectroscopic data used to characterize chiral coordination compounds more commonly makes use of the relationship between absorption and optical rotation.

In coordination chemistry the wavelength-dependence of optical rotation is used to discern information about compounds' electronic spectra. This measurement of the wavelength dependence of optical rotation is called **optical rotatory dispersion (ORD)** and the resulting plots are called optical rotatory dispersion or ORD spectra or curves. Such ORD curves are useful for characterizing the chiral environment in a coordination complex because the ORD curves exhibit a characteristic shape. This characteristic shape is because according to the **Cotton Effect,** the optical rotation changes sign at the absorption maximum of a chromophore in the compound. For one configuration the rotation will go from negative to positive with increasing wavelength and is called a **positive cotton effect**; for the other configuration the rotation will go from positive to negative or exhibit a **negative cotton effect**. This behavior is summarized in the top two curves of Figure 7.5.14.

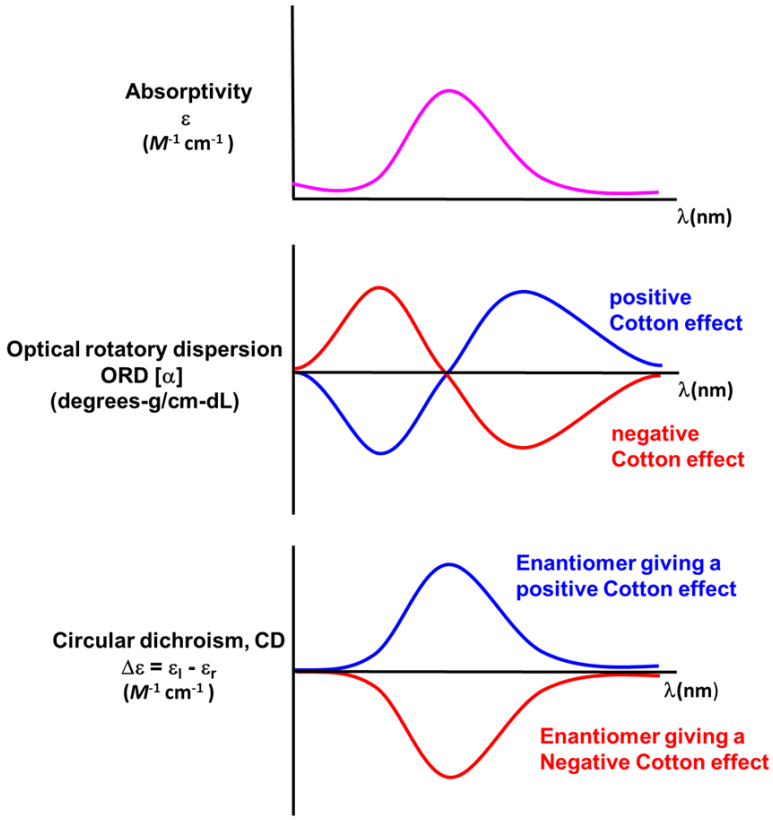


Figure 7.5.14. Idealized relationship between absorbance, ORD, and CD spectra for enantiomers exhibiting a positive and negative Cotton effect. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

A technique used even more often than ORD is **circular dichroism (CD)**, represented by the lowest spectrum in Figure 7.5.14. Circular dichroism arises from the differential absorption of left and right circularly polarized light by a chiral compound. This gives elliptically polarized light as shown in Figure 7.5.15.

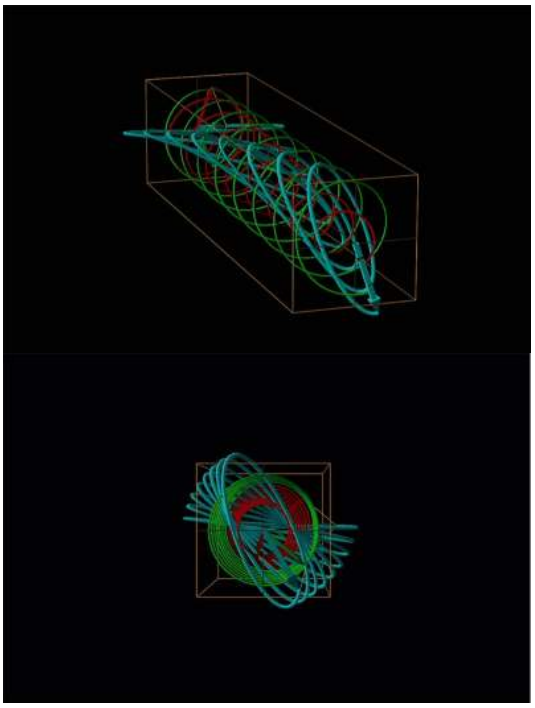


Figure 7.5.15. Angled and front view of plane polarized light (light blue) as it passes through a medium (represented by the orange box) in which left circularly polarized light (red) both experiences a higher refractive index and greater absorption than right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim) with a refractive index of 1.05 and an extinction coefficient of 0.05 for left circularly polarized light and a refractive index of 1.00 and extinction coefficient of 0 for right circularly polarized light. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In circular dichroism (CD) spectroscopy a sample is irradiated with polarized light resulting in the transmission of elliptically polarized light due to differential refraction and absorption of the polarized light's left and right circularly polarized components. For achiral molecules the handedness doesn't affect absorbance, but for chiral molecules, which chiral ground and excited states the handedness of an EM wave affects can determine how readily that wave can distort the chiral ground state into the chiral excited one. For this reason chiral molecules absorb left and right circularly polarized light differently.

In CD spectroscopy the magnitudes of the left and right circularly polarized components of light that is transmitted by the sample are measured and used to determine how much light of each was absorbed (just as in regular absorbance spectroscopy). The difference in absorption between left and right circularly polarized light constitutes the primary signal in CD spectroscopy. More specifically, circular dichroism spectra (CD spectra) show the difference in extinction coefficients for left and right circularly polarized light, $\Delta\epsilon$, as a function of wavelength, where

$$\Delta\epsilon = \epsilon_l - \epsilon_r$$

where Missing open brace for subscript and Missing open brace for subscript are the extinction coefficients observed with left and right circularly polarized light, respectively.

As with ORD spectra, the signs of the features in CD spectra like that of Δ–$[Co(en)_3]Cl_3$ given in Figure 7.5.16 are enantiomer-dependent. As illustrated in the lower spectrum in Figure 7.5.14 , the CD spectra of enantiomers mirror one another. Because of this difference in behavior it is possible in principle to determine the absolute configuration of a complex from its CD spectrum.

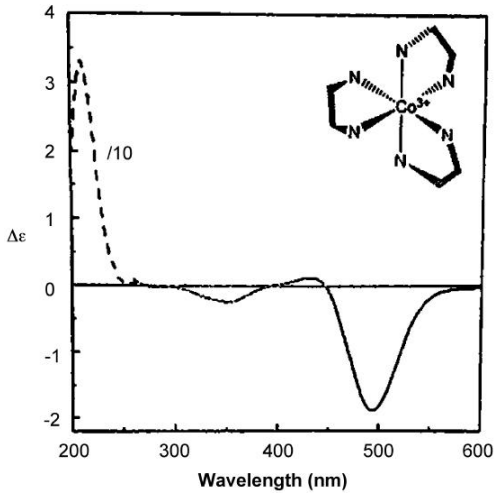


Figure 7.5.16. CD spectrum of Δ–$[Co(en)_3]Cl_3$. Taken from reference 6.

There are several ways that ORD and CD spectra can be useful for determining the absolute configuration of a chiral complex.

1. First, the sign of the Cotton effect and peaks in CD spectra exhibited by a given absolute configuration is often consistent across a series of compounds. Thus if a new member of the series is isolated, its configuration can be determined based on which enantiomer has the same Cotton effect. For instance, if both the Λ isomer of a metal diimine complex like $[Ru(bpy)_3]^{2+}$ exhibit a positive Cotton effect and a newly resolved metal diimine exhibits a negative Cotton effect it might reasonably be inferred that the newly-resolved complex is in the opposite or Δ configuration.
2. Second, for some systems the expected sign of the Cotton effect and CD peaks for each enantiomer may be predicted semi-empirically based on the spatial locations of substituents relative to the chromophore (the part of the molecule that changes electronic structure during the transition), although the details are beyond the scope of the present discussion.
3. Consideration of interactions between multiple chromophores in a compound can be used to infer absolute configuration. Again, the details are beyond the scope of the present discussion. Interested readers are referred to reference 7 for details.

Common patterns of Diastereomerism

Geometric isomerism

Geometric isomerism involves differences in the geometric placement of atoms in a compound. In coordination chemistry, geometric isomerism involves differences in the relative placement of a set of ligands about a metal center. There are two main types:

cis and *trans* isomerism

This type of isomerism has to do with how two ligands are oriented relative to one another in a square planar or octahedral complex. As shown in Figure 7.5.17, ligands that are next to one another with a L-M-L bond angle of 90° are said to be *cis*; those on opposite sides of the metal with a L-M-L bond angle of 180° are in the *trans* arrangement.



Figure 7.5.17. *cis* and *trans* arrangement of ligands around (A) square planar and (B) octahedral metal centers. Since both types of complexes feature 90° L-M-L bond angles, the arrangements are fundamentally the same in both cases. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Simple *cis* and *trans* geometric isomers can be identified when there are two identical ligands (A) or chelating ligands with distinguishable attachment points (A~B) oriented about either a square planar or octahedral center. Examples are given in Figure

7.5.18. Notice from the example given in Figure 7.5.18C that multidentate ligands have the potential to constrain complexes to adopt a particular geometry.

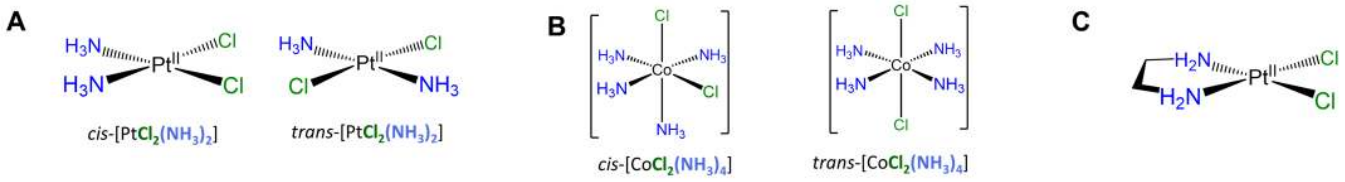


Figure 7.5.18. Examples of square planar and octahedral *cis* and *trans* isomers. (A) *cis* and *trans* isomers of $[PtCl_2(NH_3)_2]$; the former is medicinally important. Sold under the name cisplatin, the *cis* isomer is used as a chemotheraphy against various forms of cancer. (B) *cis* and *trans* isomers of $[CoCl_2(NH_3)_4]$, a compound of more academic interest. (C) $PtCl_2$(en) only exists as the *cis* isomer because the chelating en ligand can only bind in a *cis* arrangement. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Slightly more involved examples involve perturbations of the simple cases above in which there are multiple distinguishable *cis* and/or *trans* relationships. Two square planar examples are given in Figure 7.5.19.

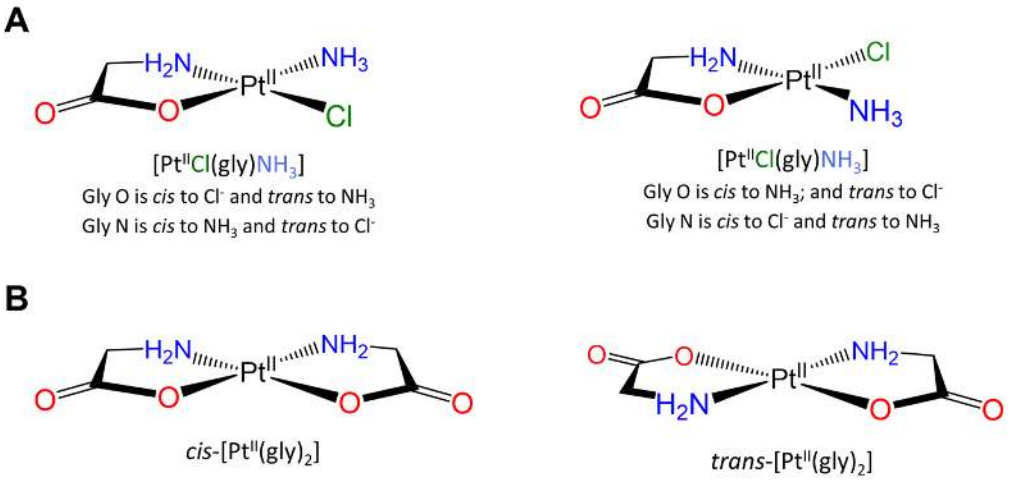


Figure 7.5.19. Examples of more complex square planar systems. (A) Geometric isomers of $[PtCl(gly)NH_3]$, a MA_2BC system for which A = gly^-, B = Cl^-, and C = NH_3. Swapping of the ammine and chloro ligands changes both the *cis* and *trans* relationships involving the Gly ligand. (B) Geometric isomers of $[Pt(gly)_2]$, an $M(A\sim B)_2$ system for which A = the κO glycine carboxy group and B its κN amine. The only possible geometric isomerism involves swapping the orientation of one glycine relative to the other. For this reason the two complexes shown can be designated as *cis* and *trans* isomers based on whether the κO and κN ends of the glycine are *cis* or *trans* to one another. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

More complex examples of *cis* and *trans* relationships between ligands in octahedral complexes are given in the exercises that conclude this page, which also demonstrates how a systematic approach may be used to identify isomers.

mer and *fac* isomerism

This type of isomerism has to do with how three ligands are oriented relative to one another in an octahedral complex. The arrangements are represented in Figure 7.5.20.

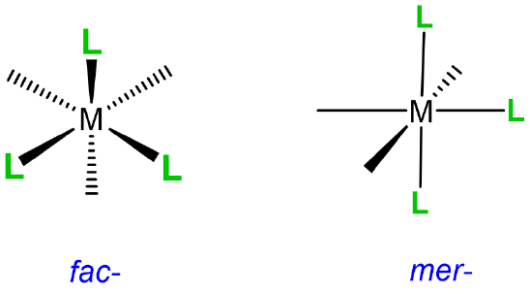


Figure 7.5.20. Simple representation of the *fac* and *mer* arrangements of ligands around an octahedral metal center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Since it can help to visualize the *mer* and *fac* geometry from multiple points of view, several representations are given in Figure 7.5.21. As shown in Figure 7.5.21, in ***fac*** or **facial arrangements**, the ligands occupy the same "face" of the octahedral coordination sphere, while in the ***mer*** or **meridional geometry** the ligands form a T shape in the same plane or its "meridian."[8]

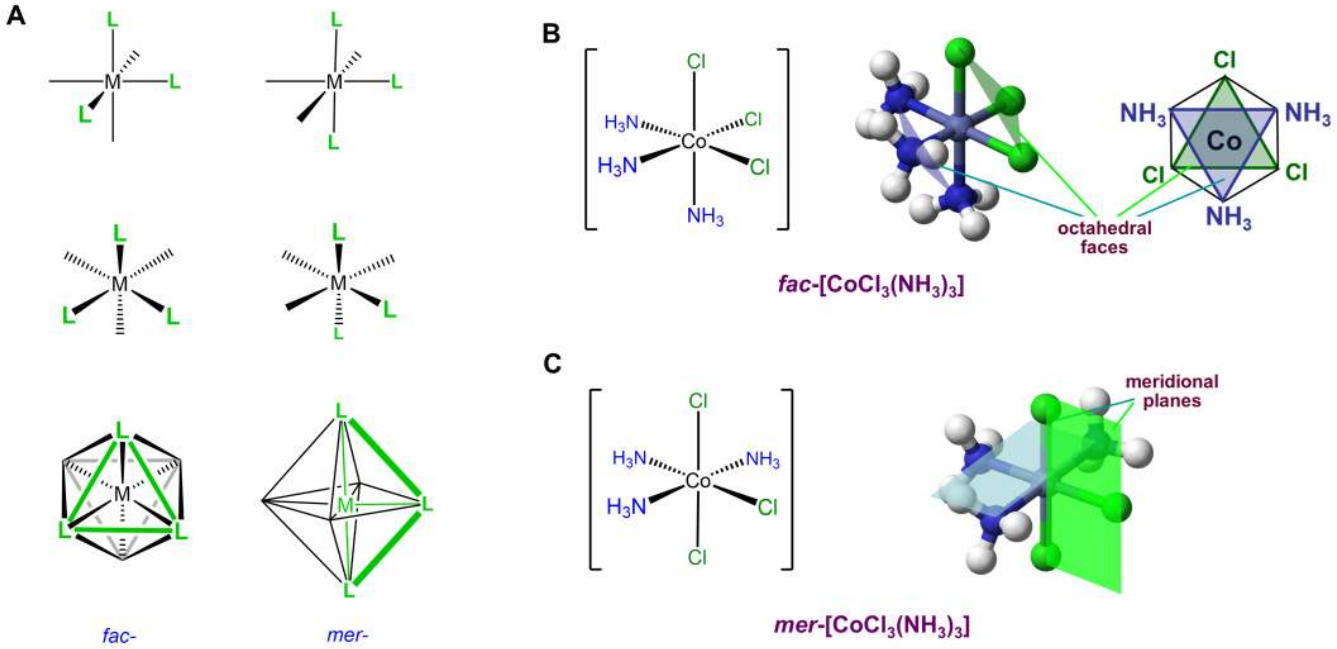
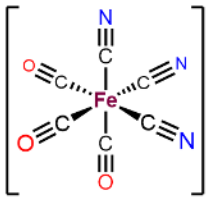
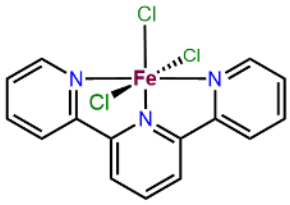
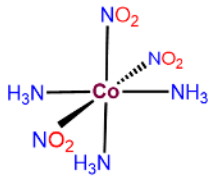


Figure 7.5.21. (A) Three projections of *fac* and *mer* arrangements of ligands around an octahedral metal center emphasizing that in the *fac* arrangement the ligands are oriented along a face of the octahedron while in the *mer* arrangement they are oriented in a plane. (B) Structure of *fac*-$[CoCl_3(NH_3)_3]$ showing the octahedral faces occupied by the chloro and amine ligands. (C) Structure of *mer*-$[CoCl_3(NH_3)_3]$ showing the planar arrangement of the chloro and ammine ligands. The ball and stick models are modified from images by Benjah-bmm27 - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=1874872 and curid=1874873. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Octahedral complexes with three identical ligands oriented about an octahedral center can only exist in *mer* and *fac* arrangements. Consequently, such complexes can be designated as *mer* and *fac* isomers. Examples are given in Figure 7.5.22.







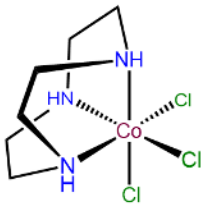


Figure 7.5.22. Examples of *fac* and *mer* octahedral complexes. Note how some chelating ligands preferentially bind to the metal in a *fac* or *mer* arrangement and, in so doing, force the other ligands to also form a *mer* or *fac* arrangement. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Diastereomerism arising from multiple ligand-associated chiral centers

Diastereomerism can also arise when two or more chiral ligands bind to a metal center. Such cases typically give rise to a complex mixture of isomers, as shown by the example in Figure 7.5.23. As may be seen from Figure 7.5.23, the differences between these isomers can arise from both changes in the stereochemical configuration of the ligand and the relationship of particular ligand centers relative to one another. For instance, the leftmost two structures in Figure 7.5.23 possess one *R* and *S* nitrogen center each but differ in whether the centers are oriented so that the *R* and *S* centers on the two ligands are *trans* or *cis* to one another.

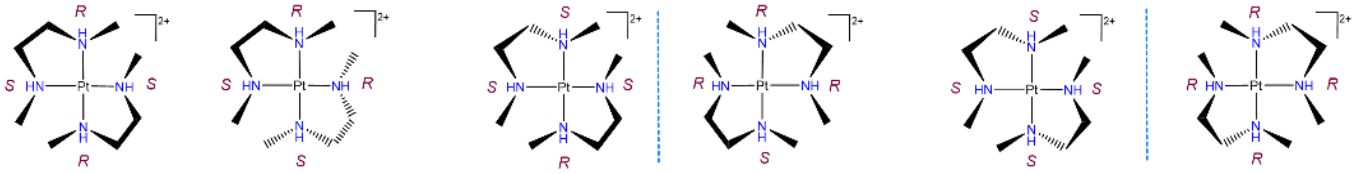


Figure 7.5.23. Diastereomers that can in principle be formed when two *N*,*N*′-dimethylethylenediamine ligands coordinate a Pt^{2+} center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Diastereomerism arising from λ and δ ring conformation isomerism.

Chelate rings are formed when a chelating ligand binds a metal

As may also be seen from the structures in Figure 7.5.23, when a multidentate ligand coordinates a metal, the ligand and metal center comprise one or more **chelate rings**. Examples of such chelate rings are shown in Figure 7.5.24.

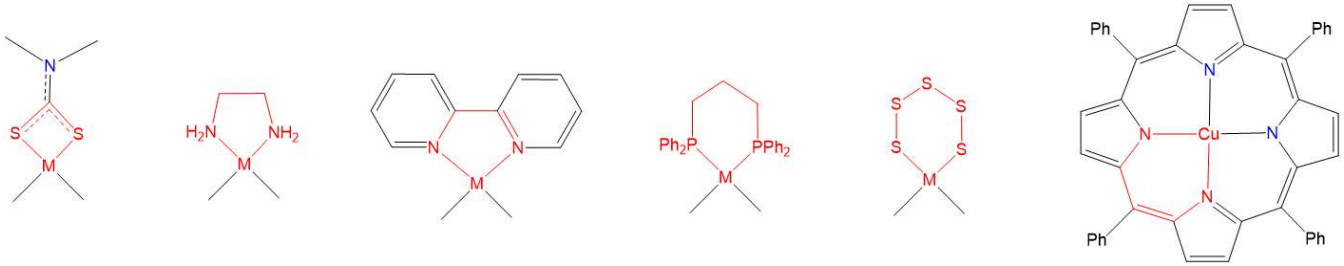


Figure 7.5.24. Four, five, and six-membered chelate rings (shown in red) formed by coordination of selected bidentate ligands to a metal center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As may be inferred from the examples in Figure 7.5.24, chelate rings may be of different sizes, although four, six, and especially five-membered rings are particularly common. Exactly which ring sizes will be more stable for a given system depends on the

coordination geometry and, due to differences in M-L bond lengths, to a lesser degree on the metal. As a result, for octahedral and square planar complexes with 90° L-M-L bond angles between *cis* ligands, *five-membered rings tend to be especially stable* (Figure 7.5.25).

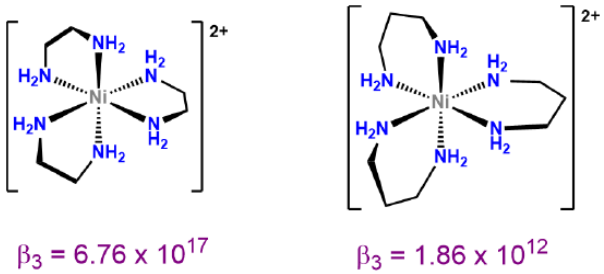


Figure 7.5.25. The greater stability of five-membered chelate rings involving Ni^{2+} and organic ligands is reflected in the higher overall formation constant (β_3) for the five-membered chelate rings contained in $[Ni(en)_3]^{2+}$ compared to that of $[Ni(et)_3]^{2+}$, which has six-membered rings. The data in this figure is taken from Stability of Metal Complexes and Chelation by Robert Lancashire. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Not all metal chelates prefer to form five-membered rings. The steric requirements of chelate rings depend on both the preferred coordination geometry of the metal center and the stereochemistry of the ligand. Both of these effects are typically considered in terms of preferred L-M-L bond angles. From the perspective of the metal center, the preferred bond angle is determined by the coordination geometry. Octahedral and square planar metals prefer 90° L-M-L bond amgles, trigonal bipyramidal systems 90 and 120° L-M-L bond angles, and tetrahedral complexes 109.5° L-M-L angles. The larger preferred bond angles in tetrahedral and trigonal bipyramidal systems often require the formation of larger six or seven-membered chelate rings for maximum stability. The size of the chelate ring actually formed between a metal and ligand is determined by the ligand's structure. As the contributor of all the atoms in the chelate ring but one, the ligand directly determines the chelate ring size. More subtly, ligands naturally prefer to coordinate metals at a particular L-M-L angle, called the **bite angle**, as shown in Figure 7.5.26A. Ligands with bite angles corresponding to the ideal L-M-L angle for a metal's preferred geometry tend to form more stable complexes, although in turn ligand bite angles can cause metals with a weak coordination geometry preference to adopt the ligand's preferred geometry instead.[10] As may be seen from the values in Figure 7.5.26B, bite angles roughly increase with the size of the chelate ring formed but are also influenced by the types of structures used to connect the ligand's Lewis base sites. This facilitates the use of diphosphine ligands to tailor the structure and reactivity of phosphine-containing organometallic catalysts.



Figure 7.5.26. (A) Definition of the bite angle as the angle at which the ligand's preferred L-M-L angle when coordinating a metal center. (B) Bite angles of selected diphosphines.[9] The bite angles of many such diphosphines have been determined to facilitate the design of phosphine-containing organometallic catalysts. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

λ and δ isomerism involves differences in the conformation of nonplanar five-membered chelate rings

As shown in Figure 7.5.27, some chelate ring systems are planar while others are not.

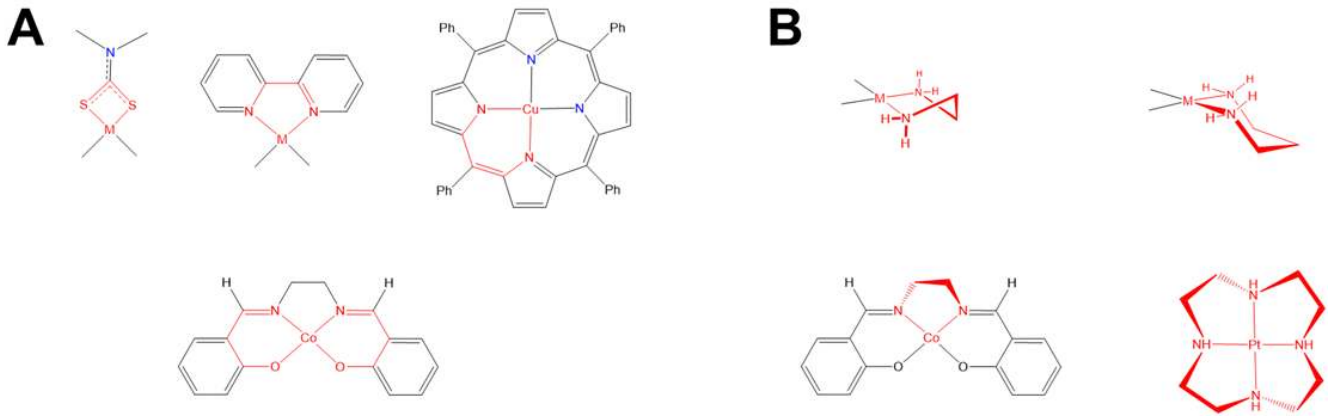


Figure 7.5.27. (A) Planar and (B) Nonplanar chelate rings shown highlighted in red. Notice how [Co(salen)] possesses a nonplanar chelate ring and two planar ones. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Among the nonplanar chelate ring systems are ligands like en and dppe, which contain tetrahedral C, N, O, P, and S atoms. Because these atoms create kinks in the chelate ring they introduce additional opportunities for diastereomerism due to differences in the chelate ring conformation, called **ring twist**. Ring twist in nonplanar systems has been most extensively explored for five-membered chelates like those formed by dppe and by en and other chelating amines. Unlike the more rigid four-membered chelate rings, five-membered chelates tend to be conformationally flexible, but not so conformationally flexible that their conformers are rapidly interconverting at room temperature (at least not when the rings are substituted to introduce additional steric strain). This balance between flexibility and rigidity enables some five-membered chelate rings to exist as mixtures of distinguishable conformational isomers at room temperature.

To understand the two most stable conformers that five-membered chelates rings tend to form, it is helpful to think of five-membered chelate rings as involving two components (Figure 7.5.28):

- a planar L-M-L group, where L are the atoms directly attached to the metal, M, and
- the remaining two ring atoms, E, which form a rigid E-E bar across the back of the chelate ring.

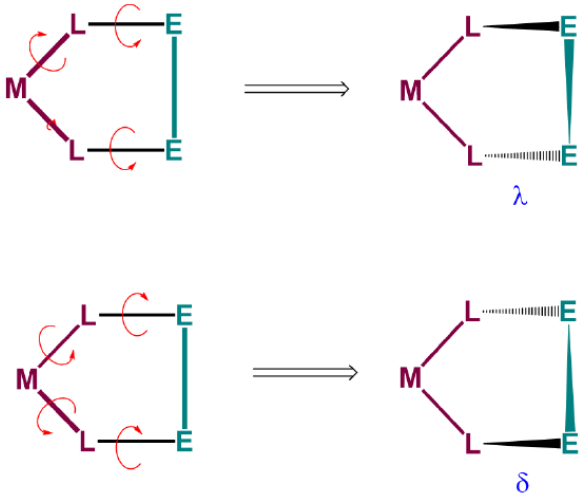


Figure 7.5.28. Five-membered chelate rings consist of a planar L-M-L group connected to a rigid E-E bar. Conformers arise as rotation about the M-L and L-E bonds causes twisting of the E-E bar relative to the L-M-L plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen from Figure 7.5.28 , rotation about the M-L and L-E bonds causes twisting of the E-E bar relative to the L-M-L plane. The two most stable conformers produced by these motions are the λ or δ conformations as shown in Figures 7.5.29 and 7.5.29.

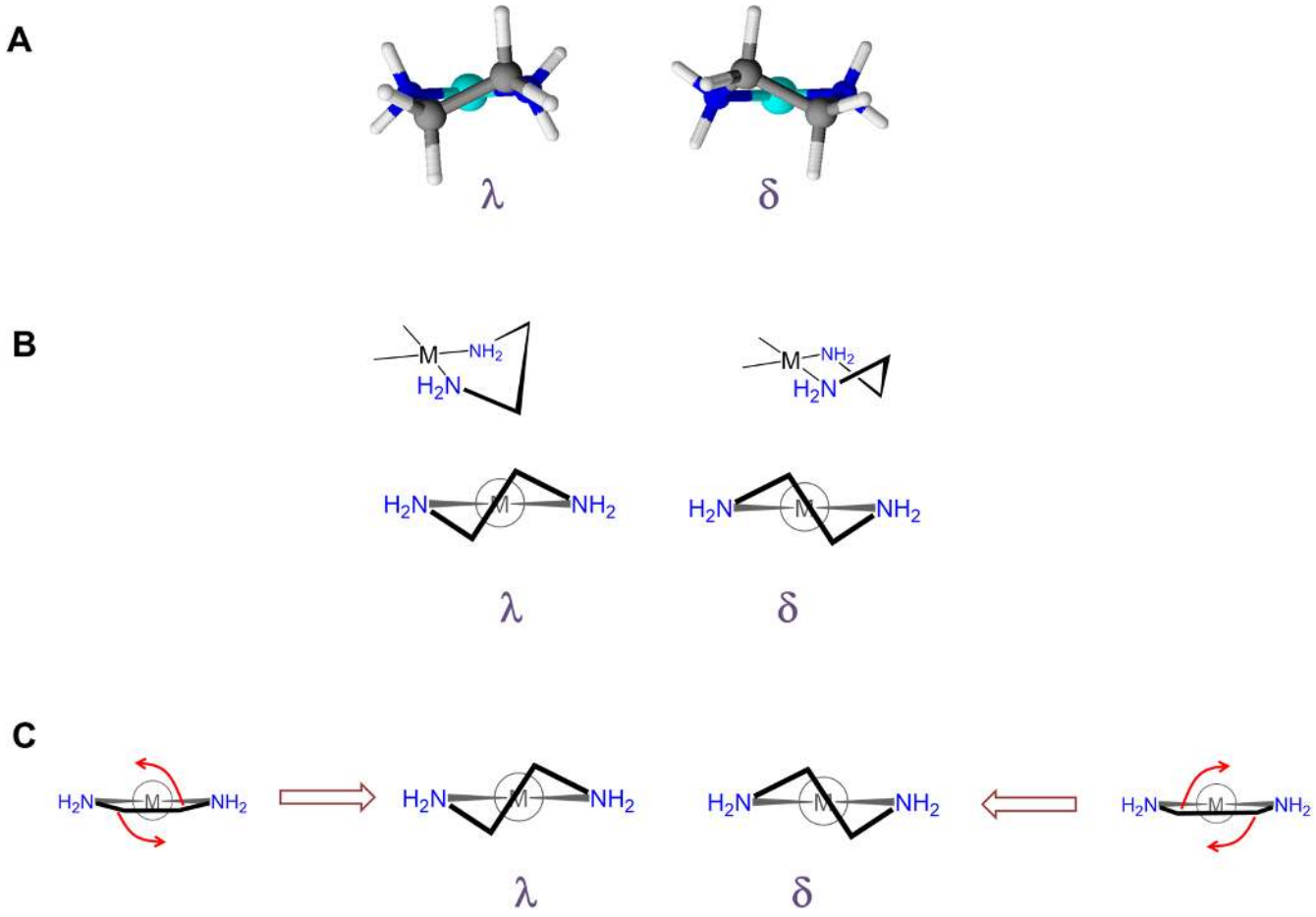


Figure 7.5.29. (A) λ and δ ring twist in a square planar metal ethylenediamine complex (B) along with several ways to represent it in line drawing form. (C) Of these, the projection looking down an axis bisecting the chelate ring makes it easiest to see that, starting with a planar chelate ring the λ conformer corresponds to a counterclockwise twist of the CH_2CH_2 bond relative to the N-M-N plane and the δ conformer a clockwise twist relative to the N-M-N plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The relative stability of the λ and δ conformers will depend on the configuration of any stereocenters present and steric factors. As with organic ring systems, steric effects tend to favor conformers in which bulky groups are placed in the less sterically strained equatorial positions while the configuration of the stereocenters present can serve to restrict the allowable ring twist conformations, as illustrated in Figure 7.5.30. A detailed treatment of such systems is beyond the scope of this page. Interested readers are referred to reference 12 for more details.

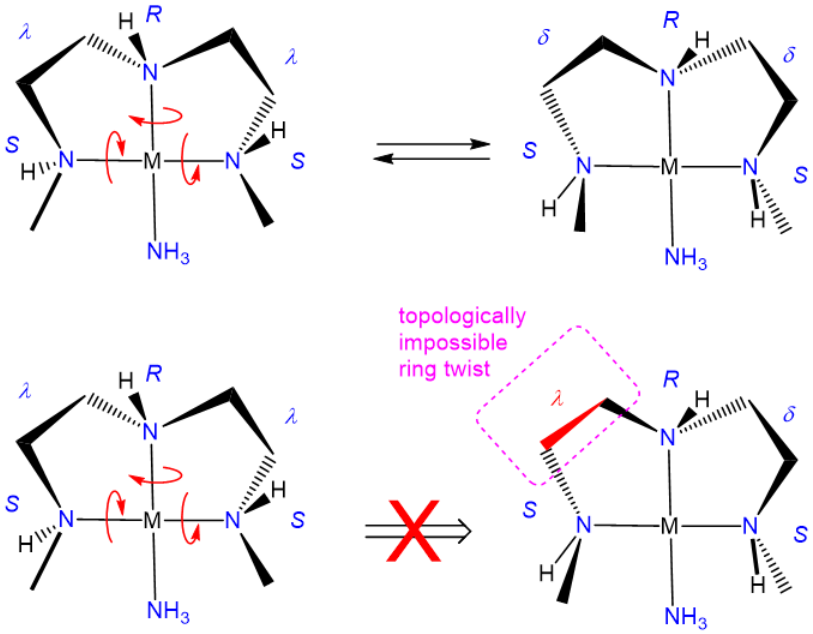


Figure 7.5.30. The configurations at nitrogen in the complex shown restrict the chelate ring conformations to either a $\lambda\lambda$ or $\delta\delta$ conformation because the rotations needed to enable a $\lambda\delta$ configuration are topologically impossible. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In closing, it should be noted that it might seem to be making much of small effects in pointing out that one source of diastereomerism in metal complexes involves the freezing out of chelate ring conformations. However, that would be to mistake the impacts that ring conformations can have on the steric accessibility of a coordination site and shaping the course of processes that might occur there. As illustrated in Figure 7.5.31, a simple shift in the conformation of one ring in a square planar, pyramidal, or octahedral complex containing coplanar ethylene diamine ligands can exert a significant effect on the steric profile of the complex perpendicular to the MN_4 square plane. Because of effects like these, ring conformation isomerism plays a role in the design of stereoselective transition metal catalysts.

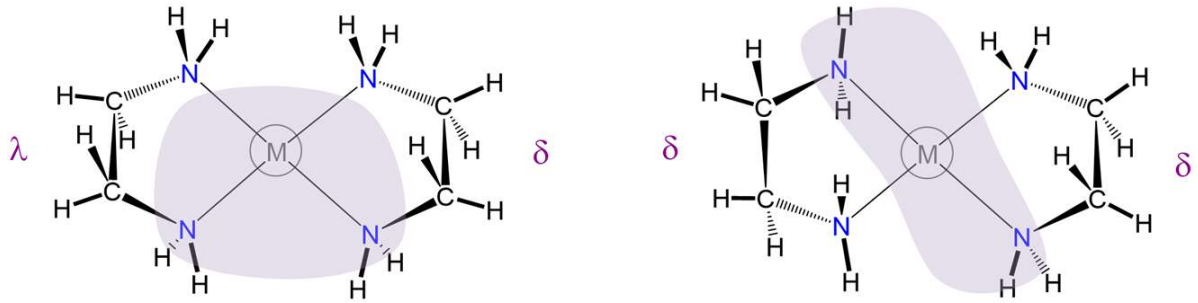


Figure 7.5.31. Schematic illustrating how the conformation of ethlyenediamine ligands bound to a metal center affects the steric accessibility of the metal (shown shaded in violet) to potential ligands attempting to bind from above the MN_4 plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Exercises

? Exercise 7.5.1. Identify the type of isomerism

What type of isomers are

a. $[CoCl(NH_3)_5](NO_3)$ and $[Co(NH_3)_5(N\text{-}NO_2)]Cl$?
b. $[Co(NH_3)_5\text{-}CN\text{-}Ru(NH_3)_5]^{4+}$ and $[Co(NH_3)_5\text{-}NC\text{-}Ru(NH_3)_5]^{4+}$
c. $[Cr(CN)_5\text{-}CN\text{-}Co(NH_3)_5]$ and $[Co(CN)_5\text{-}CN\text{-}Cr(NH_3)_5]$
d. *cis*-$[Mn(en)_2(CN)_2]$ and *trans*-$[Mn(en)_2(CN)_2]$

Answer a.

Ionization isomers.

Answer b.

Linkage isomers.

Answer c.

Coordination isomers.

Answer d.

Geometric isomers, specifically *cis*/*trans* isomers.

? Exercise 7.5.2. Assigning metal oxidation states in a complex

Many properties of transition metal complexes depend on the metal's oxidation state. For instance,

- octahedral complexes of Co^{II} lose and gain ligands rapidly
- octahedral complexes of Co^{III} lose and gain ligands very slowly
- four-coordinate complexes are generally tetrahedral
- EXCEPT four-coordinate complexes of metals like Pt^{II} , Pd^{II} , Rh^{I}, and Ir^{I}, among others, are square planar

For this reason it is important to be able to estimate the formal oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state, the ligands can be treated as having an oxidation state equal to their charge - *i.e.*, the charge they possess in the form in which they coordinate the metal - so if they need to lose a proton to bind, don't forget to account for that.

Given the above, estimate the oxidation state of the metal in the following real and hypothetical complexes.

a. $Na_4[Fe(CN)_6]$
b. $[Cu(phen)_2]BF_4$
c. $[PtF_4(NH_3)_2]$
d. $[Ni(en)_2]SO_4$
e. $Co(acac)_3$
f. [MnCl(O)(salen)]

Answer for $Na_4[Fe(CN)_6]$.

This contains $[Fe(CN)_6]^{4-}$; so $O.S._{Fe}$ + 6 x (-1) (for CN^-) = -4 (the complex's charge) so $O.S._{Fe}$ = +2 or Fe^{2+}.

Answer for $[Cu(phen)_2]BF_4$.

Since tetrafluoroborate is a monoanion, the complex is $[Cu(phen)_2]^+$ so $O.S._{Cu}$ + 0 x 2 (for phen) = +1 (the complex's charge) so $O.S._{Cu}$ = +1 or Cu^+.

Answer for $[PtF_4(NH_3)_2]$.

$O.S._{Pt}$ + 4 x (-1) (for F^-) + 0 x 2 (for NH_3) = +0 (the complex's charge) so $O.S._{Pt}$ = +4 or Pt^{4+}.

Answer $[Ni(en)_2]SO_4$.

The complex is $[Ni(en)_2]^+$ so $O.S._{Ni}$ + 0 x 2 (for en) = +2 (the complex's charge) so $O.S._{Ni}$ = +2 or Ni^{2+}.

Answer $Co(acac)_3$.

$O.S._{Co}$ + 3 x (-1) (for acac; see table 9.2.2) = +0 (the complex's charge) so $O.S._{Co}$ = +3 or Co^{3+}.

Answer [MnCl(O)(salen)].

$O.S._{Mn}$ + 1 x (-1) (for Cl^-) + 1 x (-2)(for oxo) + 1 x (-2) (for salen; see table 9.2.2) = +0 (the complex's charge) so $O.S._{Mn}$ = +5 or Mn^{5+}.

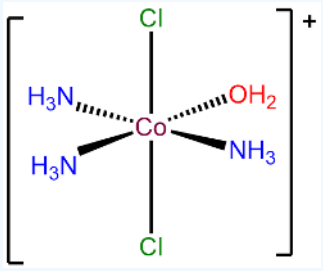
Exercise 7.5.3. Drawing isomers from descriptions

Draw structures that match the descriptions given, assuming that

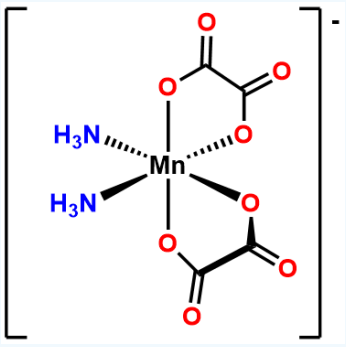
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. *mer*-triammineaqua-*trans*-dichlorocobalt(III) ion
b. Δ-diaminebis(oxalato)manganate(III)
c. $[CoCl_4]^{2-}$
d. *trans*-diamminebis(ethylenediamine)Nickel(2+) tetracyanopalladate(2-)
e. Λ-bis(ethylenediamine)cobalt(III)- μ-amido μ-hydroxo-Δ-bis(ethylenediamine)cobalt(III)

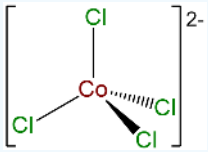
Answer a. *mer*-triammineaqua-*trans*-dichlorocobalt(III) ion.



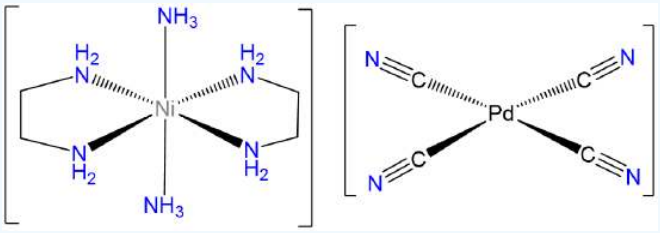
Answer b. Δ-diaminebis(oxalato)manganate(III).



Answer c. $[CoCl_4]^{2-}$.

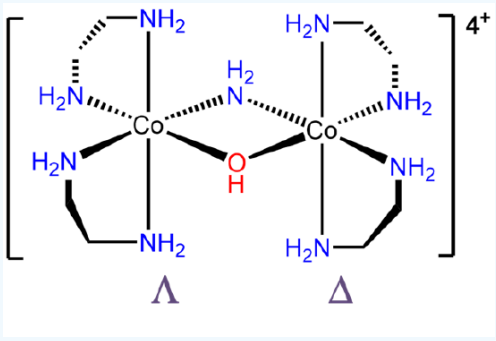


Answer d. *trans*-diamminebis(ethylenediamine)Nickel(2+) tetracyanopalladate(2-).



Note that since the Pd in $[Pd(CN)_4]^{2-}$ is Pd^{2+} it will be square planar.

Answer e. Λ-bis(ethylenediamine)cobalt(III)- μ-amido μ-hydroxo-Δ-bis(ethylenediamine)cobalt(III).



Exercise 7.5.4. Stereoisomers of complexes containing only monodentate ligands.

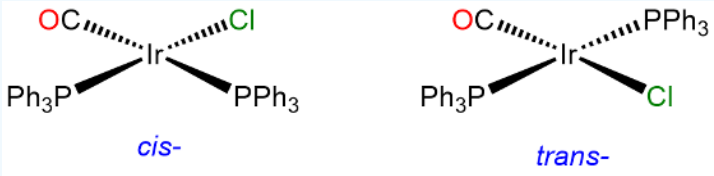
Draw all the stereoisomers of the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[IrCl(CO)(PPh_3)_2]$
b. $[CoCl_3(NH_3)_3]$
c. $[CoCl_2(H_2O)_2(NH_3)_2]^+$
d. $[CoBrCl(H_2O)_2(NH_3)_2]^+$
e. $[CoBrClI(NH_3)_3]$

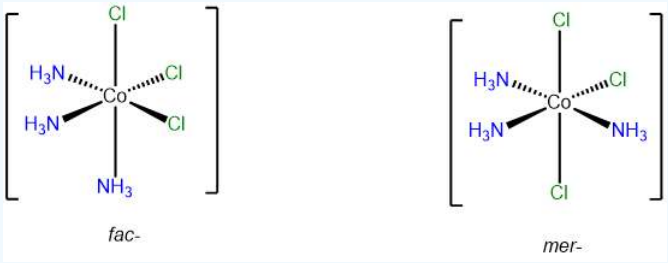
Answer a. $[IrCl(CO)(PPh_3)_2]$

This is a 4-coordinate Ir^{I} complex and, as such will be square planar. Since two of the ligands are identical, it will have *cis* and *trans* isomers. The *trans* isomer is famous for its ability to form adducts and is called Vaska's complex.



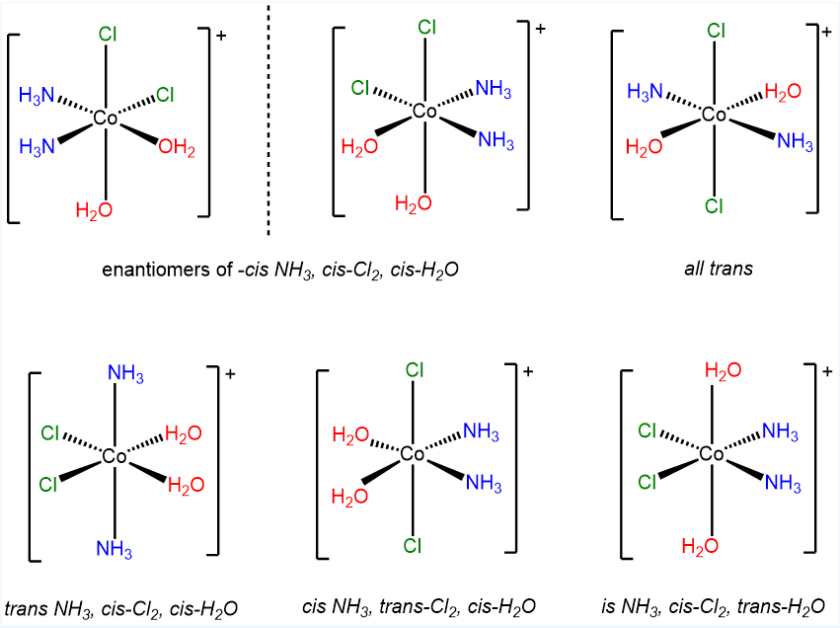
Answer b. $[CoCl_3(NH_3)_3]$

This complex contains three ammine and three chloro ligands and so will have *fac* and *mer* isomers.



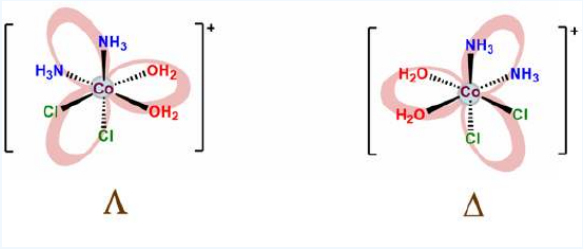
Answer c. $[CoCl_2(H_2O)_2(NH_3)_2]^+$

This is a case of an $MA_2B_2C_2$ system (A = Cl^-, B = H_2O, C = NH_3) involving multiple *cis* and *trans* relationships. The six stereoisomers are shown below.



Since it may not be obvious how to arrive at a set of isomers like the ones above, it is worth considering how one might work through the possibilities for a system of ligands like this one. Several systems may be used to systematically identify isomers. Once approach is the Macbdef system described in Note 7.5.1 at the end of these exercises. The solutions presented here and in subsequent problems employ a variant of that approach.

- Start by fixing one set of ligands. In this case the chloro ligands were first fixed as *cis* to one another. Then the remaining ligands might be *cis* or *trans* to one another, although since the *chloro* ligands are already *cis*, the ammine and aqua ligands cannot both be *trans* at the same time. Thus for *cis* chloro ligands the possibilities for the others are:
  - *cis*-H_2O ,*cis*-NH_3,
  - *cis*--H_2O, *trans*-NH_3
  - *trans*-H_2O, *cis*-NH_3
- Swap the configuration of the ligand set you started with. In this case it means placing the chloro ligands *trans* to one another. From that configuration, the possibilities for the ammine and aqua ligands are
  - *cis*-H_2O ,*cis*-NH_3,
  - *trans*-H_2O, *trans*-NH_3
- Check for enantiomers and create mirror images of any chiral complexes you drew. The easiest way to do this is to assign point groups. However, it turns out that the octahedral all-*cis* case is D_3 and formally equivalent to the symmetry of a tris chelate, as shown below.

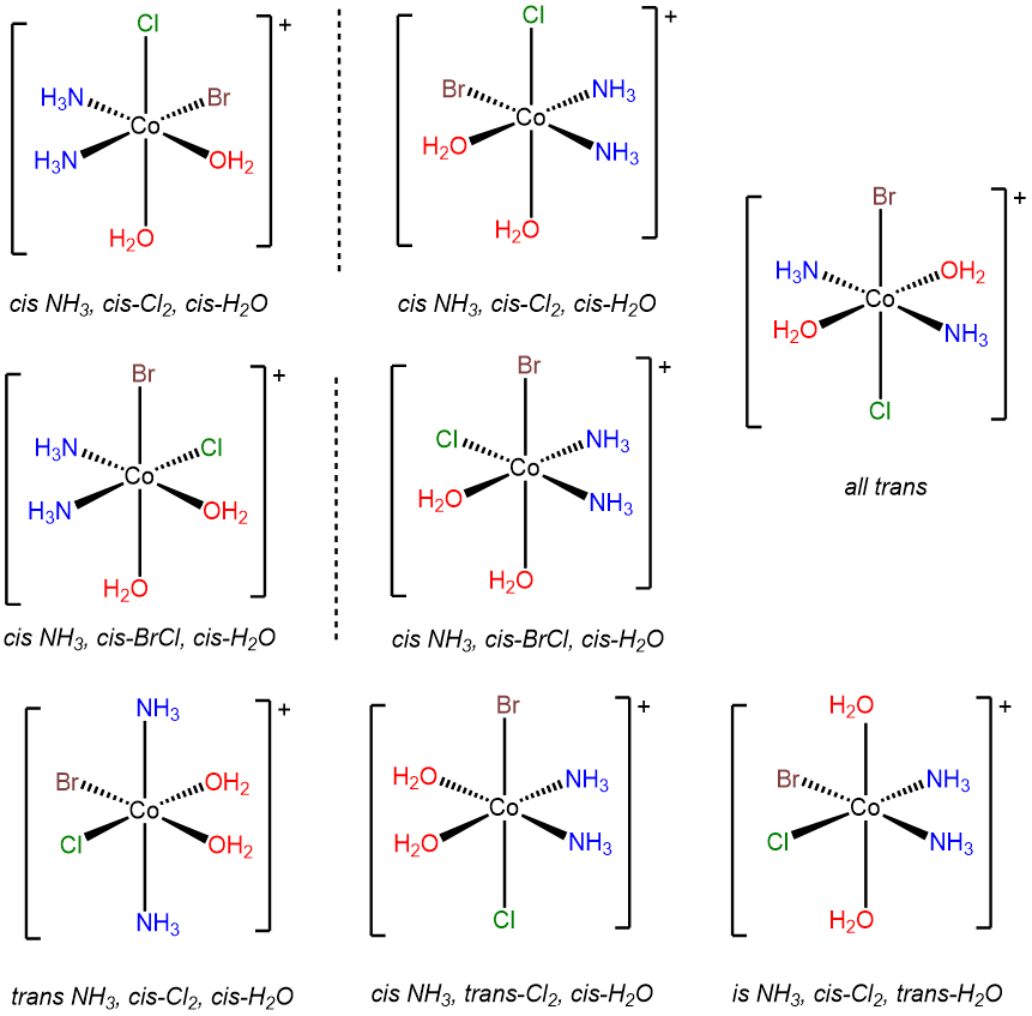


- finally, check to make sure you didn't include the same complex twice. Humans do make mistakes after all.

Answer d. $[CoBrCl(H_2O)_2(NH_3)_2]^+$

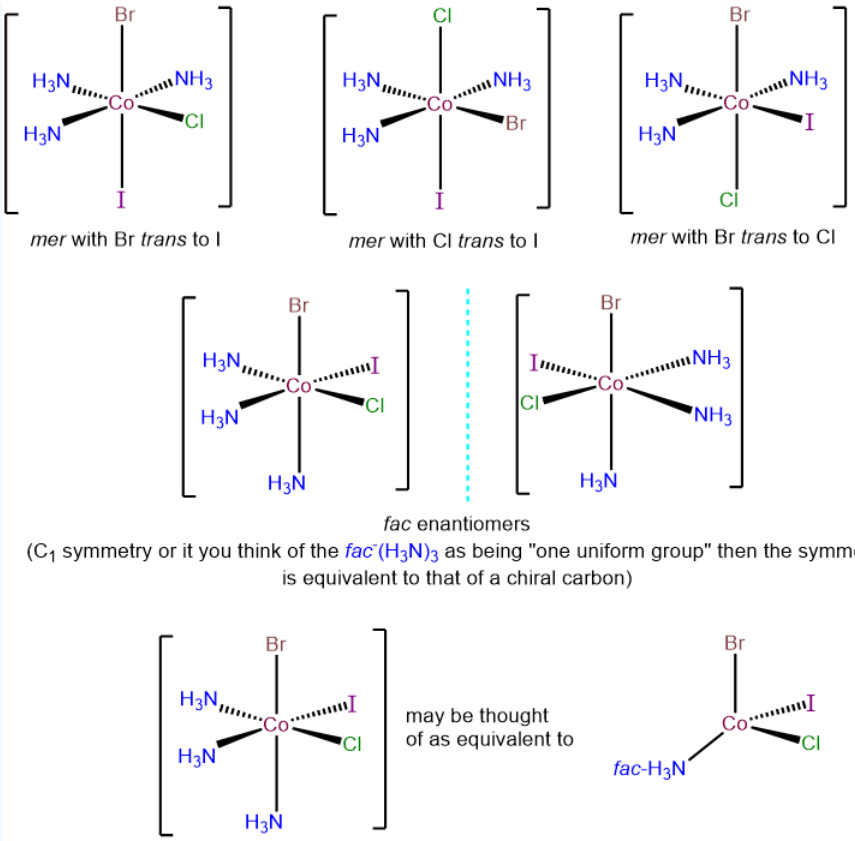
This problem is analogous to the one above except that this complex contains a bromo and chloro ligand in place of the two chloro ligands in $[CoCl_2(H_2O)_2(NH_3)_2]^+$. Consequently, when the bromo and chloro ligands are *cis* to one

another, additional possibilities for isomers arise based on whether ammine or aqua ligands are *trans* to the chloro and bromo. The result is eight isomers.



Answer e. $[CoBrClI(NH_3)_3]$

There are two possibilities for this complex - a *fac*-$(NH_3)_3$ and a *mer*-$(NH_3)_3$ arrangement. These may be taken as starting points for examining the possible permutations for the Cl^-, Br^-, and I^- ligands. The top row presents the three possibilities within the *mer*-$(NH_3)_3$ arrangement; each corresponds to a different ligand *trans* to an ammine ligand. The bottom row presents the two possible isomers with a *fac*-$(NH_3)_3$ arrangement. In each, the Cl^-, Br^-, and I^- ligands are *trans* to ammine ligands. However, the complexes possess C_1 symmetry and so are chiral and exist as enantiomers.



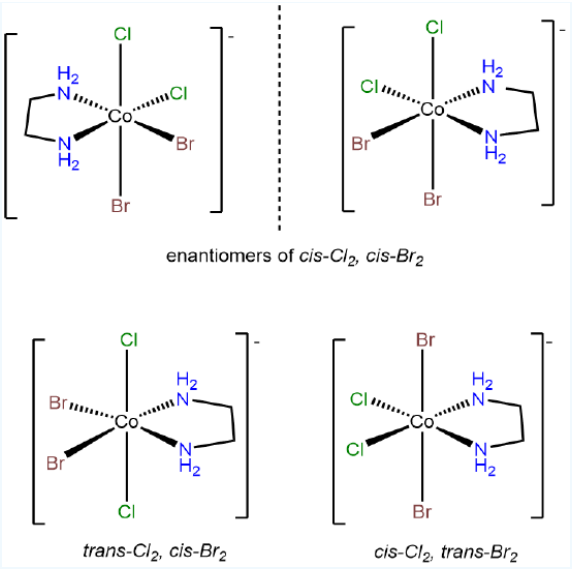
? Exercise 7.5.5. Stereoisomers of complexes with bidentate ligands (ignoring ring twist).

Ignoring ring twist, draw all the stereoisomers of the following real and hypothetical octahedral complexes.

a. $[CoBr_2Cl_2(en)]^-$
b. $[CoBrCl(en)_2]^+$
c. $[CoBrCl(gly)_2]^-$
d. $[Co(en)_3]^{3+}$
e. $[Co(gly)_3]$

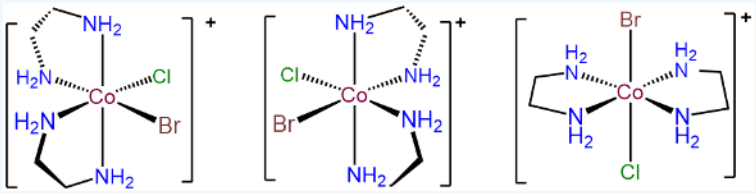
Answer a. $[CoBr_2Cl_2(en)]^-$

This complex is analogous to $[CoCl_2(H_2O)_2(NH_3)_2]^+$ in possessing pairs of identical ligating groups. The main difference is that in $[CoBr_2Cl_2(en)]^-$ the two amine ligating group of the en ligand are restricted to a *cis* arrangement. Under the MABCDEF system explained in Note 7.5.1, $[CoCl_2(H_2O)_2(NH_3)_2]^+$ may be $MA_2B_2C_2$, but this complex, $[CoBr_2Cl_2(en)]^-$, is $M(AA)B_2C_2$. The isomers are:



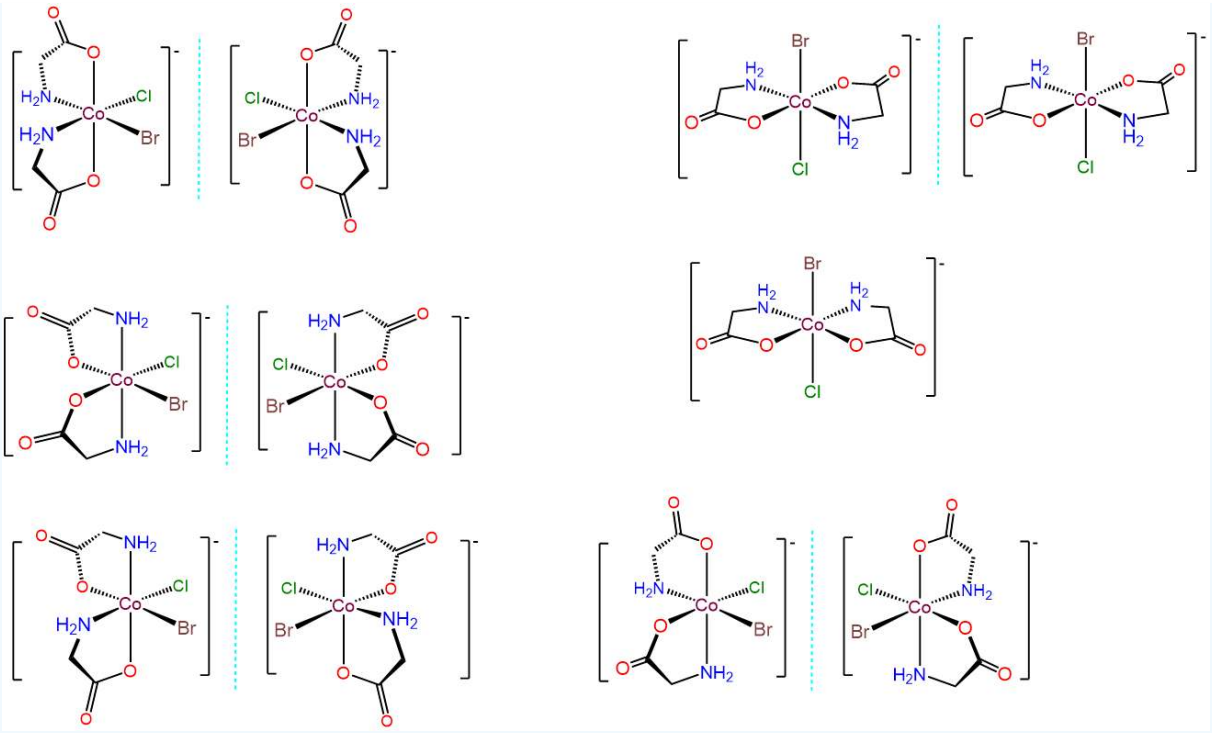
Answer b. $[CoBrCl(en)_2]^+$

The key to problems like this is to focus on the unique ligands, in this case Br^- and Cl^-. These can exist in either a *cis* or *trans* arrangement. The *trans* form is achiral, but in the case where Br^- and Cl^- are *cis*, Λ and Δ enantiomers are possible. The result is three isomers.



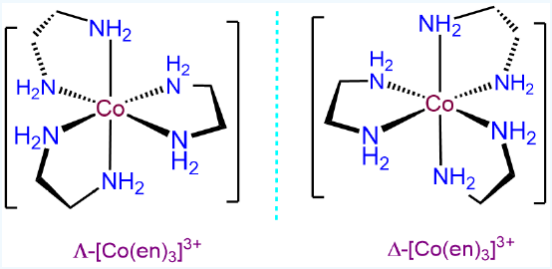
Answer c. $[CoBrCl(gly)_2]^-$

This case is analogous to the one above, but this time the bidentate ligand, gly, possesses distinguishable binding sites. Thus there are additional permutations involving how the gly ligands are bound relative to one another and/or whether the O or N end of the gly is bound *trans* to Br or Cl. The result is 11 different isomers, which are given below.



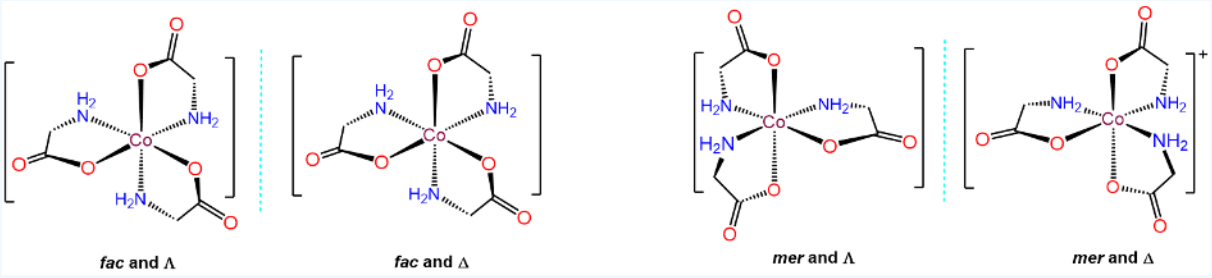
Answer d. $[Co(en)_3]^{3+}$

As a tris-chelate of symmetric bidentate ligands, ignoring ring twist, $[Co(en)_3]^{3+}$ will only exhibit Λ and Δ isomerism.



Answer e. $[Co(gly)_3]$

Since there are three gly ligands, each of which have carboxy and amine ends, the allowable arrangements involve whether the resulting three carboxy and three amine ends are oriented in a *mer* or *fac* arrangement. This gives two possibilities, each of which can exist as either the Λ or Δ enantiomer, for a total of four isomers, which are given below.



Exercise 7.5.6. More stereoisomers: Now featuring linkage isomerism

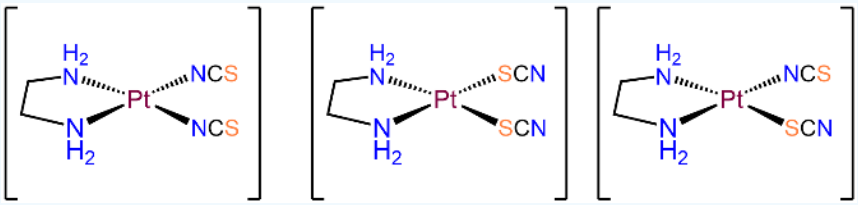
Ignoring ring twist, draw all chemically reasonable stereoisomers for the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[Pt(en)(SCN)_2]$
b. $[Pt(NH_3)_2(SCN)_2]$
c. $[Co(en)_2(SCN)_2]^+$

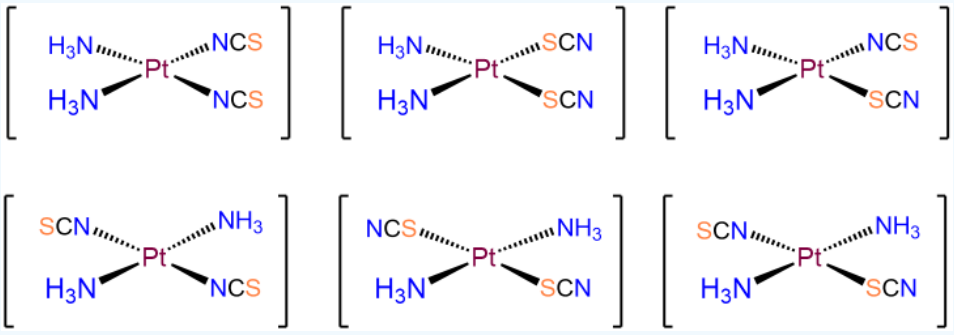
Answer a. $[Pt(en)(SCN)_2]$

The Pt in this neutral complex must be Pt^{2+} to balance the negative charges of the two SCN^- ligands. Complexes of Pt^{2+} are square planar and four coordinate, consistent with the bidentate en and two thiocyanato ligands. Of the ligands, the en ligand must bind in a *cis* arrangement. Consequently, the two SCN^- ligands will be in a *cis* arrangement as well. The isomers will therefore only differ in whether the two SCN^- bind κN or κS. The possibilities are:

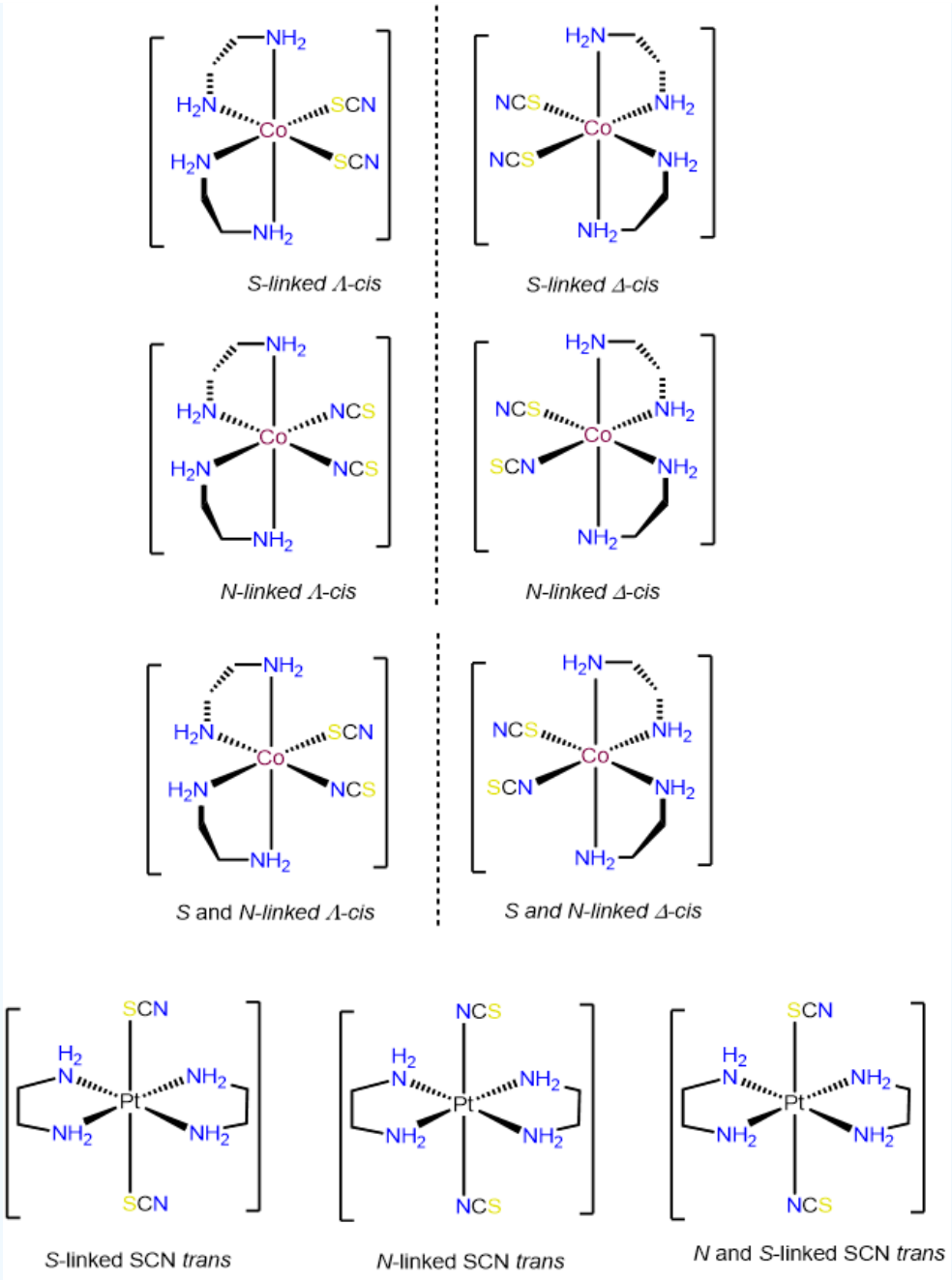


Answer b. $[Pt(NH_3)_2(SCN)_2]$

As with the preceding example, this will be a square planar Pt^{2+} complex. The main difference is that this time the coordinated nitrogens are not constrained to adopt a *cis* arrangement so there will be both *cis* and *trans* isomers.



Answer c. $[Co(en)_2(SCN)_2]^+$



? Exercise 7.5.7. Stereoisomer free for all.

Ignoring ring twist, draw all chemically reasonable stereoisomers for the following real and hypothetical complexes. You may assume that

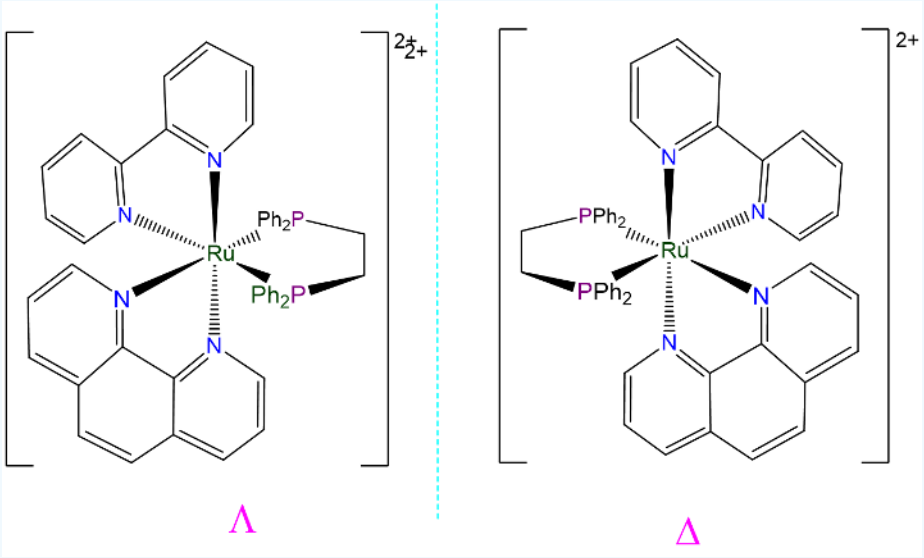
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[Ru(bpy)(phen)(dppe)]^{2+}$
b. $[CoClF(PPh_3)(py)]^{-}$
c. $[Ni(en)_2(NO_2)_2]$

d. $[Fe(H_2O)_3(SCN)_3]$
e. $[PtClF(PPh_3)(py)]$
f. $[CoBr_2Cl(NH_3)_3]$

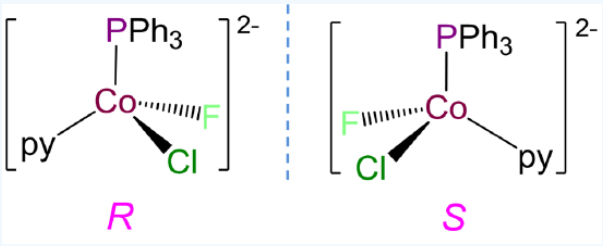
Answer a. $[Ru(bpy)(phen)(dppe)]^{2+}$

This complex is an octahedral tris-chelate containing symmetric ligands. As such it will exhibit Λ and Δ isomers:



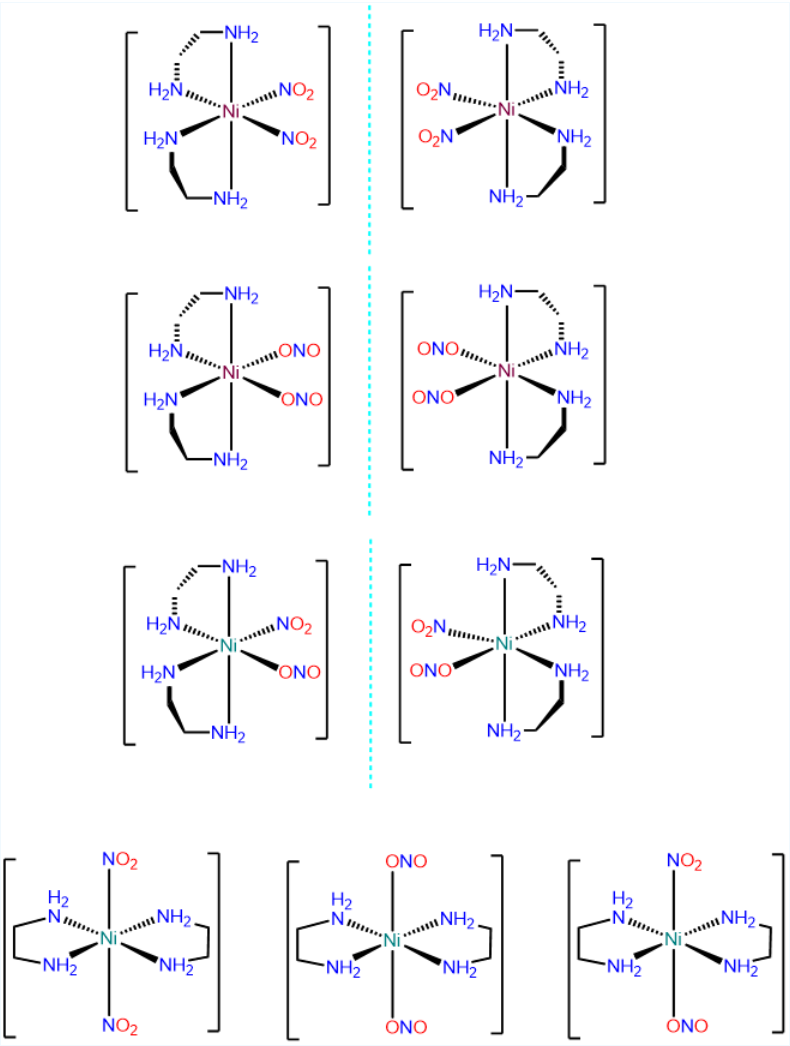
Answer b. $[CoClF(PPh_3)(py)]^-$

This complex has a coordination number of 4 and contains a Co^{2+} ion with a d^7 electron configuration, so a tetrahedral geometry is expected. Tetrahedral complexes like this one with four different ligands are chiral and can form *R* and *S* enantiomers.



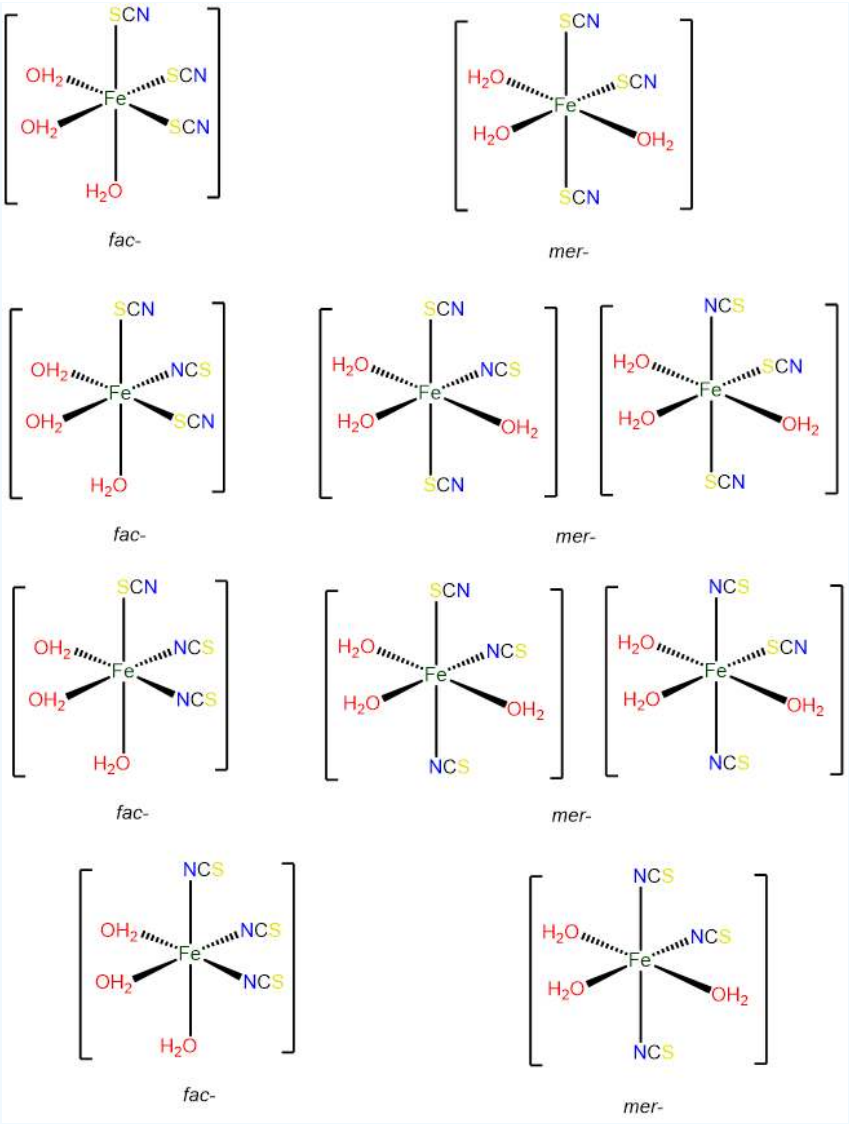
Answer c. $[Ni(en)_2(NO_2)_2]$

This is an octahedral bis-chelate and will exist in Λ and Δ configurations. Within each configuration the NO_2^- ligands can exist as *κN* and *κO*, leading to the following possibilities:



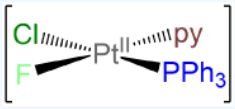
Answer d. $[Fe(H_2O)_3(SCN)_3]$

As an octahedral complex with three identical ligands it can exist in *mer* and *fac* configurations, with the ambidentate SCN ligand providing additional possibilities for isomerism.



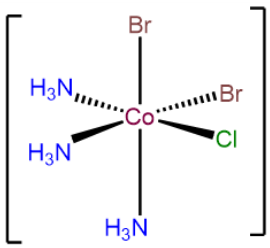
Answer e. [PtClF(PPh$_3$)(py)]

As a square planar complex with four nonidentical ligands, this complex exists as a single isomer.

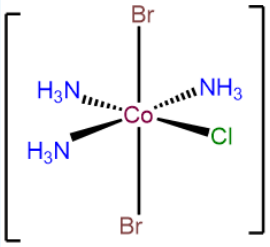


Answer f. [CoBr$_2$Cl(NH$_3$)$_3$]

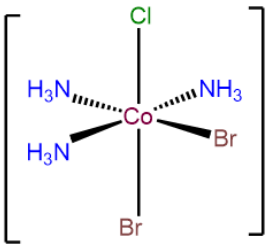
As an octahedral complex with three identical ligands it will exhibit *mer* and *fac* isomerism. In addition, it will have two *mer* configurations that differ in terms of the cis and trans relationships between the bromo and chloro ligands.



fac



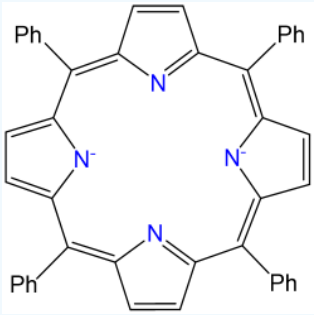
mer with Br *trans* to Br



mer with Cl *trans* to Br

Exercise 7.5.8

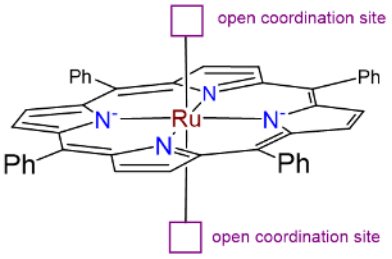
Complexes of formula $Ru(TPP)py_2$ have been prepared, in which TPP is tetraphenylporphyrin, which binds metals in the form given below. Draw all isomers of $Ru(TPP)py_2$.

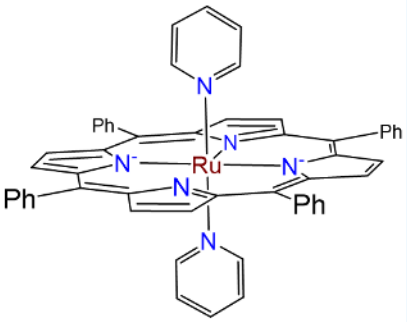


Answer

There is only one isomer. While normally complexes containing two identical ligands (in this case py) can exhibit *cis* and *trans* isomerism, in this case the planar tetraphenylporphyrin ring ligates the Ru^{2+} ion in a square planar arrangement, as shown at left in the image below. This leaves only a pair of *trans* coordination sites for the chloro ligands to occupy, giving the isomer shown at right below.

When TPP ligates Ru^{2+} it leaves only *trans* open coordination sites so only the *trans* isomer can form.

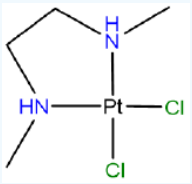




trans-[Ru(py)$_2$(TPP)]

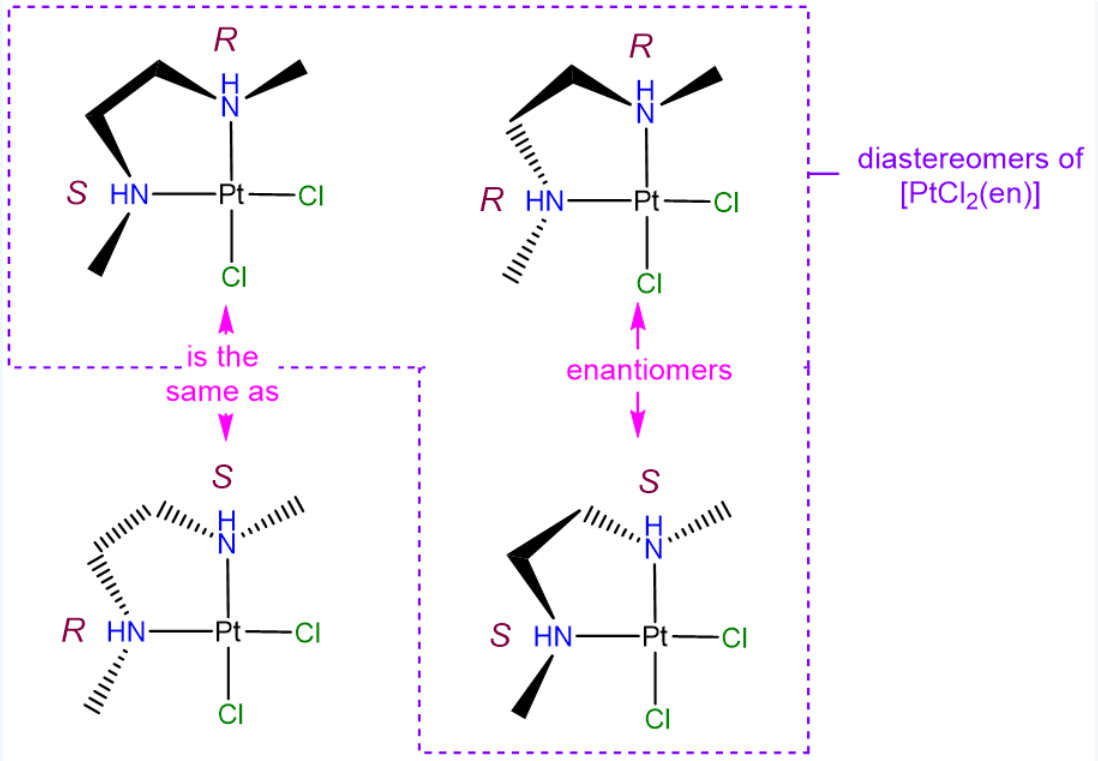
Exercise 7.5.9

Draw the diastereomers formed due to the chirality of the amine nitrogen atoms in [$PtCl_2$(*N*,*N*'-dimethylethane-1,2-diamine)] which has the atomic connectivity represented below



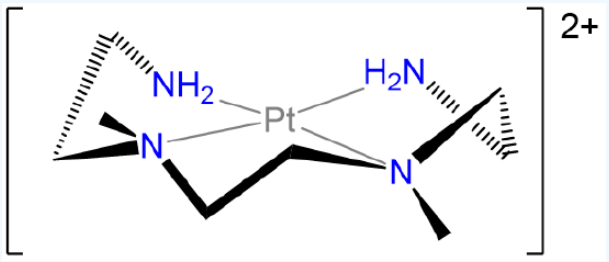
Answer

The diastereomers will differ in whether the N atoms adopt an *R* or *S* configuration at the nitrogen atoms. The possible permutations are (*R*,*R*), (S,*S*), (*R*,*S*), and (S,*R*). However, as may be seen from the image below, the (*R*,*S*) and (S,*R*) configurations are identical (the two projections shown can be interconverted through a C_2 rotation along an axis bisecting the Cl-Pt-Cl unit). As a result there are only three unique isomers. Of these, the (*R*,*R*) and (S,*S*) configurations are enantiomers (they are mirror images by reflection in the $PtCl_2N_2$ plane). Note that in solving problems like this one it can be helpful to keep track of possible isomers by assigning the stereochemistry at each chiral center as *R* or *S* using the Cahn-Ingold-Prelog-convention, though it is not strictly necessary to do so.

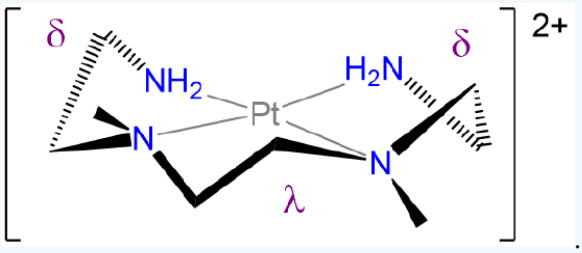


? Exercise 7.5.10

Label the conformations of all chelate rings in the structure below.



Answer



Appendix: The MABCDEF bookkeeping system for identifying isomers

The Mabcdef or MABCDEF system is one method for identifying the number of isomers in an octahedral complex, although since it is really just a bookkeeping and organizational system it can easily be extended to other geometries as well. The M in Mabcdef stands for metal and the other letters are used to stand in for ligands. The basic approach involves

- classifying the ligands as A, B, C, D, E, or F in order of multiplicity. Thus for

$[Cr(NH_3)_6]^{3+}$ A = NH_3; there are no B, C, D,E, or F ligands; and the complex is classified as MA_6

$[CoCl(NH_3)_5]^{2+}$ A = NH_3, B = Cl^-, and the complex is MA_5B

$[CrCl_2(H_2O)_2(NH_3)_2]^+$ A = Cl^-, B = H_2O, C = NH_3, and the complex is $MA_2B_2C_2$

- in the classification above, multidentate ligands are typically classified before monodentate ones and are designated AA, AB, ABC, ABA, etc. based on the symmetry of the attachment points. Thus

  en has identical attachment amine points and is AA

  gly has a carboxy and amine attachment points and is AB

  trien is ABA

  $CoCl_2(en)_2^+$ is $M(AA)_2B_2$

  $CoCl_2(gly)_2^-$ is $M(AB)_2C_2$

  $CoCl_2(en)(gly)$ is $M(AA)(AB)C_2$

- Systematically list out the possible *trans* arrangements of ligands by
  1. assigning one pair of ligands to be *trans* to one another.
  2. Then systematically list out the other possible *trans* pairs by permuting the remaining trans arrangements. It can help to organize the permutations in a table, such as that shown below for an MABCDEF complex where A and B are assigned *trans*. In looking at the table notice how the second set of trans permutations is systematically varied. This helps ensure that no possibility is skipped.
  3. Go through the list of isomers and remove any duplicates you generated so far. For instance, notice in the table below that the last three stereoisomers are identical with the first three (*e.g.*, stereoisomer 4 is identical to stereoisomer 3, 5 with 2, and 6 with 1).

Stereoisomer 1	Stereoisomer 2	Stereoisomer 3	Stereoisomer 4 (same as isomer 3)	Stereoisomer 5 (same as isomer 2)	Stereoisomer 6 (same as isomer 1)
trans AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)
trans CD	*trans* CE	*trans* CF	*trans* DE	*trans* DF	*trans* EF
trans EF	*trans* DF	*trans* DE	*trans* CF	*trans* CE	*trans* CD

  4. If the complex possesses multidentate ligands that demand that certain groups exist and *cis* pairs, then also remove any configurations which do not agree with the known binding capability of the ligand (*e.g.*, the two amine groups of ethylenediamine cannot be *trans* to one another, so if you have an en ligand, remove configurations like that from the list).

5. Next, swap or permute the original *trans* pair and repeat the process you just followed. In the case of Mabcdef this gives the following results:

Isomer	"fixed" trans pair	Additional trans pairs	
1	AB	CD	EF
2	AB	CE	DF
3	AB	CF	DE
4	AC	BD	EF
5	AC	BE	BF
6	AC	BF	DE
7	AD	BC	EF
8	AD	BE	CF
9	AD	BF	CE
10	AE	BC	DF
11	AE	BD	CF
12	AE	BF	CD
13	AF	BC	DE
14	AF	BD	CE
15	AF	BE	CD

- Since the procedure explained above only identifies isomers based on unique *trans* pairings, **it does not identify when a configuration is chiral and corresponds to a pair of enantiomers.** Any enantiomers can be identified by drawing out the complexes and either classifying their point groups or by drawing their mirror images and checking if they are superimposable. In the MABCDEF case - *i.e.*, where all the ligands are different - all of the isomers identified have C_1 symmetry so are chiral. This means there will be a pair of enantiomers for each, giving 15 x 2 = 30 different stereoisomers.

References

1. These examples are taken from http://wwwchem.uwimona.edu.jm/courses/inorgnom.html

2. Contakes S. M.; Rauchfuss, T.B. *Chem. Commun.* 2001, 553-554.

3. Shriver, D. F.; Shriver, S. A.; Anderson, S. E., *Inorg. Chem.* 1965, *4(5)*, 725-730.

4. Zelewsky, A. v., *Stereochemistry of Coordination Compounds* Wiley, 1996.

5. In the past it was difficult to determine absolute configurations from X-ray data alone, but recent advances have made it easier to do so.

6. Pavan M. V. Raja & Andrew R. Barron "Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species" in *Physical Methods in Chemistry and Nano Science* https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/07%3A_Molecular_and_Solid_State_Structure/7.07%3A_Circular_Dichroism_Spectroscopy_and_its_Application_for_Determination_of_Secondary_Structure_of_Optically_Active_Species

7. Berova, N.; Bari, L. D.; Pescitelli, G., *Chemical Society Reviews* 2007, 36 (6), 914-931.

8. Of course, if one set of ligands occupies a meridional plane, then the other three ligands will be oriented in an equatorial one. The reason they may both be considered meridional is because if the complex were rotated, the equatorial plane would be meridional and vice versa. From that point of view both might be considered meridional planes - albeit not at the same time.

9. Bite angles are taken from Mansell, S. M., Catalytic applications of small bite-angle diphosphorus ligands with single-atom linkers. Dalton Transactions 2017, 46 (44), 15157-15174.

10. Hancock, R. D., The pyridyl group in ligand design for selective metal ion complexation and sensing. Chemical Society Reviews 2013, 42 (4), 1500-1524.

11. Sasi, D.; Ramkumar, V.; Murthy, N. N., Bite-Angle-Regulated Coordination Geometries: Tetrahedral and Trigonal Bipyramidal in Ni(II) with Biphenyl-Appended (2-Pyridyl)alkylamine N,N'-Bidentate Ligands. ACS Omega 2017, 2 (6), 2474-2481.

12. Ehnbom, A.; Ghosh, S. K.; Lewis, K. G.; Gladysz, J. A., Octahedral Werner complexes with substituted ethylenediamine ligands: a stereochemical primer for a historic series of compounds now emerging as a modern family of catalysts. Chemical Society Reviews 2016, 45 (24), 6799-6811.

This page titled 7.5: Isomerism is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.4: Isomerism** by Stephen M. Contakes is licensed CC BY 4.0.

7.6: Complex-Ion Equilibria

When a metal ion reacts with a Lewis base in solution a complex ion is formed. This reaction can be described in terms of chemical equilibria.

Introduction

A complex ion is comprised of two important parts: the central atom and its surrounding ligands. The central atom can be any metallic ion (usually a transition metal). The ligands are any combination of anions that can donate an electron pair, effectively meaning they are all Lewis bases. When combined they form coordinate covalent bonds.

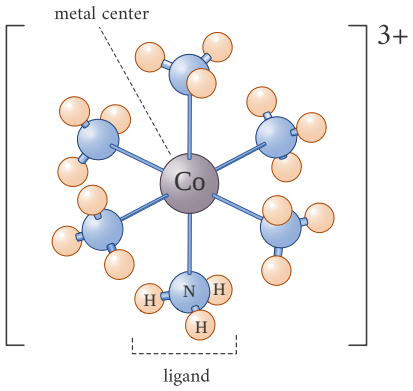


Figure 7.6.1: Separation of metal center and ligands in a complex ion. (CC BY 4.0 Unported; Ümit Kaya via LibreTexts)

Formation Constant

In general, chemical equilibrium is reached when the forward reaction rate is equal to the reverse reaction rate and can be described using an equilibrium constant, K.

$$x\mathrm{M}\,(\mathrm{aq}) + y\mathrm{L}\,(\mathrm{aq}) \rightleftharpoons \mathrm{M}_x\mathrm{L}_y(aq)$$

Complex ion equilibria are no exception to this and have their own unique equilibrium constant. This *formation constant*, K_f, describes the formation of a complex ion from its central ion and attached ligands. This constant may be called a **stability constant** or **association constant**; the units depend on the specific reaction it is describing. Common metal/ligand K_f values are tabulated in Table E4.

At its most basic level, K_f can be explained as the following, where M is a metal ion, L is a ligand, and x and y are coefficients:

$$K_f = \frac{[\mathrm{M}_x\mathrm{L}_y]}{[\mathrm{M}]^x[\mathrm{L}]^y}$$

K_f values are very large in magnitude for complex ion formation reactions heavily favor the product and very small for poorly forming complex ions. For example, observe the formation reaction of the dicyanoargentate(I) complex ion

$$\mathrm{Ag}^+\,(\mathrm{aq}) + 2\,\mathrm{CN}^-\,(\mathrm{aq}) \rightleftharpoons \mathrm{Ag(CN)_2}^-\,(\mathrm{aq})$$

and the resulting formation constant expression:

$$K_f = \frac{[\mathrm{Ag(CN)_2}^-]}{[\mathrm{Ag}^+][\mathrm{CN}^-]^2}$$
$$= 5.6 \times 10^{18}$$

The larger the K_f value of a complex ion, the more stable it is. Due to how large formation constants often are it is not uncommon to see them listed as logarithms in the form $\log K_f$. You may also see them in the form of a **dissociation constant**, K_d (which

should not be confused with pK_a). This is merely the inverse value of the formation constant and as such describes the instability of a complex ion. It may help to think of K_f and K_d as stability and instability constants, respectively.

Using the above example, the dissociation constant expression would be:

$$\begin{aligned} K_d &= \frac{1}{K_f} \\ &= \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} \\ &= 1.8 \times 10^{-19} \end{aligned}$$

In logarithm form K_f and K_d would be:

$$\log K_f = \log(5.6 \times 10^{18}) = 18.7$$
$$\log K_d = \log(1.8 \times 10^{-19}) = -18.7$$

Example 7.6.1: Stepwise Equilbria

One might assume that the formation of complex ions is a one step process, however this is not always the case. As an example let's look at the formation of tetraamminecopper(II) ion in solution:

$$[\mathrm{Cu(H_2O)_4}]^{2+}\,(\mathrm{aq}) + 4\,\mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}\,(\mathrm{aq}) + 4\,\mathrm{H_2O}\,(\mathrm{l})$$

The reason for using the hydrated form of the copper ion is that cations in solution usually exist in their hydrated form. It is because of this that the creation of tetraamminecopper(II) ion is a multi-step process, the ammine ligands have to displace the existing aqua ligands. In calculations however, the concentration of water and the number of aqua ligands are effectively constant meaning that they can be safely ignored. Each step of this process has its own formation constant, and as with other chemical equilibria, the overall reaction constant is the product of these stepwise formation constants.

Ligand Exchange Step 1:

$$[\mathrm{Cu(H_2O)_4}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(H_2O)_3(NH_3)}]^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \qquad \text{(step 1)}$$

$$K_1 = \frac{[[Cu(H_2O)_3(NH_3)]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]} = 1.9 \times 10^4$$

Ligand Exchange Step 2:

$$[\mathrm{Cu(H_2O)_3(NH_3)}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(H_2O)_2(NH_3)_2}]^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \qquad \text{(step 2)}$$

$$K_2 = \frac{[[Cu(H_2O)_2(NH_3)_2]^{2+}]}{[[Cu(H_2O)_3(NH_3)]^{2+}][NH_3]} = 3.9 \times 10^3$$

Ligand Exchange Step 3:

$$[\mathrm{Cu(H_2O)_2(NH_3)_2}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(H_2O)(NH_3)_3}]^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \qquad \text{(step 3)}$$

$$K_3 = \frac{[[Cu(H_2O)(NH_3)_3]^{2+}]}{[[Cu(H_2O)_2(NH_3)_2]^{2+}][NH_3]} = 1.0 \times 10^3$$

Ligand Exchange Step 4:

$$[\mathrm{Cu(H_2O)(NH_3)_3}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \qquad \text{(step 4)}$$

$$K_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)(NH_3)_3]^{2+}][NH_3]} = 1.5 \times 10^2$$

Total

$$\begin{aligned} K_f &= K_1 \times K_2 \times K_3 \times K_4 \\ &= \frac{[[Cu(H_2O)_3(NH_3)]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]} \times \frac{[[Cu(H_2O)_2(NH_3)_2]^{2+}]}{[[Cu(H_2O)_3(NH_3)]^{2+}][NH_3]} \\ &\quad \times \frac{[[Cu(H_2O)(NH_3)_3]^{2+}]}{[[Cu(H_2O)_2(NH_3)_2]^{2+}][NH_3]} \times \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)(NH_3)_3]^{2+}][NH_3]} \\ &= \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]^4} \\ &= 1.1 \times 10^{13} \end{aligned}$$

If you wanted to find the formation constant of one of the intermediate steps, you would simply take the product of the K values up until that point. For example the formation constant of $[Cu(H_2O)_2(NH_3)_2]^{2+}$ would be $\beta_2 = K_1 \times K_2 = 7.4 \times 10^7$. As seen here and above the standard notation for these values is a lowercase beta.

Example 7.6.2: Using Formation Constants as a Metric of Stability

Based on the given values, rank the following complex ions from most to least stable.

- $[Cr(OH)_4]^-$ with $K_f = 8.0 \times 10^{29}$
- $[Ni(CN)_4]^{2-}$ with $\log(K_d) = -31.3$
- $[Co(NH_3)_6]^{3+}$ with $K_d = 2.2 \times 10^{-34}$
- $[Cu(CN)_4]^{3-}$ with $\log(K_f) = 30.3$

Solution

The key to solving this problem is to convert all of the given values into the same form. In this case we will convert all of them into the form K_f though any other form could be used as long as you are consistent.

- $[Cr(OH)_4]^-$ with $K_f = 8.0 \times 10^{29}$
- $[Ni(CN)_4]^{2-}$ with $\log(K_d) = -31.3 \longrightarrow K_f = 2.0 \times 10^{31}$
- $[Co(NH_3)_6]^{3+}$ with $K_d = 2.2 \times 10^{-34} \longrightarrow K_f = 4.5 \times 10^{33}$
- $[Cu(CN)_4]^{3-}$ with $\log(K_f) = 30.3 \longrightarrow K_f = 2.0 \times 10^{30}$

After converting it is easy to rate the ions in terms of stability. From most to least stable:

$$[Co(NH_3)_6]^{3+} > [Ni(CN)_4]^{2-} > [Cu(CN)_4]^{3-} > [Cr(OH)_4]^-.$$

You may notice that each stepwise formation constant is smaller than the one before it. This decreasing trend is due to the effects of entropy, causing each step to be progressively less likely to occur. You can think of this in the following way, continuing with the previous example (Figure 7.6.2). When the first ammine ligand goes to displace an aqua ligand it has four sites from which to choose from, making it "easier" to displace one. Yet with every step the number of sites decreases making it increasingly more difficult. As always though, there are exceptions to this rule. If the values do not continually decrease then the structure of the complex ion likely changed during one of the steps.

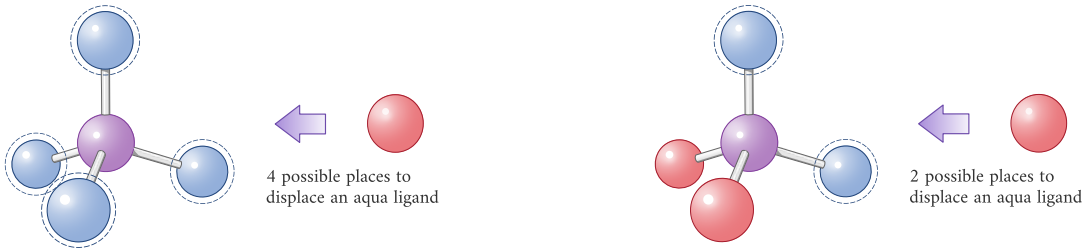


Figure 7.6.2: Ligand exchange in the tetrahedral complex. The first exchange step can occur with four ligands, while the third step has only two possible ligands to replace. (CC BY 4.0 Unported; Ümit Kaya via LibreTexts)

Chelation Effect

Generally, complex ions with polydentate ligands have much higher formation constants than those with monodentate ligands. This additional stability is known as the chelation effect. For example, the formation of the bis(ethylenediamine)copper(II) ion is identical to the tetraamminecopper(II) ion above except the ethylenediamine ligands displace two aqua ligands at a time. Observe the differences in formation constant (Table E4):

Complex Ion	K_f
$[Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$[Cu(en)_2]^{2+}$	1.0×10^{20}

Example 7.6.3

Of $[Ni(en)_3]^{2+}$, $[Ni(EDTA)]^{2-}$, and $[Ni(NH_3)_6]^{2+}$, which would you expect to have the largest K_f value? The smallest? Explain.

Solution

This is a question involving the effects of chelation. When the complex ion with EDTA is formed, the EDTA ligand displaces six aqua ligands at once. Ethylenediamine ligands displace two at a time and ammine ligands displace one at a time. Based on this we would expect $[Ni(EDTA)]^{2-}$ to be the most stable and $[Ni(NH_3)_6]^{2+}$ to be the least stable.

Solubility Effects

The formation of complex ions can sometimes explain the solubility of certain compounds in solution. For example, let's say we have a saturated solution of silver bromide ($AgBr$) which also contains additional undissolved solid silver bromide. If high enough concentrations of ammonia are added to the solution, the solid silver bromide will dissolve despite the solution previously having been saturated. This is because of the formation diammineargentate(I) ion, illustrated by the following chemical equation:

$$AgBr\,(s) + 2\,NH_3\,(aq) \rightarrow [Ag(NH_3)_2]^+\,(aq) + Br^-\,(l)$$

Example 7.6.4

The creation of $[Ni(en)_3]^{2+}$ is a three step process with the following stepwise formation constants $K_1 = 3.3 \times 10^7$, $K_2 = 1.9 \times 10^6$, and $K_3 = 1.8 \times 10^4$. Using this information find the overall formation constant and the formation constant for each of the intermediate steps.

Solution

Take the product of the stepwise formation constants up until the step you are trying to find.

$[Ni(H_2O)_4\,(en)]^{2+}$ with $\beta_1 = K_1 = 3.3 \times 10^7$

$[Ni(H_2O)_2(en)_2]^{2+}$ with $\beta_2 = K_1 \times K_2 = 6.8 \times 10^{13}$

$[Ni(en)_3]^{2+}$ with $\beta_3 = K_f = K_1 \times K_2 \times K_3 = 1.1 \times 10^{18}$

References

1. Beck, Mihály T. *Chemistry of Complex Equilibria*. Revised ed. New York: Halsted Press, 1990.
2. Brown, Theodore, Eugene Lemay, Bruce Bersten, and Catherine Murphey. Chemistry: The Central Science. 10th ed. Andalusia, Alabama: Pearson Publications Company, 2006.
3. Petrucci, Harwood, Herring, and Madura. General Chemistry: Principles and Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson Education, 2007.
4. Wilkinson, Geoffrey, Robert D. Gillard, and Jon A. McCleverty, eds. Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties & Applications of Coordination Compounds. First ed. Vol. 1. Oxford, England: Pergamon Press, 1987. N. pag. 7 vols.

This page titled 7.6: Complex-Ion Equilibria is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Gianna Navarro, Katherine Barrett, Christopher May, & Christopher May.

- **Complex-Ion Equilibria** by Christopher May, Gianna Navarro, Katherine Barrett is licensed CC BY-NC-SA 4.0.

7.7: Hard-Soft Acid-Base Theory

The Hard Soft Acid Base Principle is a Conceptual Tool for Thinking About Patterns of Lewis Acid-Base Reactivity

The explanation of the trends in metal distribution, halide salt solubility, and preferred metal coordination patterns is rooted in Arland, Chatt, and Davies' observation that *Lewis acids and bases could be classified into two groups based on their propensity to form stable compounds with one another* (*e.g.* acids in a class tend to form more stable adducts with bases in the same class than they did with bases in the other).[1] Arland, Chatt, and Davies somewhat boringly termed these groups class a and class b but today they are known by Ralph Pearson's name for them. Pearson called the class a acids and bases hard and class b acids and bases soft. These terms reflect how "soft" these substance's electron clouds are towards distortion or, in other words, their polarizability (Figure 7.7.1). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard.**

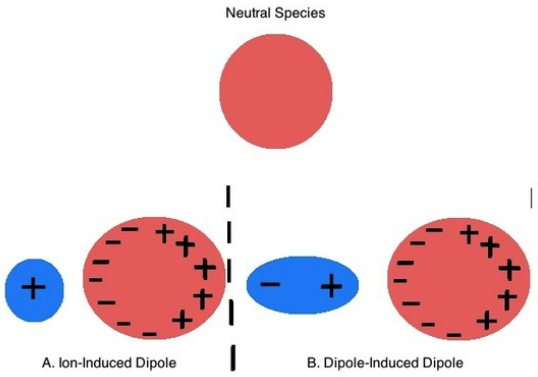


Figure 7.7.1: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. A fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability"

Recognizing Hard and Soft Acids and Bases

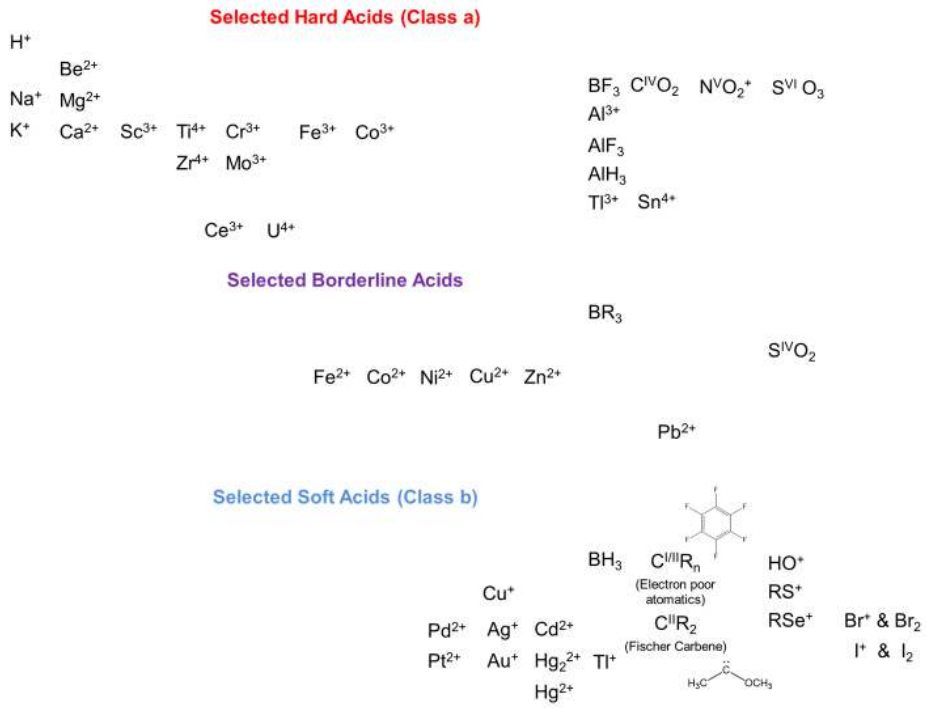
Hard acids and bases come in two varieties:

1. hard acid and base sites that possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acid hard acids towards the left of the periodic table.
2. hard acid and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

Soft acids and bases also come in two varieties

1. soft acids and bases which posses many valence electrons and so are more readily polarized. In consequence, all other things being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.



As expected, hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents while soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Illustrative hard, soft, and borderline bases are given below. Again, notice how these substances illustrate the general trends.

Selected Hard Bases (Class a)

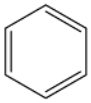
Nitrogen bases	Oxygen bases		small halides
NH_2^-	OH^-	CO_3^{2-}	F^-
NH_3	H_2O	RCO_2^-	Cl^-
RNH_2	ROH	NO_3^-	
NH_2NH_2	ROR	PO_4^{3-}	
		SO_4^{2-}	

Selected Borderline Bases

electron-poor Nitrogen bases		low oxidation state element oxyanions	intermediate halides
N_3^-		NO_2^-	
NO_2^-			Br^-
SCN^-		SO_3^{2-}	
N_2			

Selected Soft Bases (Class b)

Carbon bases	P and As bases	Sulfur bases	large halides & pseudohalides
R^-	PR_3	RS^-	H^-
CO	$P(OR)_3$	RSH	I^-
CN^-	AsR_3	RSR	
RNC		SCN^-	
$R_2C{=}CR_2$ (alkenes)			



(electron-rich aromatics)

Qualitative Estimation of the Relative Hardness and Softness of Lewis Acids and Bases

As can be seen from the examples above, **hard acids are relatively electron-poor and hard bases electron-rich** since they have comparatively

- small frontier orbitals, reflective of their relatively small atom/ion/fragment sizes
- high (for acids) or low (for bases) oxidation states on the base atom, reflected in a large positive formal charge (for acids) or negative formal charge (for bases)
- low polarizability, due to loss or gain of substantial numbers of electrons, or the localization of
  - positive charge on an electropositive element or an atom bearing electron-withdrawing substituents
  - negative charge on an electronegative element or an atom bearing electron-donating substituents

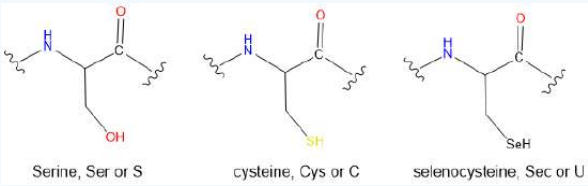
In contrast to hard acids and bases, **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- large frontier orbitals, reflective of their relatively large atom/ion/fragment sizes
- low oxidation states, often resulting in small or nonexistent atomic charges
- high polarizability, as might be expected of species in which electron-electron repulsions are lower and electrons are spread over a large volume. Sometimes this is indicated by
  - positive charge on an electronegative element or an atom bearing electron-donating substituents
  - negative charge on an electropositive element or an atom bearing electron-withdrawing substituents

Exercise 7.7.1

Rank the acids or bases in each set in increasing order of expected hardness.

a. Cr^{2+} and Cr^{3+}
b. H^+, Cs^+, and Tl^+
c. SCN^- (acting as a base at N) and SCN^- (acting as a base at S)
d. AlF_3, AlH_3, $AlMe_3$
e. The side chains of the following proteinogenic amino acids

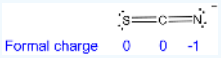


Answer

(a) $Cr^{2+} < Cr^{3+}$ All other things being equal, hardness increases with oxidation state.

(b) $Tl^+ < Cs^+ < H^+$ The order reflects Cs^+ and Tl^+'s larger size relative to H^+ (which doesn't possess any electrons that can be polarized anyway) and that Tl^+ still possesses two valence electrons while Cs^+ possesses none.

(c) SCN^- (acting as a base at S) < SCN^- (acting as a base at N). The order reflects the greater electronegativity of N than S and N's possession of a more negative formal charge of -1.



(d) $AlH_3 < AlMe_3 < AlF_3$. The hardness increases as the substituents on the Lewis acid Al center become less electron donating and more electron withdrawing (and, incidentally, harder bases) as their electronegativity increases in the order H^- < CH_3^- < F^-. Note that the order of electron donating ability for H^- and CH_3^- is the opposite observed for carbocations, for which hyperconjugation plays a larger role.

(e) Sec < Cys < Ser. The hardness increases as the electronegativity of the Lewis base chalcogen increases on going from a selenol to a thiol to an alcohol.

The Hard-Soft Acid-Base Principle (HSAB Principle)

The **Hard-Soft acid-base principle (HSAB Principle) explains patterns in Lewis acid-base reactivity in terms of a *like reacts with like preference***. Both thermodynamically and kinetically, hard acids prefer hard bases and soft acids soft bases. Specifically,

- Thermodynamically, hard acids form stronger acid-base complexes with hard bases while soft acids form stronger complexes with soft bases.
- Kinetically, hard acids/electrophiles react more quickly with hard bases/nucleophiles while soft acids/electrophiles react more quickly with soft bases/neucleophiles.

Applications of the HSAB principle include

1. Predicting the equilibrium or speed of *Lewis acid-base metathesis and displacement reactions.* In a Lewis acid-base **metathesis reaction** the acids and bases swap partners

$$A_1 : B_1 + A_2 : B_2 \overset{k_1,\ K_{eq}}{\rightleftharpoons} A_1 : B_2 + A_2 : B_1$$

For example, the equilibrium position of the metathesis reaction between TlF and K_2S favors the products:

$$2\,TlF + H_2S \rightleftharpoons Tl_2S + 2\,KF$$

consistent with the HSAB's hard-hard and soft-soft preference.



The HSAB principle also allows for prediction of the position of displacement reactions, in which a Lewis acid or base forms an adduct using a base or acid from an existing Lewis acid-base complex. In these reactions, the displacement of acid or base from the reactant complex may be thought of as a sort of metathesis reaction, one in which in the unbound acid or base switches places with one in the complex. For example, the reaction between HI and methylmercury cation

$$\mathrm{HI} + \mathrm{HgSCH_3}^+ \rightleftharpoons \mathrm{CH_3SHgI} + \mathrm{H}^+$$

involves displacement of an iodide from HI to give $\mathrm{CH_3HgI}$. The position of the equilibrium favors $\mathrm{CH_3HgI}$ since both $\mathrm{CH_3Hg}^+$ and I^- are soft, while H^+ is a hard acid.



Exercise 7.7.2

Predict the position of equilibrium for the following reaction.

$$\mathrm{Fe_2O_3} + 3\,\mathrm{Ag_2S} \rightleftharpoons \mathrm{Fe_2S_3} + 3\,\mathrm{Ag_2O}$$

Answer

The equilibrium will favor the reactants (K<1) since the hard-hard and soft-soft interactions in the reactants are more stable than the hard-soft interactions in the products.



Exercise 7.7.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $2\,\mathrm{HF} + (\mathrm{CH_3Hg})_2\mathrm{S} \rightleftharpoons 2\,\mathrm{CH_3HgF} + \mathrm{H_2S}$
b. $\mathrm{Ag(NH_3)_2}^+ + 2\,\mathrm{PH_3} \rightleftharpoons \mathrm{Ag(PH_3)_2}^+ + 2\,\mathrm{NH_3}$
c. $\mathrm{Ag(PH_3)_2}^+ + 2\,\mathrm{H_3B{-}SH_2} \rightleftharpoons 2\,\mathrm{H_3B{-}PH_3} + \mathrm{Ag(SH_2)_2}^+$
d. $\mathrm{H_3B{-}NH_3} + \mathrm{F_3B{-}SH_2} \rightleftharpoons \mathrm{H_3B{-}SH_2} + \mathrm{F_3B{-}NH_3}$

Answer

a. K< < 1 since the reactant adducts are hard-hard and soft-soft while the products involve hard-soft interactions.

b. K>>1 since the reactant complex, diamine silver(I), is a complex of a hard base, NH_3, with the soft acid, Ag^+, while the product is a complex of the same soft acid with the soft base phosphine.

c. K~1 since all the adducts amongst the reactants and products involve soft acids and bases.

d. K>>1 since BH_3 is a softer acid than BF_3, so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

2. Predicting the relative strengths of a given set of *Lewis acids or bases towards a particular substrate*. Consider, for example, the relative strengths of a BH_3, BMe_3, and BF_3 towards group 15 hydrides like NH_3, PH_3, and AsH_3. Of the

boranes listed, the hardest acid BF_3 is the strongest acid towards the hard base NH_3 while BH_3 is the strongest towards AsH_3.[†]

? Exercise 7.7.4

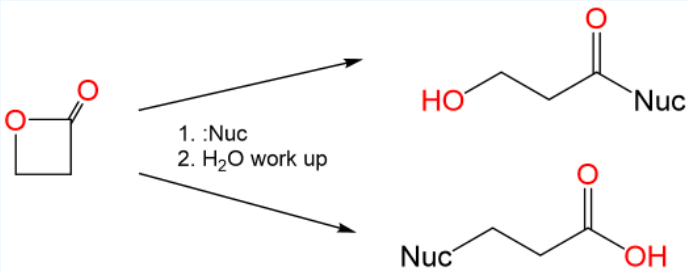
Which acid will form the most stable complex with CO: BH_3, BF_3, or BMe_3?

Answer

BH_3. Since CO forms complexes primarily through its carbon lone pair, it is a soft base and so will form the strongest complex with the softest Lewis acid.

? Exercise 7.7.5

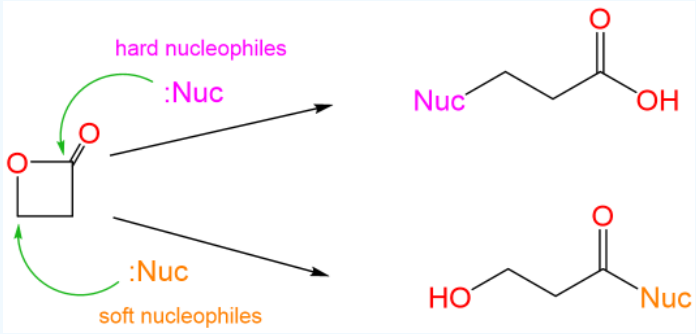
When lactones react with nucleophiles, they can undergo ring opening reactions to give either an alcohol or a carboxylic acid, as shown for propiolactone below:



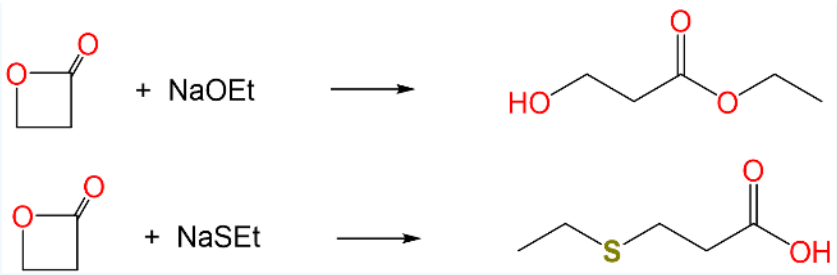
In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer

The two reaction products correspond to nucleophilic attack at the lactones' two electrophilic carbon centers. Specifically, the acid is produced by attack at the softer C^{I} center of the CH_2 directly attached to the ester oxygen and the alcohol by nucleophilic attack at the harder C^{III} center of the ester carbonyl.



Consequently, it is reasonable to expect that the harder base ethoxide will nucleophilically attack the harder carbonyl carbon while the softer thioethoxide will attack the softer methylene carbon.



The theoretical interpretation of the hard-soft acid-base principle is that hard-hard preferences reflect superior electrostatic stabilization while soft-soft preferences reflect superior covalent stabilization.

The hard-hard and soft-soft preferences in Lewis acid-base interactions reflect that

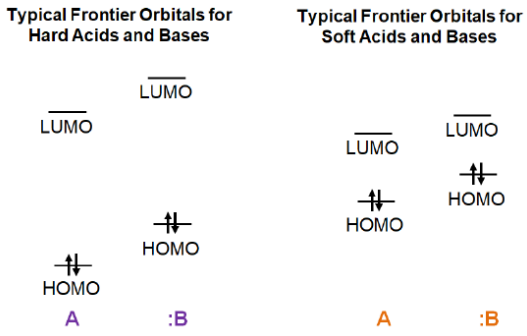
- The lone pair of a hard base is strongly stabilized electrostatically by a hard acid.
- The lone pair of a soft base is strongly stabilized by forming a covalent bond with a soft acid.
- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

To see why this is the case it is helpful to divide the contributions to the interaction energy between an acid and a base as follows:

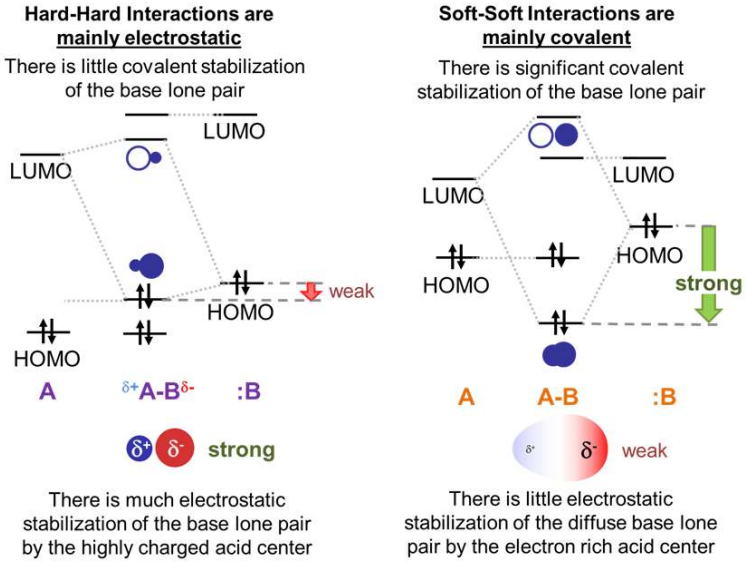
$$\text{Interaction Energy} = \underbrace{\text{Electrostatic attractions and repulsions of partial atomic charges}}_{\text{Ionic term}} + \underbrace{\text{Interactions between filled orbitals on one fragment and unfilled orbitals on the other}}_{\text{Covalent term}} + \underbrace{\text{Electrostatic repulsions between filled orbitals on the two fragments}}_{\text{Steric term}}$$

Of the three contributions to the interaction energy, only the ionic and covalent terms directly relate to the hardness of the interacting acid and base. One approach to thinking about how hardness influences the ionic and covalent contributions is to consider the frontier orbitals involved in the acid-base interaction. This is sometimes done through the use of the Salem-Klopman equation,[1,*] although in the treatment which follows a more qualitative approach will be employed.

Both hard acids and bases will have comparatively low energy HOMO levels and high energy LUMO levels, with a correspondingly high HOMO-LUMO gap. In contrast, soft acids and bases will have comparatively high-energy HOMO levels and low-energy LUMO levels, giving a comparatively smaller HOMO-LUMO gap.



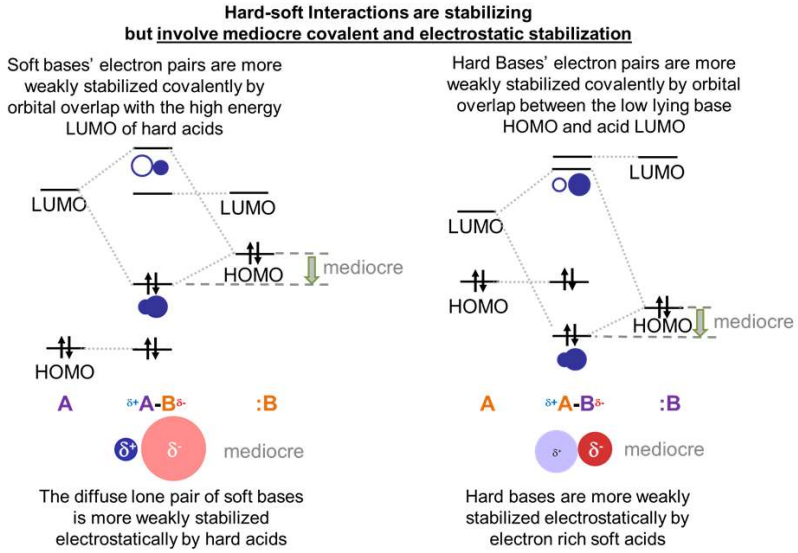
Given this, consider the frontier orbital interactions involved in the formation of an acid-base complex for the possible cases, as illustrated schematically below.



The large gap in energy between hard bases' highly stabilized HOMO lone pairs and the high energy LUMO of hard acids ensures that in **hard acid-hard base adducts the dominant stabilizing interaction will involve electrostatic attraction between the base lone pair and the electropositive Lewis acid center**. Fortunately, since the electron clouds in hard bases are relatively dense and electron rich while hard Lewis acids are highly charged and small, these electrostatic interactions are strong.

In contrast, in **soft acid-soft base adducts, the dominant stabilizing interaction will be covalent.** This is because the small gap in energy between a soft base HOMO and soft acid LUMO enables the formation of a well-stabilized bonding orbital with significant electron density between the acid and base.

The orbitals' interactions between hard acids and soft bases and soft acids and hard bases are intermediate between the hard acid-hard base and soft acid-soft base cases.



This means that the adducts are stable relative to free acid and base – just not as well stabilized as in the hard acid and hard base case. In the case of hard acids and soft bases the hard acids are less able to stabilize the soft bases' relatively diffuse electron pair electrostatically and there isn't as much covalent stabilization as in adducts of soft acids and bases due to the hard acid's high energy.

References

1. Ahrland, S.; Chatt, J.; Davies, N. R., The relative affinities of ligand atoms for acceptor molecules and ions. Quarterly Reviews, Chemical Society 1958, 12 (3), 265-276.

2. Pearson, R. G., Hard and Soft Acids and Bases. Journal of the American Chemical Society 1963, 85 (22), 3533-3539.

3. Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010.

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

†† For more on the Salem-Klopman equation see Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010; pp. 138-143.

This page titled 7.7: Hard-Soft Acid-Base Theory is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **6.6.2: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts** by Stephen M. Contakes is licensed CC BY 4.0.

CHAPTER OVERVIEW

8: NMR and IR Spectroscopy

8.1: Infrared (IR) Spectroscopy
8.2: Interpreting Infrared Spectra
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
8.4: Chemical Shifts
8.5: Proton Equivalence
8.6: Chemical Shifts in \(^1H\) NMR Spectroscopy
8.7: Peak Integration
8.8: Peak Splitting

This page titled 8: NMR and IR Spectroscopy is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

8.1: Infrared (IR) Spectroscopy

Objectives

After completing this section, you should be able to

1. identify (by wavelength, wavenumber, or both) the region of the electromagnetic spectrum which is used in infrared (IR) spectroscopy.
2. interconvert between wavelength and wavenumber.
3. discuss, in general terms, the effect that the absorption of infrared radiation can have on a molecule.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- infrared spectrum
- wavenumber (reciprocal centimetres)

Study Notes

Notice that the scale at the bottom of the infrared spectrum for 2-hexanone shown is calibrated in wavenumbers (cm^{-1}). A wavenumber is the reciprocal of a wavelength (1/λ); thus, a wavenumber of 1600 cm^{-1} corresponds to a wavelength of

$$\frac{1}{1600\,cm^{-1}} = 6.25 \times 10^{-4} cm \text{ or } 6.25\,\mu m$$

Organic chemists find it more convenient to deal with wavenumbers rather than wavelengths when discussing infrared spectra.

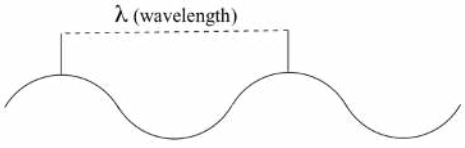
You will obtain infrared spectra for a number of the compounds you will synthesize in the laboratory component of this course.

The inverted peaks observed in the spectra correspond to molecular stretching and bending vibrations that only occur at certain quantized frequencies. When infrared radiation matching these frequencies falls on the molecule, the molecule absorbs energy and becomes excited. Eventually the molecule returns to its original (ground) state, and the energy which was absorbed is released as heat.

The electromagnetic spectrum

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$E = hc/\lambda$

where E is energy in kcal/mol, **λ** (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00 x 10^{8} m/s (the speed of light), and *h* is 9.537 x 10^{-14} kcal·s·mol^{-1}, a number known as Planck's constant.

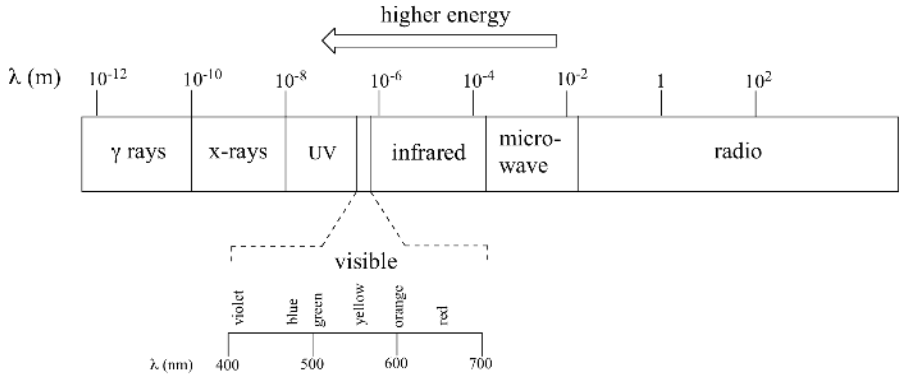
Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$\lambda\nu = c$

where **ν** (the Greek letter '*nu*') is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29 x 10^{14} Hz, and an energy of 40.9 kcal per mole of photons.

The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



Notice in the figure above that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

? Exercise \PageIndex1

Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kcal/mol of photons?

Answer

Using $\lambda\nu = c$, we first rearrange to $\nu = c/\lambda$ to solve for frequency.

For light with a wavelength of 400 nm, the frequency is 7.50×10^{14} Hz:

$$\nu = \frac{3 \times 10^{8}\ \text{m s}^{-1}}{400 \times 10^{-9}\ \text{m}} = 7.50 \times 10^{14}\ \text{s}^{-1}$$

In the same way, we calculate that light with a wavelength of 700 nm has a frequency of 4.29×10^{14} Hz.

To calculate corresponding energies using hc/λ. We find for light at 400 nm:

$$E = \frac{(6.626 \times 10^{-34}\ \text{J s mol}^{-1})(3.00 \times 10^{8}\ \text{m s}^{-1})}{400 \times 10^{-9}\ \text{m}}$$

$$= 4.97 \times 10^{-19}\ \text{J per photon}$$

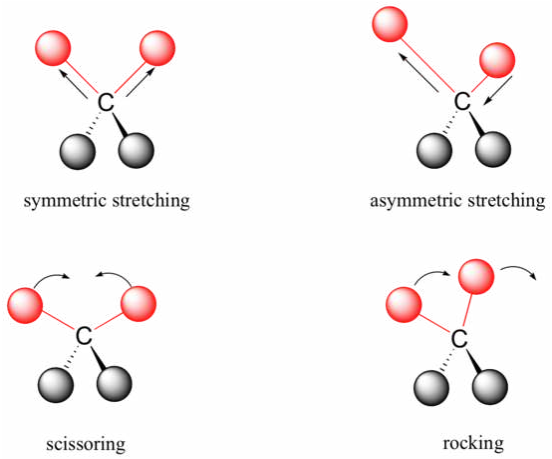
$$E\ (\text{one mole}) = E \times N$$

$$= (4.97 \times 10^{-19}\ \text{J})(6.02 \times 10^{23}\ \text{mol}^{-1})$$

$$= 299\ \text{kJ mol}^{-1}$$

Using the same equation, we find that light at 700 nm corresponds to 171 kJ mol^{-1}

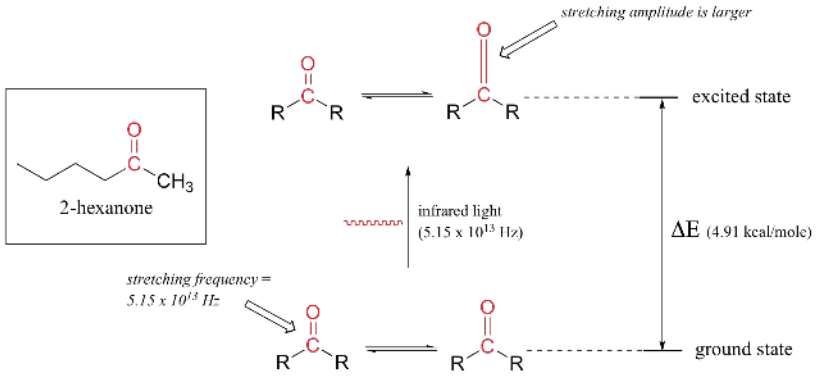
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.



The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

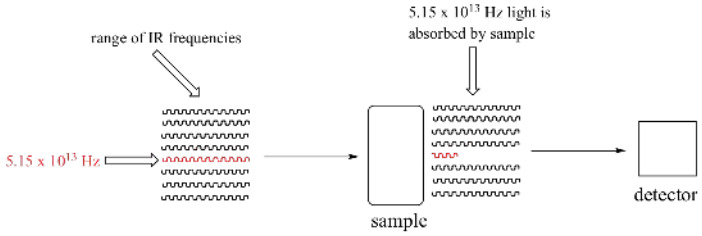
Let's take 2-hexanone as an example. Picture the carbonyl bond of the ketone group as a spring. This spring is constantly bouncing back and forth, stretching and compressing, pushing the carbon and oxygen atoms further apart and then pulling them together. This is the **stretching mode** of the carbonyl bond. In the space of one second, the spring 'bounces' back and forth 5.15×10^{13} times - in other words, the ground-state frequency of carbonyl stretching for a the ketone group is about 5.15×10^{13} Hz.

If our ketone sample is irradiated with infrared light, the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83×10^{-6} m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.



The value of **ΔE** - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about 10^{13} to 10^{14} Hz is passed though our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.



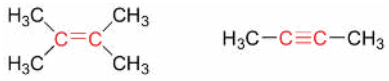
Our 5.15 x 10^{13} Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of 5.11 - 5.18 x 10^{13} Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range 6.30 - 6.80 x 10^{13} Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

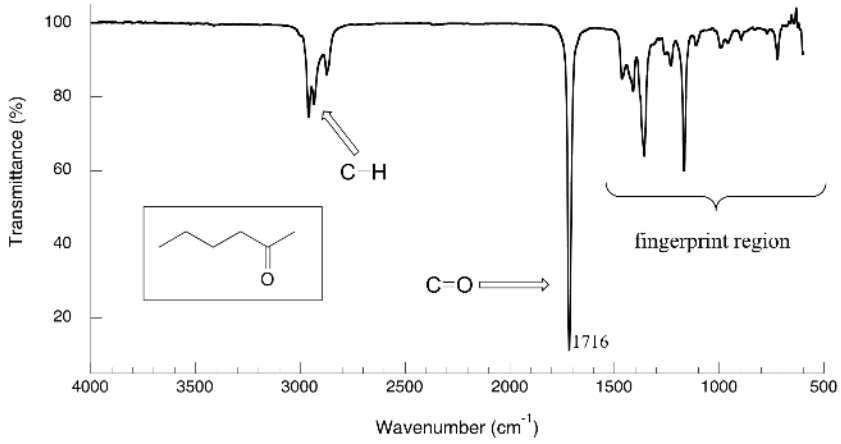
Some bonds absorb infrared light more strongly than others, and some bonds do not absorb at all. *In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule*. Such vibrations are said to be **infrared active**. In general, the greater the polarity of the bond, the stronger its IR absorption. The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon triple bond in most alkynes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkyne groups absorb rather weakly compared to carbonyls.

Some kinds of vibrations are **infrared inactive**. The stretching vibrations of completely symmetrical double and triple bonds, for example, do not result in a change in dipole moment, and therefore do not result in any absorption of light (but other bonds and vibrational modes in these molecules *do* absorb IR light).



infrared-inactive double and triple bonds

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** (cm^{-1}), which tells us how many waves fit into one centimeter. On the vertical axis we see '**% transmittance**', which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of % transmittance for every wavelength – the 'peaks' (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The 'upside down' vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn't want to make things too easy for you!

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

This page titled 8.1: Infrared (IR) Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **12.5: Spectroscopy and the Electromagnetic Spectrum** by Dietmar Kennepohl, Steven Farmer, William Reusch is licensed CC BY-SA 4.0.

8.2: Interpreting Infrared Spectra

Objectives

After completing this section, you should be able to

1. describe how the so-called “fingerprint region” of an infrared spectrum can assist in the identification of an unknown compound.
2. identify the functional group or groups present in a compound, given a list of the most prominent absorptions in the infrared spectrum and a table of characteristic absorption frequencies.
3. identify the broad regions of the infrared spectrum in which occur absorptions caused by
   a. N−H, C−H, and O−H
   b. C≡C and C≡N
   c. C=O, C=N, and C=C

Key Terms

Make certain that you can define, and use in context, the key term below.

- fingerprint region

Study Notes

When answering assignment questions, you may use this IR table to find the characteristic infrared absorptions of the various functional groups. However, you should be able to indicate in broad terms where certain characteristic absorptions occur. You can achieve this objective by memorizing the following table.

Region of Spectrum (cm^{-1})	Absorption
2500-4000	N − H, O − H, C − H
2000-2500	C≡C, C≡N
1500-2000	C=O, C=N, C=C
below 1500	Fingerprint region

The Origin of Group Frequencies

An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3200 and 2800cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.

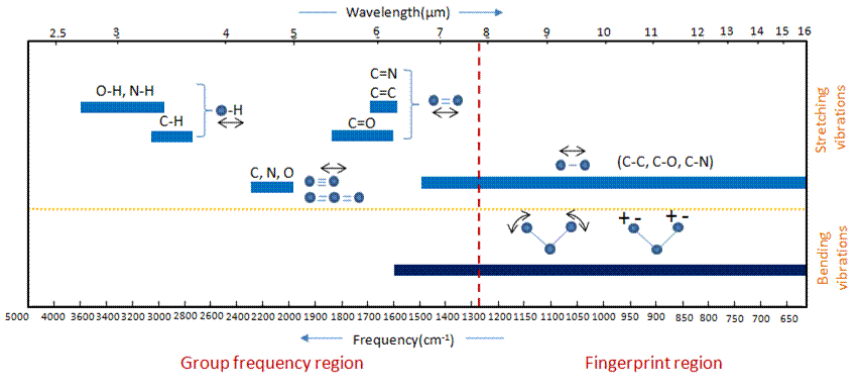
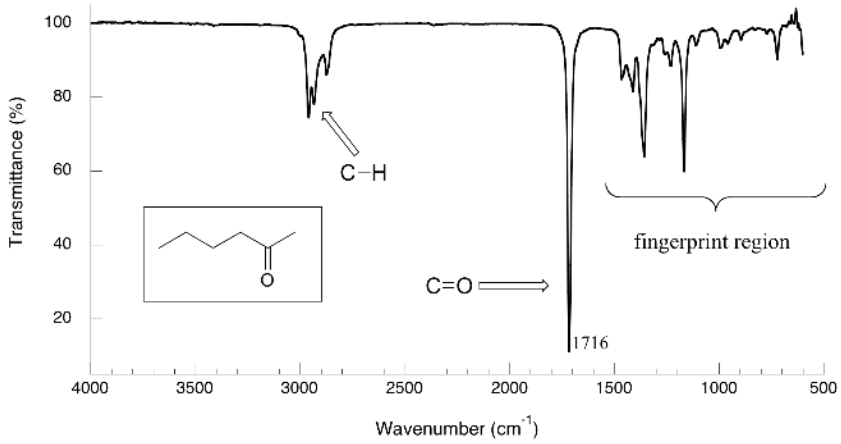


Figure 2. Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm^{-1} is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted. However, the utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule.



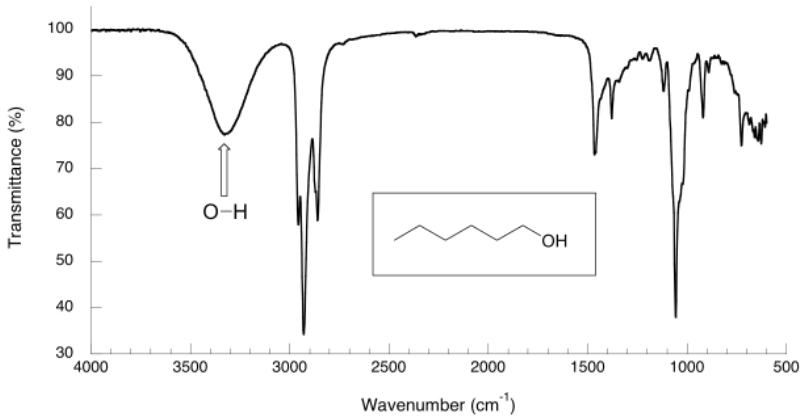
The key absorption peak in this spectrum is that from the carbonyl double bond, at 1716 cm^{-1} (corresponding to a wavelength of 5.86 mm, a frequency of 5.15 x 10^{13} Hz, and a **Δ**E value of 4.91 kcal/mol). Notice how strong this peak is, relative to the others on the spectrum: *a strong peak in the 1650-1750 cm^{-1} region is a dead giveaway for the presence of a carbonyl group*. Within that range, carboxylic acids, esters, ketones, and aldehydes tend to absorb in the shorter wavelength end (1700-1750 cm-1), while conjugated unsaturated ketones and amides tend to absorb on the longer wavelength end (1650-1700 cm^{-1}).

The jagged peak at approximately 2900-3000 cm^{-1} is characteristic of tetrahedral carbon-hydrogen bonds. This peak is not terribly useful, as just about every organic molecule that you will have occasion to analyze has these bonds. Nevertheless, it can serve as a familiar reference point to orient yourself in a spectrum.

You will notice that there are many additional peaks in this spectrum in the longer-wavelength 400 -1400 cm^{-1} region. This part of the spectrum is called the **fingerprint region**. While it is usually very difficult to pick out any specific functional group identifications from this region, it does, nevertheless, contain valuable information. The reason for this is suggested by the name: just like a human fingerprint, the pattern of absorbance peaks in the fingerprint region is unique to every molecule, meaning that the data from an unknown sample can be compared to the IR spectra of known standards in order to make a positive identification. In the mid-1990's, for example, several paintings were identified as forgeries because scientists were able to identify the IR

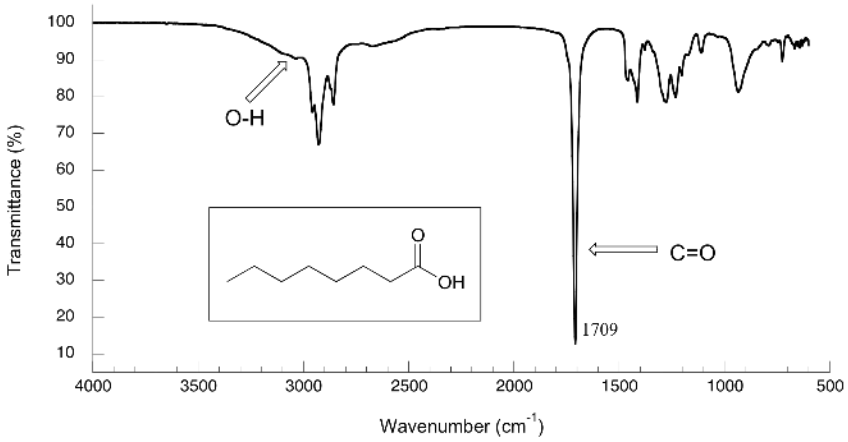
footprint region of red and yellow pigment compounds that would not have been available to the artist who supposedly created the painting (for more details see Chemical and Engineering News, Sept 10, 2007, p. 28).

Now, let's take a look at the IR spectrum for 1-hexanol.



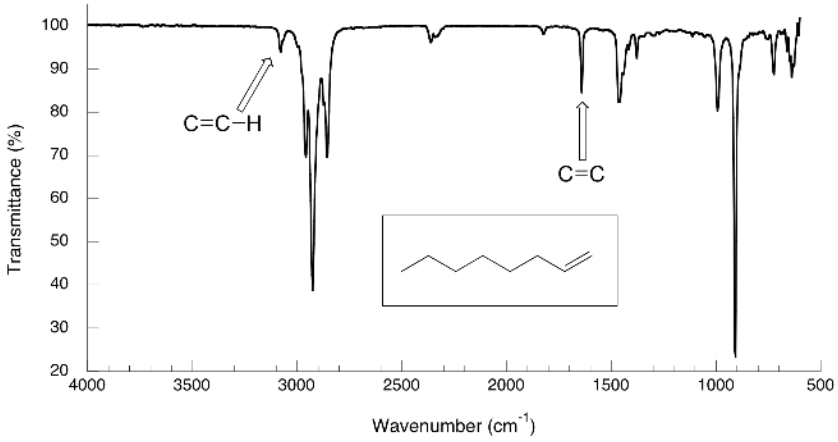
As you can see, the carbonyl peak is gone, and in its place is a very broad 'mountain' centered at about 3400 cm^{-1}. This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 cm^{-1}.



We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.

The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 cm^{-1} is due to stretching of the carbon-carbon double bond, and the one at 3079 cm-1 is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



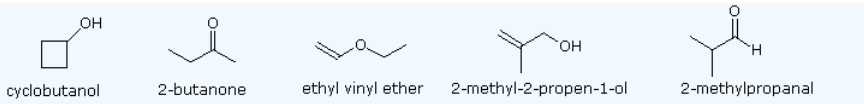
Alkynes have characteristic IR absorbance peaks in the range of 2100-2250 cm^{-1} due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm-1, due to stretching of the bond between the sp-hybridized carbon and the terminal hydrogen.

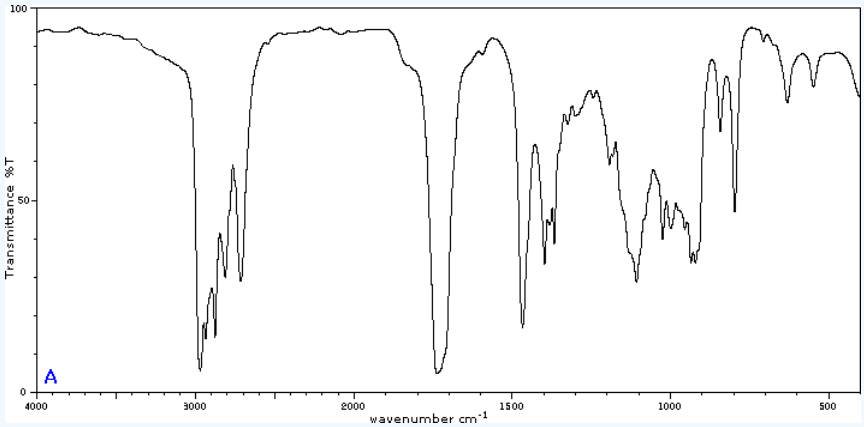
It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in this table.

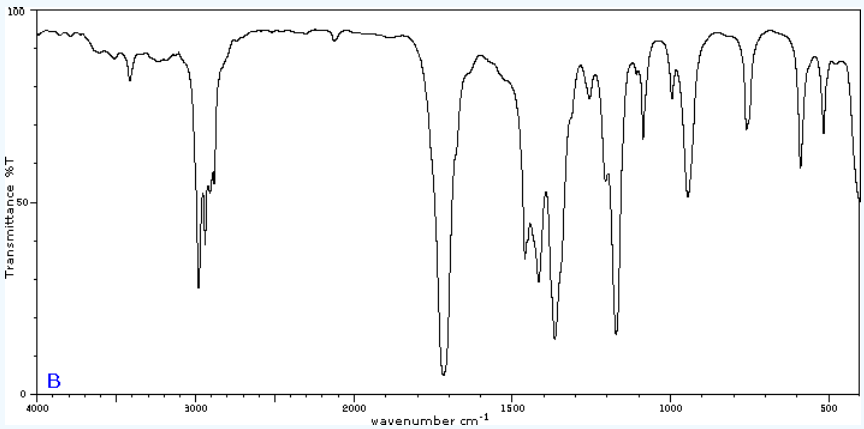
As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol.

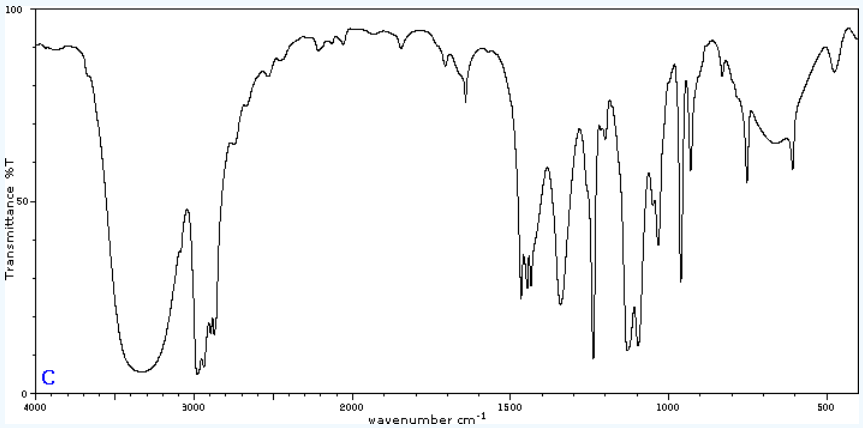
✔ Example \PageIndex1

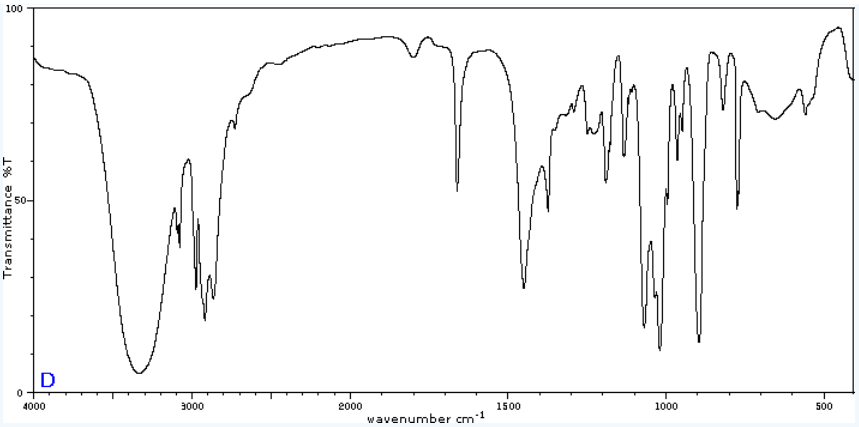
To illustrate the usefulness of infrared absorption spectra, examples for five C_4H_8O isomers are presented below their corresponding structural formulas. Try to associate each spectrum with one of the isomers in the row above it.

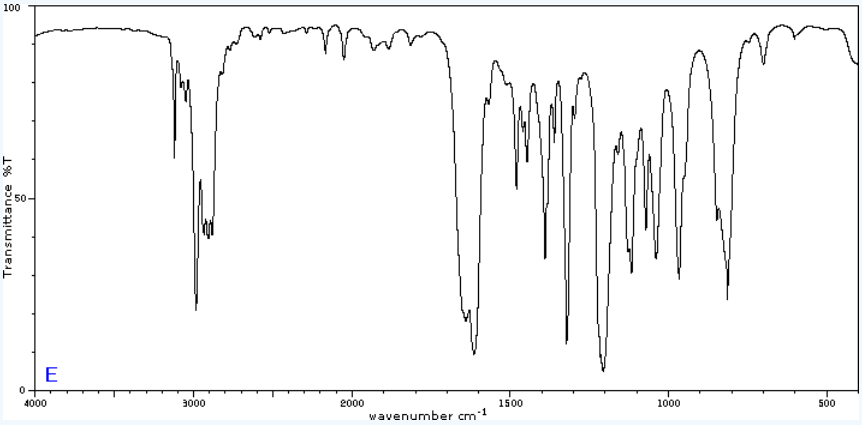

OH
cyclobutanol
O
2-butanone
O
ethyl vinyl ether
OH
2-methyl-2-propen-1-ol
O
H
2-methylpropanal


100
50
0
Transmittance %T
A
4000
3000
2000
1500
1000
500
wavenumber cm-1

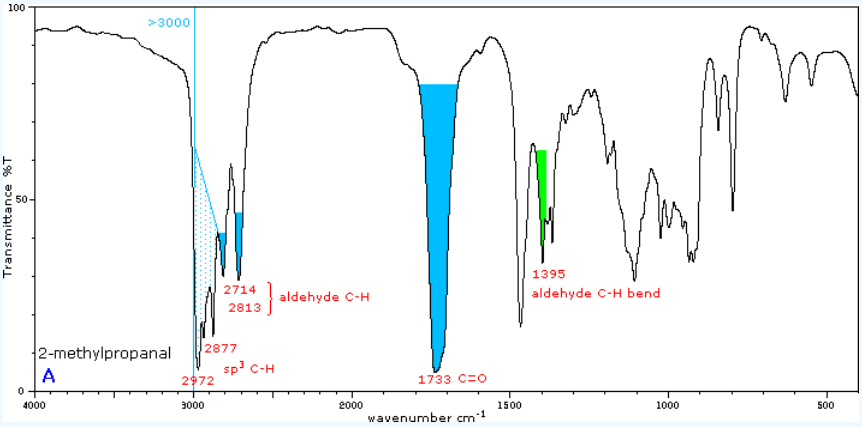

100
50
0
Transmittance %T
B
4000
3000
2000
1500
1000
500
wavenumber cm-1

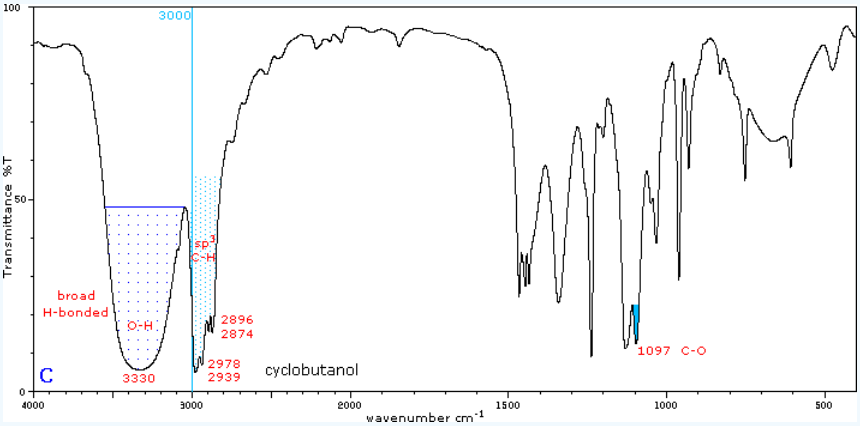

100
50
0
Transmittance %T
C
4000
3000
2000
1500
1000
500
wavenumber cm-1

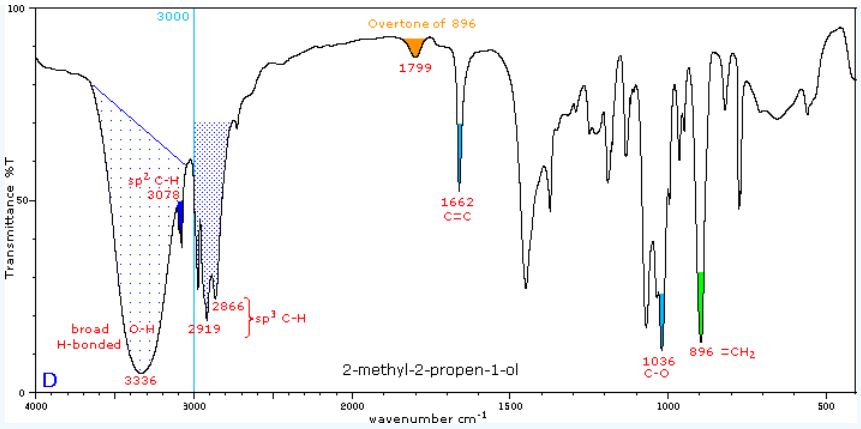

Transmittance %T
100
50
0
D
4000
3000
2000
1500
1000
500
wavenumber cm-1

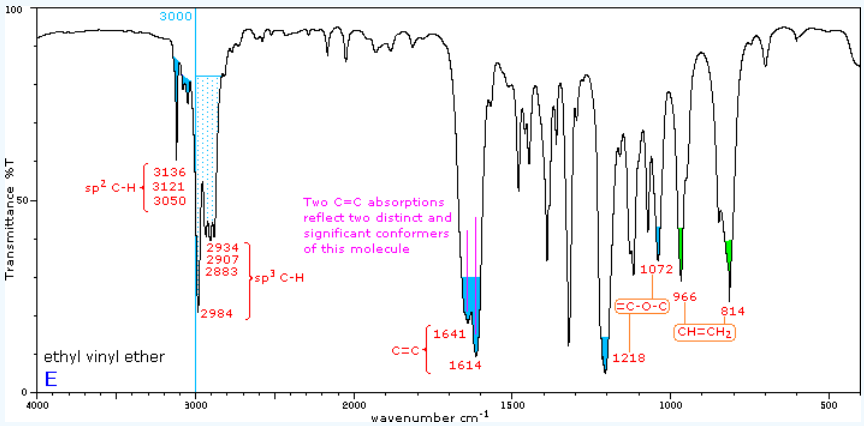

Transmittance %T
100
50
0
E
4000
3000
2000
1500
1000
500
wavenumber cm-1

Solution


Transmittance %T
100
50
0
>3000
2714
2813
aldehyde C-H
2877
2972
sp3 C-H
1733 C=O
1395
aldehyde C-H bend
2-methylpropanal
A
4000
3000
2000
1500
1000
500
wavenumber cm-1


Transmittance %T
100
50
0
3000
broad
H-bonded
O-H
3330
sp3
C-H
2896
2874
2978
2939
1097 C-O
cyclobutanol
C
4000
3000
2000
1500
1000
500
wavenumber cm-1





Exercises

? Exercise \PageIndex1

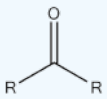
What functional groups give the following signals in an IR spectrum?

A – 1700 cm^{-1}

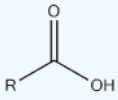
B – 1550 cm^{-1}

C – 1700 cm^{-1} and 2510-3000 cm^{-1}

Answer

A)  Carbonyl

B)  Nitro

C)  Carboxylic Acid

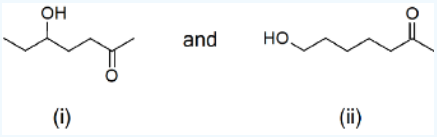
Exercise \PageIndex2

How can you distinguish the following pairs of compounds through IR analysis?

A) CH_3OH (methanol) and $CH_3CH_2OCH_2CH_3$ (diethylether)

B) Cyclopentane and 1-pentene.

C)



Answer

A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

Questions

Q12.7.1

What functional groups give the following signals in an IR spectrum?

A) 1700 cm^{-1}

B) 1550 cm^{-1}

C) 1700 cm^{-1} and 2510-3000 cm^{-1}

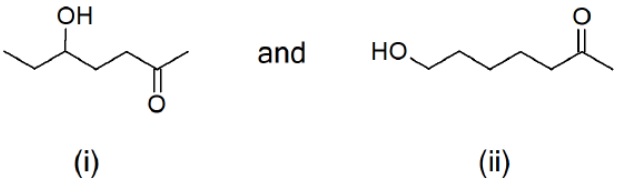
Q12.7.2

How can you distinguish the following pairs of compounds through IR analysis?

A) CH_3OH (Methanol) and $CH_3CH_2OCH_2CH_3$ (Diethylether)

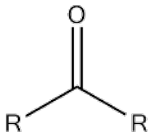
B) Cyclopentane and 1-pentene.

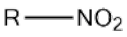
C)

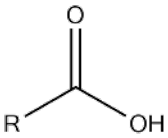


Solutions

S12.7.1

A)  Carbonyl

B)  Nitro

C)  Carboxylic Acid

S12.7.2

A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- **Organic Chemistry With a Biological Emphasis** by Tim Soderberg (University of Minnesota, Morris)

This page titled 8.2: Interpreting Infrared Spectra is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance (NMR) is a nuclei (Nuclear) specific spectroscopy that has far reaching applications throughout the physical sciences and industry. NMR uses a large magnet (Magnetic) to probe the intrinsic spin properties of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation (radio frequency waves) to promote transitions between nuclear energy levels (Resonance). Most chemists use NMR for structure determination of small molecules.

Introduction

In 1946, NMR was co-discovered by Purcell, Pound and Torrey of Harvard University and Bloch, Hansen and Packard of Stanford University. The discovery first came about when it was noticed that magnetic nuclei, such as ^{1}H and ^{31}P (read: proton and Phosphorus 31) were able to absorb radio frequency energy when placed in a magnetic field of a strength that was specific to the nucleus. Upon absorption, the nuclei begin to resonate and different atoms within a molecule resonated at different frequencies. This observation allowed a detailed analysis of the structure of a molecule. Since then, NMR has been applied to solids, liquids and gasses, kinetic and structural studies, resulting in 6 Nobel prizes being awarded in the field of NMR.

Spin and Magnetic Properties

The nucleus consists of elementary particles called neutrons and protons, which contain an intrinsic property called spin. Like electrons, the spin of a nucleus can be described using quantum numbers of I for the spin and m for the spin in a magnetic field. Atomic nuclei with even numbers of protons and neutrons have zero spin and all the other atoms with odd numbers have a non-zero spin. Furthermore, all molecules with a non-zero spin have a magnetic moment, μ, given by

$$\mu = \gamma I \tag{8.3.1}$$

where γ is the gyromagnetic ratio, a proportionality constant between the magnetic dipole moment and the angular momentum, specific to each nucleus (Table 1).

Table 8.3.1: The gyromagnetic ratios for several common nuclei

Nuclei	Spin	Gyromagetic Ratio (MHz/T)	Natural Abundance (%)
^{1}H	1/2	42.576	99.9985
^{13}C	1/2	10.705	1.07
^{31}P	1/2	17.235	100
^{27}Al	5/2	11.103	100
^{23}Na	3/2	11.262	100
^{7}Li	3/2	16.546	92.41
^{29}Si	1/2	-8.465	4.68
^{17}O	5/2	5.772	0.038
^{15}N	1/2	-4.361	0.368

The magnetic moment of the nucleus forces the nucleus to behave as a tiny bar magnet. In the absence of an external magnetic field, each magnet is randomly oriented. During the NMR experiment the sample is placed in an external magnetic field, B_0, which forces the bar magnets to align with (low energy) or against (high energy) the B_0. During the NMR experiment, a spin flip of the magnets occurs, requiring an exact quanta of energy. To understand this rather abstract concept it is useful to consider the NMR experiment using the nuclear energy levels.

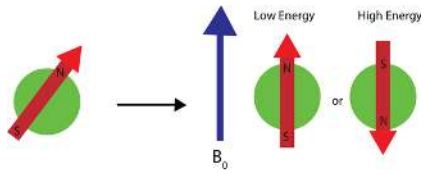


Figure 8.3.1: Application of a magnetic field to a randomly oriented bar magnet. The red arrow denotes magnetic moment of the nucleus. The application of the external magnetic field aligns the nuclear magnetic moments with or against the field.

Nuclear Energy Levels

As mentioned above, an exact quanta of energy must be used to induce the spin flip or transition. For any m, there are 2m+1 energy levels. For a spin 1/2 nucleus, there are only two energy levels, the low energy level occupied by the spins which aligned with B_0 and the high energy level occupied by spins aligned against B_0. Each energy level is given by

$$E = -m\hbar\gamma B_0 \tag{8.3.2}$$

where m is the magnetic quantum number, in this case +/- 1/2. The energy levels for $m > 1/2$, known as *quadrupolar nuclei*, are more complex and information regarding them can be found here.

The energy difference between the energy levels is then

$$\Delta E = \hbar\gamma B_0 \tag{8.3.3}$$

where $\hbar$ is Planks constant.

A schematic showing how the energy levels are arranged for a spin=1/2 nucleus is shown below. Note how the strength of the magnetic field plays a large role in the energy level difference. In the absence of an applied field the nuclear energy levels are degenerate. The splitting of the degenerate energy level due to the presence of a magnetic field in known as Zeeman Splitting.

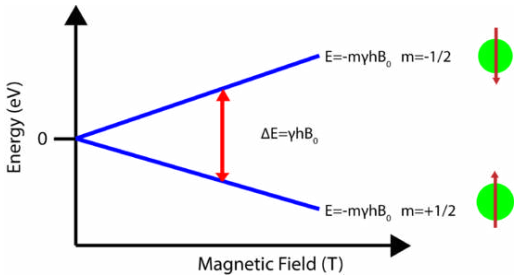


Figure 8.3.2: The splitting of the degenerate nuclear energy levels under an applied magnetic field. The green spheres represent atomic nuclei which are either aligned with (low energy) or against (high energy) the magnetic field.

Energy Transitions (Spin Flip)

In order for the NMR experiment to work, a spin flip between the energy levels must occur. The energy difference between the two states corresponds to the energy of the electromagnetic radiation that causes the nuclei to change their energy levels. For most NMR spectrometers, B_0 is on the order of Tesla (T) while γ is on the order of 10^7. Consequently, the electromagnetic radiation required is on the order of 100's of MHz and even GHz. The energy of a photon is represented by

$$E = h\nu \tag{8.3.4}$$

and thus the frequency necessary for absorption to occur is represented as:

$$\nu = \frac{\gamma B_0}{2\pi} \tag{8.3.5}$$

For the beginner, the NMR experiment measures the resonant frequency that causes a spin flip. For the more advanced NMR users, the sections on NMR detection and Larmor frequency should be consulted.

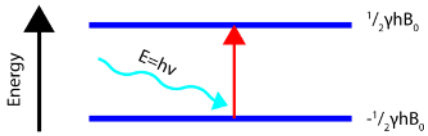


Figure 8.3.3: Absorption of radio frequency radiation to promote a transition between nuclear energy levels, called a spin flip.

Nuclear Shielding

The power of NMR is based on the concept of nuclear shielding, which allows for structural assignments. Every atom is surrounded by electrons, which orbit the nucleus. Charged particles moving in a loop will create a magnetic field which is felt by the nucleus. Therefore the local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels! This is known as shielding. Nuclei that experience different magnetic fields due to the local electronic interactions are known as inequivalent nuclei. The change in the energy levels requires a different frequency to excite the spin flip, which as will be seen below, creates a new peak in the NMR spectrum. The shielding allows for structural determination of molecules.

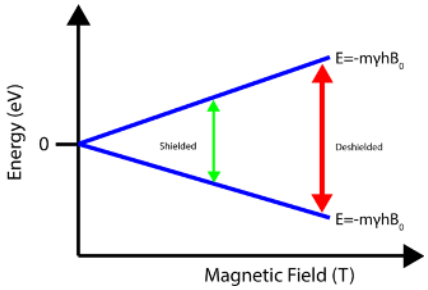


Figure 8.3.4: The effect that shielding from electrons has on the splitting of the nuclear energy levels. Electrons impart their own magnetic field which shields the nucleus from the externally applied magnetic field. This effect is greatly exaggerated in this illustration.

The shielding of the nucleus allows for chemically inequivalent environments to be determined by Fourier Transforming the NMR signal. The result is a spectrum, shown below, that consists of a set of peaks in which each peak corresponds to a distinct chemical environment. The area underneath the peak is directly proportional to the number of nuclei in that chemical environment. Additional details about the structure manifest themselves in the form of different NMR interactions, each altering the NMR spectrum in a distinct manner. The x-axis of an NMR spectrum is given in parts per million (ppm) and the relation to shielding is explained here.

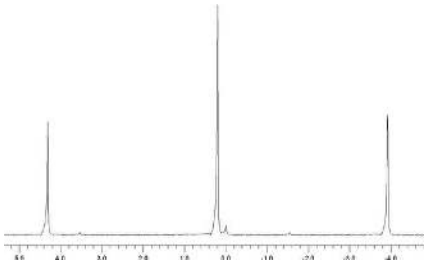


Figure 8.3.5: ^{31}P spectrum of phosphinic acid. Each peak corresponds to a distinct chemical environment while the area under the peak is proportional to the number of nuclei in a given environment.

Relaxation

Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels. The energy absorbed when a transition from a lower energy level to a high energy level occurs is released when the opposite happens. This can be a fairly complex process based on different timescales of the relaxation. The two most common types of relaxation are spin lattice relaxation (T_1) and spin spin relaxation (T_2). A more complex treatment of relaxation is given elsewhere.

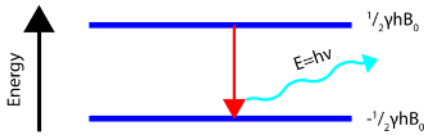


Figure 8.3.6: The process of relaxation

To understand relaxation, the entire sample must be considered. By placing the nuclei in an external magnetic field, the nuclei create a bulk magnetization along the z-axis. The spins of the nuclei are also coherent. The NMR signal may be detected as long as the spins are coherent with one another. The NMR experiment moves the bulk magnetization from the z-axis to the x-y plane, where it is detected.

- **Spin-Lattice Relaxation** (T_1): T_1 is the time it takes for the 37% of bulk magnetization to recovery along Z-axis from the x-y plane. The more efficient the relaxation process, the smaller relaxation time (T_1) value you will get. In solids, since motions between molecules are limited, the relaxation time (T_1) values are large. Spin-lattice relaxation measurements are usually carried out by pulse methods.
- **Spin-Spin Relaxation** (T_2): T_2 is the time it takes for the spins to lose coherence with one another. T_2 can either be shorter or equal to T_1.

Applications

The two major areas where NMR has proven to be of critical importance is in the fields of medicine and chemistry, with new applications being developed daily

Nuclear magnetic resonance imaging, better known as magnetic resonance imaging (MRI) is an important medical diagnostic tool used to study the function and structure of the human body. It provides detailed images of any part of the body, especially soft tissue, in all possible planes and has been used in the areas of cardiovascular, neurological, musculoskeletal and oncological imaging. Unlike other alternatives, such as computed tomography (CT), it does not used ionized radiation and hence is very safe to administer.

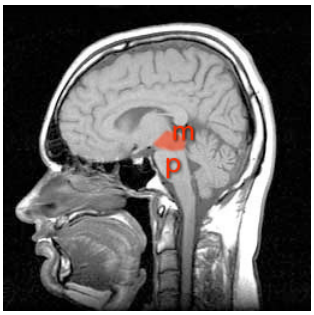


Figure 8.3.7: ^{1}H MRI of a human head showing the soft tissue such as the brain and sinuses. The MRI also clearly shows the spinal column and skull.

In many laboratories today, chemists use nuclear magnetic resonance to determine structures of important chemical and biological compounds. In NMR spectra, different peaks give information about different atoms in a molecule according specific chemical environments and bonding between atoms. The most common isotopes used to detect NMR signals are ^{1}H and ^{13}C but there are many others, such as ^{2}H, ^{3}He, ^{15}N, ^{19}F, etc., that are also in use.

NMR has also proven to be very useful in other area such as environmental testing, petroleum industry, process control, earth's field NMR and magnetometers. Non-destructive testing saves a lot of money for expensive biological samples and can be used again if more trials need to be run. The petroleum industry uses NMR equipment to measure porosity of different rocks and permeability of different underground fluids. Magnetometers are used to measure the various magnetic fields that are relevant to one's study.

Problems

1. Calculate the magnetic field, B_0 that corresponds to a precession frequency of 600 MHz for ^{1}H.
2. What is the field strength (in tesla) needed to generate a ^{1}H frequency of 500 MHz?
3. How do spin-spin relaxation and spin-lattice relaxation differ from each other?

4. The ^{1}H NMR spectrum of toluene shows that it has two peaks because of methyl and aromatic protons recorded at 60 MHz and 1.41 T. Given this information, what would be the magnetic field at 400 MHz?
5. What is the difference between ^{13}C and ^{1}H NMR?

Solutions

1. B_0= 14.1 T.
2. Using the equation used in problem 1 and solving it for B_0we get a field strength of 11.74 T.
3. Look under relaxation.
4. Since we know that the NMR frequency is directly proportional to the magnetic strength, we calculate the magnetic field at 400 MHz: B_0 = (400 MHz/60MHz) x 1.41 T = 9.40 T
5. Look under applications.

References

- Atta-ur-Rahman. Nuclear Magnetic Resonance. New York: Springer-Verlag, 1986.
- Freeman, Ray. Magnetic Resonance in Chemistry and Medicine. New York: Oxford University Press, 2003.
- Lambert, Joseph B and Eugene P Mazzola. Nuclear Magnetic Resonance Spectroscopy: An Introduction to Princliples, Applications, and Experimental Methods. Upper Saddle River: Pearson Education, 2004.
- Chang, Raymond. Physical Chemistry for the Biosciences. University Science Books, 2005

This page titled 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **Introduction to NMR** by Derrick Kaseman, Revathi Srinivasan Ganesh Iyer is licensed CC BY 4.0.

8.4: Chemical Shifts

Objectives

After completing this section, you should be able to

1. describe the delta scale used in NMR spectroscopy.
2. perform calculations based on the relationship between the delta value (in ppm), the observed chemical shift (in Hz), and the operating frequency of an NMR spectrometer (in Hz).

Key Terms

Make certain that you can define, and use in context, the key terms below.

- chemical shift
- delta scale
- upfield/downfield

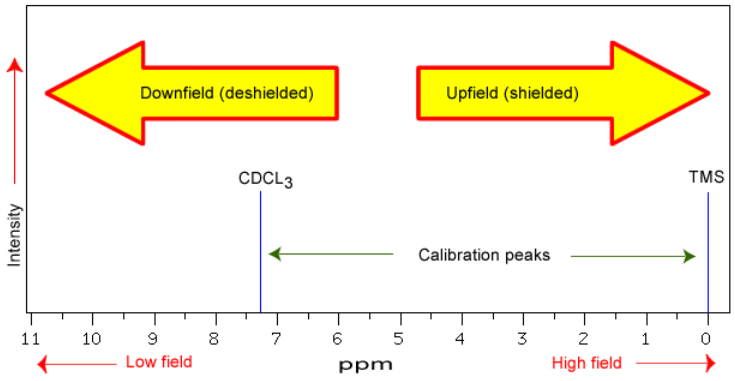
Study Notes

Although the calculations described in this section will help you understand the principles of NMR, it is the actual delta values, not the calculations, which are of greatest importance to the beginning organic chemist. Thus, we shall try to focus on the interpretation of NMR spectra, not the mathematical aspects of the technique.

In Section 13.9 we discuss ^{1}H NMR chemical shifts in more detail. Although you will eventually be expected to associate the approximate region of a ^{1}H NMR spectrum with a particular type of proton, you are expected to use a general table of ^{1}H NMR chemical shifts such as the one shown in Section 13.9.

Chemical Shifts

The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.



The position on the plot at which the nuclei absorbs is called the **chemical shift**. Since this has an arbitrary value a standard reference point must be used. The two most common standards are TMS (tetramethylsilane, $(Si(CH_3)_4)$ which has been assigned a chemical shift of zero, and $CDCl_3$ (deuterochloroform) which has a chemical shift of 7.26 for ^{1}H NMR and 77 for ^{13}C NMR.

The scale is commonly expressed as parts per million (ppm) which is independent of the spectrometer frequency. The scale is the **delta (δ) scale**.

$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

The range at which most NMR absorptions occur is quite narrow. Almost all ^1H absorptions occur downfield within 10 ppm of TMS. For ^{13}C NMR almost all absorptions occurs within 220 ppm downfield of the C atom in TMS.

Shielding in NMR

Structural features of the molecule will have an effect on the exact magnitude of the magnetic field experienced by a particular nucleus. This means that H atoms which have different chemical environments will have different chemical shifts. This is what makes NMR so useful for structure determination in organic chemistry. There are three main features that will affect the shielding of the nucleus, electronegativity, magnetic anisotropy of π systems and hydrogen bonding.

Electronegativity

The electrons that surround the nucleus are in motion so they created their own electromagnetic field. This field opposes the the applied magnetic field and so reduces the field experienced by the nucleus. Thus the electrons are said to **shield** the nucleus. Since the magnetic field experienced at the nucleus defines the energy difference between spin states it also defines what the chemical shift will be for that nucleus. Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus and result in a larger chemical shift. Compare the data in the table below.

Compound, CH_3X	**CH_3F**	**CH_3OH**	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_4**	**$(CH_3)_4Si$**
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ (ppm)	4.26	3.4	3.05	2.68	2.16	0.23	0

As can be seen from the data, as the electronegativity of X increases the chemical shift, δ increases. This is an effect of the halide atom pulling the electron density away from the methyl group. This exposes the nuclei of both the C and H atoms, "deshielding" the nuclei and shifting the peak downfield.

The effects are cumulative so the presence of more electron withdrawing groups will produce a greater deshielding and therefore a larger chemical shift, *i.e.*

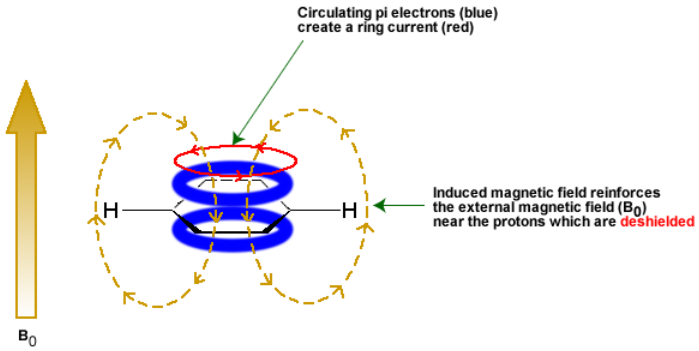
Compound	**CH_4**	**CH_3Cl**	**CH_2Cl_2**	**$CHCl_3$**
δ (ppm)	0.23	3.05	5.30	7.27

These **inductive effects** are not only felt by the immediately adjacent atoms, but the deshielding can occur further down the chain, *i.e.*

NMR signal	$-CH_2-CH_2-CH_2Br$
δ (ppm)	1.25 1.69 3.30

Magnetic Anisotropy: π Electron Effects

The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below).

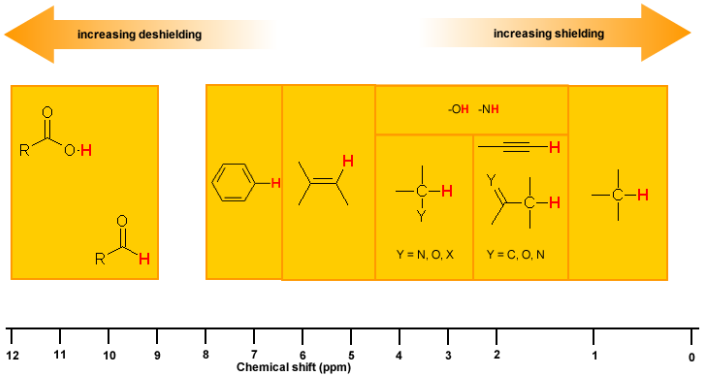


This effect is common for any atoms near a π bond, *i.e.*

Proton Type	Effect	Chemical shift (ppm)
C_6H_5-H	highly deshielded	6.5 - 8
C=C-H	deshielded	4.5 - 6
C≡C-H	shielded*	~2.5
O=C-H	very highly deshielded	9 - 10
* the acetylene H is shielded due to its location relative to the π system		

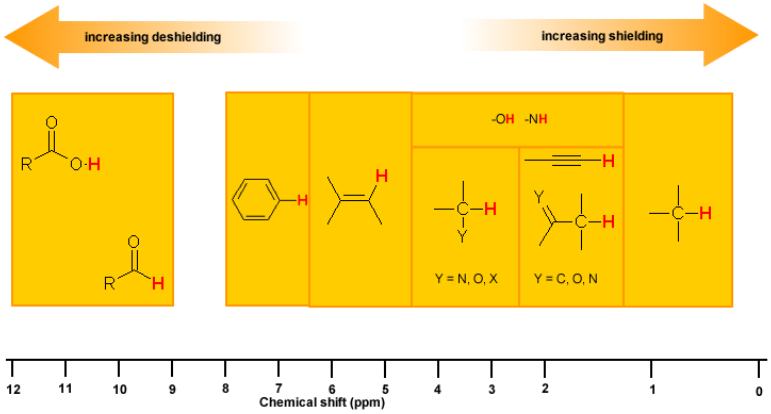
Hydrogen Bonding

Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This as well as solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms.



Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.

- run the normal H-NMR experiment on your sample
- add a few drops of D_2O
- re-run the H-NMR experiment
- compare the two spectra and look for peaks that have "disappeared"



Exercises

Exercise 8.4.1

The following peaks were from a H^1 NMR spectra from a 400 MHz spectrometer. Convert to δ units

A. $CHCl_3$ 1415 Hz

B. CH_3Cl 610 Hz

C. CH_3OH 693 Hz

D. CH_2Cl_2 1060 Hz

Answer

A. 3.627 ppm

B. 1.525 ppm

C. 1.732 ppm

D. 2.65 ppm

Exercise 8.4.2

Butan-2-one shows a chemical shit around 2.1 on a 300 MHz spectrometer in the H^1 NMR spectrum.

A. How far downfield is this peak from TMS in Hz?

B. If the spectrum was done with a 400 MHz instrument, would a different chemical shift be seen?

C. On this new 400 MHz spectrum, what would be the difference in Hz from the chemical shift and TMS?

Answer

A. Since TMS is at 0 δ = 0 Hz for reference, the difference between the two would be 630 Hz

B. No not a different chemical shift, but a different frequency would be seen, 840 Hz

C. 840 Hz

Questions

Q13.3.1

The following peaks were from a H^1 NMR spectra from a 400 MHz spectrometer. Convert to δ units

A. $CHCl_3$ 1451 Hz

B. CH_3Cl 610 Hz

C. CH_3OH 693 Hz

D. CH_2Cl_2 1060 Hz

Q13.3.2

Butan-2-one shows a chemical shift around 2.1 on a 300 MHz spectrometer in the H^1 NMR spectrum.

A. How far downfield is this peak from TMS in Hz?

B. If the spectrum was done with a 400 MHz instrument, would a different chemical shift be seen?

C. On this new 400 MHz spectrum, what would be the difference in Hz from the chemical shift and TMS?

Solutions

S13.3.1

A. 3.627 ppm

B. 1.525 ppm

C. 1.732 ppm

D. 2.65 ppm

S13.3.2

A. Since TMS is at 0 δ = 0 Hz for reference, the difference between the two would be 630 Hz

B. No not a different chemical shift, but a different frequency would be seen, 840 Hz

C. 840 Hz

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Dr. Richard Spinney (The Ohio State University)

This page titled 8.4: Chemical Shifts is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

8.5: Proton Equivalence

Objectives

After completing this section, you should be able to

1. identify those protons which are equivalent in a given chemical structure.
2. use the ^{1}H NMR spectrum of a simple organic compound to determine the number of equivalent sets of protons present.

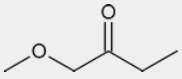
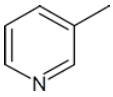
Key Terms

Make certain that you can define, and use in context, the key terms below.

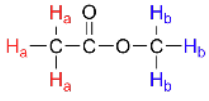
- diastereotopic
- enantiotopic
- homotopic

Study Notes

It is important at this stage to be able to identify equivalent protons in any organic compound given the structure of that compound. Once you know the number of different groups of equivalent protons in a compound, you can predict the number (before coupling) and relative strength of signals. Look at the following examples and make sure you understand how the number and intensity ratio of signals are derived from the structure shown.

Structure	Number of Signals	Ratio of Signals	
$CH_3OCH_2CH_2Br$	3	A : B : C	3 : 2 : 2
	1		
	3	A : B : C	2 : 2 : 6 (or 1 : 1 : 3)
	3	A : B : C	2 : 4 : 2 (or 1 : 2 : 1)
	4	A : B : C : D	3 : 2 : 2 : 3
	5	A : B : C : D : E	3 : 1 : 1 : 1 : 1

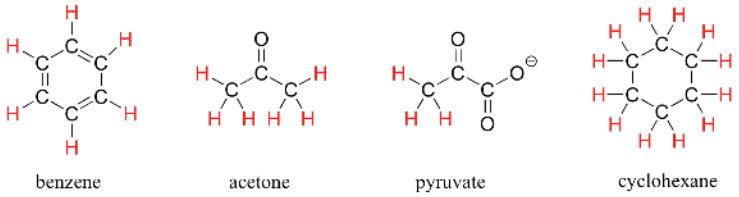
If all protons in all organic molecules had the same resonance frequency in an external magnetic field of a given strength, the information in the previous paragraph would be interesting from a theoretical standpoint, but would not be terribly useful to organic chemists. Fortunately for us, however, resonance frequencies are not uniform for all protons in a molecule. *In an external magnetic field of a given strength, protons in different locations in a molecule have different resonance frequencies, because they are in non-identical electronic environments.* In methyl acetate, for example, there are two 'sets' of protons. The three protons labeled H_a have a different - and easily distinguishable – resonance frequency than the three H_b protons, because the two sets of protons are in non-identical environments: they are, in other words, chemically nonequivalent.



https://chem.libretexts.org/@go/page/537279

On the other hand, the three H_a protons are all in the same electronic environment, and are chemically equivalent to one another. They have identical resonance frequencies. The same can be said for the three H_b protons.

The ability to recognize chemical equivalency and nonequivalency among atoms in a molecule will be central to understanding NMR. In each of the molecules below, all protons are chemically equivalent, and therefore will have the same resonance frequency in an NMR experiment.



benzene acetone pyruvate cyclohexane

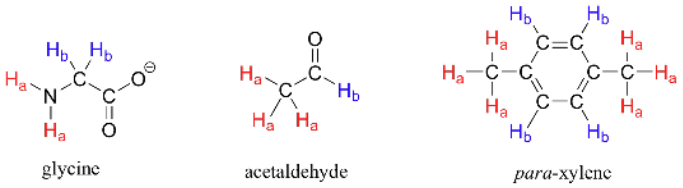
You might expect that the equitorial and axial hydrogens in cyclohexane would be non-equivalent, and would have different resonance frequencies. In fact, an axial hydrogen *is* in a different electronic environment than an equitorial hydrogen. Remember, though, that the molecule rotates rapidly between its two chair conformations, meaning that any given hydrogen is rapidly moving back and forth between equitorial and axial positions. It turns out that, except at extremely low temperatures, this rotational motion occurs on a time scale that is much faster than the time scale of an NMR experiment.



ring-flip process is *fast* compared to the NMR time-scale

In this sense, NMR is like a camera that takes photographs of a rapidly moving object with a slow shutter speed - the result is a blurred image. In NMR terms, this means that all 12 protons in cyclohexane are equivalent.

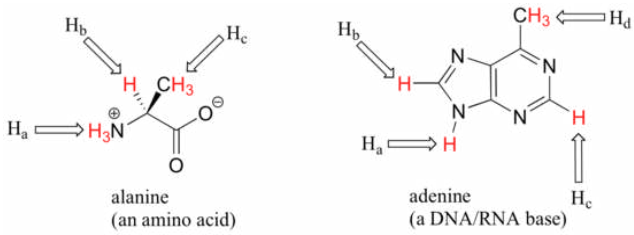
Each the molecules in the next figure contains *two* sets of protons, just like our previous example of methyl acetate, and again in each case the resonance frequency of the H_a protons will be different from that of the H_b protons.



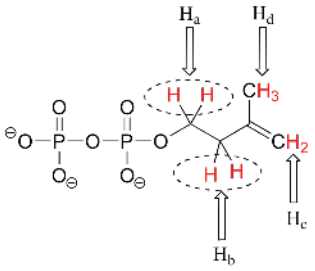
glycine acetaldehyde *para*-xylene

Notice how the symmetry of *para*-xylene results in there being only two different sets of protons.

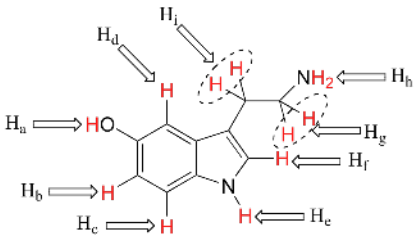
Most organic molecules have several sets of protons in different chemical environments, and each set, in theory, will have a different resonance frequency in ^{1}H-NMR spectroscopy.



alanine (an amino acid) adenine (a DNA/RNA base)

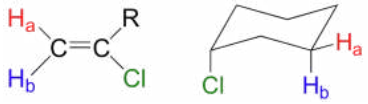


isopentenyl diphosphate
(a lipid building block)

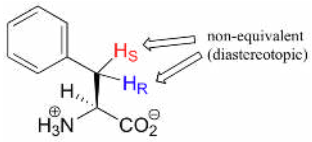


seratonin (a neurotransmitter)

When stereochemistry is taken into account, the issue of equivalence vs nonequivalence in NMR starts to get a little more complicated. It should be fairly intuitive that hydrogens on different sides of asymmetric ring structures and double bonds are in different electronic environments, and thus are non-equivalent and have different resonance frequencies. In the alkene and cyclohexene structures below, for example, H_a is *trans* to the chlorine substituent, while H_b is *cis* to chlorine.

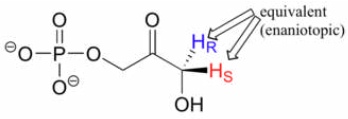


What is not so intuitive is that diastereotopic hydrogens (section 3.10) on chiral molecules are also non-equivalent:

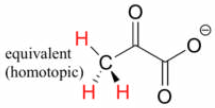


phenylalanine

However, enantiotopic and homotopic hydrogens are chemically equivalent.



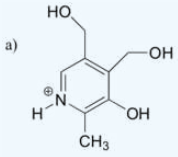
dihydroxyacetone
phosphate



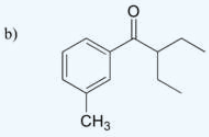
pyruvate

Example 13.8.1

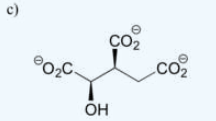
How many different sets of protons do the following molecules contain? (count diastereotopic protons as non-equivalent).



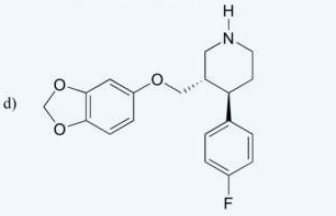
pyridoxine
(vitamin B_6)



DEET
(an insect repellent)



isocitrate
(a citric acid cycle intermediate)



paroxetine
(an antianxietry drug, trade name Paxil)

Solution

a) 8 b) 8 c) 5 d) 18

Exercise

? Exercise \PageIndex1

How many non-equivalent hydrogen are in the following molecules; how many different signals will you see in a H^1 NMR spectrum.

A. $CH_3CH_2CH_2Br$

B. $CH_3OCH_2C(CH_3)_3$

C. Ethyl Benzene

D. 2-methyl-1-hexene

Answer

A. 3

B. 3

C. 5

D. 7

Questions

Q13.8.1

How many non-equivalent hydrogen are in the following molecules; how many different signals will you see in a H^1 NMR spectrum.

A. $CH_3CH_2CH_2Br$

B. $CH_3OCH_2C(CH_3)_3$

C. Ethyl Benzene

D. 2-methyl-1-hexene

Solutions

S13.8.1

A. 3; B. 3; C. 5; D. 7

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

This page titled 8.5: Proton Equivalence is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

8.6: Chemical Shifts in 1 H NMR Spectroscopy

Objectives

After completing this section, you should be able to

1. state the approximate chemical shift (δ) for the following types of protons:
   a. aromatic.
   b. vinylic.
   c. those bonded to carbon atoms which are in turn bonded to a highly electronegative element.
   d. those bonded to carbons which are next to unsaturated centres.
   e. those bonded to carbons which are part of a saturated system.
2. predict the approximate chemical shifts of each of the protons in an organic compound, given its structure and a table of chemical shift correlations.

Study Notes

You should not attempt to memorize the chemical shifts listed in the table of this section, although it is probable that you will need to refer to it quite frequently throughout the remainder of this course. To fulfil Objective 1, above, you should be familiar with the information presented in the figure of chemical shift ranges for organic compounds. If you have an approximate idea of the chemical shifts of some of the most common types of protons, you will find the interpretation of ^{1}H NMR spectra less arduous than it might otherwise be. Notice that we shall not try to understand why aromatic protons are deshielded or why alkynyl protons are not deshielded as much as vinylic protons. These phenonomena can be explained, but the focus is on the interpretation of ^{1}H NMR spectra, not on the underlying theory.

^{1}H NMR Chemical Shifts

Chemical shift is associated with the Larmor frequency of a nuclear spin to its chemical environment. Tetramethylsilan[TMS; $(CH_3)_4Si$] is generally used for standard to determine chemical shift of compounds: δ_{TMS}=0ppm. In other words, frequencies for chemicals are measured for a ^{1}H or ^{13}C nucleus of a sample from the ^{1}H or ^{13}C resonance of TMS. It is important to understand trend of chemical shift in terms of NMR interpretation. The proton NMR chemical shift is affect by nearness to electronegative atoms (O, N, halogen.) and unsaturated groups (C=C,C=O, aromatic). Electronegative groups move to the down field (left; increase in ppm). Unsaturated groups shift to downfield (left) when affecting nucleus is in the plane of the unsaturation, but reverse shift takes place in the regions above and below this plane. ^{1}H chemical shift play a role in identifying many functional groups. Figure 1. indicates important example to figure out the functional groups.

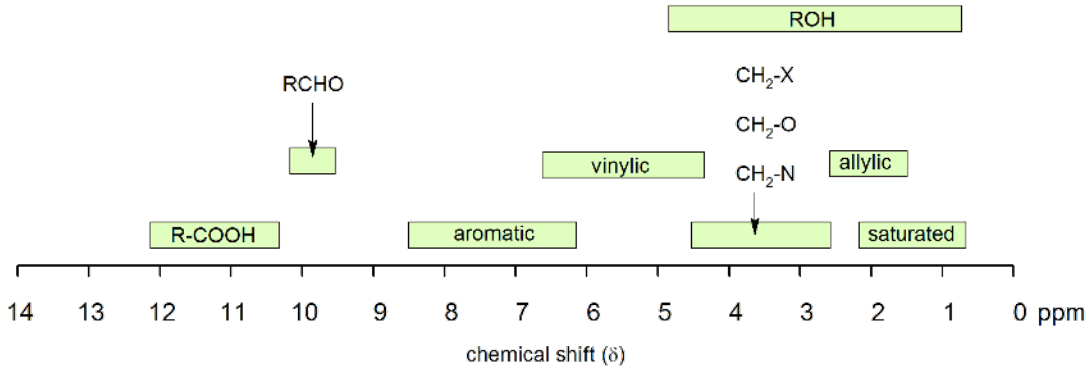
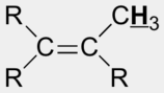
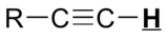
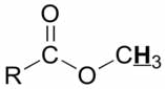
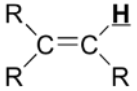
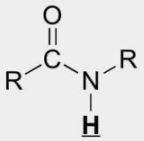
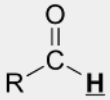
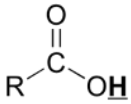


Figure 1. *1H chemical shift ranges for organic compounds*

https://chem.libretexts.org/@go/page/537280

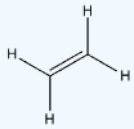
Chemical shift values are in parts per million (ppm) relative to tetramethylsilane.

Hydrogen type	Chemical shift (ppm)
$RC\underline{H}_3$	0.9 - 1.0
$RC\underline{H}_2R$	1.2 - 1.7
$R_3C\underline{H}$	1.5 – 2.0
	2.0 – 2.3
	1.5 – 1.8
$RN\underline{H}_2$	1 - 3
$ArC\underline{H}_3$	2.2 – 2.4
	2.3 – 3.0
$ROC\underline{H}_3$	3.7 – 3.9
	3.7 – 3.9
$RO\underline{H}$	1 - 5
	3.7 – 6.5
	5 - 9
$Ar\underline{H}$	6.0 – 8.7
	9.5 – 10.0
	10 - 13

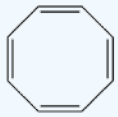
Exercises

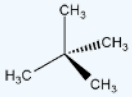
Exercise 8.6.1

The following have one H^1 NMR peak. Predict where these peaks would be in a spectra. (MAY not be exact, but will be close)

A) 

B) 

C) 

D) 

Answer

A. 5.20 δ

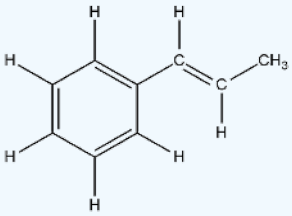
B. 1.50 δ

C. 6.40 δ

D. 1.00 δ

Exercise 8.6.2

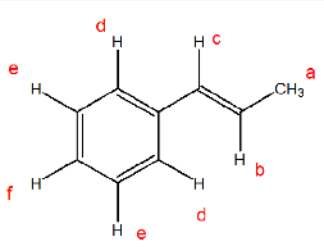
Identify the different protons in the following molecule and predict where they would be on a chemical spectrum.



Answer

There are 6 different protons in this molecule

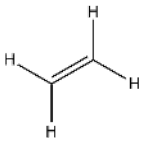
The shifts are (close) to the following: a. 2 δ; b. 6 δ; c. 6.5 δ; d. 7 δ; e. 7.5 δ; f. 7 δ



Questions

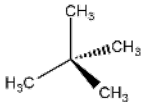
Q13.9.1

The following have one H^1 NMR peak. In each case predict approximately where this peak would be in a spectra.

A) 

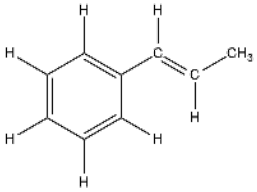
B) 

C) 

D) 

Q13.9.2

Identify the different equivalent protons in the following molecule and predict their expected chemical shift.



Solutions

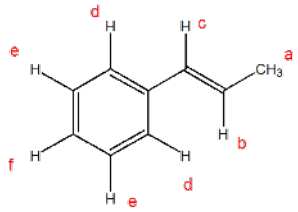
S13.9.1

A. 5.20 δ; B. 1.50 δ; C. 6.40 δ; D. 1.00 δ

S13.9.2

There are 6 different protons in this molecule

The shifts are (close) to the following: (a) 2 δ; (b) 6 δ; (c) 6.5 δ; (d) 7 δ; (e) 7.5 δ; (f) 7 δ



Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

This page titled 8.6: Chemical Shifts in ^1H NMR Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

8.7: Peak Integration

Objectives

After completing this section, you should be able to

1. explain what information can be obtained from an integrated ^{1}H NMR spectrum, and use this information in the interpretation of such a spectrum.
2. use an integrated ^{1}H NMR spectrum to determine the ratio of the different types of protons present in an organic compound.

Study Notes

The concept of peak integration is that the area of a given peak in a 1H NMR spectrum is proportional to the number of (equivalent) protons giving rise to the peak. Thus, a peak which is caused by a single, unique proton has an area which measures one third of the area of a peak resulting from a methyl (CH_3) group in the same spectrum.

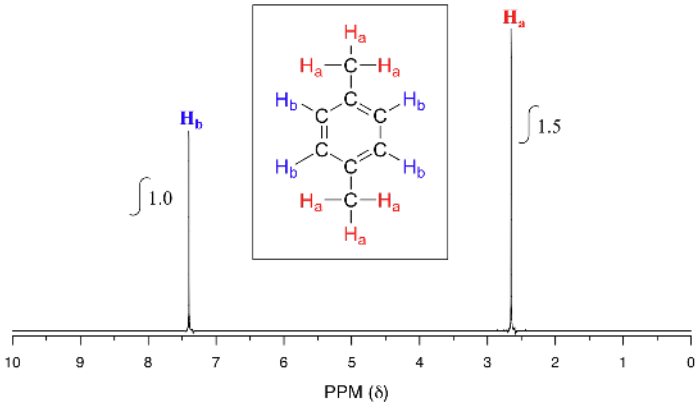
In practice, we do not have to measure these areas ourselves: it is all done electronically by the spectrometer, and an integration curve is superimposed on the rest of the spectrum. The integration curve appears as a series of steps, with the height of each step being proportional to the area of the corresponding absorption peak, and consequently, to the number of protons responsible for the absorption.

As it can be difficult to decide precisely where to start and stop when measuring integrations, you should not expect your ratios to be exact whole numbers.

Signal integration

The computer in an NMR instrument can be instructed to automatically integrate the area under a signal or group of signals. This is very useful, because *in ^{1}H-NMR spectroscopy the area under a signal is proportional to the number of hydrogens to which the peak corresponds*. The two signals in the methyl acetate spectrum, for example, integrate to approximately the same area, because they both correspond to a set of three equivalent protons.

Take a look next at the spectrum of *para*-xylene (IUPAC name 1,4-dimethylbenzene):



This molecule has two sets of protons: the six methyl (H_a) protons and the four aromatic (H_b) protons. When we instruct the instrument to integrate the areas under the two signals, we find that the area under the peak at 2.6 ppm is 1.5 times greater than the area under the peak at 7.4 ppm. This (along with the actual chemical shift values, which we'll discuss soon) tells us which set of protons corresponds to which NMR signal.

The integration function can also be used to determine the relative amounts of two or more compounds in a *mixed* sample. If we have a sample that is a 50:50 (mole/mole) mixture of benzene and acetone, for example, the acetone signal should integrate to the same value as the benzene sample, because both signals represent six equivalent protons. If we have a 50:50 mixture of acetone and

cyclopentane, on the other hand, the ratio of the acetone peak area to the cylopentane peak area will be 3:5 (or 6:10), because the cyclopentane signal represents ten protons.

Example 8.7.1

You take a ^{1}H-NMR spectrum of a mixed sample of acetone ($CH_3(CO)CH_3$) and dichloromethane (CH_2Cl_2). The integral ratio of the two signals (acetone : dichloromethane) is 2.3 to 1. What is the molar ratio of the two compounds in the sample?.

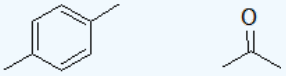
Solution

The acetone:dichloromethane molar ratio is 0.76:1. If the molar ratio was a 1:1 ratio, the signal integration ratio would be 3:1 because acetone has 6 protons while dichloromethane has 2. So, you need to divide the 2.3 integral value by a factor of 3 to get 0.76.

Example 8.7.2

You take the ^{1}H-NMR spectrum of a mixed sample of 36% *para*-xylene and 64% acetone in $CDCl_3$ solvent. How many peaks do you expect to see?

What is the expected ratio of integration values for these peaks? (set the acetone peak integration equal to 1.0)



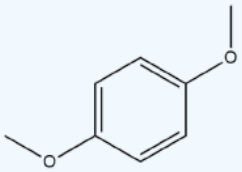
Solution

There are three peaks: two from *para*-xylene and one from acetone. The acetone peak and the *para*-xylene methyl peak both represent six protons, so the ratio of their integration values is simply 64 to 36 or 1 to 0.56. The ratio of the *para*-xylene methyl peak to the *para*-xylene aromatic peak is 6 to 4, or 0.56 to 0.37. So the final integral ratio of acetone:methyl:aromatic signals should be 1 to 0.56 to 0.37.

Exercise

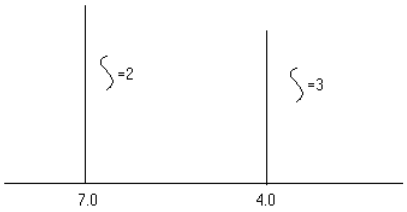
Exercise 8.7.1

Predict how many signals the following molecule would have? Sketch the spectra and estimate the integration of the peaks.



Answer

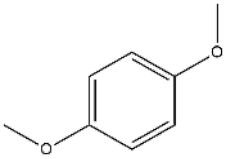
There will be two peaks in a ratio (integration) of 2 to 3 of benzene to methyl protons.



Questions

Q13.10.1

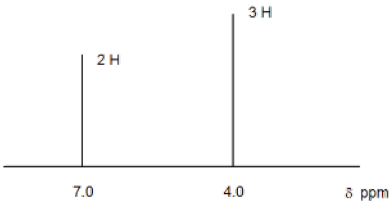
Predict how many signals the following molecule would have? Sketch the spectra and estimate the integration of the peaks.



Solutions

S13.10.1

There will be two peaks. Ideal general spectrum shown with integration.



Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

This page titled 8.7: Peak Integration is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

8.8: Peak Splitting

Objectives

After completing this section, you should be able to

1. explain the spin-spin splitting pattern observed in the ^{1}H NMR spectrum of a simple organic compound, such as chloroethane or 2-bromopropane.
2. interpret the splitting pattern of a given ^{1}H NMR spectrum.
3. determine the structure of a relatively simple organic compound, given its ^{1}H NMR spectrum and other relevant information.
4. use coupling constants to determine which groups of protons are coupling with one another in a ^{1}H NMR spectrum.
5. predict the splitting pattern which should be observed in the ^{1}H NMR spectrum of a given organic compound.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- coupling constant
- multiplet
- quartet
- triplet
- doublet

Study Notes

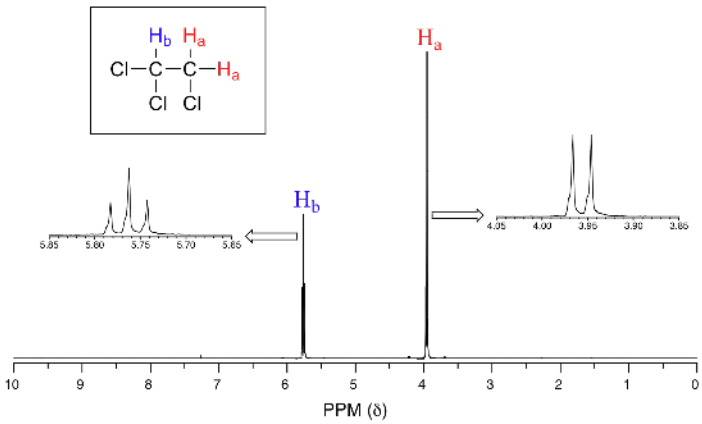
From what we have learned about ^{1}H NMR spectra so far, we might predict that the spectrum of 1,1,2-trichloroethane, $CHCl_2CH_2Cl$, would consist of two peaks—one, at about 2.5-4.0 δ, expected for CH_2-halogen compounds and one shifted downfield because of the presence of an additional electronegative chlorine atom on the second carbon. However, when we look at the spectrum it appears to be much more complex. True, we see absorptions in the regions we predicted, but these absorptions appear as a group of two peaks (a *doublet*) and a group of three peaks (a *triplet*). This complication, which may be disturbing to a student who longs for the simple life, is in fact very useful to the organic chemist, and adds greatly to the power of NMR spectroscopy as a tool for the elucidation of chemical structures. The split peaks (*multiplets*) arise because the magnetic field experienced by the protons of one group is influenced by the spin arrangements of the protons in an adjacent group.

Spin-spin coupling is often one of the more challenging topics for organic chemistry students to master. Remember the $n + 1$ rule and the associated coupling patterns.

The source of spin-spin coupling

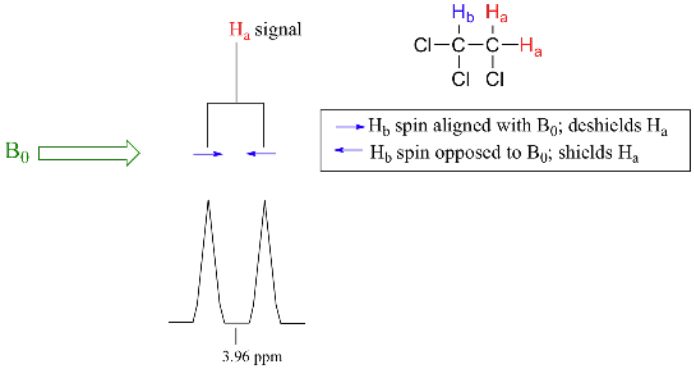
The ^{1}H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the ^{1}H-NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks. Rather than being a complication, however, this splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, we show enlargements of individual signals so that the signal splitting patterns are recognizable.

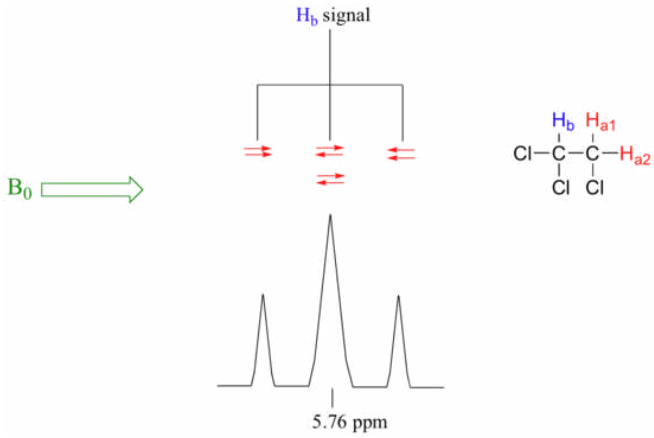


The signal at 3.96 ppm, corresponding to the two H_a protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The H_b signal at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2 trichloromethane example, the H_a and H_b protons are spin-coupled to each other. Here's how it works, looking first at the H_a signal: in addition to being shielded by nearby valence electrons, each of the H_a protons is also influenced by the small magnetic field generated by H_b next door (remember, each spinning proton is like a tiny magnet). The magnetic moment of H_b will be aligned *with* B_0 in (slightly more than) half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to B_0. The B_{eff} 'felt' by H_a is a slightly weaker if H_b is aligned against B_0, or slightly stronger if H_b is aligned with B_0. In other words, in half of the molecules H_a is *shielded* by H_b (thus the NMR signal is shifted slightly upfield) and in the other half H_a is *deshielded* by H_b(and the NMR signal shifted slightly downfield). What would otherwise be a single H_a peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal. These ideas an be illustrated by a **splitting diagram**, as shown below.

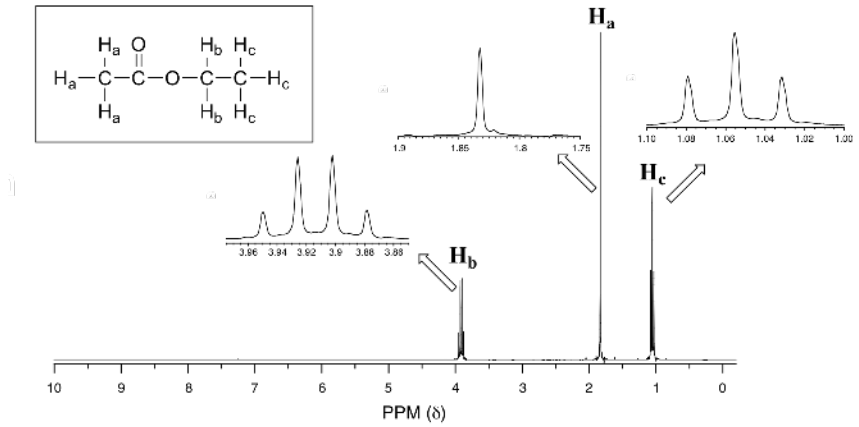


Now, let's think about the $H_b$signal. The magnetic environment experienced by H_b is influenced by the fields of both neighboring H_a protons, which we will call H_{a1} and H_{a2}. There are four possibilities here, each of which is equally probable. First, the magnetic fields of both H_{a1} and H_{a2} could be aligned with B_0, which would deshield H_b, shifting its NMR signal slightly downfield. Second, both the H_{a1} and H_{a2} magnetic fields could be aligned opposed to B_0, which would shield H_b, shifting its resonance signal slightly upfield. Third and fourth, H_{a1} could be with B_0 and H_{a2} opposed, or H_{a1}opposed to B_0 and H_{a2} with B_0. In each of the last two cases, the shielding effect of one H_a proton would cancel the deshielding effect of the other, and the chemical shift of H_b would be unchanged.



So in the end, the signal for H_b is a **triplet**, with the middle peak twice as large as the two outer peaks because there are *two* ways that H_{a1} and H_{a2} can cancel each other out.

Now, consider the spectrum for ethyl acetate:



We see an unsplit '**singlet**' peak at 1.833 ppm that corresponds to the acetyl (H_a) hydrogens – this is similar to the signal for the acetate hydrogens in methyl acetate that we considered earlier. This signal is unsplit because there are no adjacent hydrogens on the molecule. The signal at 1.055 ppm for the H_c hydrogens is split into a triplet by the two H_b hydrogens next door. The explanation here is the same as the explanation for the triplet peak we saw previously for 1,1,2-trichloroethane.

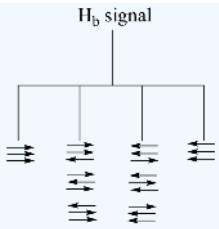
The $H_b$hydrogens give rise to a **quartet** signal at 3.915 ppm – notice that the two middle peaks are taller then the two outside peaks. This splitting pattern results from the spin-coupling effect of the *three* H_c hydrogens next door, and can be explained by an analysis similar to that which we used to explain the doublet and triplet patterns.

Example 13.11.1

a. Explain, using left and right arrows to illustrate the possible combinations of nuclear spin states for the H_c hydrogens, why the H_b signal in ethyl acetate is split into a quartet.
b. The integration ratio of doublets is 1:1, and of triplets is 1:2:1. What is the integration ratio of the H_b quartet in ethyl acetate? (Hint – use the illustration that you drew in part a to answer this question.)

Answer

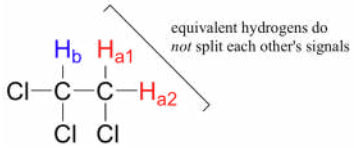
a)



b) The figure above demonstrates that the quartet subpeaks integrate to 1:3:3:1 (eg., there are three ways for two spins to be aligned with B_0 and one against B_0). As an analogy, if you flip three coins at once, you have a 1 in eight chance of getting all heads, 1 in 8 chance of all tails, a 3 in 8 chance of two heads and a tail, and a 3 in 8 chance of two tails and a head.

By now, you probably have recognized the pattern which is usually referred to as the ***n* + 1 rule**: if a set of hydrogens has *n* neighboring, non-equivalent hydrogens, it will be split into *n* + 1 subpeaks. Thus the two H_b hydrogens in ethyl acetate split the H_c signal into a triplet, and the three H_c hydrogens split the H_b signal into a quartet. This is very useful information if we are trying to determine the structure of an unknown molecule: if we see a triplet signal, we know that the corresponding hydrogen or set of hydrogens has two `neighbors`. When we begin to determine structures of unknown compounds using ^{1}H-NMR spectral data, it will become more apparent how this kind of information can be used.

Three important points need to be emphasized here. First, signal splitting only occurs between non-equivalent hydrogens – in other words, H_{a1} in 1,1,2-trichloroethane is *not* split by H_{a2}, and vice-versa.

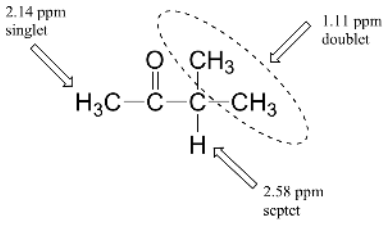


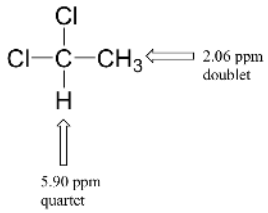
Second, splitting occurs primarily between hydrogens that are separated by three bonds. This is why the H_a hydrogens in ethyl acetate form a singlet– the nearest hydrogen neighbors are five bonds away, too far for coupling to occur.

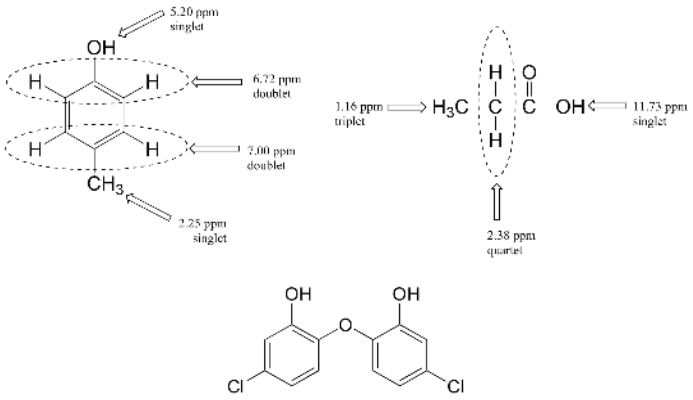


Occasionally we will see four-bond and even 5-bond splitting, but in these cases the magnetic influence of one set of hydrogens on the other set is much more subtle than what we typically see in three-bond splitting (more details about how we quantify coupling interactions is provided in section 5.5B). Finally, splitting is most noticeable with hydrogens bonded to carbon. Hydrogens that are bonded to heteroatoms (alcohol or amino hydrogens, for example) are coupled weakly - or not at all - to their neighbors. This has to do with the fact that these protons exchange rapidly with solvent or other sample molecules.

Below are a few more examples of chemical shift and splitting pattern information for some relatively simple organic molecules.







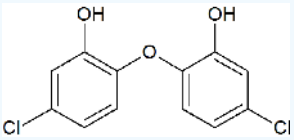
Multiplicity in Proton NMR

The number of lines in a peak is always one more (n+1) than the number of hydrogens on the neighboring carbon. This table summarizes coupling patterns that arise when protons have different numbers of neighbors.

# of lines	ratio of lines	term for peak	# of neighbors
1	-	singlet	0
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

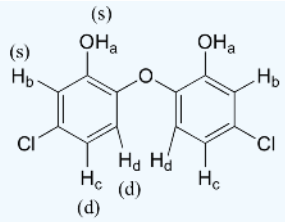
Example 13.11.2

How many proton signals would you expect to see in the ^{1}H-NMR spectrum of the structure shown below? For each of the proton signals, predict the splitting pattern. Assume that you see only 3-bond coupling.



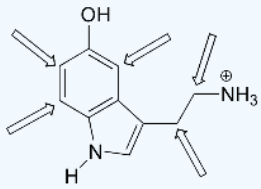
Answer

Because of the symmetry in the molecule, there are only four proton signals. Predicted splitting is indicated.

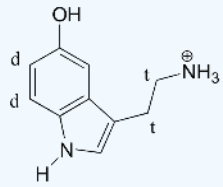


Example 13.11.3

Predict the splitting pattern for the ^{1}H-NMR signals corresponding to the protons at the locations indicated by arrows (the structure is that of the neurotransmitter serotonin).



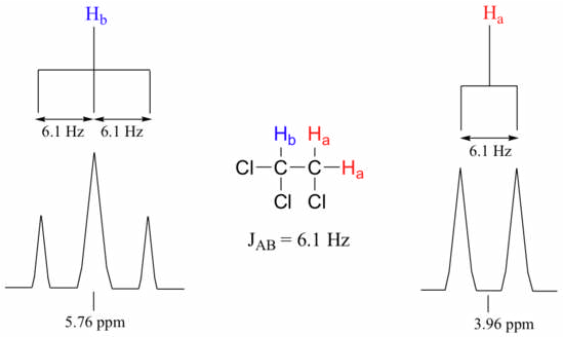
Answer



(recall that splitting is generally not seen with protons on heteroatoms)

Coupling constants

Chemists quantify the spin-spin coupling effect using something called the **coupling constant**, which is abbreviated with the capital letter *J*. The coupling constant is simply the difference, expressed in Hz, between two adjacent sub-peaks in a split signal. For our doublet in the 1,1,2-trichloroethane spectrum, for example, the two subpeaks are separated by 6.1 Hz, and thus we write $^{3}J_{a\text{-}b}$ = 6.1 Hz.

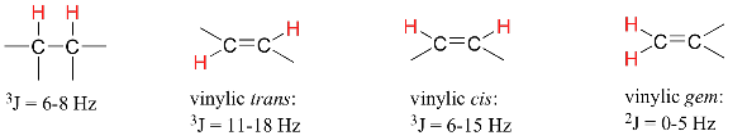


The superscript 3 tells us that this is a three-bond coupling interaction, and the a-b subscript tells us that we are talking about coupling between H_a and H_b. Unlike the chemical shift value, *the coupling constant, expressed in Hz, is the same regardless of the applied field strength of the NMR magnet*. This is because the strength of the magnetic moment of a neighboring proton, which is the source of the spin-spin coupling phenomenon, does *not* depend on the applied field strength.

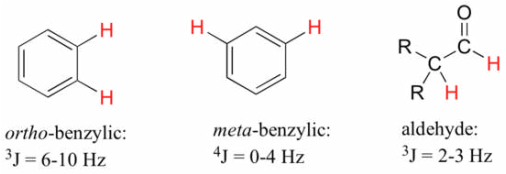
When we look closely at the triplet signal in 1,1,2-trichloroethane, we see that the coupling constant - the `gap` between subpeaks - is 6.1 Hz, the same as for the doublet. This is an important concept! The coupling constant $^{3}J_{a\text{-}b}$ quantifies the magnetic interaction between the H_a and H_b hydrogen sets, and *this interaction is of the same magnitude in either direction*. In other words, H_a

influences H_b to the same extent that H_b influences H_a. When looking at more complex NMR spectra, this idea of **reciprocal coupling constants** can be very helpful in identifying the coupling relationships between proton sets.

Coupling constants between proton sets on neighboring sp^3-hybridized carbons is typically in the region of 6-8 Hz. With protons bound to sp^2-hybridized carbons, coupling constants can range from 0 Hz (no coupling at all) to 18 Hz, depending on the bonding arrangement.



For vinylic hydrogens in a *trans* configuration, we see coupling constants in the range of ^3J = 11-18 Hz, while *cis* hydrogens couple in the ^3J = 6-15 Hz range. The 2-bond coupling between hydrogens bound to the same alkene carbon (referred to as geminal hydrogens) is very fine, generally 5 Hz or lower. *Ortho* hydrogens on a benzene ring couple at 6-10 Hz, while 4-bond coupling of up to 4 Hz is sometimes seen between *meta* hydrogens.

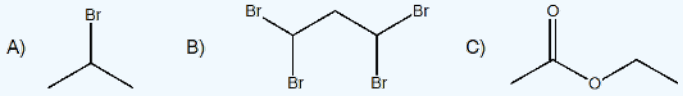


Fine (2-3 Hz) coupling is often seen between an aldehyde proton and a three-bond neighbor. Table 4 lists typical constant values.

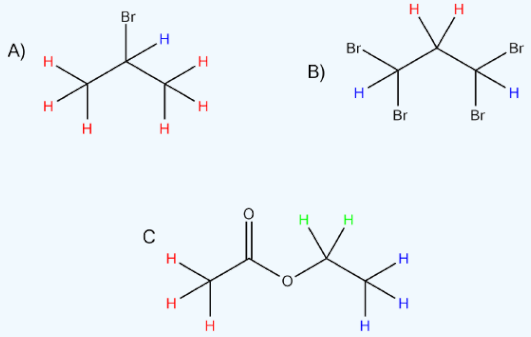
Exercises

Exercise 8.8.1

Predict the splitting patterns of the following molecules.



Answer



A. H: Doublet. H: Septet

B. H: Triplet, H: Triplet

C. H: Singlet, H: Quartet, H: Triplet

Exercise 8.8.2

Draw the following according to the criteria given.

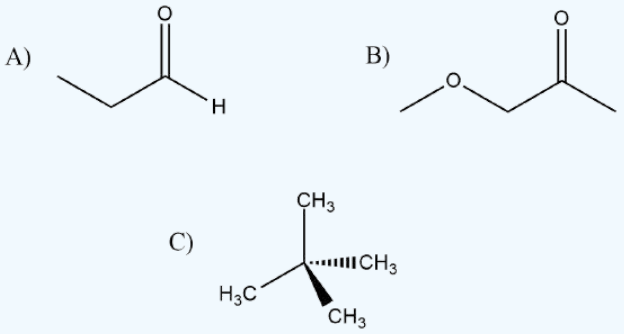
A. C_3H5O; two triplet, 1 doublet

B. $C_4H_8O_2$; three singlets

C. C_5H_{12}; one singlet

Answer

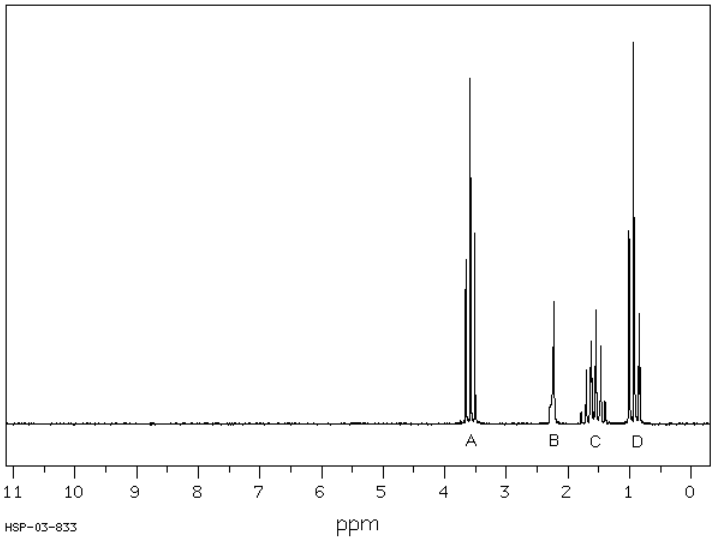
These are just some drawings, more may be possible.



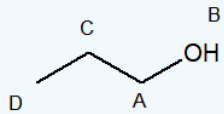
Exercise 8.8.3

The following spectrum is for C_3H_8O. Determine the structure.

A; triplet, B; Singlet, C; Sextet, D; Triplet



Answer



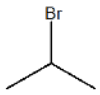
Propanol

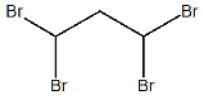
Note: Remember, chemically equivalent protons do not couple with one another to give spin-spin splitting.

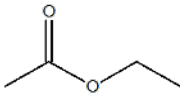
Questions

Q13.11.1

Predict the splitting patterns of the following molecules:

A) 

B) 

C) 

Q13.11.2

Draw the following according to the criteria given.

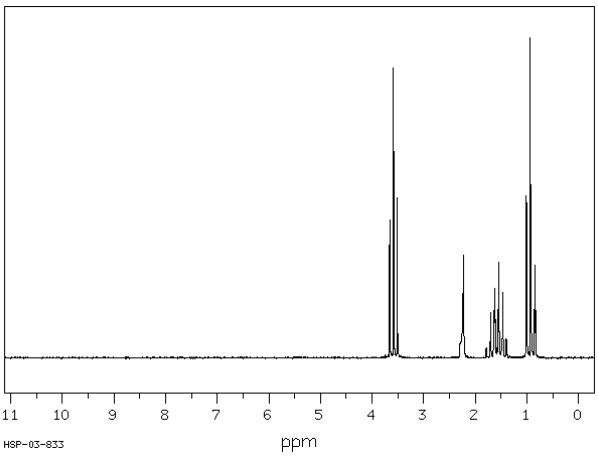
A. C_3H_5O; two triplet, 1 doublet

B. $C_4H_8O_2$; three singlets

C. C_5H_{12}; one singlet

Q13.11.3

The following spectrum is for C_3H_8O. Determine the structure.



A triplet; B singlet; C sextet; D triplet

Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 3 December 2016)

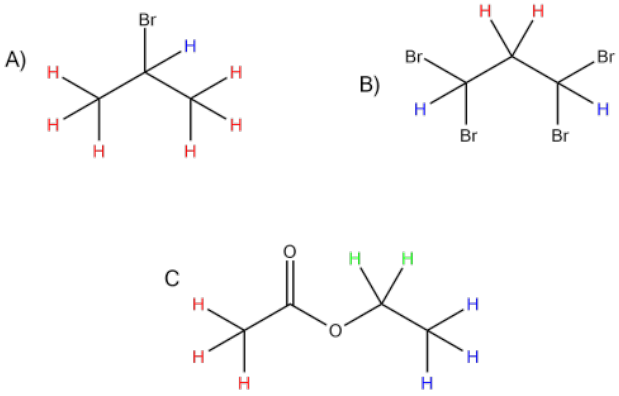
Solutions

S13.11.1

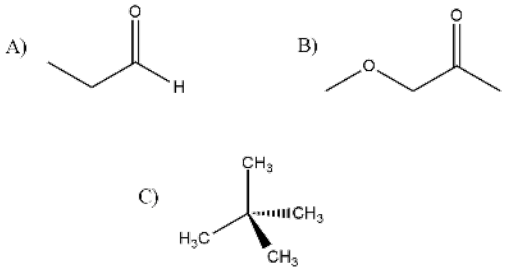
A. H: Doublet. H: Septet

B. H: Doublet, H: Triplet

C. H: Singlet, H: Quartet, H: Triplet

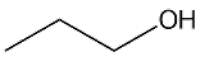


S13.11.2



These are just some drawings, more may be possible.

S13.11.3



Propane

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 8.8: Peak Splitting is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

CHAPTER OVERVIEW

9: Symmetry

9.1: Symmetry Elements
9.2: Point Groups
9.3: Assigning Point Groups
9.4: Character Tables
9.5: Applications of Symmetry - Chirality

This page titled 9: Symmetry is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

9.1: Symmetry Elements

Symmetry in Chemistry

Symmetry is actually a concept of mathematics and not of chemistry. However, symmetry, and the underlying mathematical theory for symmetry, group theory, are of tremendous importance in chemistry because they can be applied to many chemistry problems. For example it helps us to classify the structures of molecules and crystals, understand chemical bonding, predict vibrational spectra, and determine the optical activity of compounds. We will therefore first discuss the general foundations of symmetry and group theory, and then apply them to chemical problems, in particular chemical bonding.

Let us first find a definition for symmetry. Symmetry is very familiar to us as we associate symmetry with beauty, but very familiar things are not necessarily easy to define scientifically. One common definition is that symmetry is the self-similarity of an object. The more similar parts it has the more symmetric it appears. For example, we would argue that the two wings of the butterfly depicted look similar. If the left wing was very different from the right wing the butterfly would look less symmetric.



Figure 2.1.1 Symmetry depicted through an image of a butterfly (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...jpg?revision=2 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

How can we measure the self-similarity, or symmetry of an object quantitatively? We can do this using the concept of the symmetry operation. It is defined as a movement of an object into an equivalent indistinguishable orientation. The number and kind of symmetry operations that can be carried out defines the symmetry of the object.

Definition: Symmetry Operation

Movement of an object into an equivalent indistinguishable orientation

Symmetry operations are carried out around so-called symmetry elements. A symmetry element is a point, line, or plane about which a symmetry operation is carried out. Let us understand know what symmetry elements and operations exist.

Definition: Symmetry Element

A point, line or plane about which a symmetry operation is carried out

The Identity Operation (*E*)

The most simple operation is the identity operation. It can be denoted by the Schoenflies symbol *E*. Schoenflies symbols are the most common symbols to denote a symmetry operation. The identity operation says that each object is self-similar to itself when you do not move it in any way. This is a trivial statement, but as we will see later, the identity operation is necessary to make the mathematical framework of symmetry, group theory, complete. The identity operation is present in any object. In the example of the depicted snail shell it is the only operation (Fig. 2.1.2).



Figure 2.1.2 Snail shell (Attribution: Petr Kratochvil http://res.publicdomainfiles.com/pdf...8045418010.jpg)

The Proper Rotation Operation

The proper rotation operation is a counter-clockwise rotation about a proper rotational axis by an angle of 360° over an integer number n. After that rotation the object must be indistinguishable from its original form. That means that the object after the rotation must superimpose the original object before the rotation. For example, when n=4, then we rotate around 90°, and after that the object must superimpose its original form. The proper rotational axis is the symmetry element associated with the proper rotation operation. It's Schoenflies symbol is C_n, whereby n is called the order of the rotational axis. A proper rotational operation has the symbol C_n^m, whereby m counts the number of times the operation is carried out. Overall we rotate by and angle of 360°× m/n when we carry out an operation C_n^m. This means that when m=n, then we have rotated around 360° (Fig. 2.1.3). Then all points in the object are at their original position. It is as though we had done nothing with the object. We can also say we have reached the identity *E*. In mathematical form we can say that C_n^n=E. If we rotated one more time, $C_n^{(n+1)}$, then this would be equal to rotating only one time, and thus $C_n^{(n+1)}=C_n^1$. For example if n=4, then rotating four times around 90° will produce the identity. We have rotated around 4 x 90°=360° which is the same a though we had not rotated at all, because all points in the object are in their original position after a 360° rotation. If we rotated 5 times around 90°, it would the same as rotating only one time.

$$C_n^m = 360° \times \frac{m}{n}$$

$$C_n^n = E$$

$$C_n^{n+1} = C_n^1$$

Figure 2.1.3 Properties of the proper rotation operation

If an object has several axes with different order n, then the one with the highest order is called the *principal axis.* If there is more than one axis of the same order, then they get distinguished by primes if they are not conjugate. We will learn about the exact definition of conjugation somewhat later, we can however often see by inspection if two axes are conjugate. This is usually the case when they pass through the object in a equivalent way, and rotate the object in an equivalent way. Axes that pass through less many bonds, get less many primes. This is just a convention, but you have to follow it. An additional rule is that an axis which is in the same position as the principal axis gets the least number of primes. For example, a square planar molecule such as $PtCl_4^{2-}$ has a C_4 principal axis standing perpendicular to the square plane of the molecule. There is an additional C_2 axis where the C_4 axis runs. It is present because one can also rotate around 180°, and not only around 90°. This C_2 axis does not get any prime. You an see that there are four additional C_2 axes, two of them are denoted C_2', and two others are denoted C_2''. You can see that the two axes which only have one prime pass through two Pt-Cl bonds, while the ones that have two primes, do not pass through any bonds. The two C_2' axes are conjugate, meaning that they transform the object in an equivalent way. The two C_2'' axes are also conjugate.

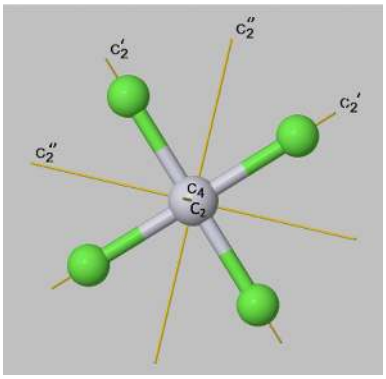


Figure 2.1.4 Proper rotational axes in the $PtCl_4^{2-}$ molecular anion. (Attribution: symotter.org/gallery)

We can now think about how we can write out the axes and their associated proper rotational operations in a systematic way. Let us first look at the symmetry elements, the proper axes: We conventionally write the principal axis first, and then all other axes from their highest to their lowest order. When there are axes of the same order, those with the least number of primes get denoted first, and those with the highest number of primes last. If there are conjugate axes then their number is placed in front of their Schoenflies symbol. For the proper axes of the $PtCl_4^{2-}$ the notation would therefore be: C_4, C_2, $2C_2'$, $2C_2''$. Now let us see how to denote the rotation operations that are associated with these symmetry elements. The notation follows the same rules as for the symmetry elements. In addition, we have to consider that we must not count identical operations twice, we also do not denote the operations that are the same as the identity. For the C_4 axis there are four operations until we reach the identity. C_4^1, C_4^2, C_4^3, and C_4^4. For each of the C_2, C_2', and C_2'' elements there are two operations until the identity is reached. C_2^1, C_2^2, $C_2^{1'}$, $C_2^{2'}$, $C_2^{1''}$, $C_2^{2''}$. The C_4^4, the C_2^2, the $C_2^{2'}$, and the $C_2^{2''}$are the same as the identity and therefore we do not consider them. In addition we can see that the C_4^2 is the same as the C_2^1. This is because the C_4 and the C_2 axes are in the same location, and rotating two times around 90° is the same as rotating one time around 180°. By convention we eliminate the operation associated with the higher order, thus the C_4^2. The overall notation would then be: C_4^1, C_4^3, C_2^1, 2 $C_2^{1'}$ 2 $C_2^{1''}$ (Fig. 2.1.5).

Rotation symmetry operations are: C_4^1, C_4^3, C_2^1, 2 $C_2^{1'}$ 2 $C_2^{1''}$

($C_4^4 = E$, $C_4^2 = C_2^1$, $C_2^2 = E$, $C_2^{2'} = E$, $C_2^{2''} = E$)

Figure 2.1.5 Proper rotation operations in $PtCl_4^{2-}$

The Reflection Operations (σ)

Let us look at reflection operations which are carried out around reflection planes, or mirror planes. Mirror planes have the Schoenflies symbol σ. When we carry out a reflection operation, then we move any point of the object to the other side of the mirror plane. There are two types of mirror planes, so-called horizontal mirror planes and vertical mirror planes. A horizontal mirror plane always stands perpendicular to the principal axis. For example in the depicted BH_3 molecule there is a horizontal mirror plane that stands perpendicular to a C_3 principal axis (Fig. 2.1.6). A horizontal mirror plane has the Schoenflies symbol σ_h.

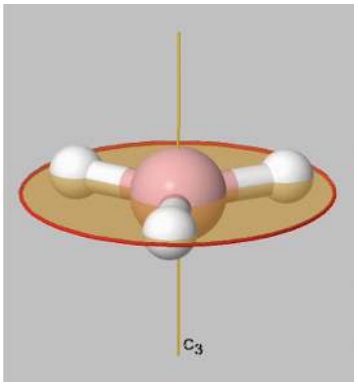


Figure 2.1.6 Visual depiction of the horizontal mirror plane of BH_3, σ_h (Attribution: symotter.org/gallery)

A vertical mirror plane has the property that it contains the principal axis, this means that it is part of the principal axis. It is denoted σ_v. The BH_3 molecule has three vertical axes that pass through the three B-H bonds. You can see that each of them contain

the principal C_3 axis (Fig. 2.1.7). The three vertical mirror planes are conjugate, and therefore they are not distinguished by primes. We can write a coefficient 3 in front of the symbol σ_v to indicate that there are three conjugate vertical mirror planes.

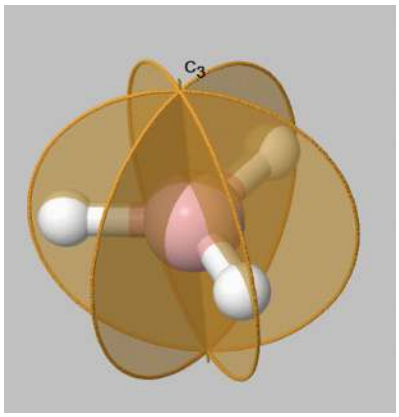


Figure 2.1.7 Visual depiction of the vertical mirror planes of BH_3, 3 σ_v (Attribution: symotter.org/gallery)

Now let us look at how many symmetry operations are associated with a particular mirror plane. Fortunately, things are simple here: There is only one reflection operation associated with one mirror plane. This because reflecting two times at a mirror plane produces the identity E: σ_v^2=E. More generally, when we reflect n times, and n is an even number then this is the same as the identity or, σ_v^n=E (n is even). When n is odd the reflecting n times is the same a reflecting only one time or, $\sigma_v^n=\sigma_v^1$ (n=odd).

The horizontal mirror plane of the BH_3 molecule deserves an additional comment. Carrying out the horizontal reflection does not change the position of any atom. It is important to understand why the operation does exist despite the fact it does not change the position of any atom. The criterion is not whether the position of an atom is changed, but whether the position of the points in the object changes. In the case of the BH_3 molecule the part of the molecule that is located above the mirror plane will be located below the mirror plane after the reflection operation has been carried out. Vice versa any part of the molecule that was formerly below the mirror plane will be located above the mirror plane after the reflection operation has been carried out. For example the lower half of the B atom with be above the mirror plane, and the half above the plane will be below the plane after the execution of the reflection operation.

Like non-conjugate proper rotations are distinguished by primes, also non-conjugate vertical mirror planes must be distinguished by primes. The smaller the number of bonds the vertical mirror plane contains, the larger the number of primes.

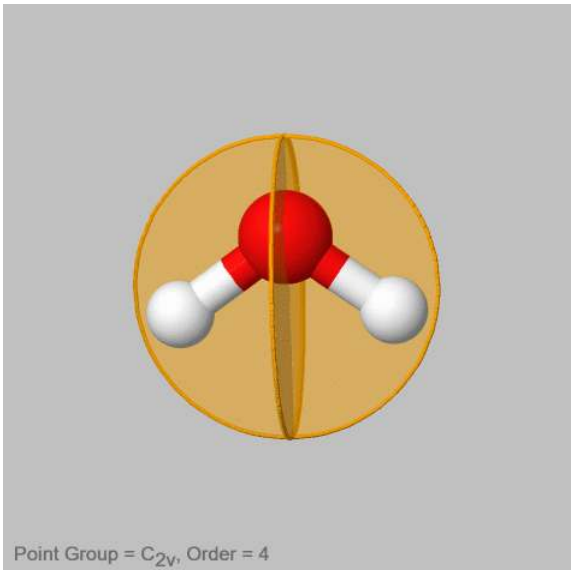


Figure 2.1.8 Non-conjugate vertical mirror planes of H_2O (Attribution: symotter.org/gallery)

For example in the water molecule (Fig. 2.1.8) there are two non-conjugate vertical mirror planes. One contains the two O-H bonds, the other stands perpendicular to the first mirror plane. It is easy to see that these two mirror planes will not move the points

in the atom in an equivalent way, and therefore they are not conjugate. The first mirror plane does not change the position of any atom, while the second one swaps the positions of the two hydrogen atoms. Therefore, the second mirror plane not containing any O-H bonds gets one prime the one that contains the O-H bonds doe not get a prime.

Dihedral Reflection Planes (σ_d)

A special case of a vertical mirror plane is a dihedral mirror plane, denoted σ_d. A dihedral mirror plane bisects the angle between two conjugate C_2 axes.

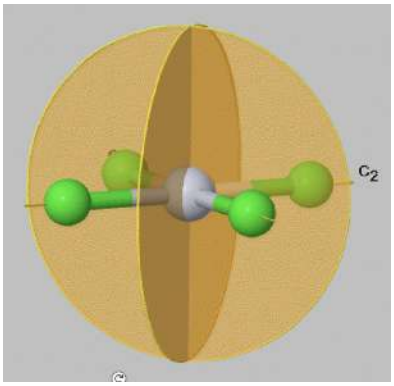


Figure 2.1.9 Dihedral mirror planes of $PtCl_4^{2-}$ (Attribution: symotter.org/gallery)

For example, in the $PtCl_4^{2-}$ anion (FIg. 2.1.9) there are two vertical mirror planes that bisect the angle between the two conjugate C_2 axes that pass through the Pt-Cl bonds. Therefore, these mirror planes are vertical mirror planes σ_d.

The Inversion Operation (*i*)

Let us look next at the inversion operation which is symbolized by a Schoenflies symbol *i*. The symmetry element associated with an inversion, is the inversion center, also called center of symmetry. It is a single point. When an inversion operation is performed, then each point of the object is moved through the inversion center to the other side. Each coordinate in the object (x,y,z) is inverted into the coordinates (-x,-y,-z).

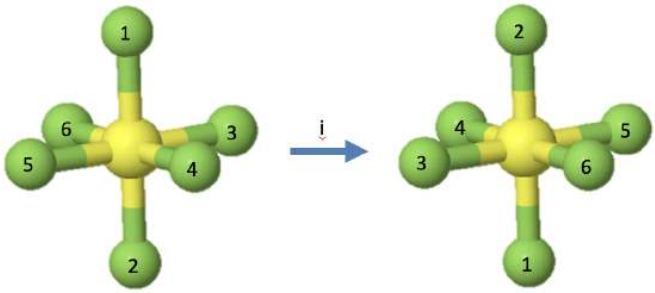


Figure 2.1.10 The inversion operation for SF_6 (Attribution: symotter.org/gallery)

For example, the octahedral molecule SF_6 has an inversion center in the center of the molecule (Fig. 2.1.10). When the inversion operation is carried out, then each fluorine atom is moved through the inversion center to the other side. This means that the fluorine atoms 1 and 2 swap up their positions, the fluorine atoms 3 and 5 swap up their positions, and so do the fluorine atoms 4 and 6. The sulfur atom does not change its position. There is only one inversion operation associated with each inversion center. Inverting two times, or more generally, an integer number of two times produces the identity. Inverting an odd number of times is the same as inverting one time.

The Rotation-Reflection Operation (S_n)

The rotation-reflection operation S_n is the most complex symmetry operation. It is carried out in two steps. First, a rotation around an improper axis is carried out. The angle is determined by the order n of the improper axis, and is 360°/n. This axis is called improper, because the object does not need to superimpose the original object after the rotation. Achieving superposition requires the second step which is the reflection at a mirror plane that stands perpendicular to the improper axis. Only after the second step

the operation is complete. The presence of the rotation-reflection does not require a proper rotational axis or a regular mirror plane σ to exist, however it also do not preclude their existence.

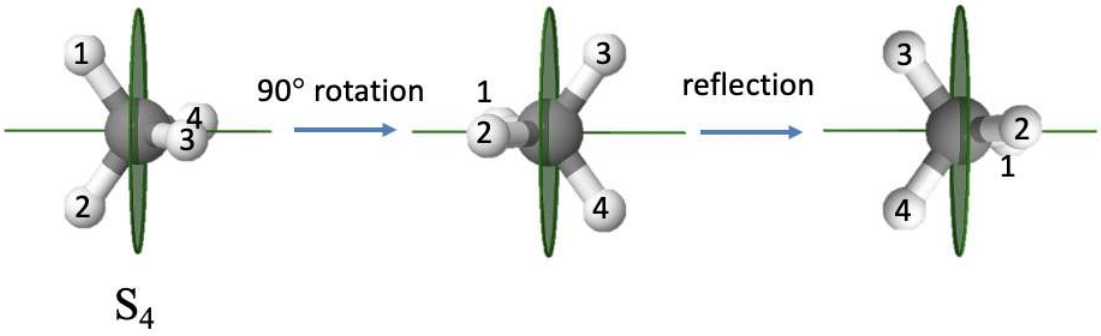


Figure 2.1.11 The improper S_4 rotation for CH_4 (Attribution: symotter.org/gallery)

An example of a molecule with an improper axis is the methane molecule (Fig. 2.1.11). It has an S_4 improper axis. The axis bisects the H-C-H tetrahedral bond angle. The order of the axis is four which requires that we rotate by 90° around this axis. You can see that after we carry out the rotation, the molecule does not superimpose the original molecule. Only after we reflect the rotated molecule at a mirror plane standing perpendicular to the improper axis the molecule superimposes the original molecule.

Properties of the Rotation-Reflection Operation (S_n)

The rotation-reflection has a number of interesting properties. One of the them is that an S_1 operation is the same as a reflection. This is because the order 1 implies a rotation around 360° which produces the identity, and all points within the object are in their original position. This is the same as though we had not rotated at all. This means actually we only did the second step, the reflection, and therefore the S_1 is identical to a "regular" reflection. The second property is that an S_2 operation is the same as an inversion. When you rotate around 180° and then reflect perpendicular to the improper axis of rotation, the positions of the points in the object change exactly the same way as they do when you invert through an inversion center.

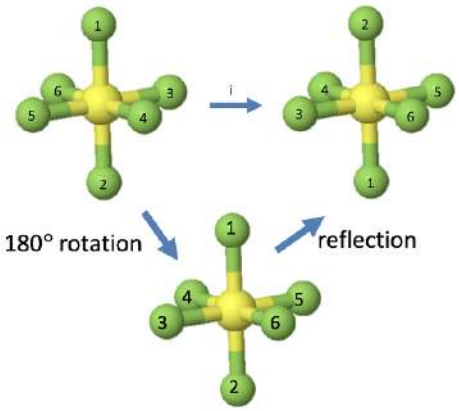


Figure 2.1.12 Rotation-Reflection operations for SF_6 (Attribution: symotter.org/gallery)

Look for example at the SF_6 molecule again (Fig. 2.1.12) which has an inversion center in the center of the atom. We previously saw that when we carry out the inversion, the atoms 1 and 2 swap their position, and so do the atoms 3 and 5, as well as the atoms 4 and 6. Let us carry out the rotation-reflection, and see if the atoms change the same way. Firstly we rotate 180° around an axis that goes through the atoms 1 and 2. This leaves the positions of the atoms 1 and 2 unchanged, but swaps up the positions of the atoms 3 and 5, as well as the atoms 4 and 6. Next we must do a reflection at a plane that stands perpendicular to the improper axis. It is the plane defined by the atoms 3, 4, 5, and 6. Reflection at this plane does not change the positions of the atoms 3, 4, 5, and 6, but it swaps up the positions of the atoms 1 and 2, which lie above and below the plane, respectively. We can see that the positions of the atoms are the same as after the inversion.

The fact that we can express a reflection by an S_1 rotation-reflection, and an inversion by a S_2 rotation-reflection means that the reflection and the inversion are not independent symmetry operations, and we would not need them. The symmetry of an object could be fully described by the identity, proper rotations, and rotation-reflections. However, by convention, we use reflections and

inversions instead of S_1 and S_2, simply because it is easier for the human mind to perform 1-step operations, rather than 2-step operations.

Improper rotations have different properties depending on whether the order of the axis is even or odd. For even orders, the presence of an S_n improper rotational axis implies that there must also be a proper rotational axis with an order n/2. For improper axes of even orders n the identity is produced after n rotation-reflections (Fig. 2.1.13).

$$S_n \text{ with n even} \rightarrow \text{molecule contains } C_{n/2}$$

$$S_n^n = E$$

Figure 2.1.13 Properties of improper rotations with even order *n*

For improper axes of odd order n, carrying out the rotation-reflection n times is the same as carrying out a reflection at a horizontal mirror plane. We need to do the rotation-reflection 2n times to reach the identity (Fig. 2.1.4).

$$S_n \text{ with n odd} \rightarrow \text{molecule contains } C_n \text{ and } \sigma_h$$

$$S_n^n = \sigma_h$$

$$S_n^{2n} = E$$

Figure 2.1.14 Properties of improper axes of odd order *n*

Rotation-Reflections of PF_5 (an example with odd order)

Let us show these properties using two examples. Let us first look at an example with an improper rotation of odd order. The PF_5 molecule has trigonal pyramidal shape with three F atoms in the equatorial plane, and two additional F atoms above and below the plane. The F atoms have been numbered from 1 to 5 as indicated by the subscripts that follow the element symbol (Fig. 2.1.15). The PF_5 has an improper rotational axis S_3 that stands perpendicular to the equatorial plane going through the P-F_1 and P-F_2 bonds. Let us carry out the S_3 symmetry operations step by step and see how the atoms move.

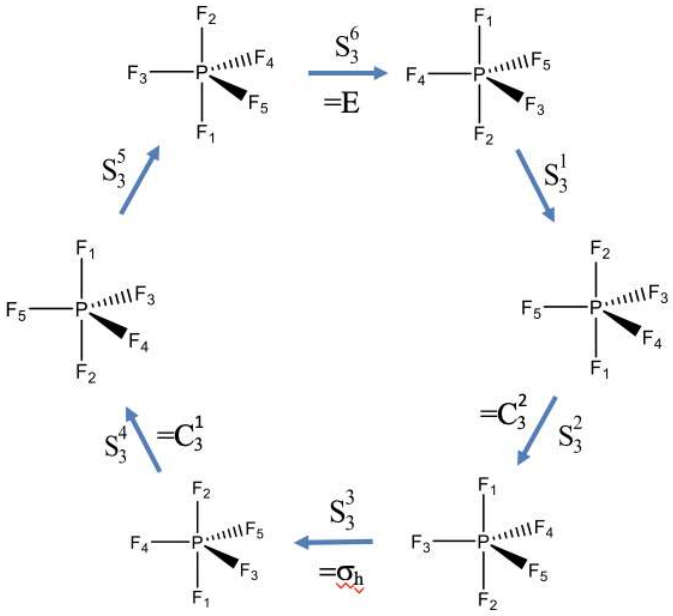


Figure 2.1.15 S_3 symmetry operations for PF_5

We would expect that after we carry out the operation six times the identity will be produced. After three rotation-reflections we would expect that the object has been moved the same way a horizontal mirror plane would do. After the first rotation-reflection the atoms F_1 and F_2 have swapped their positions, and the three F atoms in the equatorial plane have been rotated by 120 degrees counter-clockwise. The F_5 atom now occupies the position of the F_4, the F_4 has been rotated into the position of the F_3, and the F_3 has been moved into the position of the F_5. The second S_3 operation again swaps up the F_2 and F_1 atoms, and rotates the remaining F atoms by 120°. Now the F_5 atoms points toward us, the F_4 atom points away from us, and the F_3 atoms is in the paper plane. Carrying out the operation a third time again swaps the F_1 and F_2 and rotates F_3, F_4, and F_5 counter-clockwise by 120°. Now let us

compare the position of the atoms with the atom positions of the molecule we started with. We see that the position of the equatorial F atoms are same as in the beginning, but the position of the axial F_1 and F_2 atoms have been swapped up. This is equivalent to a reflection at a horizontal mirror plane located within the equatorial plane. This horizontal mirror plane would only swap up the axial F atoms, but would not move the equatorial ones. The S_3^4 operation again swaps up the position of the F_1 and the F_2 atoms, and rotates the equatorial F atoms by 120° counter-clockwise. Now, F_4 points toward us, F_3 points away, and F_5 is in the paper plane. After the fifth rotation-reflection F_1 and F_2 are again swapped so that F_1 is below and F_2 is above the equatorial plane. The atoms F_3, F_4 and F_5 are rotated so that F_3 is in the paper plane, F_5 points toward us, and F_4 points away from us. The sixth rotation-reflection again swaps up F_1 and F_2, and rotates the other F atoms around 120° counter-clockwise. We can now see that the produced molecule is the same as the one we started with, and the identity has been produced.

It is also noteworthy that the S_3^2 and the S_3^4 operation can be expressed by simpler operations, namely C_3^2 and C_3^1 proper rotation operations. We can understand this considering that an S_3^2 operation requires that we reflect two times, and reflecting two times is just like not reflecting at all. So effectively, we only have two rotations around 120° which is equivalent to C_3^2. Similarly, the S_3^4 operation requires to reflect four times, which is the same as not reflecting at all. Thus, effectively, we only rotate four times around 120°. This is the same as rotating only one time around this angle, which is equivalent to a C_3^1 operation.

Using similar considerations, we can also understand why the S_3^3 operation is equivalent to a σ_h. In this case, we rotate 3 x 120° = 360°, and rotating around 360° is the same as not rotating at all. In addition, we carry out a reflection three times. Reflecting an odd number of times is the same as reflecting only one time. Thus overall, we effectively carry out a single reflection only.

Overall, only the S_3^1 and the S_3^5 operations are unique, all others can be expressed by other, simpler operations.

Rotation-Reflections of CH_4 (an example with even order)

Let us illustrate the properties of an improper rotational axis with even order using the example methane (Fig. 2.1.16).

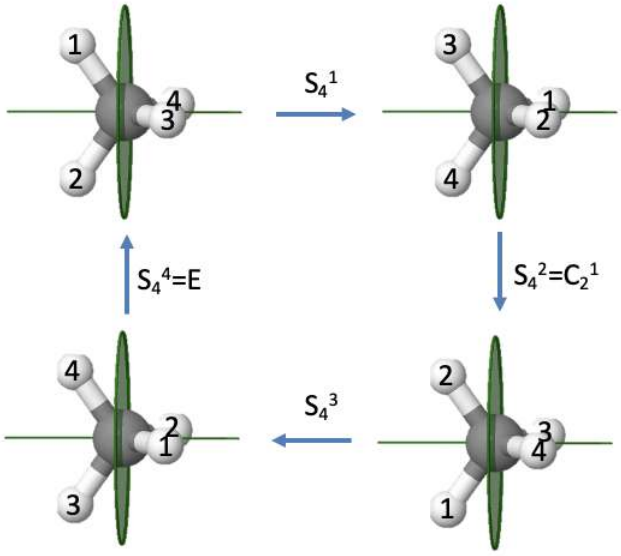


Figure 2.1.16 S_4 symmetry operations for CH_4 (Attribution: symotter.org/gallery)

We previously saw that the methane molecule has an S_4 improper axis. Executing the symmetry operation once moves the H atoms 1 and 2 to the right, whereby atom 1 points to the back and atom 2 points to the front. After the second rotation-reflection the atoms 1 and 2 are reflected back to the left side, but because we have rotated two times by 90° atom 2 points up, and atom 1 points down. Similarly, atoms 3 and 4 are reflected back to the right side, but atom four points toward us and atom 3 points to the back. After three rotation-reflections, the atoms 1 and 2 are again on the right side with atom 2 pointing to the back and atom 1 pointing to the front. Atoms 3 and 4 are on the left with atom 4 pointing up, and atom 3 pointing downward. After the operation is carried out four times, all atoms are back in their original position, meaning the identity has been produced. This is what we expected for an improper rotation of even order. We can see in addition that the S_4^2 operation is the same as an C_2 operation. Rotating two times about 90° is the same as rotating about 180°. Reflecting two times is the same as not reflecting at all. Therefore, effectively, we

only rotated by 180° which is the same as what a C_2^1 operation does. Because an S_4^2 can be expressed by a C_2^1, and an S_4^4 is the same as the identity, only the S_4^1 and the S_4^3 are unique symmetry operations.

The Symmetry of a Molecule

We have now discussed all types of symmetry elements and operations that can exist in an object. Next, let us think about how we can define the overall symmetry of an object. The **overall symmetry** of an object is defined as the sum of all the symmetry operations for this object. If two objects have exactly the same symmetry elements and operations then their symmetry is the same. Using the mathematical language of group theory, the mathematical theory for symmetry, we can say they belong to the same point group. The name point group comes from the fact, that it has at least one invariant point. The number of symmetry operations belonging to a point group is called the order of the point group. Let us see next what different point groups we know and how we can systematically classify them.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 9.1: Symmetry Elements is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **2.1: Symmetry Elements and Operations** by Kai Landskron is licensed CC BY 4.0.

9.2: Point Groups

The Low Symmetry Point Groups

C_1 Point Group

Overall, we divide point groups into three major categories: High symmetry point groups, low symmetry point groups, dihedral point groups, and rotational point groups. Let us begin with the low symmetry point groups. As the name says, these point groups only have few symmetry elements and operations. The point group C_1 is the point group with the lowest symmetry. Molecules that belong to this point group only have the identity as symmetry element.

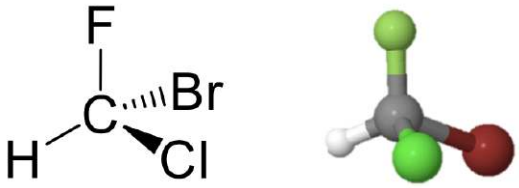


Figure 2.2.1 C_1 point group of bromochlorofluromethane (Attribution: symotter.org/gallery)

An example is the bromochlorofluromethane molecule (Fig. 2.2.1). It has no symmetry element, but the identity. The name C_1 comes from the symmetry element C_1. A C_1 operation is the same as the identity.

C_s Point Group

The point group C_s has a mirror plane in a addition to the identity. An example is the 1,2-bromochloroethene molecule (Fig. 2.2.2).

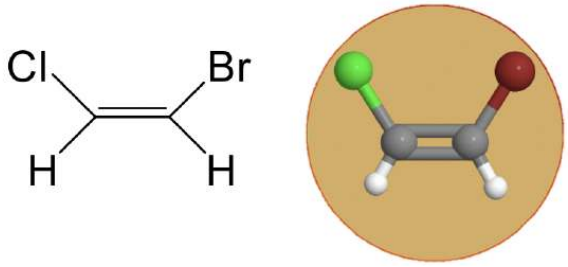


Figure 2.2.2 C_s point group of 1, 2-bromochloroethene (Attribution: symotter.org/gallery)

This is a planar molecule and the mirror plane is within the plane of the molecule. This mirror plane does not move any atoms when the reflection operation is carried out, nonetheless it exists because any point of the molecule above the mirror plane will be found below the mirror plane after the execution of the operation. Vice versa, any point below the mirror plane will be above the mirror plane. This mirror plane does not have a vertical or horizontal mirror plane designation because no proper rotational axes exist.

C_i Point Group

The point group C_i has the inversion as the only symmetry element besides the identity. The point group C_i is sometimes also called S_2 because an S_2 improper rotation-reflection is the same as an inversion. An example is the 1,2-dibromo 1,2-dichloro ethane (Fig. 2.2.3).

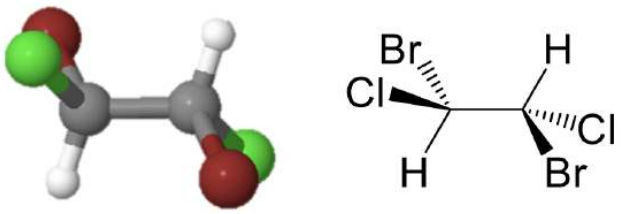


Figure 2.2.3 The C_i point group: 1,2-dibromo 1,2-dichloro ethane (Attribution: symotter.org/gallery)

This molecule looks quite symmetric, but it has inversion center in the middle of the carbon-carbon bond as the only symmetry element. Upon execution of the inversion operation, the two carbons swap up their positions, and so do the two bromine, the two chorine, and the two hydrogen atoms.

The High Symmetry Point Groups

The symmetry elements of the high symmetry point groups can be more easily understood when the properties of platonic solids are understood first. Platonic solids are polyhedra made of regular polygons. In a platonic solid all faces, edges, and vertices (corners) are symmetry-equivalent. We will see that this is a property that can be used to understand the symmetry elements in high symmetry point groups. There are only five possibilities to make platonic solids from regular polygons (Fig. 2.2.4).

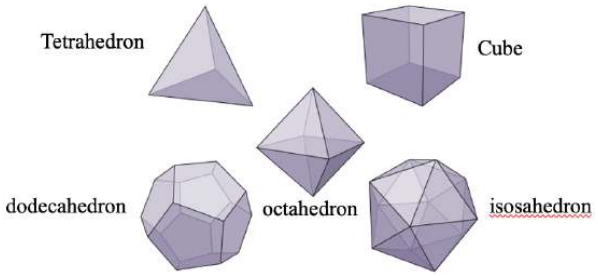


Figure 2.2.4 The platonic solids (Attribution: Drummyfish [CC0] https://commons.wikimedia.org/wiki/F...ransparent.svg)

The first possibility is to construct a tetrahedron from four regular triangles. The second platonic solid is the octahedron made of eight regular triangles. The third possibility is the icosahedron made of twenty triangles. In addition, six squares can be connected to form a cube, and twelve pentagons can be connected to form a dodecahedron. There are no possibilities to connect other regular polygons like hexagons to make a platonic solid.

The icosahedron is the most complex of all platonic solids. If you would like to see and study an icosahedron from the outside and inside, there is one for study on the playground of the Allentown Cedar Beach Park, in Allentown, Pennsylvania.



Figure 2.2.5 Icosahedron at Allentown Cedar Beach Park

The T_d Point Group

The tetrahedron, as well as tetrahedral molecules and anions such as CH_4 and BF_4- belong to the high symmetry point group T_d. Let us find the symmetry elements and symmetry operations that belong to the point group T_d. First, we should not forget the identity operation, E. Next, it is useful to look for the principal axes.

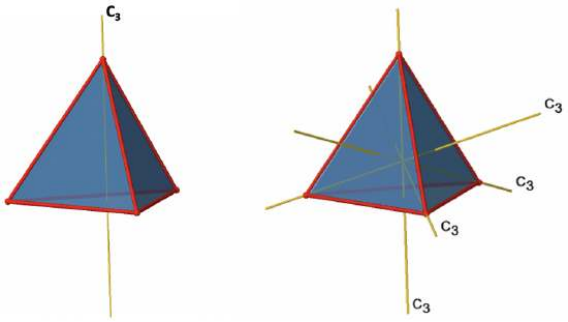


Figure 2.2.6 The C_3 axes in a tetrahedron (Attribution: symotter.org/gallery)

The tetrahedron has four principal C_3 axes (Fig. 2.2.6). It is a property of the high-symmetry point groups that they have more than one principal axis. The C_3 axes go through the vertices of the tetrahedron. Because each C_3 axis goes through one vertex, there are four vertices, and we know that in a platonic solid all vertices are symmetry-equivalent, we can understand that there are four C_3 axes. How many unique C_3 operations are associated with these axes? After three rotations around 120° we reach the identity. Therefore C_3^3=E, and we only need to consider the C_3^1 and the C_3^2 rotation about 120 and 240° respectively. Because there are four C_3 axes, there are four C_3^1 and four C_3^2 operations and eight C_3 operations overall. We can express this by writing the respective numbers as coefficients in front of the Schoenflies symbol for the operations (Fig. 2.2.7).

Symmetry operations: E, $8C_3$

Symmetry operations in detail: E, 4 C_3^1, 4 C_3^2 ($C_3^3 = E$)

Figure 2.2.7 Symmetry operations associated with the C_3 axes in the point group T_d

In addition to the C_3 axes there are C_2 axes (Fig. 2.2.8).

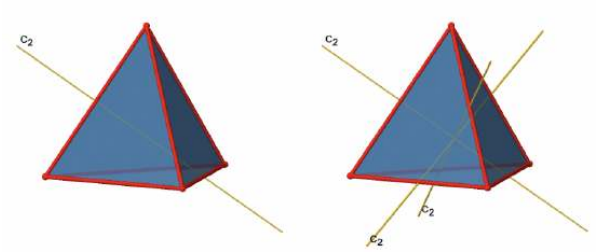


Figure 2.2.8 The C_2 axes in a tetrahedron belonging to the point group T_d (Attribution: symotter.org/gallery)

You can see that a C_2 axis goes through two opposite edges in the tetrahedron. Because a tetrahedron has six edges, and each C_2 axis go through two edges there are 6/2=3 C_2 axes. There is only one C_2 symmetry operation per C_2 axis because we produce the identity already after two rotations. Therefore there are three C_2^1 operations overall (Fig. 2.2.9).

Symmetry operations: $3C_2$

Symmetry operations in detail: 3 C_2^1

Figure 2.2.9 Symmetry operations associated with the C_2 axes in the point group T_d

In addition, the T_d point group has S_4 improper rotation reflections. Like the C_2 axes, they pass through the middle of two opposite edges. This also means that they are superimposing the C_2 axes. Because there are six edges, and two S_4 axes per edge there are 6/2=3 S_4 axes (Fig. 2.2.10).

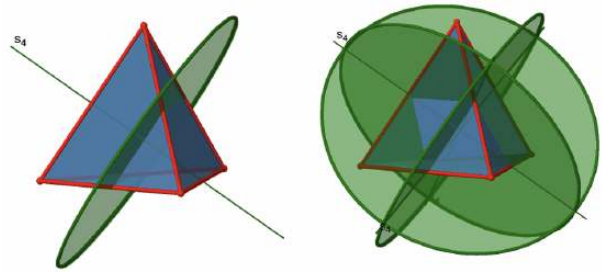


Figure 2.2.10 The S_4 axes in a tetrahedron (Attribution: symotter.org/gallery)

How many operations are associated with these S_4 axes? The order of the axes are even, and therefore we need four S_4 operations to produce the identity. The S_4^2 operation is the same as a C_2^1 operation because reflecting two times is equivalent to not reflecting at all, and rotating two times by 90° is the same as rotating about 180°. Therefore overall, only S_4^1 and S_4^3 operations are unique operations. S_4^2 and S_4^4 can be expressed by the simpler operations C_2^1 and E respectively. Because there are 3 S_4 axes, there are three S_4^1 and three S_4^3 operations. Overall there are six S_4 operations (Fig. 2.2.11).

Symmetry operations: $6S_4$

Symmetry operations in detail: $3\ S_4^1, 3\ S_4^3$

$(S_4^4 = E, S_4^2 = C_2^1)$

Figure 2.2.11 Symmetry operations associated with the S_4 axes in the point group T_d

There are also mirror planes (Fig. 2.2.11). The planes contain a single edge of the tetrahedron, thereby bisecting the tetrahedron. There a six edges in a tetrahedron, and therefore there are 6/1=6 mirror planes.

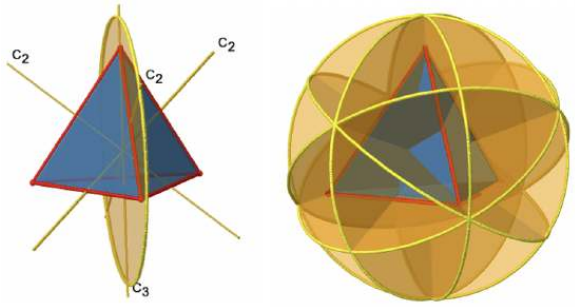


Figure 2.2.12 The mirror planes and C_2 axes in a tetrahedron belonging to the point group T_d (Attribution: symotter.org/gallery)

These planes are dihedral planes because each plane contains a C_3 principal axis and is bisects the angle between two C_2 axes. Overall, there are three C_2 axes and three C_2 operations. There is one reflection operation per mirror plane because reflecting two times produces the identity. Therefore, there are six σ_d reflection operations (Fig. 2.2.12, right and Fig. 2.2.13).

Symmetry operations: $6\sigma_d$

Symmetry operations in detail:$6\ \sigma_d$

Figure 2.2.13 Reflection operations associated with the σ_d mirror planes in T_d

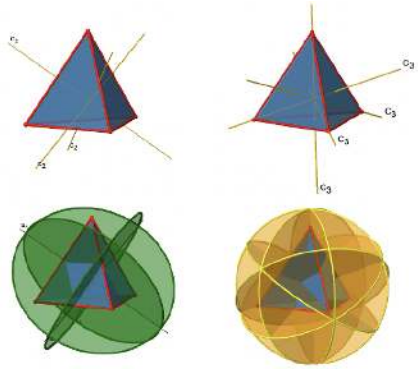


Figure 2.2.14 Summary of symmetry axes and planes in a tetrahedron with the point group T_d (Attribution: symotter.org/gallery)

In sum (Fig.2.2.14 and 2.2.15) we can denote the overall symmetry of the T_d point group the following way: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$. In detail the unique symmetry operations are E, $4C_3^1$, $4C_3^2$, $3C_2^1$, $3S_4^1$, $3S_4^3$, $6\sigma_d$.

Symmetry operations: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$

Symmetry operations in detail: E, $4\ C_3^1$, $4\ C_3^2$, $3\ C_2^1$, $3\ S_4^1$, $3\ S_4^3$, $6\ \sigma_d$

$(C_3^3 = E, S_4^4 = E, S_4^2 = C_2^1)$

Figure 2.2.15 Summary of the symmetry operations for the point group T_d

The Rotational Subgroup T

The high symmetry point group T is the so-called rotational subgroup of the point group T_d. A rotational subgroup is a point group in which all symmetry operations but the identity and the proper rotations have been removed from a high-symmetry point group. For the point group T this leaves the $4C_3$, the four C_3^2 and the three C_2 operations (Fig. 2.2.17). The S_4 rotation-reflections and the mirror planes have been removed. The point group T is rare.

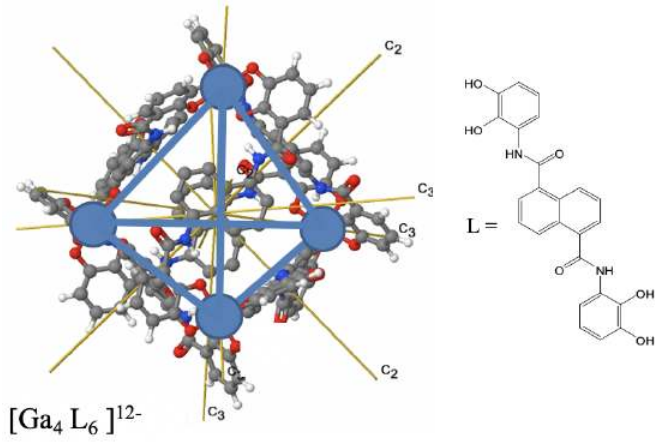


Figure 2.2.16 Symmetry elements in the Ga_4L_6 cage belonging to the point group T (Attribution: symotter.org/gallery)

An example is the depicted Ga_4L_6 cage (Fig. 2.2.16). The Ga atoms occupy the vertices of a tetrahedron, but the point group is not T_d but T because of the shape of the ligands that connect the four Ga atoms.

Symmetry operations: E, $4C_3$, $4C_3^2$, $3C_2$

Figure 2.2.17 Symmetry operations for the Ga_4L_6 cage

The Octahedral Point Group O_h

Another high symmetry point group is the point group O_h. Both the octahedron as well as the cube belong to this point group despite their very different shape (Fig. 2.2.18). Because they belong to the same point group they must have the same symmetry elements and operations. There are many octahedrally shaped molecules, such as the SF_6.

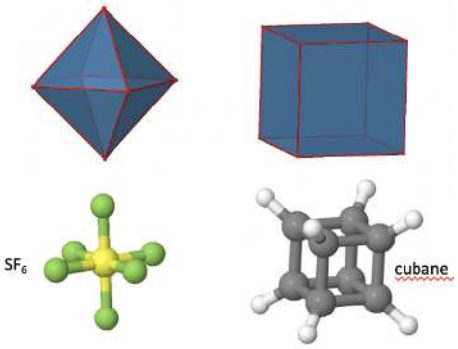


Figure 2.2.18 SF_6 and cubane with cubic and octahedral shape, respectively, belong to the point group O_h (Attribution: symotter.org/gallery)

Molecules with cubic shapes are far less common, because a cubic shape often leads to significant strain in the molecule. An example is cubane C_8H_8. Let us determine the symmetry elements and operations for the point group O_h using the example of the octahedron. If we used the cube, we would get exactly the same results.

There are three C_4 principal axes in the octahedron. They go through two opposite vertices of the octahedron (Fig. 2.2.19). There are three C_4 axes because an octahedron has six vertices which are all symmetry-equivalent because the octahedron is a platonic solid.

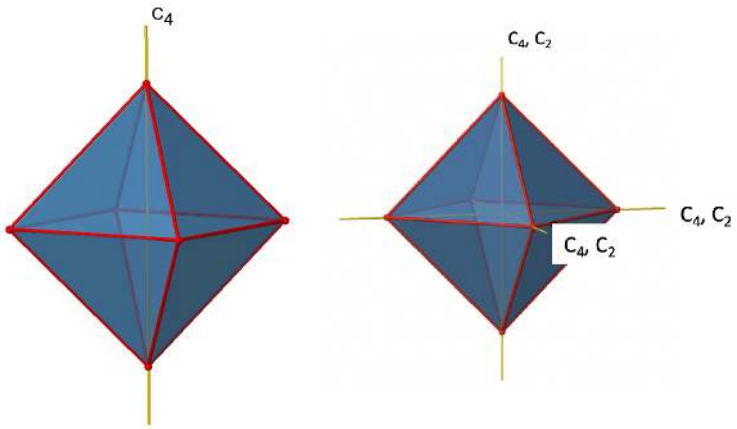


Figure 2.2.19 The C_4 and C_2 axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

We can see that there are also C_2 axes where the C_4 axes run. This is because rotating two times around 90° is the same as rotating around 180°. What are the symmetry operations associated with these symmetry elements? Rotating four times around 90° using the C_4 axes produces the identity. So we have to consider the operations C_4^1, C_4^2, C_4^3 and C_4^4. How many of these are unique? C_4^4 is the same as the identity, so it is not unique, In addition a C_4^2 is identical to a C_2^1, and thus C_4^2 is also not unique, and can be expressed by the simpler operation C_2^1. That leaves the C_4^1 and the C_4^3 as the only unique symmetry operations. Because we have three C_4 axes, there are 2x3=6 C_4 operations, in detail there are $3C_4^1$ and three C_4^3 operations. In addition, there are the three C_2^1 operations belonging the the three C_2 axes (Fig. 2.2.20).

Symmetry elements: E, $3C_4$, 3 C_2

Symmetry operations: E, 6 C_4, 3 C_2
In detail: E, 3 C_4^1, 3 C_4^3
($C_4^2 = C_2^1$, C_4^4 = E)

Figure 2.2.20 C_4 and C_2 symmetry operations in the octahedral point group O_h

In addition, there are four C_3 axes (Fig. 2.2.21). They are going through the center of two opposite triangular faces of the octahedron.

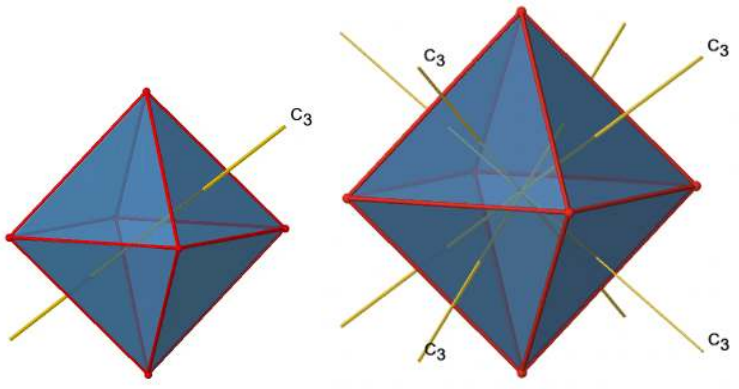


Figure 2.2.21 The C_3 axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

You see above a single C_3 axis, and on the right hand side all four of these axes. How can we understand that there are four axes? An octahedron has overall eight triangular faces, and each C_3 axis goes through two opposite faces, so there are 8/2=4 C_3 axes. Each C_3 axis has the C_3^1 and the C_3^2 as unique symmetry operations. The C_3^3 is the same as the identity. So overall we have 4x2=8 operations, four of them are C_3^1, and four of them are C_3^2 (Fig. 2.2.22).

Symmetry elements: $4C_3$
Symmetry operations: $8\ C_3$
In detail: $4\ C_3^1$, $4\ C_3^2$
$(C_3^3 = E)$

Figure 2.2.22 Symmetry operations of C_3 in the octahedral point group O_h

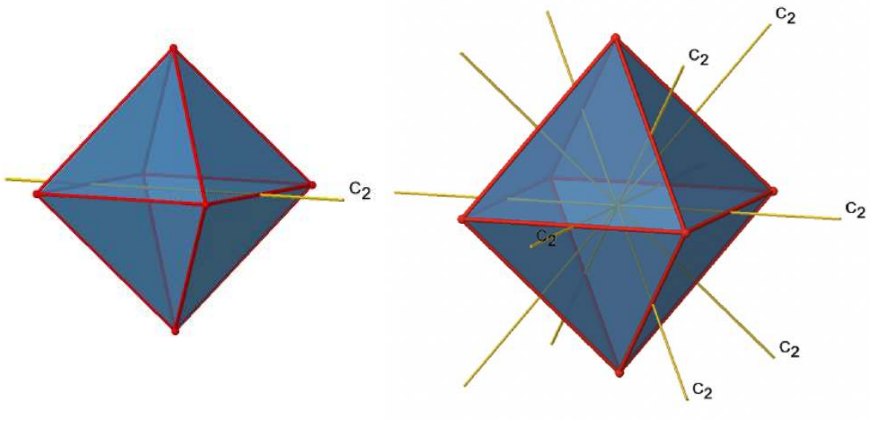


Figure 2.2.23 The C_2' axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

In addition to the C_2 axes that superimpose the C_4 axes, there are C_2' axes which go though two opposite edges of the octahedron (Fig. 2.2.23). How many of them are there? An octahedron has twelve edges, and because each C_2' passes through two edges, there must be 12/2=6 C_2' axes. These axes have primes because they are not conjugate to the C_2 axes that superimpose the C_4 axes. For each C_2' axis there is only the C_2' ^{1} as the unique symmetry operation, and therefore there are overall 6 C_2'^{1} symmetry operations (Fig. 2.2.24).

Symmetry elements: $6\ C_2$'
Symmetry operations: $6\ C_2$'^{1}

Figure 2.2.24 Symmetry operations of C_2' in the octahedral point group O_h

Let us look at the mirror planes next (Fig. 2.2.25). There are horizontal mirror planes that stand perpendicular to the C_4 principle axes. You can see a single one of them below on the left.

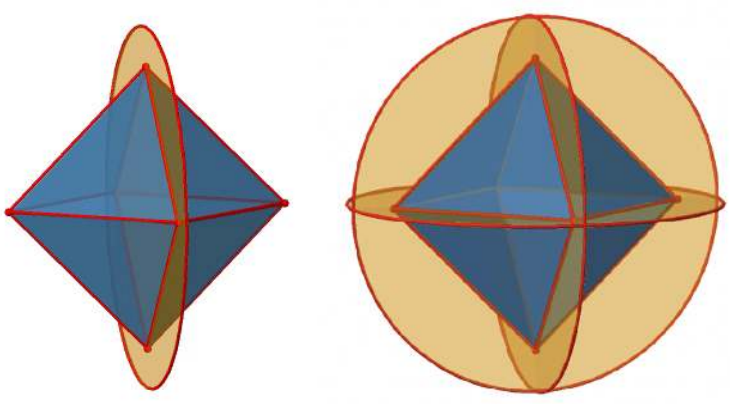


Figure 2.2.25 The horizontal mirror planes in the octahedral point group O_h (Attribution: symotter.org/gallery)

Note that this mirror plane also contains two axes, in addition to the one to which it stands perpendicular. Because it contains two principal C_4 axes, it has also properties of a vertical mirror plane. Nonetheless, we call it a horizontal mirror plane because it stands perpendicular to the third C_4. The horizontal properties trump the vertical ones, so to say. You can see that a single mirror plane contains four edges of the octahedron. Because there are twelve edges, there are 12/4=3 horizontal mirror planes. There is one

mirror plane per principal C_4 axis. There are three horizontal reflection operations because there is always only one reflection operation per mirror plane (Fig. 2.2.26).

Symmetry elements: $3\sigma_h$
Symmetry operations: $3\sigma_h$

Figure 2.2.26 Symmetry operations associated with horizontal mirror planes in the octahedral point group O_h

Next let us look for vertical mirror planes (Fig. 2.2.27). A vertical mirror plane is depicted below on the left.

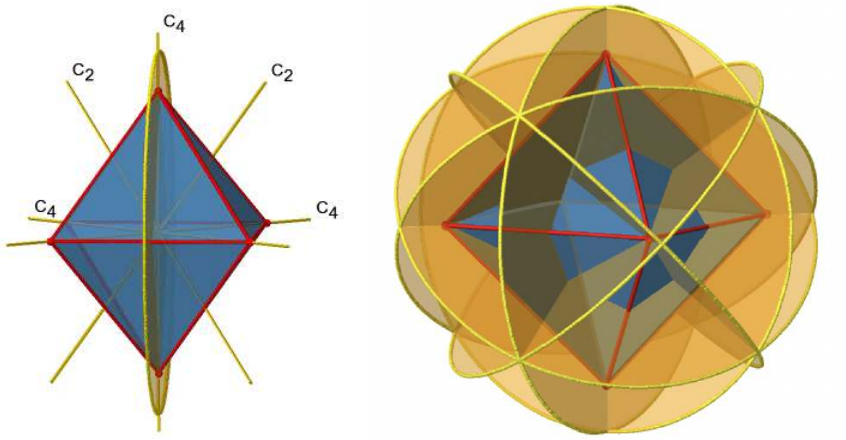


Figure 2.2.27 The vertical mirror planes in the octahedral point group O_h (Attribution: symotter.org/gallery)

You can see that - contrast to the horizontal mirror planes - it does not contain any edges. Rather, it cuts through two opposite edges. You can see that this plane contains a C_4 axis, but it does not stand perpendicular to the other two C_4 axes. Therefore it has only the properties of a vertical mirror plane. You can see however, that the mirror plane bisects the angle between two C_2' axes which also depicted. This makes the vertical mirror planes dihedral mirror planes, σ_d. How may of them do we have? As previously mentioned, each mirror plane cuts through two opposite edges. There are twelve edges in an octahedron, and thus there are 12/2=6 dihedral mirror planes. You can see all of them on the right side of Fig. 2.2.27. Each mirror plane is associated with one reflection operation, therefore there are six dihedral reflection operations (Fig. 2.2.28).

Symmetry elements: $6\ \sigma_d$
Symmetry operations: $6\ \sigma_d$

Figure 2.2.28 Symmetry operations associated with vertical mirror planes in the octahedral point group O_h

Next we can ask if the point group O_h has an inversion center? Yes, there is one in the center of the octahedron (Fig. 2.2.29)!

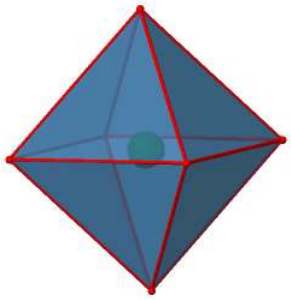


Figure 2.2.29 The inversion center of the octahedral point group O_h (Attribution: symotter.org/gallery)

Each point in the octahedreon can be moved through the inversion center to the other side, and the produced octahedron will superimpose the original one. There is always one inversion operation associated with an inversion center (Fig. 2.2.30).

Symmetry elements: i
Symmetry operations: i

Figure 2.2.30 Symmetry operations associated with the inversion center in the octahedral point group

Next, let us look for rotation-reflections. You can see an S_6 rotation-reflection operation below (Fig. 2.2.31, left).

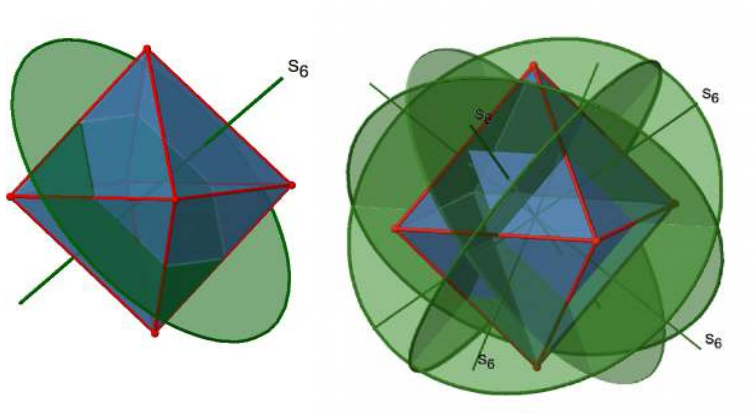


Figure 2.2.31 The S_6 rotation-reflection element of the octahedral point group O_h (Attribution: symotter.org/gallery)

The improper S_6 axis passes though the centers of two opposite triangular faces. One can see that rotation about 60° alone does not make the octahedron superimpose. The reflection at a plane perpendicular to the improper axis is required to achieve superposition. Overall, the rotation-reflection swaps up the position of the two opposite triangular faces. How many S_6 improper axes are there? Since each S_6 passes through two faces, and an octahedron has 8 faces there must be 8/2=4 S_4 axes. You can see all of them above (Fig. 2.2.31, right). Note that they are in the same position as the $4C_3$ axes we previously discussed. How many unique operations are associated with them? For an S_6 axis we need to consider operations from S_6^1 to S_6^6. S_6^6 is the same as the identity so it is not unique. The S_6^2 is the same as a C_3^1 because rotating two times round 60° is the same as rotating around 120°, and reflecting twice is the same as not reflecting at all. Similarly, an S_6^4 is the same as an C_3^2. Rotating four time by 60° is the same as rotating two times by 120° and reflecting four times is the same as not reflecting at all. Further, an S_6^3 is the same as an inversion. After three 60° rotations we have rotated by 180°. If we reflect after that, then this is the same as an S_2^1 operation which is the same as an inversion. Therefore, only the S_6^1 and the S_6^5 operations are unique, all other operations can be expressed by simpler operations (Fig. 2.2.32).

Symmetry elements: 4 S_6
Symmetry operations: 8 S_6
In detail $4S_6^1$, $4S_6^5$
($S_6^2=C_3^1$, $S_6^3=i$, $S_6^4=C_3^2$, $S_6^6=E$)

Figure 2.2.32 Symmetry operations of the rotation-reflection S_6 of the octahedral point group O_h

The octahedron also has S_4 improper axes, and you can see one of them below (Fig. 2.2.33, right).

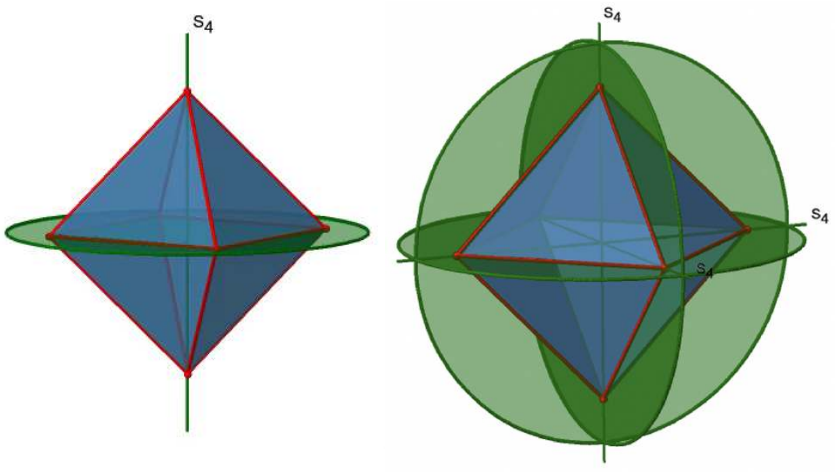


Figure 2.2.33 The S_4 improper axis of the octahedral point group O_h (Attribution: symotter.org/gallery)

It goes through two opposite corners of the octahedron. The S_4 improper axis seemingly does the same as the C_4 axis that goes through the same two opposite vertices, but actually does not. While rotating around 90° already makes the octahedron superimpose with its original form, executing the reflection operation after the rotation swaps up the position of the two vertices, and generally all points of the octahedron above and below the plane, respectively. Overall the S_4 moves the points within the object differently compared to the C_4 which makes it an additional, unique symmetry element. There are overall three S_4 improper axes because the octahedron has six vertices and one S_4 passes through two vertices (Fig. 2.2.34).

Symmetry elements: 3 S_4
Symmetry operations: 6 S_4
In detail: $3S_4^1$, $3S_4^3$
($S_4^2=C_2'$, $S_4^4=E$)

Figure 2.2.34 Symmetry operations associated with the S_4 improper axis of the octahedral point group O_h

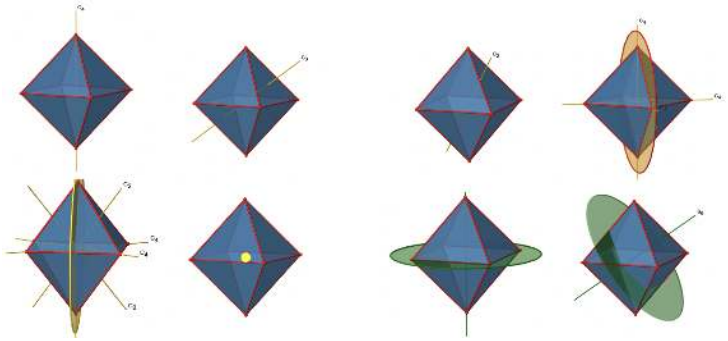


Figure 2.2.35 An overview over all symmetry elements in the octahedral point group O_h (Attribution: symotter.org/gallery)

Here is an overview over all the symmetry elements and operations (Fig. 2.2.35 and 2.2.36). Overall, there are 48 different unique operations that one can perform!

Symmetry elements: E, i, $4S_6$, $4C_3$, $3S_4$, $3C_4$, $6C_2$, $3\,C_2$, $3\sigma_h$, $6\sigma_d$
Symmetry operations: E, i, $8\,S_6$, $8\,C_3$, $6\,S_4$, $6\,C_4$, $6\,C_2$, $3\,C_2$, $3\,\sigma_h$, $6\,\sigma_d$
In detail: E, i, $4\,S_6^1$, $4\,S_6^5$, $4\,C_3^1$, $4\,C_3^2$, $3\,S_4^1$, $3\,S_4^3$, $3\,C_4^1$, $3\,C_4^3$, $6\,C_2$, $3\,C_2$, $3\,\sigma_h$, $6\,\sigma_d$
($S_6^2=C_3^1$, $S_6^3=i$, $S_6^4=C_3^2$, $S_6^6=E$; $C_3^3=E$. $S_4^2=C_2^1$, $S_4^4=E$, $C_4^2=C_2^1$, $C_4^4=E$)

Figure 2.2.36 Summary over all symmetry operations and elements of the octahedral point group O_h

Like the point group T_d , also the point group O_h has a rotational subgroup, named O. It has the identity and the same proper rotations as the point group O_h, but no other symmetry operations (Fig. 2.2.38). An example is the polyoxometalate cluster core shown below (Fig. 2.2.37). Polyoxometalates are cluster anions of the group 5 and 6 elements.

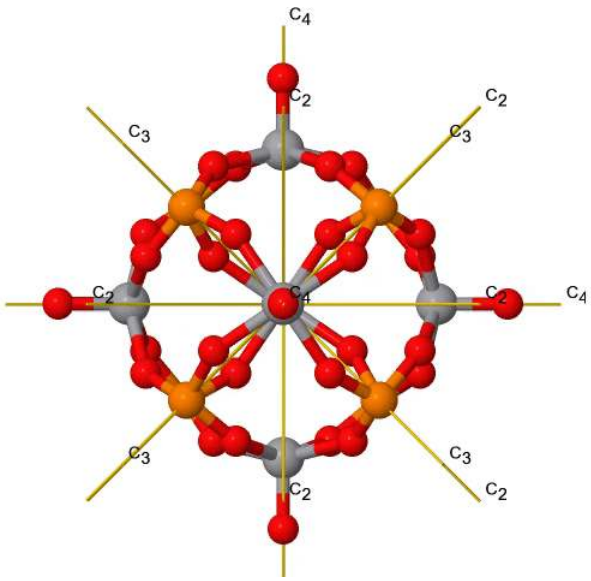


Figure 2.2.37 Proper rotations in a $V_6P_8O_{24}$ polyoxometalate cluster core. The C_3 rotation is animated. (Attribution: symotter.org/gallery)

The point group O is generally rare.

Symmetry elements: E, ~~i, $4S_6$~~, $4C_3$, ~~$3S_4$~~, $3C_4$, $6C_2$, $3\ C_2$, ~~$3\sigma_h$, $6\sigma_d$~~
Symmetry operations: E, ~~i, $8\ S_6$~~, $8\ C_3$, ~~$6\ S_4$~~, $6\ C_4$, $6\ C_2$, $3\ C_2$, ~~$3\ \sigma_h$, $6\ \sigma_d$~~
In detail: E, ~~i, $4\ S_6^1$, $4\ S_6^5$~~, $4\ C_3^1$, $4\ C_3^2$, ~~$3\ S_4^1$, $3\ S_4^3$~~, $3\ C_4^1$, $3\ C_4^3$, $6\ C_2$, $3\ C_2$, ~~$3\ \sigma_h$, $6\ \sigma_d$~~

Figure 2.2.38 Symmetry elements and operations in the point group O (relative to O_h)

Another high symmetry point group is the point group T_h. It can also be derived from the point group O_h. In this case the S_4, the C_4, the C_2', and the σ_d operations are removed from the octahedral symmetry. An example is the hexapyridyl iron (2+) cation (Fig. 2.2.39).

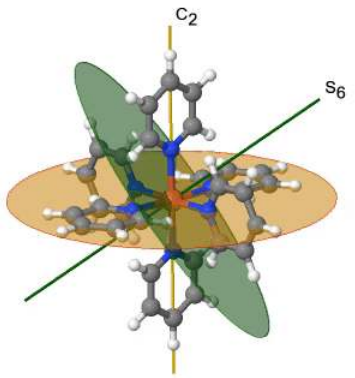


Figure 2.2.39 The hexapyridyl iron (2+) cation and its S_6 and C_2 symmetry elements. An S_6 operation is animated.

You can see that the N-atoms of the pyridyl-ligands surround the Fe atoms octahedrally, but the symmetry is reduced from O_h to T_h because of the planar shape of the pyridyl-ligands. In particular the C_4 symmetry is reduced to C_2. This reduction in symmetry leads to elimination of the S_4, the C_2', and the σ_d symmetry elements (Fig. 2.2.40).

T_h group (symmetry elements: E, i, $4S_6$, $4C_3$, $3C_2$, $3s_h$) can also be considered as a result of reducing **O_h** group symmetry (E, i, $4S_6$, $4C_3$, ~~$3S_4$, $3C_4$, $6C_2$~~, $3\ C_2$, $3\sigma_h$, ~~$6\sigma_d$~~)
by eliminating C_4, S_4 and some C_2 axes and s_d planes

Symmetry operations: i, $8\ S_6$, $8\ C_3$, $3\ C_2$, $3\ \sigma_h$,

Figure 2.2.40 Symmetry operations in $Fe(py)_6^{2+}$ in the point group T_h

The I_h Point Group

The two remaining platonic solids, the icosahedron and the dodecahedron, belong both to the icosahedral point group I_h. This is despite they are made of different polygons (Fig. 2.2.41).

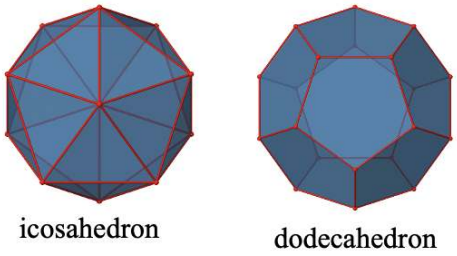


Figure 2.2.41 The icosahedron and dodecahedron of the I_h point group (Attribution: symotter.org/gallery)

Because they belong to the same point group, they have exactly the same symmetry operations. An example for a molecule with icosahedral shape is the molecular anion $B_{12}H_{12}^{2-}$. An example for a molecule with dodecahedral shape is the dodecahedrane $C_{20}H_{20}$.

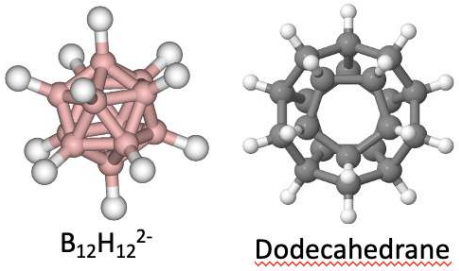


Figure 2.2.42 $B_{12}H_{12}^{2-}$ and the dodecahedrane (Attribution: wikiwand.com https://upload.wikimedia.org/Wikipedia/commons/thumb/9/97/Dodecaborane-3D-balls.png/640px-Dodecaborane-3D-balls.png)

Let us determine the symmetry elements and symmetry operations for the example of the icosahedron. We could also use the dodecahedron, and the results would be the same. The principal axes of the icosahedron are the C_5 axes. You can see one of them, going through the center of the pnetagon comprised of five triangular faces below (Fig. 2.2.43).

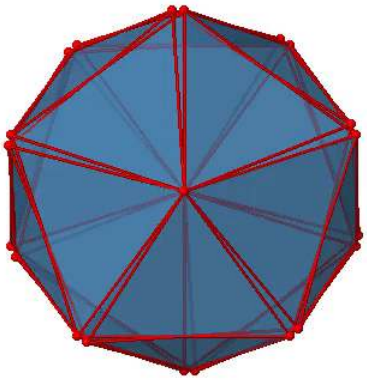


Figure 2.2.43 One of the C_5 axes of the icosahedron stands perpendicular to the paper plane going through the center of a pentagon of the icosahedron (Attribution: symotter.org/gallery)

You can understand that there is a C_5 when considering that there are five triangular faces making a pentagon. The C_5 axis sits in the center of the pentagon. We can see that when we rotate around this C_5 axis, then the produced icosahedron superimposes the original one. The C_5 axis goes through two opposite vertices of the icosahedron. Because an isosahedron has 12 vertices, there must be six C_5 axes overall. You can see all of them below (Fig. 2.2.44).

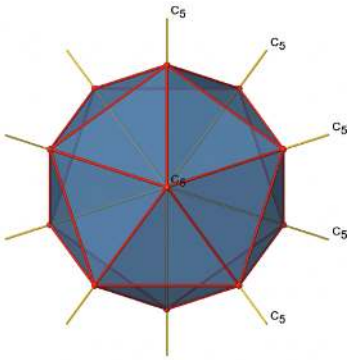


Figure 2.2.44 The C_5 axes of the icosahedron (Attribution: symotter.org/gallery)

There are four unique symmetry operations associated with a single C_5 axis, namely the C_5^1, the C_5^2, the C_5^3, and the C_5^4. The C_5^5 is the same as the identity. Because there are six C_5 axes, there are overall 6x4=24 C_5 symmetry operations (Fig. 2.2.45).

Symmetry elements: 6 C_5
Symmetry operations: 24 C_5
In detail: 6 C_5^1, 6 C_5^2, 6 C_5^3, 6 C_5^4 (C_5^5=E)

Figure 2.2.45 Symmetry operations associated with the C_5 axis of icosahedral point group

In addition, there are C_3 axes. One of them is shown below, and you can see that it passes through the centers of two opposite triangular faces (Fig. 2.2.46).



Figure 2.2.46 One of the C_3 axes of the icosahedral point group (Attribution: symotter.org/gallery)

As one rotates by 120° the atoms on the triangular faces change their position, and the resulting icosahedron superimposes the original one. As the name icosahedron says, there are twenty faces overall.

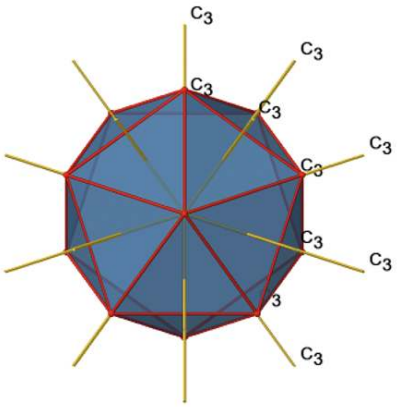


Figure 2.2.47 The C_3 axes of the icosahedral point group (Attribution: symotter.org/gallery)

Because one C_3 passes through two opposite axes, there are 20/2=10 C_3 axes overall (Fig. 2.2.47). Each C_3 axis is associated with two symmetry operations, namely C_3^1, and C_3^2. Thus, there are overall 10x2=20 C_3 symmetry operations.

Symmetry elements: 10 C_3
Symmetry operations: 20 C_3
In detail: 10 C_3^1, 10 C_3^2 (C_3^3=E)

Figure 2.2.48 Symmetry operations of the C_3 axes of the icosahedral point group

There are also C_2 axes (Fig. 2.2.49). They pass through the centers of two opposite edges of the icosahedron. Rotating around the C_2 axis shown makes the icosahedron superimpose.

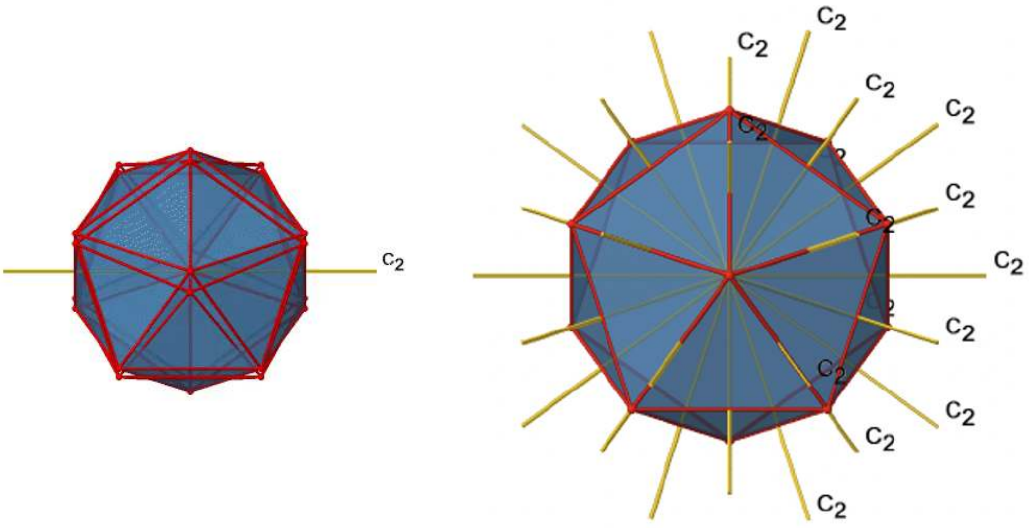


Figure 2.2.49 The C_2 axes of the icosahedral point group (Attribution: symotter.org/gallery)

An isosahedron has overall 30 edges. Because one C_2 axis passes through the centers of two opposite edges, we can understand that there are 30/2=15 C_2 axes. There is one unique C_2 operation per axis, and therefore there are 15 C_2 operations (Fig. 2.2.50).

Symmetry elements: 15 C_2
Symmetry operations: 15 C_2'
In detail: 15 C_2'^{1}

Figure 2.2.50 Symmetry operations associated with the C_2 axes of the icosahedral point group

We have now found all proper rotations. Let us look for mirror planes, next. You can see a mirror plane below (Fig. 2.2.51).

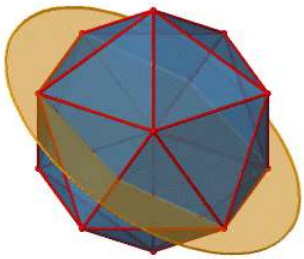


Figure 2.2.51 A mirror plane in the icosahedral point group (Attribution: symotter.org/gallery)

It contains two opposite edges. It also bisects two other edges. An icosahedron has overall 30 edges, therefore there are 30/2=15 mirror planes. You can see all of them below (Fig. 2.2.52 and Fig. 2.2.53)).

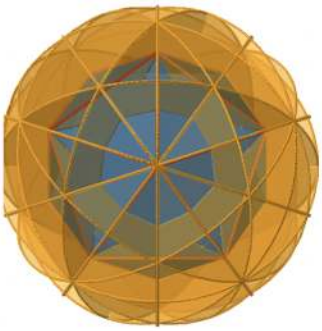


Figure 2.2.52 All the mirror planes in the icosahedral point group (Attribution: symotter.org/gallery)

Symmetry elements: 15 σ
Symmetry operations: 15 σ

Figure 2.2.53 Symmetry operations of the mirror planes in the icosahedral point group

The icosahedron also has an inversion center in the center of the icosahedron (Fig. 2.2.54 and Fig. 2.2.55)).



Figure 2.2.54 The inversion center in the icosahedron (Attribution: symotter.org/gallery)

As we carry out the associated, one symmetry operation, all points in the isosahedron move through the inversion center to the other side.

Symmetry elements: i
Symmetry operations: i

Figure 2.2.55 Symmetry operations of the inversion planes in the icosahedral point group

Let us now look for improper rotations. The improper rotational axes with the highest order are S_{10} axes. They are located in the same position as the C_5 axes, and go through two opposite corners (Fig. 2.2.56).

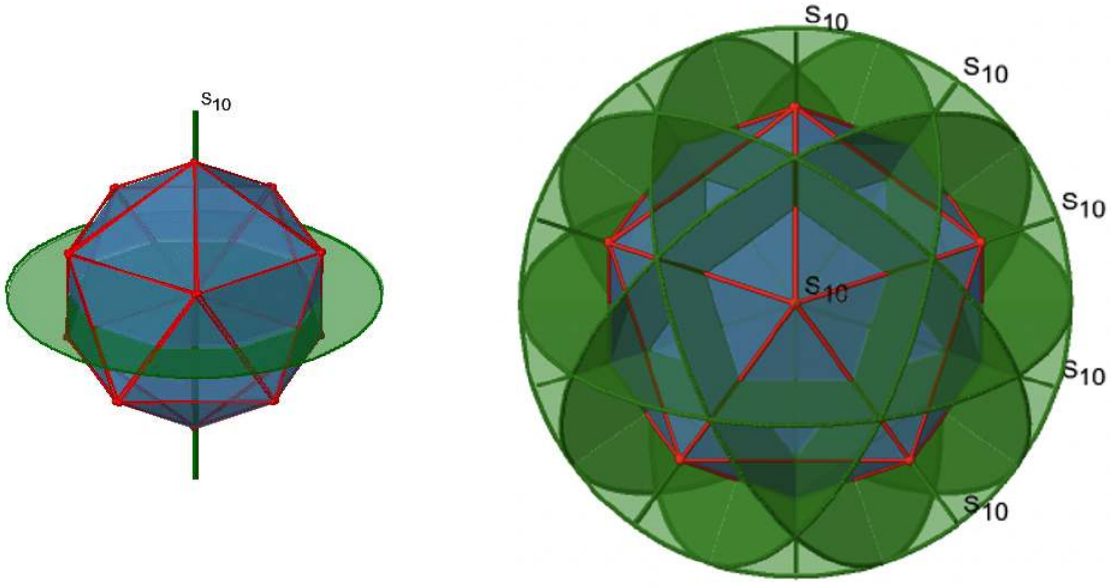


Figure 2.2.56 The S_{10} improper rotational axes in the icosahedral point group (Attribution: symotter.org/gallery)

The S_{10} exists because in an icosahedron there are pairs of co-planar pentagons that are oriented staggered relative to each other. The rotation around 36° brings one pentagon in eclipsed position relative to the other, but superposition is only achieved after the reflection at the mirror plane perpendicular to the rotational axis. Because one S_{10} passes through two opposite vertices, and there

are 12 vertices there are 6 S_{10} improper axes. For each axis there are four unique symmetry operations, the S_{10}^1, the S_{10}^3, the S_{10}^7, and the S_{10}^9. Therefore, there are overall 4x6=24 operations possible (Fig. 2.2.57).

Symmetry elements: 6 S_{10}
Symmetry operations: 24 S_{10}
In detail: 6 S_{10}^1, 6 S_{10}^3, 6 S_{10}^7, 6 S_{10}^9 ($S_{10}^2=C_5^1$, $S_{10}^4=C_5^2$, $S_{10}^5=i$, $S_{10}^6=C_5^3$, $S_{10}^8=C_5^4$)

Figure 2.2.57 Symmetry operations associated with the S_{10} improper rotational axes of the icosahedral point group

Are the lower order improper rotational axes? Yes, there are S_6 axes that pass through the centers of two opposite triangular faces (Fig. 2.2.58). This symmetry element exists because the two triangular faces are in staggered orientation to each other. Rotation alone brings one face in eclipsed orientation relative to the other, but reflection at a mirror plane perpendicular to the axis is required to achieve superposition. The S_6 axes are in the same location as the C_3 axes.

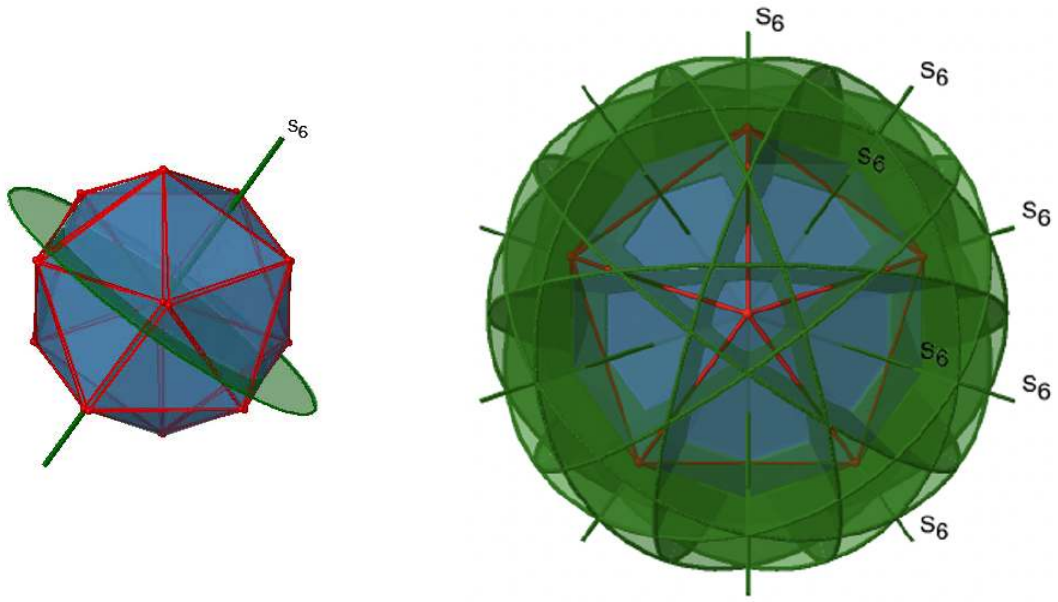


Figure 2.2.58 The S_6 rotation-reflections in the icosahedral point group (Attribution: symotter.org/gallery)

There are 10 S_6 axes because there are twenty faces and one axis passes through two opposite faces. Only the S_6^1 and the S_6^5 operations are unique S_6 operations, all others can be expressed by simpler operations. Therefore there are overall 10 S_6^1+10 S_6^5 = 20 S_6 operations (Fig. 2.2.59).

Symmetry elements: 10 S_6
Symmetry operations: 20 S_6
In detail: 10S_6^1, 10 S_6^5 ($S_6^2=C_3^1$, $S_6^3=i$, $S_6^4=C_3^2$)

Figure 2.2.59 Symmetry operations associated with the S_6 rotation-reflections in the icosahedral point group

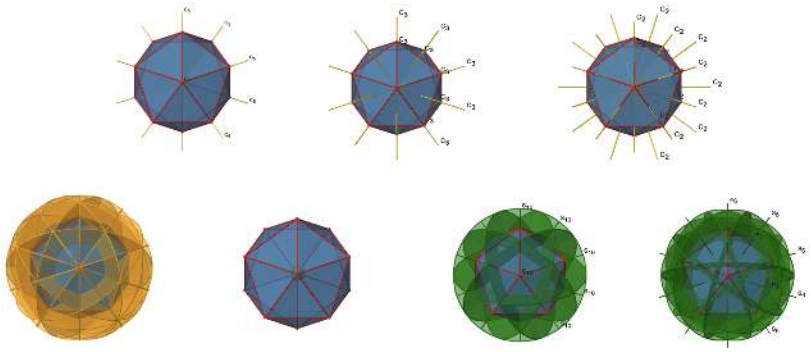


Figure 2.2.60 The symmetry elements of the icosahedral point group (Attribution: symotter.org/gallery)

We have now found all symmetry operations for the I_h symmetry. There are overall 120 operations making the point group I_h the point group with the highest symmetry (Fig. 2.2.60 and Fig. 2.2.61).

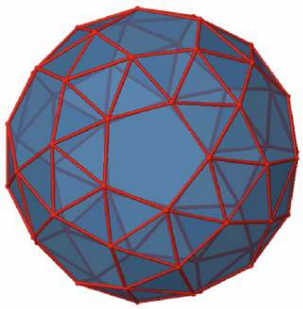
Symmetry elements: E, 6 C_5, 10 C_3, 15 C_2, 15 σ, i, 6 S_{10} , 10 S_6

Symmetry operations: E, 24 C_5, 20 C_3 , 30 C_2', 15 σ, i, 24 S_{10}, 20 S_6

In detail: E, 6 C_5^1, 6 C_5^2, 6 C_5^3, 6 C_5^4, 10 C_3^1, 10 C_3^2, 30 C_2'^{1}, 15 σ, i, 6 S_{10}^1, 6 S_{10}^3, 6 S_{10}^7, 6 S_{10}^9, 10S_6^1, 10 S_6^5

Figure 2.2.61 Summary of the symmetry operations of the icosahedral point group

Also the point group I_h has a rotational subgroup.



Snub-dodecahedron

Figure 2.2.62 The snub-dodecahedron belonging to the point group I (Attribution: symotter.org/gallery)

It is called I. An example of an object with this symmetry is the snub-dodecahedron (Fig. 2.2.62). It has the identity, and all the proper rotation operations of the point group O_h, but the inversion, the rotation-reflections, and the mirror planes are eliminated (Fig. 2.2.63).

Symmetry elements: E, 6 C_5, 10 C_3, 15 C_2, ~~15 σ, i, 6 S_{10} , 10 S_6~~

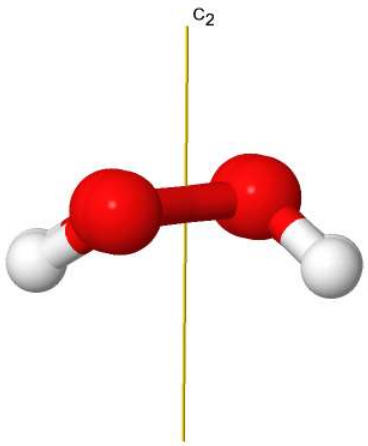
Symmetry operations: E, 24 C_5, 20 C_3 , 30 C_2', ~~15 σ, i, 24 S_{10}, 20 S_6~~

In detail: E, 6 C_5^1, 6 C_5^2, 6 C_5^3, 6 C_5^4, 10 C_3^1, 10 C_3^2, 30 C_2'^{1}, ~~15 σ, i, 6 S_{10}^1, 6 S_{10}^3, 6 S_{10}^7, 6 S_{10}^9, 10S_6^1, 10 S_6^5~~

Figure 2.2.63 Symmetry operations of the icosahedral rotational sub group I (relative to I_h)

Cyclic Point Groups

After having discussed high and low symmetry point groups, let us next look at cyclic point groups. They have the property that they have only a single proper n-fold rotational axis, but no other proper axes. In the most simple case they do not have any additional symmetry element such as mirror planes or rotation-reflections. These point groups are denoted C_n whereby n is the order of the proper axis. An example is the hydrogen peroxide molecule H_2O_2 (Fig. 2.2.64).



Point Group = C_2, Order = 2

Figure 2.2.64 The C_2 rotational axis of hydrogen peroxide

It has a so-called roof-structure due to its non-planarity. One hydrogen atom points toward us, and the other points away from us. This structure is due to the two electron-lone pairs at each sp^3-hybridized oxygen atom. These electron-lone pairs consume somewhat more space than the H atoms, and there is electrostatic repulsion between the electron lone pairs. Therefore, the electron lone pairs at the different oxygen atoms try to achieve the greatest distance from each other. This forces the H-atoms out of the plane, leading to the roof-structure of the hydrogen peroxide. Because the H_2O_2 molecule is not planar, it only has a single C_2 axis, but no other symmetry element besides the identity. The C_2 axis passes through the center of the O-O bond. Execution of the C_2 operation swaps up both the O and the H atoms.

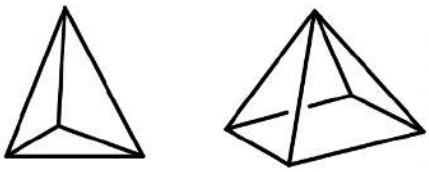
$$C_2 - H_2O_2 \text{ (elements: E, } C_2)$$

Figure 2.2.65 Symmetry elements in the hydrogen peroxide molecule

Definition: Cyclic Groups C_n

Cyclic groups have one rotational axiPyramidal Groups

Another class of groups are the pyramidal groups, denoted C_{nv}. They have n vertical mirror planes containing the principal axis C_n in addition to the principal axis C_n. Generally molecules belonging to pyramidal groups are derived from an n-gonal pyramid. An n-gonal pyramid has an n-gonal polygon as the basis which is capped (Fig. 2.2.66).



N-gonal pyramid

Figure 2.2.66 n-gonal pyramids (n=3,4)

For example a trigonal pyramid has a triangular basis which is capped, a tetragonal pyramid has a square which is capped, and so on. The proper axis associated with a specific pyramid has the order n and goes through the tip of the pyramid and the center of the polygon. An example of a molecule with a trigonal pyramidal shape is the NH_3 (Fig. 2.2.67).

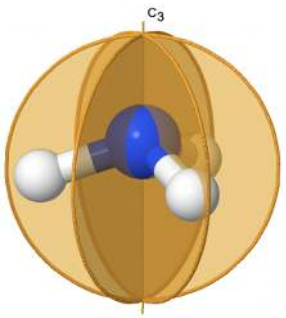


Figure 2.2.67 C_3 axis and vertical mirror planes in NH_3

The three H atoms form the triangular basis of the pyramid, which is capped by the N atom. The NH_3 molecule belongs to the point group C_{3v}. The C_3 axis goes though the N atom which is the tip of the pyramid, and the center of the triangle defined by the H atoms. There are three vertical mirror planes that contain the C_3 axis. Each of them goes through an N-H bond (Fig. 2.2.68).

$$C_{3v} - NH_3 \text{ (elements: E, } C_3, 3\sigma_v)$$

Figure 2.2.68 Symmetry elements in NH_3

Definition: Pyramidal Groups C_{nv}

Pyramidal groups have n vertical plane(s) in addition to the principal axis C_n.

The Linear Group $C_{\infty v}$

A special n-gonal polygon is the cone. A cone can be conceived as an n-gonal pyramid with an infinite number *n* of corners at the base (Fig. 2.2.69).

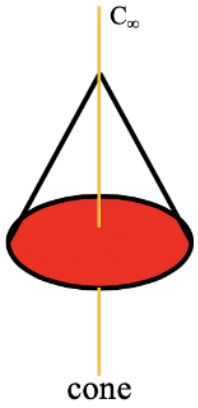


Figure 2.2.69 Cone having a proper rotational axis with infinite order.

In this case the order of the rotational axis that passes through the tip of the cone and the center of the circular basis is infinite. This also means that there is an infinite number of vertical mirror planes that contain the C_∞ axis (Fig. 2.2.71). The point group describing the symmetry of a cone is called the linear point group $C_{\infty v}$. Polar, linear molecules such as CO, HF, N_2O, and HCN belong to this point group. You can see the HCN molecule with its C_∞ axis and its infinite number of vertical mirror planes below (Fig. 2.2.70).

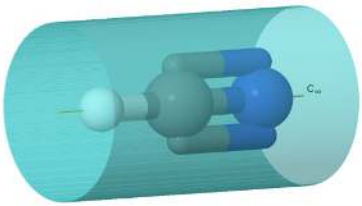


Figure 2.2.70 C_∞ axis of the HCN molecule

The infinite number of mirror planes, shown in blue are forming a cylinder that surround the molecule.

(**elements**: E, C_∞, $\infty\sigma_v$)

Figure 2.2.71 Symmetry elements of polar linear molecules

Definition: Linear group $C_{\infty v}$

The linear group $C_{\infty v}$ has an infinite number of vertical mirror planes containing a C_∞ axis

Reflection Groups

If we add a horizontal mirror plane instead of n vertical mirror planes to a proper rotational axis C_n we arrive at a the reflection point group type C_{nh}. The presence of the horizontal mirror planes also generates an improper axis of the order n. This is because when one can rotate and reflect perpendicular to the rotational axes independently, then it must also be possible to do it in combination. An example of a molecule belong to a reflection group is the trans-difluorodiazene N_2F_2 (Fig. 2.2.72).

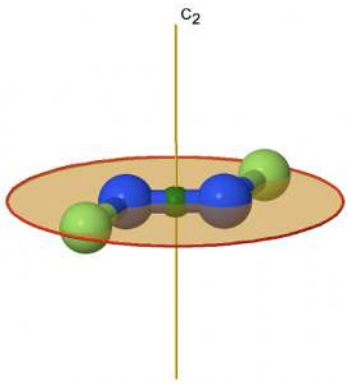


Figure 2.2.72 C_2 axis and horizontal mirror plane in trans-N_2F_2

It is a planar molecule with a C_2 axis going through the middle of the N-N double bond, and standing perpendicular to the plane of the molecule. The horizontal mirror plane stands perpendicular to the C_2 axis, and is within the plane of the molecule. There is an additional inversion center because an S_2 must exist which is the same as an inversion center. The inversion center is in the middle of the N-N bonds. Overall, the molecule has the symmetry C_{2h}.

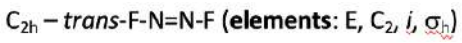


Figure 2.2.73 Symmetry elements in N_2F_2

Definition: Reflection Group C_{nh}

A reflection group has a horizontal plane perpendicular to the principal axis C_n

Dihedral Groups

Dihedral groups are point groups that have n additional C_2 axes that stand perpendicular to the principal axis of the order n. If there are no other symmetry elements, then the point group is of the type D_n.

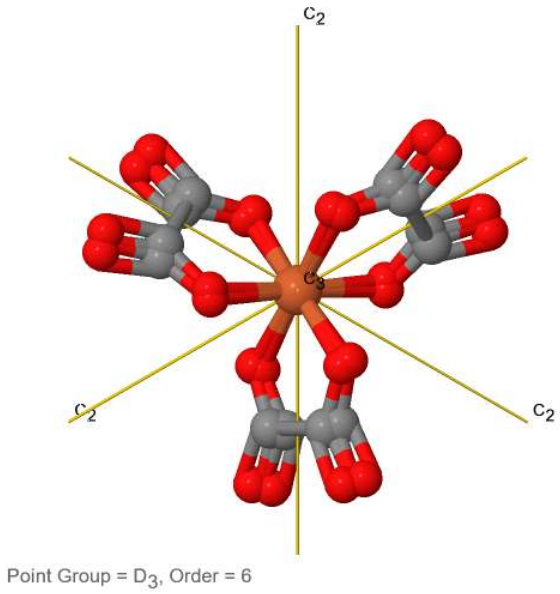


Figure 2.2.74 The tris-oxolato ferrate (3-) ion and its symmetry elements

For example in the point group D_3 there is a C_3 principal axis, and three additional C_2 axes, but no other symmetry element (Fig. 2.2.75). The tris-oxolato ferrate (3-) ion belongs to this point group (Fig. 2.2.75). You can see that the C_3 axis stands perpendicular to the paper plane, and there are three C_2 axes in the paper plane.

D_3 – (**elements**: E, C_3, $3C_2$)

Figure 2.2.75 Symmetry elements in the dihedral group D_3

Definition: Dihedral Groups D_n

In a point group of the type D_n there is a principal axis of order n, n C_2 axes, but no other symmetry elements.

If a horizontal mirror plane is added to the C_n axis and the n C_2 axes we arrive at the prismatic point groups D_{nh} (Fig. 2.2.76). The addition of the horizontal mirror plane generates further symmetry elements namely an S_n and n vertical mirror planes.

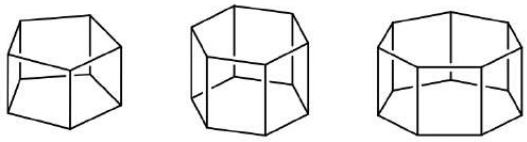


Figure 2.2.76 N-gonal prisms belong to the point group type D_{nh}

Generally, molecules belonging to this point group derive from n-gonal prisms. The order of the principal axis is the same as the number of corners of the polygons the prism are made of.

Definition: Prismatic Groups D_{nh}

In prismatic point groups there is a horizontal mirror plane perpendicular to the principal axis C_n. There are also n C_2 axes.

An example for a molecule belonging to a prismatic point group is PF_5 (Fig. 2.2.77).

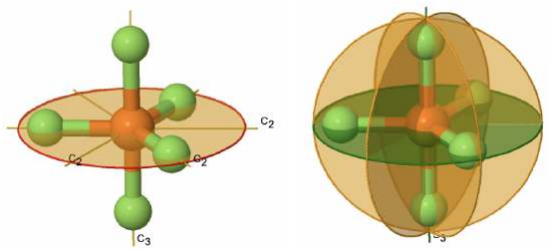


Figure 2.2.77 The PF_5 molecule belonging to the point group D_{3h} and its symmetry elements.

It has a trigonal bipyramidal shape. The C_3 axis goes through the axial F atoms of the molecule, and the three C_2 axes go through the three equatorial F atom. The horizontal mirror plane stands perpendicular to the principal C_3 axis and is located within the equatorial plane of the molecule. In addition, there are the vertical mirror planes that contain the C_3 axis, and go through the three equatorial P-F bonds. There is also an S_3 axis which superimposes the C_3 axis. In sum:

D_{3h} – PF_5 (**elements**: E, C_3, $3C_2$, σ_h, S_3, $3\sigma_v$)

Figure 2.2.78 Symmetry elements of PF_5

A special case of a D_{nh} group is the linear group $D_{\infty h}$. An object that has this symmetry is a cylinder. A cylinder can be conceived as a prism with an infinite number of vertices. Thus, the principal axis that passes through a cylinder has infinite order. Because of the infinite order of the principal axis, there is an infinite number of C_2 axes that stand perpendicular to the principal axis. You can see one such C_2 going though the cylinder (Fig. 2.2.79).

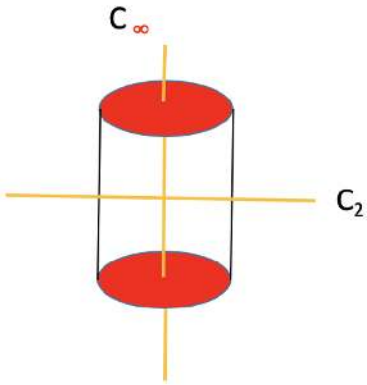


Figure 2.2.79 Cylinder as an example of linear group $D_{\infty h}$

There is now also an improper axis of infinite order, as well as an infinite number of vertical mirror planes. Non-polar linear molecules like H_2, CO_2, and acetylene C_2H_2 belong to the point group $D_{\infty h}$. You can see the C_∞ axis passing through a CO_2 molecule below (Fig. 2.2.80).

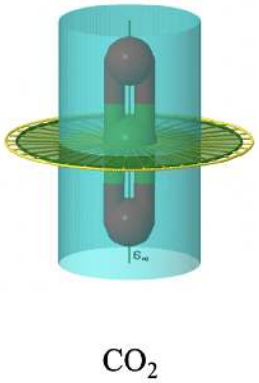


Figure 2.2.80 C_∞ in a CO_2 molecule

You can see the infinite number of vertical mirror planes as a blue cylinder. The infinite number of C_2 axes is shown a yellow lines going around the molecule. In sum:

$$E, C_\infty \infty C_2, \sigma_h, S_\infty, \infty \sigma_v, i$$

Figure 2.2.81 Symmetry elements of linear group $D_{\infty h}$

Definition: Linear Group D_{ooh}

In the point group $D_{\infty h}$ there is an infinite number of n C_2 axes in addition to the principal axis of infinite order, an infinite number of vertical mirror planes, and one horizontal mirror plane.

If we add n vertical mirror planes to the principal axis and the n C_2 axes, we arrive at the point group D_{nd}. The vertical mirror planes are dihedral mirror planes because they bisect the angle between the C_2 axes. An example is the ethane molecule in staggered conformation which has the symmetry D_{3d} (Fig. 2.2.82).

Figure 9.2.1: Paste Caption Here

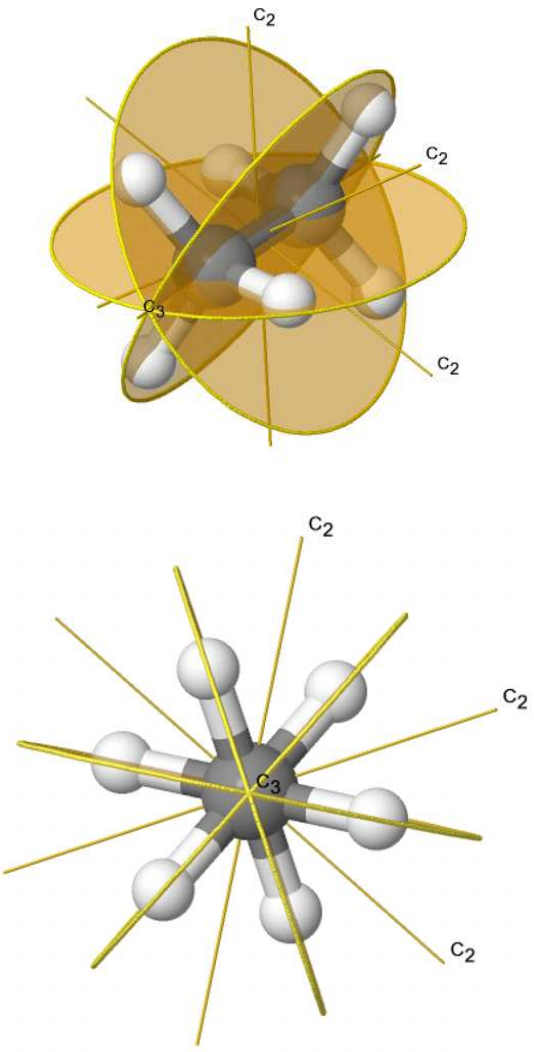


Figure 2.2.82 The ethane molecule in the staggered conformation belongs to the point group type D_{nd}

The C_3 axis goes along the C-C bond, and the $3C_2$ axes pass through the middle of the carbon-carbon bond, and bisect the angle between two hydrogens and one carbon atom. The three dihedral mirror planes pass through the C-H bonds. In addition, the ethane molecule has an S_6 axis, and an inversion center. In sum:

D_{3d} – ethane/staggered (elements: E, C_3, S_6, $3C_2$, 3 σ_d, i)

Figure 2.2.83 Symmetry elements in ethane

Definition: D_{nd}

In this point group type there are n dihedral mirror planes that contain the C_n and bisect the angle between adjacent C_2 axes

Improper Rotational Point Groups

The last class of point groups to be discussed are the improper rotation point groups. The only have one proper rotational axis, and an improper rotational axis that has twice the order of the proper rotational axis (Fig. 2.2.85). There may be an inversion center

present depending on the order of the proper and improper axes. An example the tetramethylcycloocta-tetraene molecule (Fig. 2.2.84).

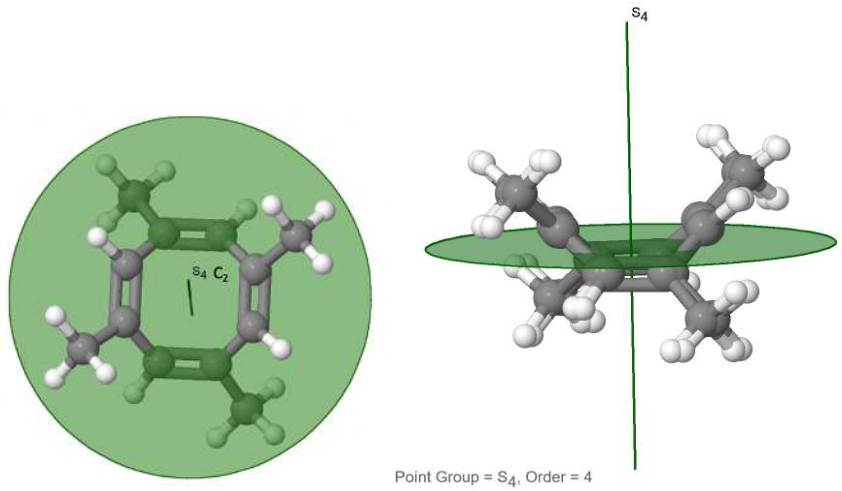


Figure 2.2.84 The S_4 and an C_2 axes of tetramethyl cycloocta-tetraene

It has an S_4 and an C_2 axis as the only symmetry elements besides the identity. Rotating by 90° alone does not superimpose the molecule because two C-C double bonds lie above the plane and two below the plane. In addition, two opposite methyl groups lie above and below the plane respectively. Therefore it needs the additional reflection to achieve superposition. There is also a C_2 axis which is in the same locations as the S_4 axis.

Symmetry elements: E, S_{2n}, C_n

May have inversion center *i*

Figure 2.2.85 Symmetry elements of improper rotational point groups

Guide for the Determination of Point Groups

With the knowledge you have, you can unambiguously identify the point group of a molecule. The key to success is that you are able to see the symmetry elements in the molecule. This takes practice. With enough practice you can identify the point group of a molecule immediately. Until, you can use guides, that you can follow to identify a point group. Such a guide asks systematic questions about the presence or absence of a symmetry element. Depending on whether you answer the question with yes or no you can follow the guide in a particular direction. Eventually, after having answered enough questions the guide will lead you to the respective point group. You can see such a chart below (Fig. 2.2.86).

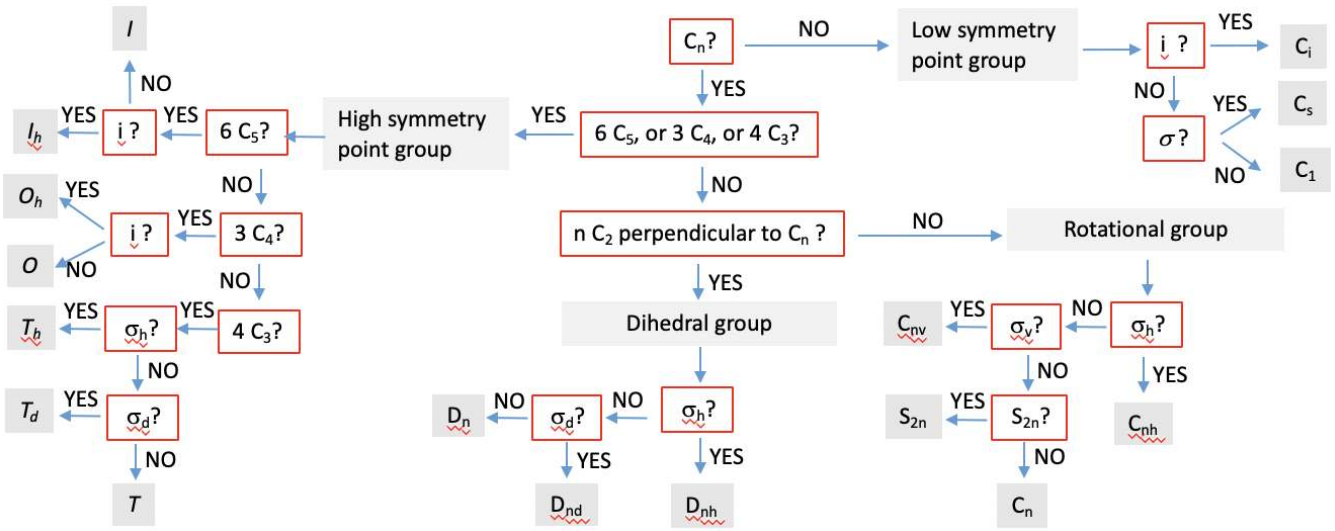


Figure 2.2.86 Guide for determination of point groups

You can first ask if there is at least one C_n present. If not, then the molecule must be in a low symmetry point group. If there is an inversion center, the point group is C_i. If not we can next ask, if there is a mirror plane. If yes it is C_s, and if not the point group is C_1. If a low symmetry point group can be ruled out, then we can ask next, if there is a high symmetry point group. This is the case when there are either $4C_3$, $3C_4$, or $6C_5$ rotational axes present, standing for tetrahedral, octahedral, and icosahedral symmetry, respectively. If there is an inversion center in case a C_5 is present, the point group is I_h. If not, it is I. Similarly, if there are $3C_4$ axes, and an inversion center, the point group must be O_h. If there is no inversion center the point group is O. If there are $4C_3$ axes, the point group must be T type. If there is a horizontal mirror plane in addition, then the point group must be T_h. If not, we can ask next is there are dihedral mirror planes. If yes, the point group is T_d, otherwise it is T. Now we have checked for all high symmetry point groups.

If a high-symmetry point groups can be ruled out, we ask if there are n C_2 axes in addition to the C_n principal axis. If this is so, then we must have a dihedral group of the D type. Next we ask, if there is a horizontal mirror plane. If yes, the point group must be D_{nh}. If not, we ask if there are dihedral mirror planes. If yes, the point group is D_{nd}. If there are no mirror planes at all, then the point group is D_n. If there are no n C_2 axes in addition to the C_n, the the group must be either a rotational group or an improper rotation group. We next ask, if there is a horizontal mirror plane. If yes, then the point group is of the type C_{nh}. If not, we ask if there are vertical mirror planes. If yes, then the point group is C_{nv}. If that is not the case, we ask if there is an S_{2n} in addition to the C_n. If yes, the point group is S_{2n}. If not, it is C_n.

Example: Dibromonaphtalene

Let us practice the point group guide by one example. Let us look at the dibromonaphtalene molecule (Fig. 2.2.87).

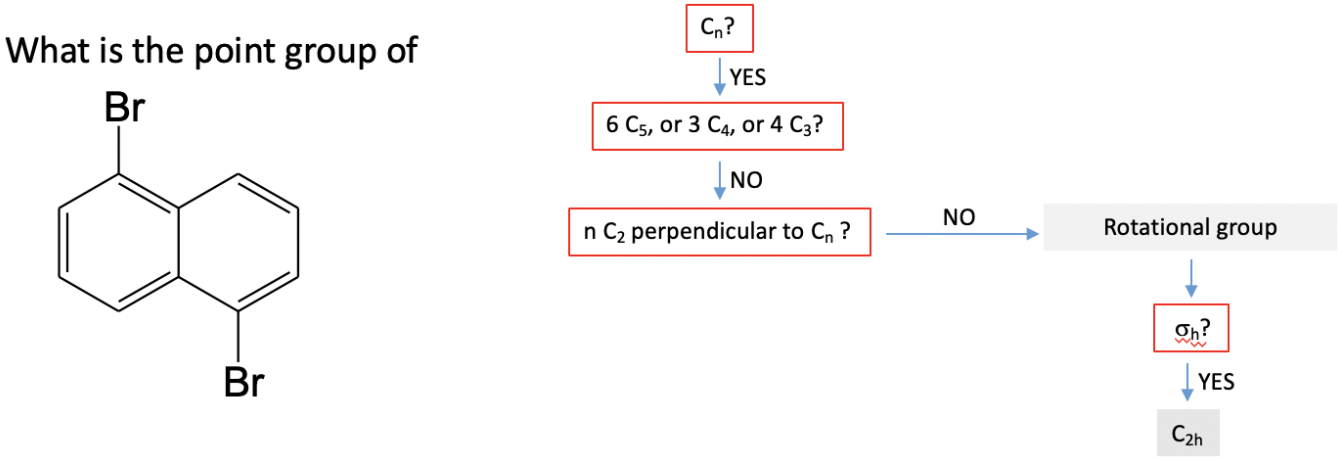


Figure 2.2.87 Guide for determining the point group of dibromonaphtalene

The first question we would ask is: Can you see at least one proper rotational axis? The answer is yes. There is a C_2 proper rotational axis that stands perpendicular to the plane of the molecule and goes through the center of the C-C bond that is shared by the two aromatic rings. Next we ask: Are the $6C_5$, $3C_4$ or $4C_3$ axes? That is clearly not the case, and thus we do not have a high symmetry point group. Next we can think about if the there are $2C_2$ axes in addition to the C_2 axes we already found. The answer is no, so the point group cannot be a dihedral group. Next, we would ask: Is there a horizontal mirror plane. This is indeed the case. There is a horizontal mirror plane in the plane of the molecule. It does not move any atoms around, but as we discussed before, a mirror does not need to do this to exist. This identifies the point group as C_{2h}.

Chiral Point Groups

A chiral point group is a point group that only has proper rotation operations in addition to the identity. This is equivalent to the statement that no improper rotations must exist in a chiral point group. This includes mirror planes and inversion centers because a mirror plane is the same as an S_1, and an inversion center is the same as an S_2. If a molecule belongs to a chiral point group, then it has a mirror image that cannot be superimposed with the original molecule. The two mirror images are called enantiomers. An example is the bromochlorofluoromethane. You can see two enantiomers separated by a dotted line (Fig. 2.2.88).

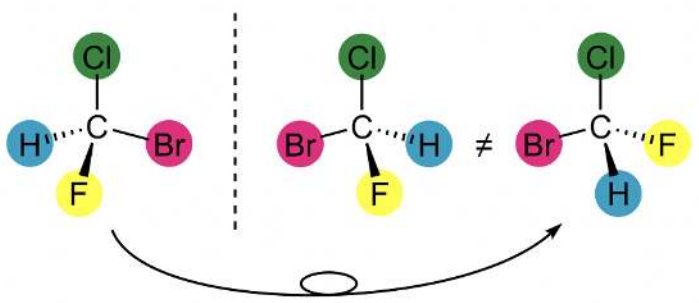


Figure 2.2.88 Chirality in bromochlorofluoromethane

The dotted line represents a mirror plane. Note that this mirror plane is not a mirror plane in the meaning of a symmetry element. You can see that the two molecules to the left and the right of the mirror plane are mirror images respective to each other. The molecules cannot be superimposed meaning that they are enantiomers. Note that the bromochlorofluoromethane molecule on the far right is not an enantiomer to the other two. It the same molecule as the enantiomer on the far left. We only need to rotate clockwise around the C-Cl axis to make the two molecules superimpose meaning that they are the same.

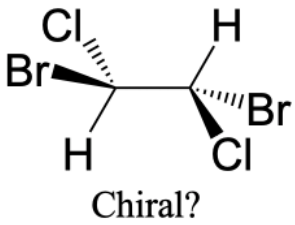


Figure 2.2.89 Dibromodichloroethane

It should be pointed out that the fact that a molecule has a carbon with four different substituents is not sufficient to make it a chiral molecule. The dibromodichloroethane molecule shown above (Fig. 2.2.89) has four different substituents around the carbon atom, but it is not chiral because there is an inversion center in the middle of the C-C bond.

Chiral High Symmetry Point Groups

Chiral groups not necessarily need to have low symmetry, in fact, the high symmetry rotational subgroups I, O, and T are chiral groups because they only have proper axes in addition to the identity (Fig. 2.2.90).

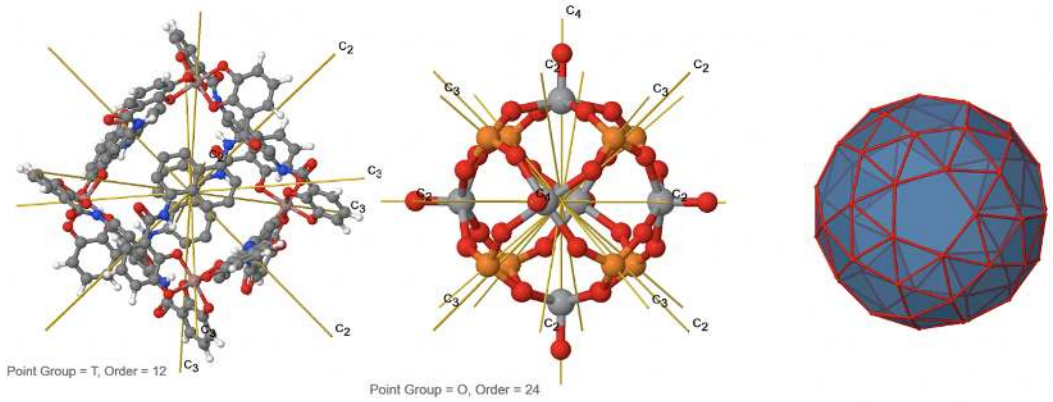


Figure 2.2.90 Objects belonging to chiral high symmetry point groups (T, O, and I from left to right).

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 9.2: Point Groups is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **2.2: Point Groups** by Kai Landskron is licensed CC BY 4.0.

9.3: Assigning Point Groups

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.

1. Determine if the molecule is of high or low symmetry.
2. If not, find the highest order rotation axis, C_n.
3. Determine if 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 if 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 if 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 if 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.

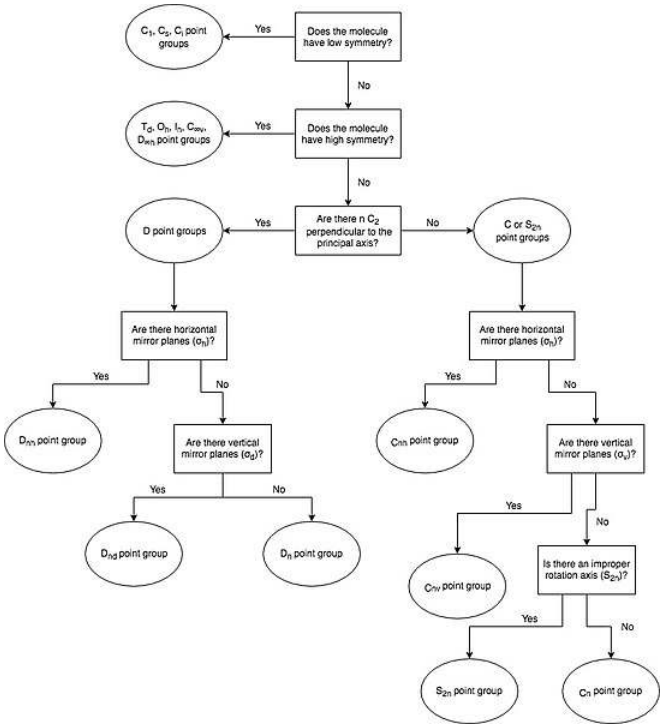


Figure 9.3.1 steps for determining a molecule's overall point group

Example 9.3.1

Find the point group of benzene (C_6H_6).

Solution

1. Highest order rotation axis: C_6

1. Highest order rotation axis: C_6
2. Benzene is neither high or low symmetry
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.

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	$B_{12}H_{12}^{2-}$

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

This page titled 9.3: Assigning Point Groups is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **1.2: Molecular Point Groups** by Wikipedia is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Advanced_Inorganic_Chemistry.

9.4: Character Tables

Matrix Representations of Symmetry Operations

Thus, far we have looked at symmetry operations qualitatively, and determined their nature by inspection. Now let us have a look how we can describe symmetry operations from a more mathematical point of view. Why do we do this? We do this to be able to understand so-called character tables which we will later need to apply symmetry to molecular orbital theory. Generally, symmetry operations can be described by matrices. When a matrix representing a symmetry operation is multiplied with coordinates of an object, then this gives the new coordinates of the object after the symmetry operation was carried out. Therefore let us briefly review matrices, and matrix multiplications in particular. A matrix is nothing but an array of numbers arranged into rows and columns. When we multiply to matrices, we must multiply each row with each column of the matrix. When the first matrix A_{ik} has i rows and k columns and the second matrix B_{kj} has k rows and j columns, then the product matrix C_{ij} has i rows and j columns. A requirement for a matrix multiplication is that the number of columns of the first matrix is the same as the number of the rows of the second column. Otherwise, one can just not multiply each row with each column of the two matrices.

A_{ik} = initial matrix with i rows and k columns
B_{kj} = initial matrix with k rows and j columns

↓

C_{ij} = product matrix with i rows and j columns

$$C_{ij} = \sum A_{ik} \times B_{kj}$$

Figure 2.3.1 Review on multiplying matrices

Let us do this by a few examples.

Example 1 of Matrix Multiplication

In the first example we multiply two 2x2 matrices, meaning that they both have two rows and two columns (Fig. 2.3.2). First, we need to check if the two matrices can be multiplied. We can see that the number columns of the first matrix is 2, and the number of rows of the second matrix is also 2. Therefore, we can multiply the two matrices.

$$\underset{\substack{i=2\\k=2}}{\begin{bmatrix}1 & 5\\ 2 & 6\end{bmatrix}} \times \underset{\substack{k=2\\j=2}}{\begin{bmatrix}7 & 3\\ 4 & 8\end{bmatrix}} = \begin{bmatrix}(1)(7)+(5)(4) & (1)(3)+(5)(8)\\ (2)(7)+(6)(4) & (2)(3)+(6)(8)\end{bmatrix} = \underset{\substack{i=2\\j=2}}{\begin{bmatrix}27 & 43\\ 38 & 54\end{bmatrix}}$$

Figure 2.3.2 Example 1 of matrix multiplication

The product matrix is expected to be also a 2x2 matrix. Now we need to multiply the first row of the first matrix with the first column of the second matrix, and that means that we to multiply 1x7 and 5x4. The sum of 1x7+5x4=27 gives us the first character of the first row of the product matrix. Next, we multiply the first row of the first matrix with the second column of the second matrix. So we have to multiply 1x3 and 5x8. The sum of the two products gives the second character of the first row of the product matrix. Because the second matrix has no additional column, there is no further column with which the first row of the first matrix could be multiplied. Therefore, we now go to the second row of the first matrix, and multiply it with the first column of the second matrix. This gives the products 2x7 and 6x4. When added together, then this gives 38, and this is now the first character of the second row of the product matrix. Lastly, we multiply the second row of the first matrix with the second row of the second matrix. This gives 2x3 and 6x8 which gives 54 when added together. This is the second character in the second row of the product matrix.

Example 2 of Matrix Multiplication

In the next example, we multiply a 1x3 matrix with a 3x3 matrix (Fig. 2.3.3). This is possible because the number of the columns of the second matrix is 3, and the number of rows of the second matrix is also 3.

$$\underset{\substack{i=1\\k=3}}{[1\ 2\ 3]} \times \underset{\substack{k=3\\j=3}}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} = \underset{\substack{i=1\\j=3}}{[1\ -2\ \ 3]}$$

$$(1)(1) + (2)(0) + (3)(0) \quad (1)(0) + (2)(-1) + (3)(0) \quad (1)(0) + (2)(0) + (3)(1)$$

Figure 2.3.3 Example 2 of matrix multiplication

The product matrix would be expected to have one row and three columns. The first matrix has only one row, so we multiply it with the three columns of the second matrix. Multiplying the first row of the first matrix with the first column of the second matrix gives (1)(1) + (2)(0) + (3)(0) = 1. This is the first character in the first, and only row in the product matrix. The multiplication of the first row of the first matrix with the second column of the second matrix is (1)(0) + (2)(-1) + (3)(0) = -2 which is the second character of the first row of the product matrix. The multiplication of the first row of the first matrix with the third column of the second matrix gives (1)(0) + (2)(0) + (3)(1) = 3. This is the third character of the first row of the product matrix. Overall, the product matrix is [1 -2 3].

Example 3 of Matrix Multiplication

In the last example let us multiply a 3x3 matrix with a 3x1 matrix (Fig. 2.3.4). Again, the number of the columns of the first matrix is the same as the number of the rows of the second matrix, they are both 3. Thus, we can multiply the two matrices.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 1 \\ -2 \\ 3 \end{bmatrix}$$

Figure 2.3.4 Example 3 of matrix multiplication

Multiplying the first row of the first matrix with the first, and in this case only column of the second matrix gives 1x1 + 0x2 + 0x3 = 1. This is the first and only character of the first row of the product matrix. The second matrix has only one column, therefore we multiply the second row of the first matrix with the only column of the second matrix in the next step. This gives 0x1 + (-1)x2 + 0x3 = -2. This the character of the second row of the product matrix. Lastly, we multiply the third row of the first matrix with the column of the second matrix. This gives 0x1 + 0x2 + 1x3 = 3. This is the character of the third row of the product matrix.

Applying Matrix Multiplications to Symmetry Operations

So what do symmetry operations have to do with the multiplication of matrices? The answer is that a symmetry operation can be described as a matrix, and the multiplication of this matrix with the matrix that represents the coordinates of the position of the points in an object, will give the new coordinates of the object after the symmetry operation has been carried out (Fig. 2.3.5).

[new coordinates] = [transformation matrix][old coordinates]

Figure 2.3.5 Relationships between symmetry operations and matrices

Example H_2O

A matrix that represents a symmetry operation is a 3x3 matrix and the matrix that describes coordinates is a 3x1 matrix. When two are multiplied then this gives a 3x1 matrix that describes the new coordinates of the object. For example, let us look at the water molecule H_2O.

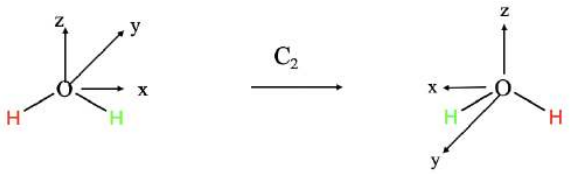


Figure 2.3.6 Transformation of coordinates in H_2O upon application of the C_2 symmetry operation

We can define a coordinate system in the water molecule so that the molecule is within the xz plane, whereby the z-axis is chosen so that it bisects the H-O-H bond angle. The y-axis would stand perpendicular and point into the board plane (Fig. 2.3.6). Any point within the water molecule, would have coordinates x,y,z that are defined by vectors $\vec{x}$, $\vec{y}$, $\vec{z}$ that point to these coordinates. For example, the center of a particular hydrogen atoms would have specific coordinates that would be described by three vectors that when added up, would point to the center of the hydrogen atom. Now let us think how the coordinates will change as we carry out a specific symmetry operations. For instance, take the C_2 symmetry operation that is carried out around the z-axis. How will the rotation change, the x,y, and z coordinates, respectively?

The x-coordinate is defined by a vector pointing into x-direction. As we rotate this vector 180° around the z-axis, it will retain its length but will point into the opposite direction (Fig. 2.3.6). Hence, we can say that the coordinate x has changed its algebraic sign, and is now –x. Now what about the y-coordinate? A vector pointing into y-direction will also be rotated around 180°, and point into the opposite direction. That means it is –y after the execution of the symmetry operation. Finally, how will the z-coordinate change? Because we rotate around z, there will not be any change to the z-vector, and thus the new coordinate z will be identical to the old coordinate z. If we represent the three vectors of the old coordinates by a 3x1 matrix $\vec{x}$, $\vec{y}$, $\vec{z}$, the new coordinates of the matrix $\vec{x}'$, $\vec{y}'$, $\vec{z}'$ are represented by the matrix $-\vec{x}$,$-\vec{y}$, $\vec{z}$. The matrix that when multiplied with the matrix for the old coordinates gives the matrix for the new coordinates, would be the matrix that would represent the symmetry operation C_2. In the case of the C_2 symmetry operation the matrix has the form below (Fig. 2.3.7).

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.7 C_2 symmetry operation for H_2O in matrix form

We can show that this matrix correctly represents the symmetry operation C_2 by applying the multiplication rules for matrices. Multiplying the first row of the matrix for C_2 with the only column of the matrix for the old coordinates would give $(-1 \times \vec{x}) + (0 \times \vec{y}) + (0 \times \vec{z}) = -\vec{x}$ for the first character of the product matrix. Multiplying the second row of the matrix representation of C_2 with the only column of the matrix for the old coordinates gives $(0 \times \vec{x}) + (-1 \times \vec{y}) + (0 \times \vec{z}) = -\vec{y}$ for the second character of the product matrix. Multiplication of the third row of the matrix for C_2 with the column of the matrix for the old coordinates gives $(0 \times \vec{x}) + (0 \times \vec{y}) + (1 \times \vec{z}) = \vec{z}$ This proves that the matrix correctly represents the symmetry operation C_2.

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} -\vec{x} \\ -\vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.8 The symmetry operation C_2 in matrix form transforming the coordinates in H_2O

We can develop the matrix representation for the σ(xz) reflection operation along the same line we did for the C_2 operation. Let us first think about how the vectors representing the coordinate changes as the reflection operation is carried out. The vectors $\vec{x}$ and $\vec{z}$ do not change because they are within the xz mirror plane. However, the $\vec{y}$vector changes its direction as it is reflected to the other side of the mirror plane. Thus, the y-coordinate changes its algebraic sign.

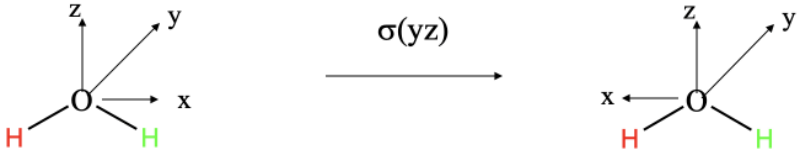


Figure 2.3.9 Transformation of coordinates of H_2O upon the application of the σ_{xz} symmetry operation

The matrix representing the new coordinates therefore has the form $\vec{x}$, - $\vec{y}$, $\vec{z}$. The matrix that when multiplied with the matrix of the old coordinates, gives the matrix of the new coordinates must be the matrix representing the symmetry operation σ_{xz}. It has the form below (Fig. 2.3.10).

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.10 σ_{xz} symmetry operation in H_2O in matrix form

We could again show using the multiplication rules for matrices that multiplication of this matrix with the matrix for the old coordinates gives the matrix for the new coordinates (Fig. 2.3.11).

$$\begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x} \\ -\vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.11 the symmetry operation for σ_{xz} in matrix form transforming the coordinates of H_2O.

We can apply the same process for the σ(yz) symmetry operation. The σ(yz) mirror plane contains the coordinates y and z, and thus their vectors do not change upon the application of the symmetry operation. However, the vector $\vec{x}$ changes its direction upon reflection at the yz plane, and thus the algebraic sign of the x-coordinate changes (Fig. 2.3.12).

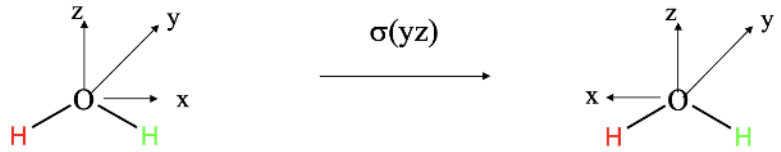


Figure 2.3.12 Transformation of the coordinates in H_2O upon the application of the σ_{yz} symmetry operation

The matrix for the new coordinates is thus -$\vec{x}$, $\vec{y}$, $\vec{z}$. In this case the matrix that when multiplied with the matrix of the old coordinates $\vec{x}$, $\vec{y}$, $\vec{z}$ gives the matrix with the new coordinates -$\vec{x}$, $\vec{y}$, $\vec{z}$ has the form below (Fig. 2.3.13).

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.13 σ_{yz} symmetry operation in H_2O in matrix form

We could again use the multiplication rules for matrices to show that the above matrix is the correct matrix representation of the symmetry operation σ(yz), Fig. 2.3.14.

$$\begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} -\vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.14 The multiplication of the σ_{yz} operation in matrix form with the coordinates of H_2O produces the new coordinates for H_2O

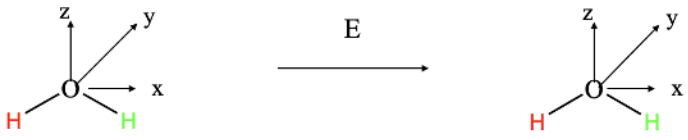


Figure 2.3.15 Transformation of the coordinates of H_2O by the E symmetry operation

Lastly, we can also determine the matrix representation of the identity operation (Fig. 2.3.15). It has the form below (Fig. 2.3.16).

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.16 E symmetry operation in H_2O in matrix form

Like previously, we could use the multiplication rules to show that this matrix produces the correct matrix for the new coordinates. Since the identity does nothing to an object (Fig. 2.3.15), the new coordinates are the same as the old coordinates (Fig. 2.3.17).

$$\begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.17 Multiplication of the symmetry operation E for H_2O with the coordinates of H_2O produces the correct, new coordinates for H_2O

Reducible and Irreducible Representations

Let us look closer at the four matrices that we just derived (Fig. 2.3.18).

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.18 The four matrices for the symmetry operations in the point group C_{2v}

It is noteworthy that all characters are zero, except those on a diagonal that goes from the top left corner in the matrix to the bottom right corner. This diagonal is called the trace of the matrix. With good justification we can say that the characters on the trace of the matrix tell us what the symmetry operation does with a coordinate. If it is a -1 the algebraic sign of the coordinate changes, if it is +1, it does not. If we write the characters of the trace of the matrices that belong to a specific coordinate on a line underneath the symmetry operations, we get what is called an irreducible representation for the specific coordinate (Fig. 2.3.19).

	E	C_2	σ_{yz}	σ_{xz}	"character"
x	1	-1	-1	1	irreducible representation
y	1	-1	1	-1	
z	1	1	1	1	
Γ	3	-1	1	1	Reducible Representation

Figure 2.3.19 The irreducible and reducible representations associates with the coordinates in H_2O

For example, for the x-coordinate the characters of the traces of the matrices for the symmetry operations E, C_2, σ_{yz}, σ_{xz}, are 1, -1, -1, and 1, respectively. For the y-coordinate the characters would be 1, -1, 1, and -1, and for the z- coordinate they are 1, 1, 1, and 1. The use of an irreducible representation is that it tells us directly in a concise form what the symmetry operations do to a specific coordinate. The sum of two or more irreducible representations is a so-called reducible representation. If we sum up the three irreducible representations of Fig. 2.3.19, then this gives a reducible representation with the characters 1+1+1=3, (-1)+(-1)+1=-1, (-1)+1+1=1, and 1+(-1)+1=1. We will see about the use of reducible representations in a little bit.

Symmetry Types of Irreducible Representations

The specific characters in an irreducible representation determine the symmetry type of the irreducible representation. It is denoted by a capital letter with subscripts and/or superscripts. For example the irreducible representation for the x-coordinate is of the type B_1 (Fig. 2.3.20)

	E	C_2	σ_v (xz)	σ_v' (yz)
B_1	1	-1	1	-1
B_2	1	-1	-1	1
A_1	1	1	1	1

Figure 2.3.20 Symmetry types of of the irreducible representations associated with the coordinates of H_2O

B means that the symmetry is anti-symmetric with regard to the principal axis (Fig. 2.3.21).

"B" means *anti-symmetric* with regard to rotation about the principle axis.

Figure 2.3.21 The definition of the B irreducible representation

Anti-symmetric means that the algebraic sign of the coordinate changes as we rotate. In this case the principal axis is the C_2 axis. We can see that the algebraic sign changes because the character of the irreducible representation for the x-coordinate underneath C_2 is -1. The subscript 1 means that the representation is symmetric to a C_2 perpendicular to the principal axis, or if lacking to a vertical σ_v (Figure 2.3.22)

Subscript 1 means the representation is *symmetric* to a C_2 perpendicular to the principal axis or, if lacking, to a vertical plane σ_v.

Figure 2.3.22 The definition of the subscript 1 in an irreducible representation

In this case, we do not have a C_2 perpendicular to the C_2 which is our principal axis, but we have two vertical mirror planes. Symmetric means that the coordinate does not change its algebraic sign as the symmetry operation is carried out. We can see that this is true for the reflection with the lower number of primes which comes first in our considerations. It is indicated by the character +1 underneath the symmetry operation.

The irreducible representation of the y-coordinate has the symmetry type B_2 (Fig.2.3.20) The symmetry type is again B, because the character underneath C_2 is -1. The subscript is 2 in this case, and this means that the representation is *antisymmetric* to a C_2 perpendicular to the principal axis or, if lacking to a vertical plane σ_v (Fig. 2.3.23)

Subscript 2 means the representation is *antisymmetric* to a C_2 perpendicular to the principal axis or, if lacking to a vertical plane σ_v.

Figure 2.3.23 The definition of the subscript 2 in the irreducible representation

We can see that the σ_v(xz) is anti-symmetric as indicated by the character -1 in the irreducible representation. Lastly, let us look at the symmetry type of the irreducible representation for the z-coordinate which is A_1 (Fig. 2.3.20) A means symmetric with regard to rotation around the principle axis (Fig. 2.3.24).

"A" means *symmetric* with regard to rotation about the principle axis.

Figure 2.3.24 The definition of the A irreducible representation

We can confirm the symmetric situation for the rotation around z by verifying that the character underneath the principal axis C_2 is +1.

Symmetry Types of Orbitals

Irreducible representations are more powerful than only telling you the symmetry type of a specific coordinate in a point group. More generally, they can tell the symmetry type of a mathematical function in a specific point group. Remember, that orbitals are mathematically wave functions. Thus, it should be possible to assign orbitals to a symmetry type within a given point group. Let us look for example, at the 2s and the 2p orbitals of the oxygen atom in the water molecule. Let us consider the 2s orbital first, and determine what the symmetry operations do with it. We can see that no symmetry operation changes the 2s orbital in any way, thus all characters of the irreducible representation that belongs to the orbital should be +1. We can see that this is only the case for the irreducible representation with the symmetry type A_1. Therefore we can say that the 2s orbital of the O-atom in the water molecule has the symmetry type A_1 (Fig. 2.3.25).

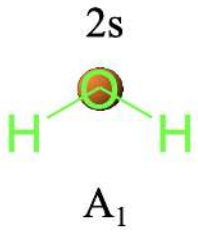


Figure 2.3.25 The 2s orbital of the O-atom in the water molecule has the symmetry type A_1

Next, let us determine the symmetry type of the $2p_z$ orbital. The $2p_z$ orbital is oriented along the z-axis around which we rotate. When carrying a C_2 operation we can see that this operation does not make any changes to the orbital. The same is true for the two reflection operations. Again, we can see that the symmetry operations do not change the $2p_z$ orbital in any way, and therefore it also must belong to the symmetry type A_1 (Fig. 2.3.26)

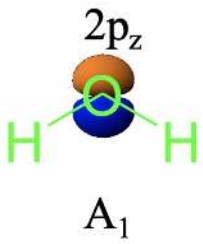


Figure 2.3.26 The $2p_z$ orbital of the O-atom in the water molecule has the symmetry type A_1

For the $2p_x$ orbital the situation is different though (Fig. 2.3.27). We can see that rotating around the C_2 axis changes the algebraic sign of the orbital. This means that the $2p_x$ orbital should belong to a symmetry type which has a character of -1 for the C_2 operation. We can see that this can be the B_1 or the B_2 symmetry type, but not A_1. This rules out the A_1 symmetry type. We still need to decide if the symmetry type is B_1 or B_2. For B_1 reflection at the $\sigma_v(xz)$ mirror plane would need to be symmetric, and for B_2 it would need to be anti-symmetric. We can see that the orbital does not change when we carry out the σ_v (xz) reflection, and thus the symmetry type must be B_1.

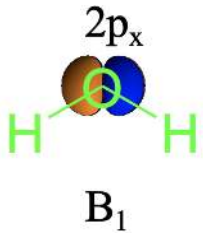


Figure 2.3.27 The $2p_x$ orbital of the O-atom in the water molecule having the symmetry type B_1

Lastly let us determine the symmetry type of the $2p_y$ orbital (Fig. 2.3.28). The $2p_y$ orbital is oriented perpendicular to the paper plane, the blue lobe points to the front, and the orange one, hardly visible points to the back. We can see that when we rotate around 180° the orange lobe points to the front, and the blue one points to the back. That means that the wave function of the orbital has changed its algebraic sign. Therefore, it must be of B symmetry type. Which one is it? B_1 or B_2? We can see that in this case the $\sigma_v(xz)$ does change the algebraic sign of the wave function because the front lobe of the orbital gets reflected to the back, and the lobe in the back gets reflected to the front. Thus, it is antisymmetric with respect to $\sigma_v(xz)$ and thus it must belong to the symmetry type B_2.

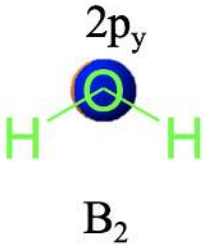


Figure 2.3.28 The $2p_y$ orbital of the O-atom in the water molecule having the symmetry type B_2

We could have determined the symmetry types of the orbitals also from a more mathematical perspective. Remember when we discussed the atomic orbitals we saw that the wave function of a p_z orbital is a linear function of the z-coordinate (Fig. 2.3.29). Therefore it has the same symmetry type as the z coordinate, namely A_1. A p_y orbital is a linear function of y, therefore it has the same symmetry type as the coordinate y: B_2. A p_x orbital is only a function of x, therefore its symmetry type is that of the coordinate x: B_1. The 2s orbital is not a function of any coordinate. Because of that it must belong to the symmetry type in which all characters are +1 which is the A_1 symmetry type in the point group C_{2v}.

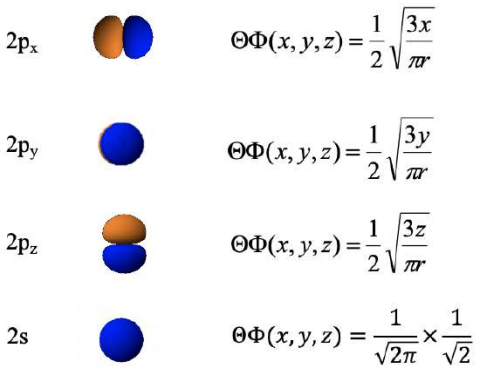


Figure 2.3.29 The angular wave functions of the 2s and 2p orbitals in cartesian coordinates.

By the same means we can also determine the symmetry type of the d orbitals of the O atom in H_2O. They are not occupied, and not involved in the bonding, but nonetheless they are possible states for the electrons. Let us determine them using the table below (Fig. 2.3.30)

			xz	yz
C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Figure 2.3.30 Character table for the point group C_{2v}

Does the $3d_{z^2}$ – orbital change when the symmetry operations are carried out (Fig. 2.3.31)? No, it does not! Therefore, it has the symmetry type A_1.

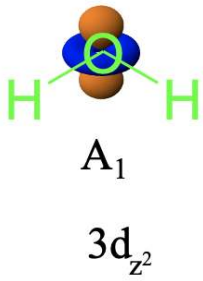


Figure 2.3.31 The $3d_{z^2}$ orbital of the O atom of the water molecule has the symmetry type A_1

What about the $3d_{xz}$? The $3d_{xz}$ orbital changes its algebraic sign when the C_2 operation is carried out, but not when the reflections are carried out. Therefore, it is of B_1 symmetry type (Fig. 2.3.32).

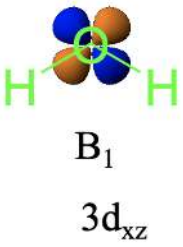
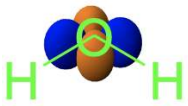


Figure 2.3.32 The $3d_{xz}$ orbital of the O atom of the water molecule has the symmetry type B_1

The $3d_{x^2-y^2}$-orbital also does not change when the symmetry operations are executed, thus it is of symmetry type A_1 (Fig. 2.3.33)

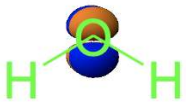


A_1

$3d_{x^2-y^2}$

Figure 2.3.33 The $3d_{x^2-y^2}$ orbital of the O atom of the water molecule has the symmetry type A_1

For the d_{yz} orbital rotation and the $\sigma_v(xz)$ reflection changes the algebraic sign, therefore it is B_2 (Fig. 2.3.24).

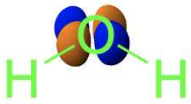


B_2

$3d_{yz}$

Figure 2.3.34 The $3d_{yz}$ orbital of the O atom of the water molecule has the symmetry type B_2

For the $3d_{xy}$ we can see that rotation does not change the orbital, but the $\sigma_v(xz)$ reflection does. This means that the symmetry type must be A_2 (Fig. 2.3.35).



A_2

$3d_{xy}$

Figure 2.3.35 The $3d_{xy}$ orbital of the O atom of the water molecule has the symmetry type A_2

This is a new symmetry type which also belongs to the point group C_{2v}. No single coordinate is of this symmetry type, but mathematical functions that are the product of the coordinates x and y, such as the $3d_{xy}$ orbital are. Similarly, because the $3d_{z^2}$ orbital is a function of z^2 and the $3d_{z^2}$ has the symmetry type A_1 any function of z^2 has this symmetry type. Analogously, any function which is the product of the x and the z coordinate belongs to the symmetry type B_1, any function which is a function of x^2-y^2 belongs to the symmetry type A_1, and any function which is a product of y and z belongs to the symmetry type B_2.

Character Tables

There is only a finite number of irreducible representations and symmetry types in a specific point group.

Generally, all the irreducible representations that are possible in a specific point group define the so-called *character table* of the point group Fig. 2.3.36).

Definition: Character Table

A complete set of irreducible representations in a point group defines its character table

Character tables describe what the symmetry operations of a point group do with a mathematical function. You can see the complete character table of the point group C_{2v} below (Fig. 2.3.36).

Symmetry operations that are conjugate are grouped in a class (column).

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Linear function	Square function
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

Figure 2.3.36 Character table for the point group C_{2v}

It is made of several rows and columns. In the first column you can find the point group symbol to the very left, and then the symbols for the different symmetry types of the irreducible representations the point group has. Then, there are several columns with symmetry operations in the first row, and the characters for the irreducible representations below. Each of these columns is called a class. Symmetry operations that are conjugate are grouped into the same column, or the same class. For the point group C_{2v}, each operation gets its own column and that means that they are all non-conjugate. But this is not always true, in many other point groups there are several symmetry operations that are conjugate, and listed in the same column. We have already discussed qualitatively that conjugate operations transform the coordinates of an object in a similar way. Now we have a more exact definition which is that whenever the characters for the operations in their irreducible representations are the same, they belong to the same class.

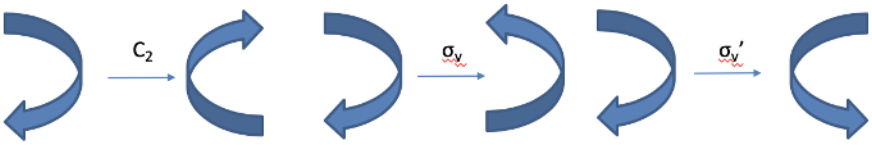


Figure 2.3.37 Transformation of a rotational vector rotating around z by the symmetry operations in the C_{2v} point group

The sum of characters underneath the identity operation E defines the dimension of the point group. For C_{2v} the dimension of the point group is 1+1+1+1=4. The order (h) of the point group is just the sum of all symmetry operations in the point group. For C_{2v} the order is 4. In the two far right columns of the character table you can find the mathematical functions that belong to the different irreducible representations. In the second column from the right linear and rotational functions are listed, and in the far right column square functions are listed. For example, the letter z is in the row associated with the symmetry type A_1. This means that any linear function of the z-coordinate has the symmetry type A_1. The letters x and y are in rows for the symmetry type B_1 and B_2 respectively. This means that any linear function of x and y has the symmetry type B_1 and B_2 respectively.

You can also see the symbols R_z, R_x, and R_y in the same column. These symbols stand for rotational functions around the z, x, and y axis respectively. R_z is in the row of the symmetry type A_2, which means that any rotational function of z has the symmetry type A_2. How can we understand that? Consider a rotational vector around z that indicates clockwise rotation (Fig. 2.3.37). If we rotate this vector by 180° counter-clockwise it will not change its direction, it will still point clock-wise, and thus the character underneath C_2 in the character table should be a 1. This rules out that the symmetry is B type, it must be either A_1 or A_2 type. We can further see that when we reflect this vector at the two vertical mirror planes, it reverses its direction, now pointing counter-clockwise. Therefore, the characters underneath the two mirror planes should be both -1. This means that the symmetry type must be A_2. If we did the same exercise with the R_x and the R_y rotational vectors we could show that they belong to the symmetry types B_2 and B_1 respectively. In the last column the square functions are listed. The row in which the function is located gives you the information about the symmetry type of the square function. For example any function of x^2, y^2, or z^2 has the symmetry type A_1, a function that is a product of x and y has the symmetry type A_2 and so forth.

Matrix Representations of Symmetry Operations in C_{3v}

Now let us go from the point group C_{2v} to the point group C_{3v} and determine the matrix representations of the symmetry operations. We will see that for this, and more generally for any point group with rotational axes with an order higher than 2, a symmetry degeneracy is possible, which means that two or even all three coordinates belong to the same symmetry type. The coordinates do not change independently upon the execution of a symmetry operation, they are linked to each other. Let us look at the ammonia molecule that belongs to the point group C_{3v}.

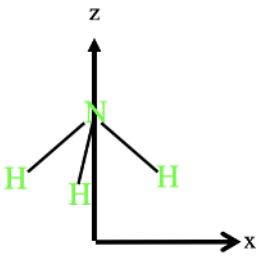
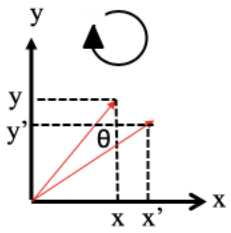


Figure 2.3.38 A suitable representation of the coordinate system in the ammonia molecule belonging to the C_{3v} point group

We can define the coordinate system so that the x-axis points to the right, the z-axis point to the to top , and the y-axis stands perpendicular to the paper plane (Fig. 2.3.38). The ammonia molecule is oriented so that its pyramid points into z-direction, and one of the three N-H bonds is within the xz plane.

Now let us see how the coordinates change when we rotate the molecule by an arbitrary general angle θ around the z-axis. In the diagram shown below, we now look along the z-axis, and the xy plane is within the paper plane (Fig. 2.3.39).



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

Figure 2.3.39 Transformation of x and y coordinates by rotation of the molecule of ammonia around an arbitrary angle θ

We can see that the rotation changes both the x and and the y coordinate together, but leaves the z-coordinate unaffected. According to trigonometry the new x-coordinate x' is x' = x cos θ - y sin θ. The new coordinate y' is y' = x sin θ + y cos θ.

The matrix representation of a symmetry operation that rotates around an arbitrary angle must be able to convert the old coordinates x,y,z into the new coordinates below (Fig. 2.3.40).

$$\begin{matrix} x\cos\theta - y\sin\theta \\ x\sin\theta + y\cos\theta \\ 1 \end{matrix}$$

Figure 2.3.40 The new coordinates (matrix form) of the NH_3 molecule after the rotation around an arbitrary angle θ

The matrix which is able to do this has the form below (Fig. 2.3.41)

$$\begin{matrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.41 Matrix representation for the rotation operation around an arbitrary angle θ

We could again use the multiplication rules for matrices to show that this matrix is the correct matrix.

The matrix that we just developed rotates around a general angle θ. What does this matrix look like in the point group C_{3v} where we rotate around 120° and 240°? Well, all we need to do is to insert the values of 120° and 240° for θ into the matrix. The sinus of 120° is -√3/2, and the sinus of 240° is √3/2. The cosinus of 120° and 240° are both -1/2 (Fig. 2.3.42).

$$\sin 120° = -\frac{\sqrt{3}}{2} \qquad \sin 240° = \frac{\sqrt{3}}{2} \qquad \text{(clockwise)}$$
$$\cos 120° = -\frac{1}{2} \qquad \cos 240° = -\frac{1}{2}$$

Figure 2.3.42 The values of sinus and cosinus for a 120° and 240° clockwise rotation

Note that these are the values for clockwise rotation. Because the C_3 operations rotate anti-clockwise, we must use the values for the 240° rotation for the C_3^1 and the values for the 120° rotation for the C_3^2 operation. Considering this, the matrix for the C_3^2 operation and the matrix for the C_3^1 operation are the matrices shown below (Fig. 2.3.43).

$$C_3^2 = \begin{matrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix} \qquad C_3^1 = \begin{matrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.43 The matrices for the C_3^2 operation and the C_3^1 operation

We can see there is a significant difference to the all the matrices we saw before. There are non-zero characters not only on the trace of the matrix, but also on other positions within the matrix, in particular in the first two rows which represent the x and the y coordinates. This is a consequence of the fact that the x and the y coordinates are no longer independent in C_{3v}, they change in a dependent way. We say that they are degenerate.

Now can we determine the remaining symmetry operations in C_{3v}. There are three conjugate vertical mirror planes to consider. The first mirror plane stands within the xz plane and passes through the N-H bond that is within the xz plane. The matrix for it is simple. It has the form below (Fig. 2.3.44).

$$1\text{st } \sigma_v' = \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.44 The matrix for the first mirror plane in the C_{3v} point group

It is straightforward to understand why the matrix has this form. Because the mirror plane is in the xz plane the coordinates x and z are not affected by the reflection at this plane. Therefore there are two +1 characters on the trace of the matrix in the rows for the x and the z coordinates, respectively, and all other characters in these rows are 0. The character in the second row on the trace of the matrix is -1 because the algebraic sign of the y-coordinate changes as we reflect at the xz plane. However, the other two mirror planes are not co-planar with any two coordinates, and for these planes the x and the y coordinates are dependent again. The matrix for the second mirror plane and the matrix for the third one are shown below (Fig. 2.3.45).

$$2\text{nd } \sigma_v' = \begin{matrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

$$3\text{rd } \sigma_v' = \begin{matrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.45 The matrices for the second mirror plane and the matrix for the third mirror plane in C_{3v}

We will not derive them in detail here. It is enough for us to understand here that these matrices have more complex forms with non-zero values outside the trace of the matrix because of the degeneracy of the x and y coordinates. Lastly, we should not forget the identity. Because the identity does nothing with an object, its matrix is always the matrix below in any point group (Fig. 2.3.46).

$$E = \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.46 The identity matrix for any point group

Because we know now the matrix representations of the symmetry operations we can understand the character table for the point group C_{3v} (Fig. 2.3.47)

C_{3v}	E	$2C_3$	$3\sigma_v$	Linear function	Square function
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y)	(x^2-y^2, xy) (xz, yz)

means “double degeneracy”

Figure 2.3.47 The character table for the point group C_{3v}

The character table has three classes for the three groups of non-conjugate symmetry operations. In the first class there is only the identity. You can see that the second class contains the C_3^1 and the C_3^2 operations, summarized as $2C_3$. The third class contains the 3 conjugate σ_v operations. In the point group C_{3v} there are three irreducible representations. The first two have the symmetry types A_1 and A_2 respectively, the third of is of type E. The last one is new to us. It stands for “double degeneracy”, and this symmetry type exists due to the double-degeneracy of the x and the y coordinate. You can see that the character table explicitly states that x and y are double-degenerate when you look into the last column of the character table. The letters x and y are in parentheses separated by a comma. The parentheses indicate the degeneracy of these two coordinates. More generally, any two functions that are linear functions of x or y are degenerate in C_{3v}. You can see that there are also other functions that are degenerate. For instance functions of x^2-y^2 and xy are degenerate. Also functions of xz and yz are degenerate.

You can see that the characters in the irreproducible representation of the E symmetry type are also unusual. Previously, we only encountered the characters 1 and -1. However, the character underneath the identity is 2, and the character in the class for the vertical mirror planes is 0. How can we understand these characters? The answer has to do with the double-degeneracy of the x and y coordinates. Because of this double-degeneracy, the characters in the irreducible representations are the sum of the characters on the trace of the matrices for the x and y coordinate. Let us check what they are. You can see the three matrices representing the three classes of the symmetry operations below (Fig. 2.3.48).

$$\begin{array}{c} \\ x \\ y \\ z \end{array} \quad \begin{array}{c} E \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array} \quad \begin{array}{c} 2C_3 \\ \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array} \quad \begin{array}{c} 3\sigma_v \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

Figure 2.3.48 The three matrices representing the three classes of symmetry operations

For the identity the sum of the two characters is 1+1=2 which explains the character 2 in the irreducible representation E. For the matrix representing the C_3 operations the characters on the trace of the matrix for x and y are -1/2. When summed up -1/2 + (-1/2) gives -1 which explains the character -1 in the irreducible representation. Lastly for the matrix representing the vertical mirror planes the characters on the trace of the matrix for the x and y coordinates are 1 and -1, respectively. -1+1=0 which explains the character 0 in the irreducible representation of the symmetry type E.

The z coordinate has the symmetry type A_1 which is straightforward to understand because the characters for z on the trace of the matrices for the three different classes of symmetry operations are all 1. You can also see from the character table that there is again an irreducible representation to which no coordinate belongs to. It is the one with the symmetry type A_2. In C_{3v} only rotational functions around z have that symmetry type.

Symmetry Types of Degenerate Irreducible Representations

There are not only double-degenerate irreducible representations, denoted by a symbol E, there can also be triply-degenerate ones, indicated by a symbol T. In this case all three coordinates x, y, and z are degenerate. Triple-degeneracy does not appear in the point group C_{3v}, but in other point groups, in particular the high-symmetry point groups (Fig. 2.3.49).

“E” indicates that the representation is doubly-degenerate.
“T” indicates that the representation is triply-degenerate (x,y,z are dependent).

Figure 2.3.49 The definition of "E" and "D" irreducible representations

Both the E and T symbols can carry subscripts and primes that have specific meanings. The prime (‘) and (“) double prime in the symmetry representation label indicates “symmetric” or “anti-symmetric” with respect to σ_h, e.g. E` or E``(Fig. 2.3.50).

The prime (‘) and (“) double prime in the symmetry representation label indicates
“symmetric” or “anti-symmetric” with respect to σ_h. E.g. E` or E``

Figure 2.3.50 The definition of prime (') and (") in irreducible representations

The subscripts g and u stand for the German words “gerade” and “ungerade” and a g and a u indicates “symmetric” or “anti-symmetric” with respect to inversion, *i*, respectively (Fig. 2.3.51).

The subscripts g (gerade) and u (ungerade) in the symmetry representation label
indicates “symmetric” or “anti-symmetric” with respect to inversion, *i*.
Example T_g or E_u

Figure 2.3.51 The definition of g (gerade) and u (ungerade) in irreducible representations

For example, there can be symmetry types like T_g or E_u. There are other subscripts possible, and we do not need to go through them exhaustively. It is enough to understand that they indicate a certain symmetry property in a symmetry type.

Character Tables and Degenerated Orbitals

One of the most useful properties of character tables are that one can identify degenerate orbitals very easily. For example, a quick look into the character table of the point group C_{3v} reveals that the $2p_x$ and the $2p_y$ orbital in NH_3 must be degenerate (Fig. 2.3.52).

C_{3v}	E	$2C_3$	$3\sigma_v$	Linear function	Square function
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y)	(x^2-y^2, xy) (xz, yz)

Degenerate orbitals are always grouped in parenthesis

Figure 2.3.52 Character table of the C_{3v} point group

This is because the $2p_x$ orbital is a linear function of x, and the $2p_y$ orbital is a linear function of y, and linear functions of x and y are listed in parentheses in the double-degenerate irreducible representation of the type E. This double-degeneracy could also be derived by inspecting the orbitals in the NH_3 molecule, but this is not as easy as looking up the character table. You can see the $2p_x$ and the $2p_y$ orbitals in the ammonia molecule below (Fig. 2.3.53).

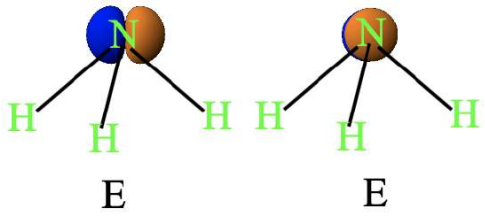


Figure 2.3.53 The $2p_x$ and $2p_y$ orbitals in ammonia

The two orbitals stand perpendicular to each other, but the NH_3 molecule has C_3 rotational symmetry. Therefore, why would the two orbitals be symmetry-degenerate? If they are degenerate, then there must be at least one symmetry operation that can interconvert the two orbitals. From the above depiction it not obvious what symmetry operation this could be.

Identifying the Double Degeneracy of $2p_x$ and $2p_y$ in NH_3

We can do a little trick to see that a reflection operation is the one that can interconvert the two orbitals. The trick is to rotate the coordinate system by 45°. You can see the ammonia molecule in the bird’s perspective below (Fig. 2.3.54).

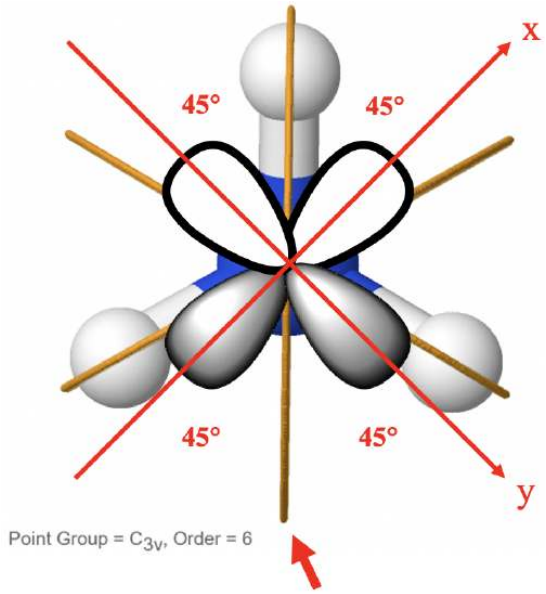


Figure 2.3.54 Ammonia in the bird's perspective with an arrow indicating the reflection plane that interconverts $2p_x$ and $2p_y$

This means that we look perpendicular to the base of the pyramid. You can see the NH_3 molecule with its three mirror planes above. Now we can choose our coordinate system so that the x and the y axes are rotated 45° with respect to one of the mirror planes. By definition, the $2p_x$ orbital must be oriented along the x-axis, and the $2p_y$ orbital must be oriented along the y-axis. You can see that one of the mirror planes, namely the one that oriented vertically, is able to interconvert the two orbitals. Upon reflection, the left and the right lobes of both orbitals will swap up their positions, so that after the symmetry operation is complete, the 2p orbitals are interconverted. Overall we can see that proving the degeneracy of two orbitals by inspection can be tricky. A quick look into the character table can tell us much more easily if two orbitals are degenerate.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 9.4: Character Tables is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **2.3: Matrix Representations of Symmetry Operations and Character Tables** by Kai Landskron is licensed CC BY 4.0.

9.5: Applications of Symmetry - Chirality

Introduction

Around the year 1847, the French scientist Louis Pasteur provided an explanation for the optical activity of tartaric acid salts. When he carried out a particular reaction, Pasteur observed that two types of crystals precipitated. Patiently and carefully using tweezers, Pasteur was able to separate the two types of crystals. Pasteur noticed that the types rotated plane-polarized light by the same amount but in different directions. These two compounds are called enantiomers.

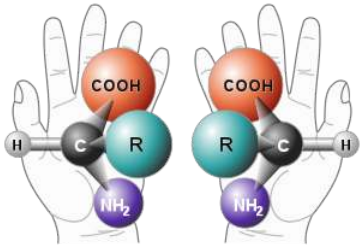


Figure 9.5.1: Two enantiomers of an amino acid (with side chain R).

What is chirality?

A molecule is **chiral** (or **dissymetric**) if it is non-superimposable on its mirror image. The two mirror images of a chiral molecule are called enantiomers. Enantiomers have the same physical properties (e.g., melting point, etc.). They differ in their ability to rotate plane polarized light and in their reactivity with other chiral molecules. Due to their ability to rotate plane polarized light, they are referred to as being *optically active*.

Using Symmetry to Determine Chirality

There are some general rules of thumb that help determine whether a molecule is chiral or achiral. The point group of the molecule, and the symmetry operations within that point group, can give clues as to whether the molecule is chiral.

Symmetry operations of chiral molecules

A chiral molecule cannot possess a plane of symmetry (σ), a center of inversion (i), or an improper rotation (S_n). Due to the fact that all groups that lack both σ and i also lack S_n, **a molecule that belongs to any group that lacks S_n is chiral**.

An example of an inorganic coordination complex is tris(ethylenediamine)cobalt(III) (Figure 9.5.1). Figure 9.5.1 shows the two enantiomers of tris(ethylenediamine)cobalt(III): the Δ and Λ isomers.

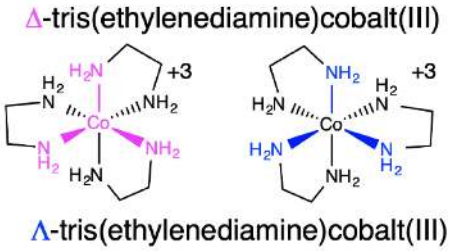


Figure 9.5.2: Two chiral enantiomers of tris(ethylenediamine)coalt(III).

You can visualize the Λ and Δ isomers by imagining that the ligands around the metal centers are blades of a fan. To push the air toward you, you would need to rotate the Δ isomer clockwise, and the Λ isomer counter-clockwise.

Exercise 9.5.1

Which point groups are possible for chiral molecules?

Answer

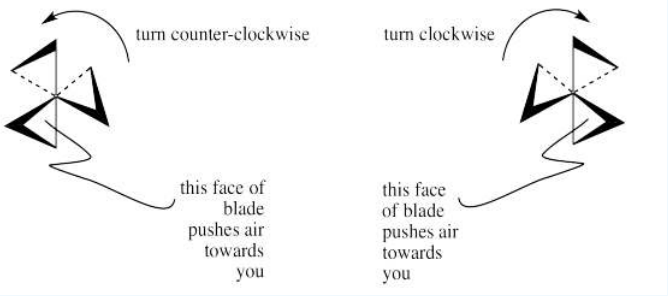


Figure 9.5.3: Another way of thinking about the chirality of the two chiral enantiomers of tris(ethylenediamine)coalt(III) shown in Figure 9.5.2. This figure was taken from Structure and Reactivity in Organic, Biological, and Inorganic Chemistry.

As a result of the previous discussion, there are a few classes of point groups that lack an improper axis. Those classes are C_1, C_n, and D_n.

This page titled 9.5: Applications of Symmetry - Chirality is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **4.4.1: Chirality** by Kathryn Haas is licensed CC BY-NC 4.0.

CHAPTER OVERVIEW

10: Molecular Orbital Theory

10.1: Molecular Orbitals

10.1.1: s-Orbital MOs

10.1.2: p-Orbital MOs

10.1.3: d-Orbital MOs

10.2: Non-bonding Orbitals

10.3: Molecular Orbital Diagrams

10.4: Orbital Mixing

10.5: Diatomic Molecules

10.6: Polar Diatomic Molecules

10.7: Polyatomic Molecules

10.7.1: Bifluoride anion

10.7.2: Carbon Dioxide

10.7.3: H_2O

10.7.4: NH_3

10.7.5: CO_2 (Revisted with Projection Operators)

10.7.6: BF_3

This page titled 10: Molecular Orbital Theory is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

10.1: Molecular Orbitals

Molecular orbital theory extends from quantum theory and the atomic orbital wavefunctions (ψ) described by the Schrödinger equation. While the Schrödinger equation defines a Ψ for electrons in individual atoms, we can approximate the molecular wavefunction (what Ψ would look like if we combined the ψ of individual atoms). The addition or subtraction of wavefunctions is termed **linear combination of atomic orbitals** (LCAO). Molecular orbital theory is applied to LCAO to describe bonding.

The LCAO for the wavefunction of two atoms (ψ_a and ψ_b) is represented by the general expression below. The coefficients c_a and c_b quantify the contribution of each atomic ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

For two atomic ψs to form a bond, three conditions must be satisfied:

- First, the **distance between the atoms** must be small enough to provide good overlap. This is because the two orbitals must be able to overlap using regions of ψ^2 where the probability of finding electrons is significant. If atoms are not close enough, ψ_a and ψ_b cannot interact productively. At the same time, the atoms must be far enough apart that their nuclei do not repel each other.
- The **symmetry of the orbitals** must be compatible such that regions of ψ_a and ψ_b with the same sign constructively interfere more than regions with opposite sign destructively interfere. In other words, for a productive interaction, there must be a relatively high probability of finding an electron between the two nuclei, and this depends on the symmetry (and sign of the ψ) of the atomic orbitals.
- Third, the **energies of the atomic orbitals** must be similar. Orbitals with similar energy combine to make the most stable bonding molecular orbitals. Atomic orbitals with very different energies form less stable bonding interactions, and the larger the difference in the atomic orbitals, the weaker the bonding interaction will be.

Atomic orbitals combine to form molecular orbitals when these three conditions are met. The result is a set of bonding molecular orbitals that are lower in energy than the original atomic orbital energies.

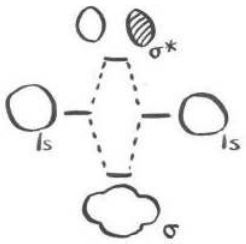
This page titled 10.1: Molecular Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.1: Formation of Molecular Orbitals from Atomic Orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

10.1.1: s-Orbital MOs

In the case of the hydrogen molecule, we took two atomic orbitals and combined them to form two molecular orbitals. These new molecular orbitals had different wavelengths than the two atomic orbitals: one had a longer wavelength and was a little lower in energy, while the other had a shorter wavelength and was a little higher in energy. If we take into account the energy of the two original atomic wavefunctions, and compare them to the total energy of the two new molecular wavefunctions, there is no change overall.

We started with two atomic orbitals, and by combining them we produced two molecular orbitals. Both of these ideas are useful in considering the formation of more complex molecules from individual atoms.

- - The average energy of the orbitals has remained almost constant.
  - Also, the number of wavefunctions has remained constant.
  - 

Of course, from the point of view of the two real electrons, some remarkable changes have occurred. Both of these electrons have adopted a longer wavelength and a lower energy and that has made all the difference. There is an occupied molecular orbital and an unoccupied molecular orbital; only the occupied orbital makes a real energetic contribution to the overall stability of the molecule. The unoccupied orbital is completely imaginary.

A bonding picture of He_2 would look exactly the same, because it would also involve the overlap of 1s electrons on one atom with 1s electrons on the other atom. There would be a different electronic energy, however. That difference would affect the prospects of helium-helium bond formation.

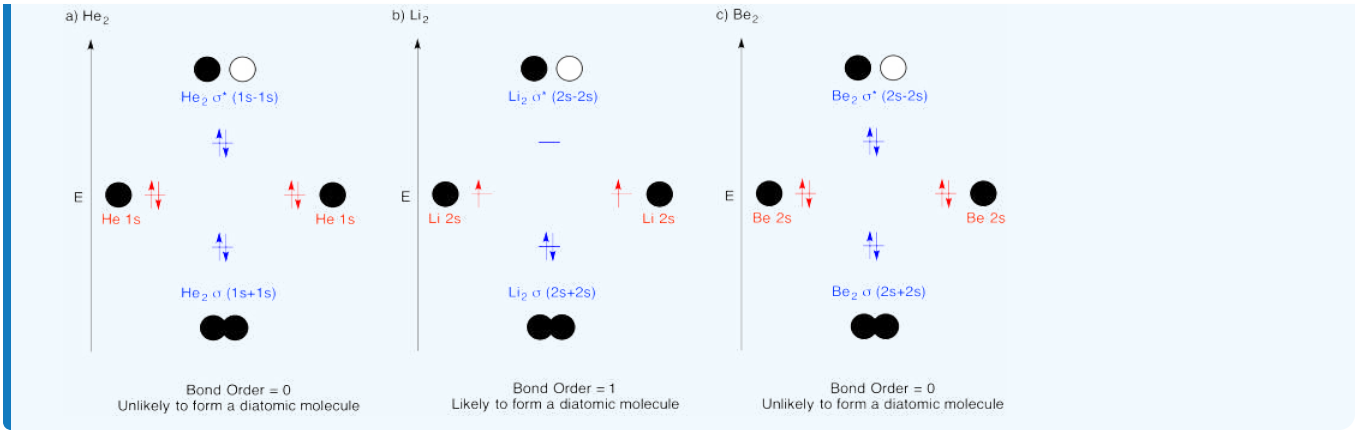
- The electrons have lower kinetic energy in the bond than they had before bonding.
- Electronic energy has decreased. A stable bond has formed.

? Exercise 10.1.1.1

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

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

Answer



This page titled 10.1.1: s-Orbital MOs is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Chris Schaller & Kathryn Haas.

10.1.2: p-Orbital MOs

Bonding with P-orbitals

Sigma bonding with p-orbitals

Other diatomic molecules in the upper right corner of the periodic table can be constructed in a similar way. Look at dinitrogen, N_2.

We can think about how dinitrogen would form if two nitrogen atoms were placed close enough together to share electrons. Nitrogen has more electrons than hydrogen, so this interaction is more complicated.

In our qualitative examination of bonding in main group diatomics, we will take the approach used in Lewis structures and just look at the valence electrons. A quantitative molecular orbital calculation with a computer would not take this shortcut, but would include all of the electrons in the atoms that are bonding together.

Nitrogen has five valence electrons, and these electrons are found in the 2s and 2p levels. There are three possible atomic orbitals in the 2p level where some of these electrons could be found: p_x, p_y and p_z. We need to look at the interaction between the s and p_x, p_y and p_z orbitals on one nitrogen atom with the s and p_x, p_y and p_z orbitals on the other nitrogen. That process could be extremely complicated, but:

- Orbital interactions are governed by symmetry.

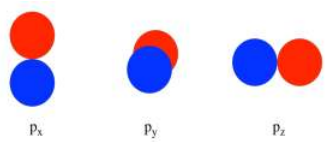
Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

- s orbitals interact with s orbitals. We can already see how that will work out in dinitrogen, because that is what happened in dihydrogen.
- p_x orbitals interact with p_x orbitals.
- p_y orbitals interact with p_y orbitals.
- p_z orbitals interact with p_z orbitals.

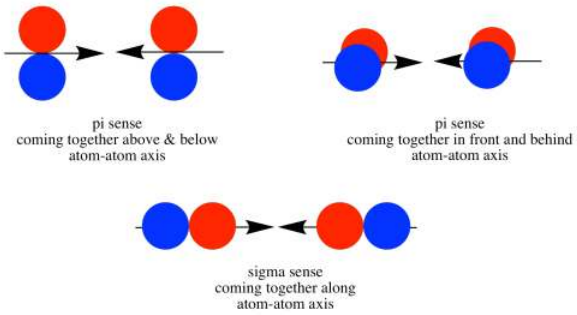
Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go lower in energy than the combinations from s orbitals? We will **simplify** and **assume** that the s and p levels remain completely separate from each other. This is not always true, but the situation varies depending on what atoms we are dealing with.

- The combination of one s orbital with another is just like in hydrogen. Two original orbitals will combine and rearrange to produce two new orbitals.
- There is a bonding combination in which the orbitals are in phase. The new orbital produced has a longer wavelength than the original orbital. It is lower in energy.
- There is an antibonding combination in which the orbitals are out of phase. The new orbital produced has a shorter wavelength than the original orbital. It is higher in energy.

In considering the interaction of two p orbitals, we have to keep in mind that p orbitals are directional. A p orbital lies along a particular axis: x, y or z. The three p orbitals on nitrogen are all mutually perpendicular (or orthogonal) to each other. That situation is in contrast to s orbitals, which are spherical and thus look the same from any direction.

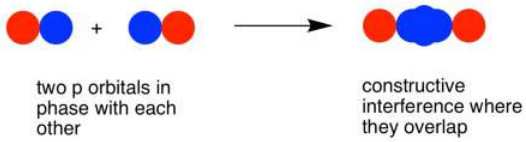


We first need to define one axis as lying along the N-N bond. It does not really matter which one. We arbitrarily say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas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

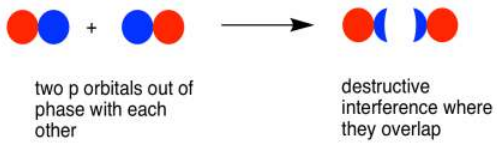


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

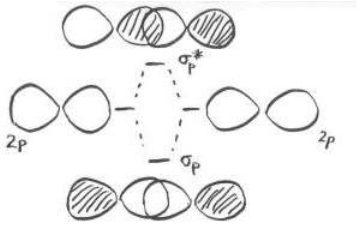
As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, so that one orbital is the mirror image of the other.) This combination is at a longer wavelength than the original orbital. It is a lower energy combination.



The out-of-phase combination (meaning in this case that the overlapping lobes are out-of-phase) results in destructive interference. This combination is at shorter wavelength than the original orbital. It is a higher energy combination.



As a result, we have two different combinations stemming from two different p orbitals coming together in two different ways. We get a low-energy, in-phase, bonding combination and a high-energy, out-of-phase, antibonding combination.

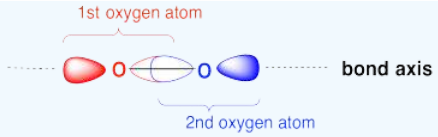


What about those other p orbitals, the ones that do not lie along the bond axis? We'll take a look at that problem on the next page.

? Exercise 10.1.2.2

Draw an MO cartoon of a sigma bonding orbital formed by the overlap of two p orbitals between two oxygen atoms. Label the positions of the oxygen nuclei with the symbol "O". Label the O-O bond axis.

Answer



Exercise 10.1.2.3

Chemical reactions can be described by MO diagrams too! Consider the following reaction in which a new sigma bond is formed.



Draw an MO diagram for the reaction above. In other words, start from the one frontier MO on each reactant to build the MO's of the new sigma bond in the product.

o Draw the orbital from the base (hydroxide) that is likely to donate its electrons.

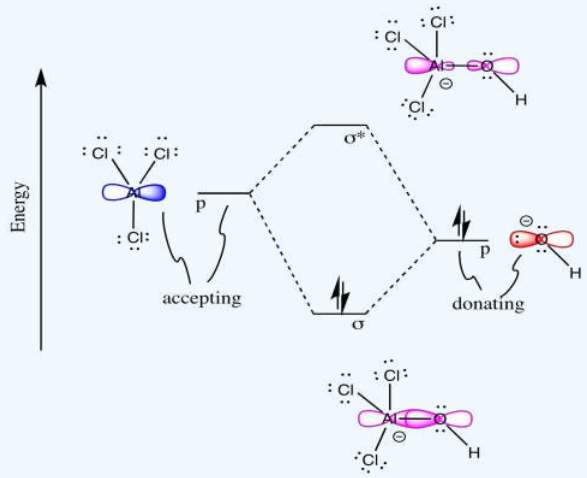
o Draw the orbital from the acid (aluminum chloride) that is likely to accept electrons.

o Complete the MO mixing diagram of these two orbitals:

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

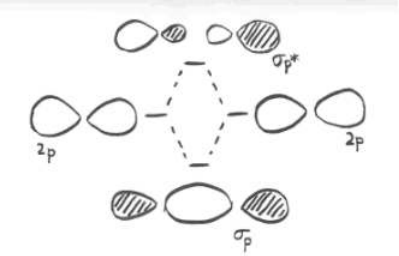
o Draw a cartoon showing each reactant and product MO that contributes to the bonding interaction.

Answer



Pi-bonding with p-orbitals

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



Parallel, but not collinear, p orbitals can also interact with each other. They would approach each other side by side, above and below the bond axis between the two atoms. They can be close enough to each other to overlap, although they do not overlap as strongly as orbitals lying along the bond axis. They can make an in-phase combination, as shown below.

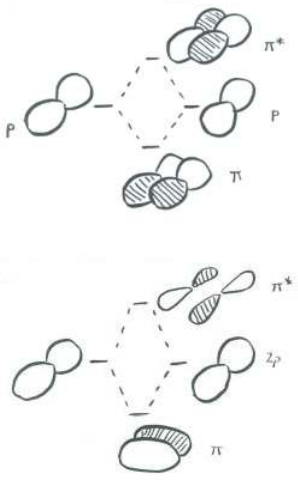


They could also make an out-of-phase combination, as shown below.



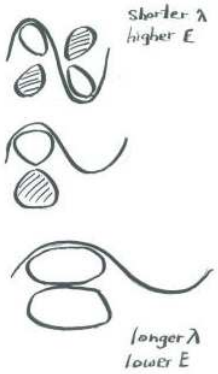
- parallel p orbitals can overlap to produce bonding and antibonding combinations.
- the resulting orbitals contain nodes along the bond axis.
- the electron density is found above and below the bond axis.
- this is called a p (pi) bond.

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

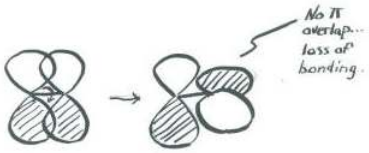


In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

Just as the sigma-bonding orbitals display progressively shorter wavelengths along the bonding axis as they go to higher energy, so do the pi bonding orbitals. In other words, there are more nodes in the higher-energy orbitals than in the lower-energy ones.



An important consequence of the spatial distribution or "shape" of a p orbital is that it is not symmetric with respect to the bond axis. An s orbital is not affected when the atom at one end of the bond is rotated with respect to the other. A p orbital is affected by such a rotation. If one atom turns with respect to the other, the p orbital would have to stretch to maintain the connection. The orbitals would not be able to overlap, so the connection between the atoms would be lost.



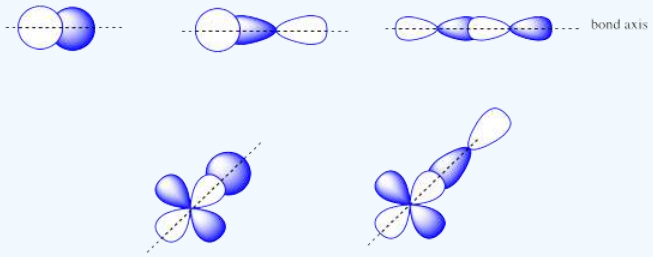
? Exercise 10.1.2.4

The combinations of _____ atomic orbitals leads to σ orbitals.

Draw pictures.

Answer

The combinations of ***s*** + ***s*** OR ***s*** + ***p*** OR ***p*** + ***p*** OR ***s*** + ***d*** OR ***p*** + ***d*** atomic orbitals can lead to σ orbitals.



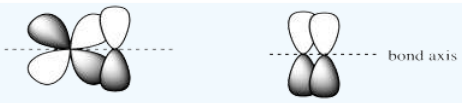
? Exercise 10.1.2.5

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer

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



Exercise 10.1.2.6

Which molecular orbital is typically the highest in energy?

a. p
b. σ
c. π*
d. π
e. σ*

Answer

e) σ*

Exercise 10.1.2.7

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

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

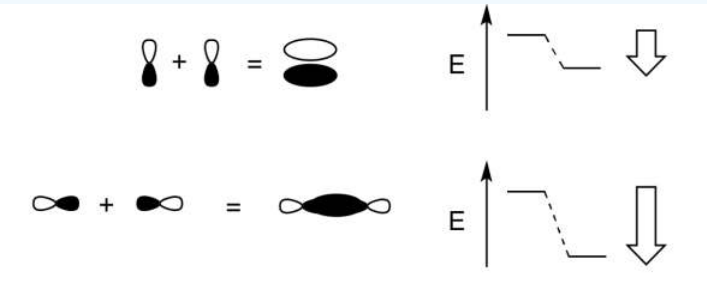
Answer

Li^+ and O^{2-} are more similar in size than K^+ and O^{2-}, so the bond between Li^+ and O^{2-} is stronger.

The energy difference between any core orbitals and valence orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

Exercise 10.1.2.8

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



Answer

When two parallel p orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

Attribution

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

Curated or created by Kathryn Haas

This page titled 10.1.2: p-Orbital MOs is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.1.2: Molecular Orbitals from p Orbitals** by Chris Schaller is licensed CC BY-NC 3.0.

10.1.3: d-Orbital MOs

In transition metals and other heavier elements, the d orbitals may combine with other orbitals of compatible symmetry (and energy) to form molecular orbitals. Generally, there are three types of bonding and antibonding interactions that may occur with d orbitals: sigma (σ), pi (π), and delta (δ) bonds.

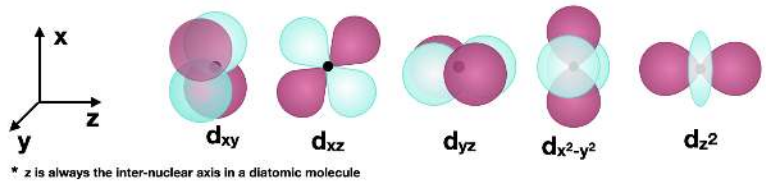


Figure 10.1.3.1: The five $3d$ orbitals are shown. The orientation of the axes is consistent and the z axis is horizontal for convenience in drawing bonding along the z axis (see examples below). (CC-BY-SA; Kathryn Haas)

Sigma (σ) bonding with d orbitals

σ bonds are symmetric with respect to the inter-nuclear axis (in a diatomic molecule, this is the z axis). An example of a σ bond formed by d orbitals is that of two d_{z^2} orbitals (see Figure 10.1.3.2). If a bonded atom is in a position other than on the z axis (in an octahedral geometry, for example), σ bonds can also form. For example, two $d_{x^2-y^2}$ orbitals on atoms bonded along the x or y axes could also form a σ bond.

d orbitals can also form σ bonds with other types of orbitals with the appropriate symmetry. Examples of orbitals with appropriate symmetry are the s orbital and certain p orbitals on another atom, as shown below in Figure 10.1.3.2.

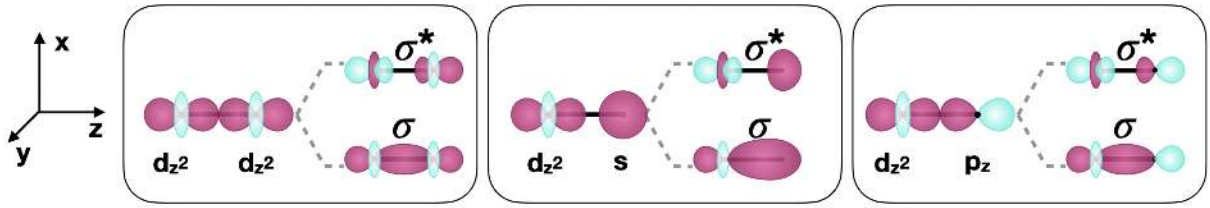


Figure 10.1.3.2: Selected examples of σ bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Pi (π) bonding with d orbitals

π bonds are those with one node that is in-plane with the internuclear axis. A π bond can form between two d orbitals or between d orbitals and other types of orbitals with comparable symmetry. An example of a π bond between two d orbitals is that formed by two d_{xz} orbitals along the z axis (shown in Figure 10.1.3.3). d orbitals can also form π bonds using p orbitals with compatible symmetry, as shown in Figure 10.1.3.3.

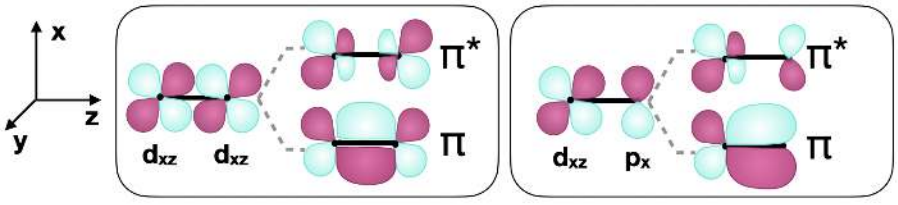


Figure 10.1.3.3: Selected examples of π bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Delta (δ) bonding with d orbitals

δ bonds are those with two nodes that are in-plane with the internuclear axis. δ bonds can form between two d orbitals with appropriate symmetry. For example, when two atoms bond along the z axis, the d_{xy} orbitals and the two $d_{x^2-y^2}$ orbitals can form δ bonds (Figure 10.1.3.4).

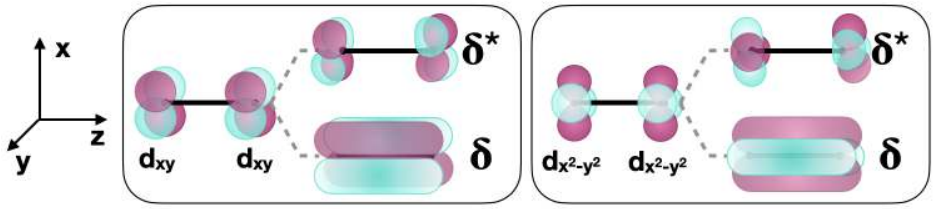


Figure 10.1.3.4: Selected examples of δ bonds involving d orbitals along the z internuclear axis (shown in bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Incompatible orbitals

In the descriptions above, we focused on how bonds (and antibonds) can be formed with d orbitals. All bonding and non-bonding interactions require that orbitals have compatible symmetry to form productive interactions. It is worth mentioning that orbitals with symmetry that is incompatible with the d orbitals will not have bonding or antibonding interactions with d orbitals. The figure below shows several sets of orbitals that are incompatible for bonding.

Curated or created by Kathryn Haas

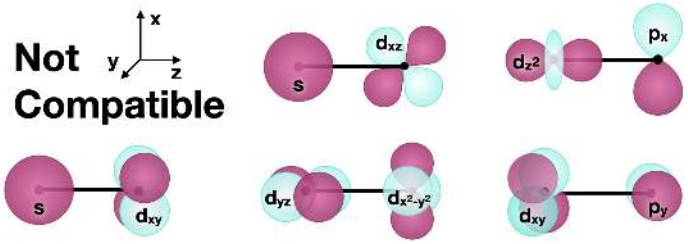


Figure 10.1.3.5: Several incompatible pairs of orbitals. (CC-BY-SA; Kathryn Haas)

This page titled 10.1.3: d-Orbital MOs is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.1.3: Molecular orbitals from d orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

10.2: Non-bonding Orbitals

The simplest case is when there is an even number of atomic orbitals that all combine to form strong bonding and antibonding orbitals. But what if there is an uneven number of atomic orbitals? Or what if there are some orbitals that don't meet the criteria for bonding? Or what if the bonding interactions are weak? In these cases, there will be molecular orbitals on the molecule that have non-bonding character.

It is important to note that the bonding, non-bonding, and antibonding nature of orbitals exist on a spectrum. Some bonding and anti-bonding orbitals may have some non-bonding character depending on where their energies lie with respect to the original atomic orbital energies. When molecular orbitals have energies similar to their original atomic orbitals, they will have some non-bonding character. The closer the energies of atomic and molecular orbitals, the more non-bonding the molecular orbitals.

Two major factors to consider

Uneven number of atomic orbitals: In the case that there is an uneven number of atomic orbitals with compatible symmetry, orbitals with non-bonding character will form. For example, in the case where three atomic orbitals combine, the most common result is formation of a low-energy bonding orbital, a high energy antibonding orbital, and a non-bonding orbital of intermediate energy (Figure 10.2.1).

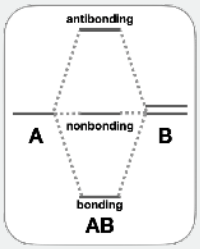


Figure 10.2.1. This figure illustrates the most common case for three atomic orbitals that combine to form three molecular orbitals; formation of one low-energy bonding, one high-energy antibonding, and one intermediate energy non-bonding molecular orbital. (CC-BY-NC-SA, Kathryn Haas)

Differences in energy: Combination of orbitals with different energies may lead to orbitals with non-bonding character. Atomic orbitals that have similar energies will have the strongest interactions, and result in bonding molecular orbitals with much lower energies than the component atomic orbitals. On the other hand, atomic orbitals with very unequal energies have a weaker interaction because the molecular orbitals are closer in energy to the atomic orbital energies, thus there is less energy benefit to putting electrons in the bonding molecular orbitals (Figure 10.2.2). When bonding or antibonding orbitals are close to the energies of the contributing atomic orbitals, those molecular orbitals may have some non-bonding character.

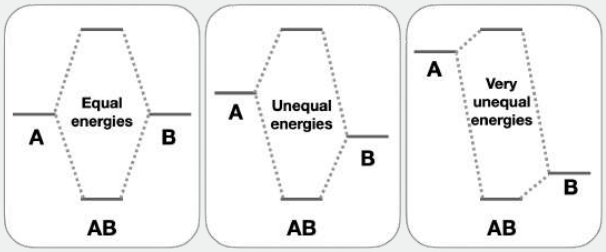


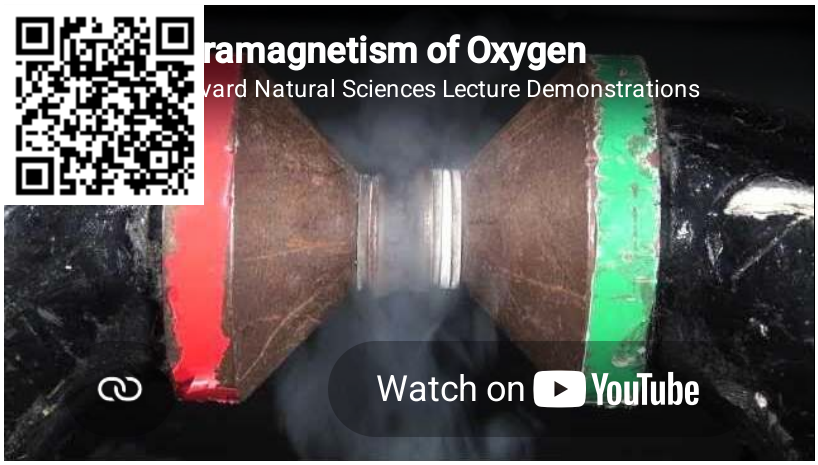
Figure 10.2.2. This figure illustrates how relative energies of atomic orbitals result in molecular orbitals that are more or less favorable. The greater the energy difference between atomic orbitals and the bonding molecular orbital, the more eneretically favorable it is for bonding to occur. (CC-BY-NC-SA, Kathryn Haas)

This page titled 10.2: Non-bonding Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.1.4: Nonbonding Orbitals and Other Factors** by Kathryn Haas is licensed CC BY-SA 4.0.

10.3: Molecular Orbital Diagrams

There are several cases where our more elementary models of bonding (like Lewis Theory and Valence Bond Theory) fail to predict the actual molecular properties and reactivity. A classic example is the case of O_2 and its magnetic properties. At very cold temperatures, O_2 is attracted to a magnetic field, and thus it must be paramagnetic (unpaired electrons give rise to magnetism). Watch the video below!



The magnetic properties of O_2 are easily rationalized by its **molecular orbital diagram**. A molecular orbital diagram is a diagram that shows the relative energies and identities of each molecular orbital in a molecule. Figure 10.3.1 shows a simplified and generic molecular orbital diagram for a second-row homonuclear diatomic molecule. The diagram is simplified in that it assumes that interactions are limited to degenerate orbitals from two atoms (see next section).

There are some things you should note as you inspect Figure 10.3.1 (and keep these in mind as you draw your own diagrams!). First, notice that there are the **same number of molecular orbitals as there are atomic orbitals**. Second, notice that **each orbital in the diagram is rigorously labeled** using labels (σ and π) that include the subscripts u and g. These labels and subscripts indicate the symmetry of the orbitals. The σ symbol indicates that the orbital is symmetric with respect to the internuclear axis, while the π label indicates that there is one node along that axis. The g and u stand for *gerade* and *ungerade*, the German words for *even* and *uneven*, respectively. The subscript g is given to orbitals that are *even*, or *symmetric*, with respect to an inversion center. The subscript u is given to orbitals that are *uneven*, or *antisymetric*, with respect to an inversion center. The pictures of calculated molecular orbitals are shown in Figure 10.3.1 to illustrate the symmetry of each orbital.

Another important thing to notice is that the diagram in Figure 10.3.1 lacks electrons (because it is generic for any second-row diatomic molecule). If this were a *complete* molecular orbital diagram it would **include the electrons for each atom and for the molecule**. Electrons in molecular orbitals are filled in the same way an atomic orbital diagram would be filled, where electrons occupy lower energy orbitals before higher energy orbitals, and electrons occupy empty degenerate orbitals before pairing. A complete molecular orbital diagram would show whether the molecule is diamagnetic or paramagnetic. It can also be used to calculate the bond order of the molecule (the number of bonds between atoms) using the formula below:

$$\text{Bond order } = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons}\\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding orbitals}\end{pmatrix}\right]$$

In general, non-valence (core) electrons can be ignored because they contribute nothing to the bond order. In fact, many molecular orbital diagrams will ignore the core orbitals, as they are insignificant for bonding interactions and reactivity.

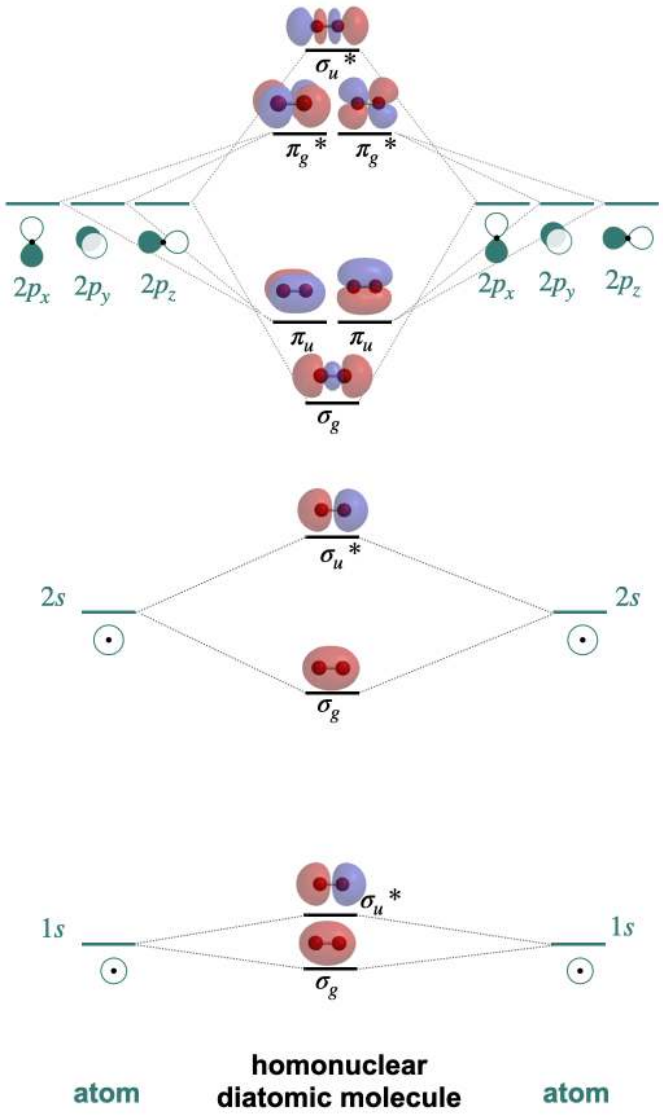


Figure 10.3.1: A generic molecular orbital diagram for a homonuclear diatomic molecule of second-row elements assuming no orbital mixing (interactions are formed by orbitals of the same energy from each atom). (CC-BY-NC-SA, Kathryn Haas)

Now, to see how this molecular orbital diagram can explain the magnetic behaviour of O_2, complete the example below.

Example 10.3.1

Let's change Figure 10.3.1 to make it specific for O_2. Re-draw the MO diagram (no need to draw the shapes of orbitals). Fill in the correct number of electrons for each oxygen atom on either side of the diagram. Then, fill in the total molecular electrons in the center. Calculate the bond order and determine whether it is diamagnetic or paramagnetic.

Solution

The diagram in Figure 10.3.1 includes core orbitals (the 1s) and valence electrons (2s, 2p). Therefore, we will consider all the electrons in an oxygen atom and a dioxygen molecule. An oxygen atom has eight total electrons. So we fill eight electrons into the atomic orbitals for the oxygen atom on the right, and eight electrons into the atomic orbitals for oxygen on the left. The total number of electrons for the molecule is sixteen, so fill in 16 electrons into the molecular orbitals, being sure to apply Hund's rule and the Aufbau principle. The result is a diagram that looks like the one drawn below in Figure 10.3.2.

The bond order is calculated using the molecular orbitals (we can ignore atomic orbitals). There are 10 electrons in binding orbitals and 6 electrons in antibonding orbitals). This gives a bond order of $\frac{1}{2}(10-6)=2$. This bond order is consistent with valence bond theory!

This diagram indicates that dioxygen is paramagnetic; it has two unpaired electrons in the π^* orbitals. This paramagnetic electron configuration explains why dioxygen is attacted to magnetic fields!

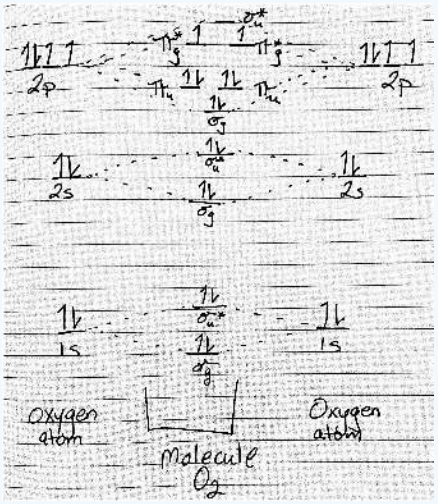


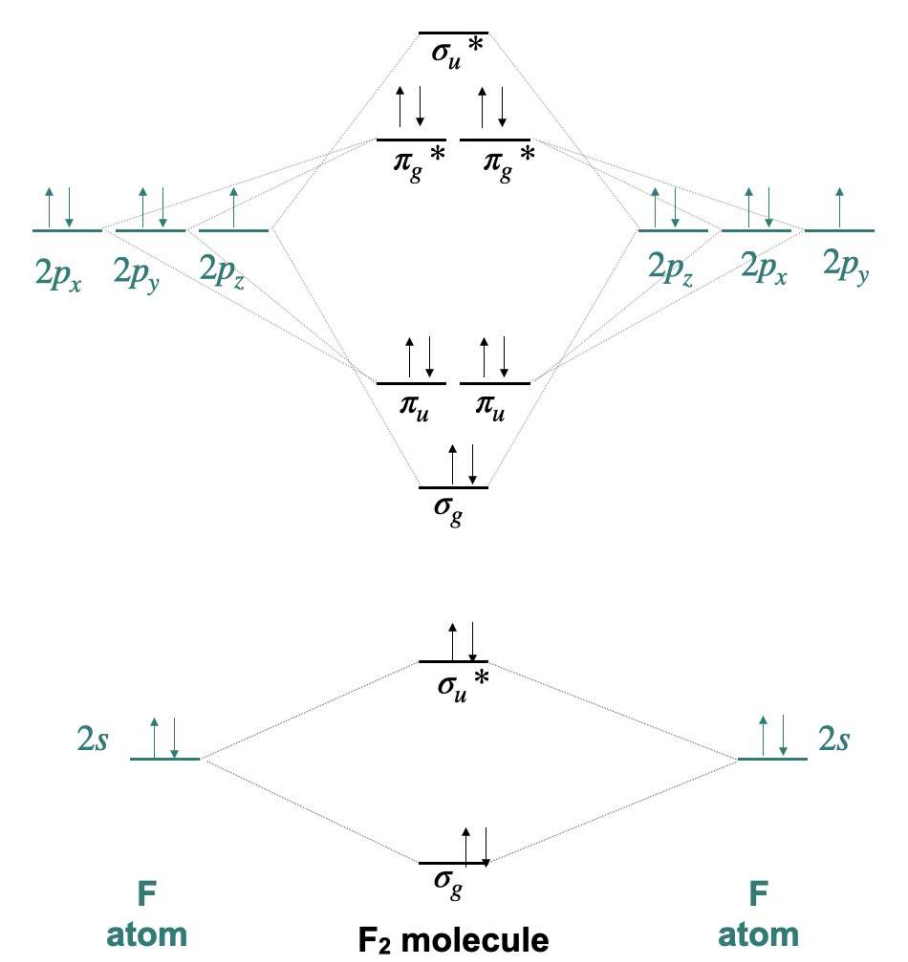
Figure 10.3.2: Hand-drawn molecular orbital diagram for dioxygen. (CC-BY-SA; Kathryn Haas)

? Exercise 10.3.1

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

Answer

The valence orbitals on an F atom are 2s and 2p. And, there are seven valence electrons in F. This gives fourteen total valence electrons. The MO diagram of the valence molecular orbitals can be constructed by combining the valence 2s and valence 2p orbitals from each F atom. The bond order is 1 and the molecule is diamagnetic.



This page titled 10.3: Molecular Orbital Diagrams is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.2.1: Molecular Orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

10.4: Orbital Mixing

In the previous section, we introduced a simplified molecular orbital (MO) diagram, assuming that interactions were limited to degenerate orbitals of compatible symmetry. A version of that *simplified* diagram for second-row homonuclear diatomics is shown on the left side of Figure 10.4.1 (only valence orbitals shown).

In reality, orbitals of compatible symmetry can combine, or mix, even when they have different energies. When sets of orbitals mix, it has the effect of decreasing the energy of the lower-energy set and increasing the energy of the higher-energy set. There are two ways to explain mixing, described in the points below. The diagram on the right of side of Figure 10.4.1 shows how energy levels are affected by orbital mixing.

- **Starting from the simplified MO diagram and mixing molecular orbitals of like symmetry**: If we start with the "no mixing" simplified diagram shown on the left, we can pick out the orbitals with like symmetry and consider what will happen if these molecular orbitals mix. For example, starting from the MO diagram on the left side of Figure 10.4.1, we see that there are two σ_g orbitals that have identical symmetry (hence they have identical symmetry labels). Upon mixing, the lower-energy $\sigma_g(2s)$ will decrease in energy while the higher-energy $\sigma_g(2p)$ will increase in energy. Likewise, there are two σ_u^* orbitals that will mix, decreasing the energy of $\sigma_u^*(2s)$ while increasing the energy of $\sigma_u^*(2p)$.
- **Starting from and mixing atomic orbitals of compatible symmetry**: Starting from the atomic orbitals, we can select the orbitals that have compatible symmetry to make productive interactions, and combine them as a set to make molecular orbitals. From the two sets of atomic orbitals on the right panel in Figure 10.4.1, there are two sets of four orbitals with compatable symmetry; one is the set of two $2s$ and two $2p_z$ orbitals. These four orbitals can combine to form molecular orbitals with σ symmetry. They combine to form one lowest-energy bonding σ_g, a highest-energy σ_u^*, and two orbitals with intermediate energy (σ_g, and σ_u^*). This treatment can be expressed as the linear combination of four atomic orbitals:

$$\Psi = c_1\psi\,(2s_a) \pm c_2\psi\,(2s_b) \pm c_3\psi\,(2p_a) \pm c_4\psi\,(2p_b)$$

  where the coefficients $c_1 = c_2$ and $c_3 = c_4$ for homonuclear diatomic molecules.

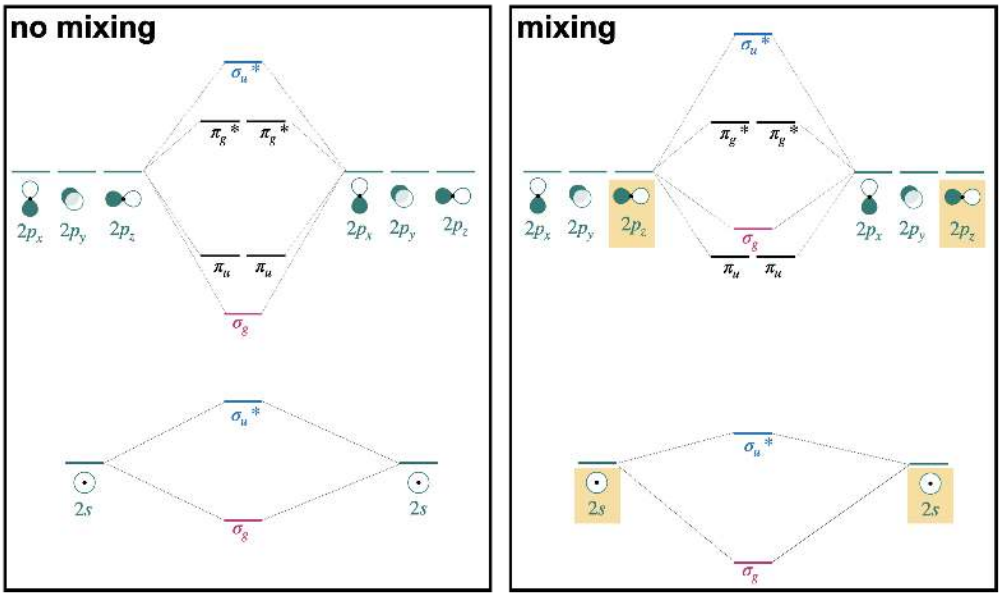


Figure 10.4.1: Mixing of orbitals with like symmetry affects the energies of molecular orbitals. The simplified case where no mixing occurs is shown on the left. The effects of mixing are shown on the right. The σ_g orbitals of like symmetry are highlighted in fuschia and the σ_u^* orbitals of like symmetry are highlighted in blue. A group of atomic orbitals of similar symmetry are highlighted in yellow boxes; these atomic orbitals combine to give all σ molecular orbitals. (CC-BY-SA, Kathryn Haas)

In the case of homonuclear diatomic molecules of the second row, orbital mixing has important consequences for the energetic order of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. This will be discussed in the next section.

This page titled 10.4: Orbital Mixing is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.2.2: Orbital Mixing** by Kathryn Haas is licensed CC BY-SA 4.0.

10.5: Diatomic Molecules

First Period Homonuclear Diatomic Molecules

In the first row of the periodic table, the valence atomic orbitals are $1s$. There are two possible homonuclear diatomic molecules of the first period:

Dihydrogen, H_2 $[\sigma_g^2(1s)]$: This is the simplest diatomic molecule. It has only two molecular orbitals (σ_g and σ_u^*), two electrons, a bond order of 1, and is diamagnetic. Its bond length is 74 pm. MO theory would lead us to expect bond order to decrease and bond length to increase if we either add or subtract one electron. The calculated bond length for the H_2^+ ion is approximately 105 pm.[1]

Dihelium, He_2 $[\sigma_g^2\sigma_u^{*2}(1s)]$: This molecule has a bond order of zero due to equal number of electrons in bonding and antibonding orbitals. Like other nobel gases, He exists in the atomic form and does not form bonds at ordinary temperatures and pressures.

Exercise 10.5.1

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

Answer

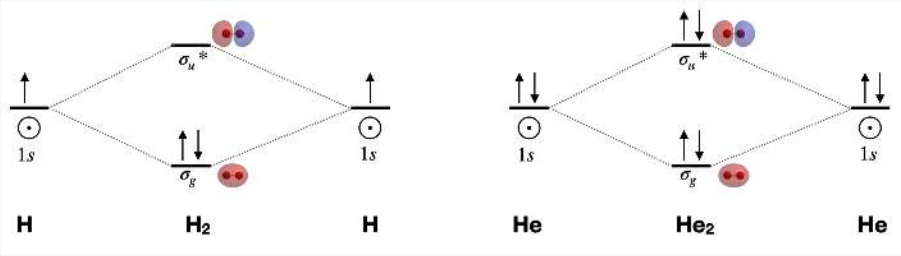


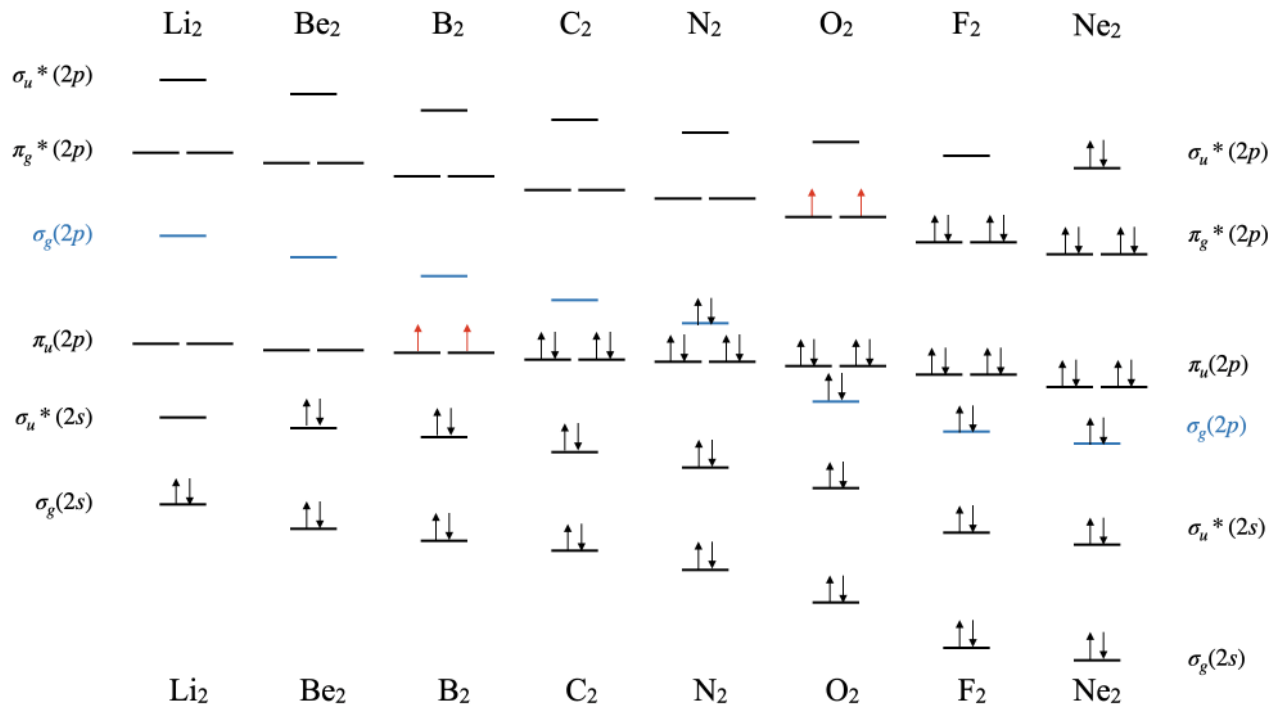
Figure for Exercise 10.5.1: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

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

Second Period Homonuclear Diatomic Molecules

The second period elements span from Li to Ne. The valence orbitals are 2s and 2p. In their molecular orbital diagrams, non-valence orbitals (1s in this case) are often disregarded in molecular orbital diagrams.

Orbital mixing has significant consequences for the magnetic and spectroscopic properties of second period homonuclear diatomic molecules because it affects the order of filling of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. Early in period 2 (up to and including nitrogen), the $\pi_u(2p)$ orbitals are lower in energy than the $\sigma_g(2p)$ (see Figure 10.5.1). However, later in period 2, the $\sigma_g(2p)$ orbitals are pulled to a lower energy. This lowering in energy of $\sigma_g(2p)$ is not unique; all of the σ orbitals in the molecule are pulled to lower energy due to the increasing positive charge of the nucleus. The π orbitals in the molecule are also affected, but to a much lesser extent than σ orbitals. The reason has to do with the high penetration of s atomic orbitals compared to p atomic orbitals (recall our previous discussion on penetration and shielding, and its effect on periodic trends). The σ molecular orbitals have more s character and thus their energy is more influenced by increasing nuclear charge. As nuclear charge increases, the energy of the $\sigma_g(2p)$ orbital is lowered significantly more than the energy of the $\pi_u(2p)$ orbitals (Figure 10.5.1).



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Unpaired e⁻	0	0	2	0	0	2	0	0
Bond Order	1	0	1	2	3	2	1	0
Experimental* Bond Length (pm)	267.3	246.0	159.0	124.3	109.8	120.8	141.2	310.0

*Experimental bond lengths from "List of Experimental Diatomic Bond Lengths", NIST, https://cccbdb.nist.gov/diatomicexpbondx.asp

Figure 10.5.1: Molecular orbital energy-level diagrams for the diatomic molecules of the period 2 elements. Unlike earlier diagrams, *only the valence molecular orbital energy levels for the **molecules** are shown here (atomic orbitals not shown for simplicity).* For Li_2 through N_2, the $\sigma_g(2p)$ orbital is higher in energy than the $\pi_u(2p)$ orbitals. In contrast, from O_2 onward, the $\sigma_g(2p)$ orbital is *lower* in energy than the $\pi_u(2p)$ orbitals because the nuclear charge increases across the row. The experimental bond lengths correlate with the calculated bond order. (CC-BY-NC-SA, Kathryn Haas)

Dilithium, Li_2 $[\sigma_g^2(2s)]$**:** This molecule has a bond order of one and is observed experimentally in the gas phase to have one Li-Li bond.

Diberylium, Be_2 $[\sigma_g^2\sigma_u^{*2}(2s)]$**:** This molecule has a bond order of zero due to the equal number of electrons in bonding and antibonding orbitals. Although Be_2 does not exist under ordinary conditions, it can be produced in a laboratory and its bond length measured (Figure 10.5.2). Although the bond is very weak, its bond length is surprisingly ordinary for a covalent bond of the second period elements.[2]

Diboron, B_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^1\pi_u^1(2p)]$**:** The case of diboron is one that is much better described by molecular orbital theory than by Lewis structures or valence bond theory. This molecule has a bond order of one. The molecular orbital description of diboron also predicts, accurately, that diboron is paramagnetic. The paramagnetism is a consequence of orbital mixing, resulting in the σ_g orbital's being at a higher energy than the two degenerate π_u^* orbitals.

Dicarbon, C_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2(2p)]$**:** This molecule has a bond order of two. Molecular orbital theory predicts two bonds with π symmetry, and no σ bonding. C_2 is rare in nature because its allotrope, diamond, is much more stable.

Dinitrogen, N_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2\sigma_g^2(2p)]$**:** This molecule is predicted to have a triple bond. This prediction is consistent with its short bond length and bond dissociation energy. The energies of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals are very close, and their relative energy levels have been a subject of some debate (see next section for discussion).

Dioxygen, O_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*1}\pi_g^{*1}(2p)]$**:** This is another case where valence bond theory fails to predict actual properties. Molecular orbital theory correctly predicts that dioxygen is paramagnetic, with a bond order of two. Here, the molecular orbital diagram returns to its "normal" order of orbitals where orbital mixing could be somewhat ignored, and where $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Difluorine, F_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}(2p)]$**:** This molecule has a bond order of one and like oxygen, the $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Dineon, Ne_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}\sigma_u^{*2}(2p)]$**:** Like other noble gases, Ne exists in the atomic form and does not form bonds at ordinary temperatures and pressures. Like Be_2, Ne_2 is an unstable species that has been created in extreme laboratory conditions and its bond length has been measured (Figure 10.5.2)

Exercise 10.5.2

Draw the complete molecular orbital diagram for O_2. Show calculation of its bond order and tell whether it is diamagnetic or paramagnetic.

Answer

O_2 is paramagnetic with a bond order of 2. Its $\sigma_g(2p)$ molecular orbital is lower in energy that the set of $\pi_u(2p)$ orbitals.

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

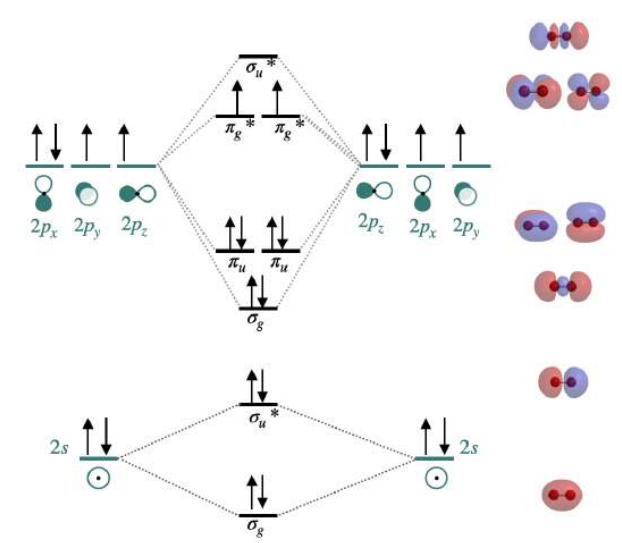


Figure for Exercise 10.5.2. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

Exercise 10.5.3: The Peroxide Ion

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

Answer

This diagram looks similar to that of O_2, except that there are two additional electrons.
$(\sigma_g(2s))^2\,(\sigma_u^*(2s))^2\,(\sigma_g(2p))^2\,(\pi_u(2p))^4\,(\pi_g(2p))^4$; bond order of 1; no unpaired electrons.

Bond Lengths in Homonuclear Diatomic Molecules

The trends in experimental bond lengths are predicted by molecular orbital theory, specifically by the calculated bond order. The values of bond order and experimental bond lengths for the second period diatomic molecules are given in Figure 10.5.1, and shown

in graphical format on the plot in Figure 10.5.2. From the plot, we can see that bond length correlates well with bond order, with a minimum bond length occurring where the bond order is greatest (N_2). The shortest bond distance is at N_2 due to its high bond order of 3. From N_2 to F_2 the bond distance increases despite the fact that atomic radius decreases.

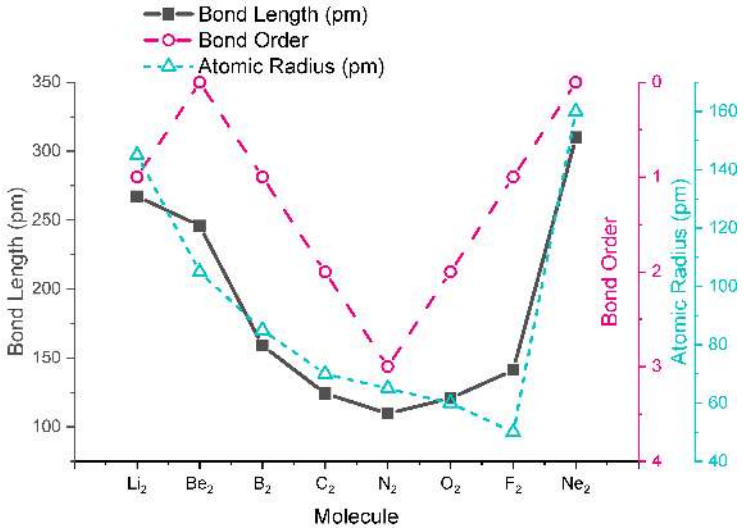


Figure 10.5.2: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

References

1. NIST, Calculated Geometries available for H_2^+ (Hydrogen cation) 2Σg+ D∞h, available at https://cccbdb.nist.gov/diatomicexpbondx.asp
2. Merritt, J. M.; Bondybey, V. E.; Heaven, M. C., Beryllium Dimer-Caught in the Act of Bonding. *Science* **2009,** *324* (5934), 1548-1551.

This page titled 10.5: Diatomic Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.2.3: Diatomic Molecules of the First and Second Periods** by Kathryn Haas is licensed CC BY-SA 4.0.
- **5.P: Problems** is licensed CC BY-SA 4.0.

10.6: Polar Diatomic Molecules

Molecular orbital diagrams for heteronuclear diatomic molecules

The molecular orbital diagram of a heteronuclear diatomic molecule is approached in a way similar to that of a homonuclear diatomic molecule. The orbital diagrams may also look similar. A major difference is that the more electronegative atom will have orbitals at a lower energy level. Two examples of heteronuclear diatomic molecules will be explored below as illustrative examples.

Carbon monoxide MO diagram

Carbon monoxide is an example of a heteronuclear diatomic molecule where both atoms are second-row elements. The valence molecular orbitals in both atoms are the $2s$ and $2p$ orbitals. The molecular orbital diagram for carbon monoxide (Figure $10.6.1$) is constructed in a way similar to how you would construct dicarbon or dioxygen, except that the oxygen orbitals have a lower potential energy than analogous carbon orbitals. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial labels according to type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts.

A consequence of unequal atomic orbital energy levels is that orbital mixing is significant. Notice the order of the molecular orbitals labeled 1π and 3σ in Figure $10.6.1$. This is a similar order of π and σ orbitals to the one we saw in the case of the σ_g and π_u orbitals of N_2 and lighter diatomics of the second period. Because the oxygen $2p_z$ orbital is close in energy to both the carbon $2p_z$ and carbon $2s$, these three orbitals will have significant interaction (mixing). The result is an increase in the energy of the 3σ orbital and a decrease in energy of the $2\sigma^*$ orbital, resulting in the diagram shown in Figure $10.6.1$.

In the case of carbon monoxide (Figure $10.6.1$), atomic orbitals contribute unequally to each molecular orbital. For example, because the $2s$ orbital of oxygen is very close in energy to the 2σ moelcular orbital, it contributes to that molecular orbital more than the $2s$ orbital from carbon. Notice the shape of this 2σ orbital and how it is unevenly distributed over the two atoms; it is more heavily distributed on the oxygen because it is most like the oxygen $2s$. This is in line with the assumption that electron density is distributed more on oxygen because it is more electronegative than carbon. Likewise, the 1π orbitals are unevenly distributed, with more distribution close to the oxygen.

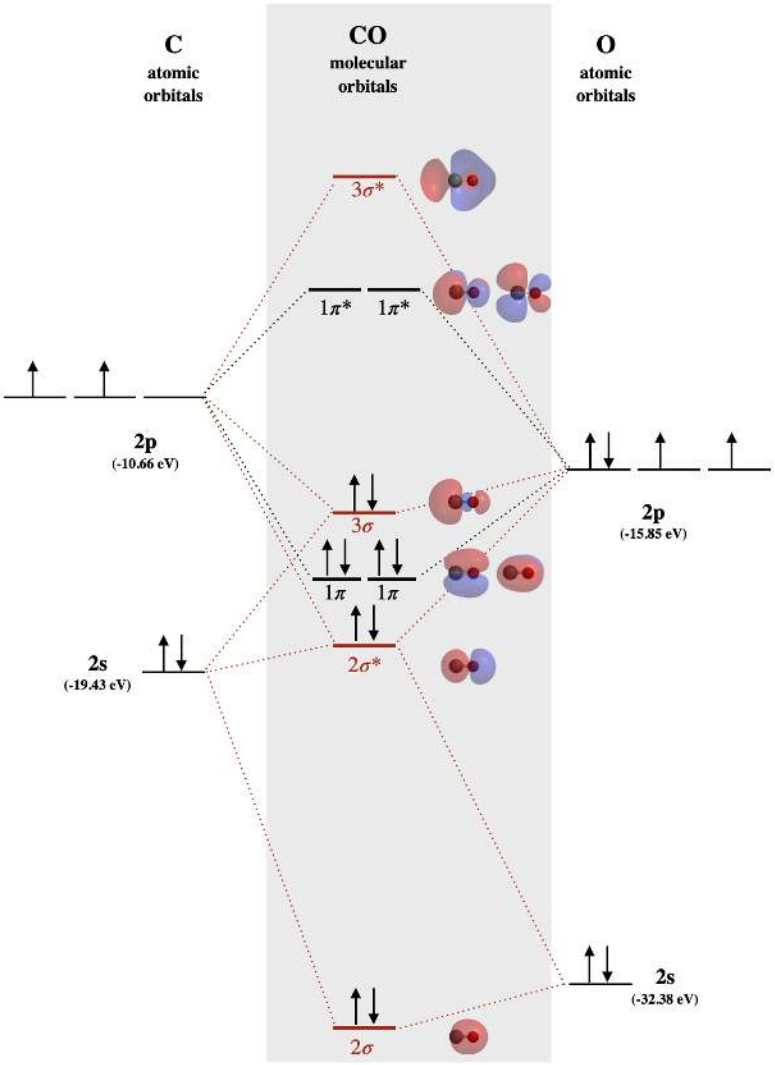
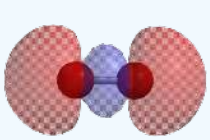


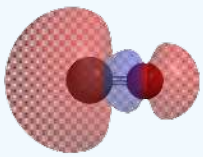
Figure 10.6.1: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts. Molecular orbital surfaces were calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

? Exercise 10.6.1

Examine the shape of the 3σ orbital of carbon monoxide in Figure 10.6.1. Describe what ways this shape is different from the shape of the σ_g orbitals from second period homonuclear diatomic molecules (see Fig. 5.2.1.1). Rationalize these differences. Both orbitals are re-created below for convenience.



σ_g of homonuclear diatomic



3σ of CO

Answer

The 3σ orbital is like the σ_g in that it has three lobes and two nodes distributed along the internuclear bond. They are different in their distribution. The two external lobes of σ_g are evenly distributed because they are an equal combination of two p_z orbitals (one from each atom). The 3σ orbital is more heavily distributed toward the carbon atom, the less electronegative atom, than toward the oxygen. The unequal distribution of 3σ is apparent in the unequal sizes of its exterior lobes and the uneven shape of the interior lobe. The heavier distribution within the exterior lobe on carbon is caused by the mixing of the carbon $2s$ orbital with carbon and oxygen $2p_z$ orbitals. The uneven shape of the interior lobe, where it leans toward oxygen, is best explained by the fact that the 3σ orbital is closer in energy to the oxygen $2p_z$ than the carbon $2p_z$.

Hydrogen fluoride MO diagram

Hydrogen fluoride is an example of a heteronuclear diatomic molecule in which the two atoms are from different periods. In this case, the valence orbital of H is $1s$ while those of F are $2s$ and $2p$. The molecular orbital diagram for HF is shown in Figure 10.6.2.

Three of these orbitals have compatible symmetry for mixing; these are the hydrogen $1s$, fluorine $2s$, and fluorine $2p$. However, the extent to which they will interact depends on their relative energies. Fluorine is more electronegative than H, and the fluorine atom has a higher first ionization energy than does hydrogen. From these trends, we can expect that the fluorine valence orbitals are lower in energy than that of hydrogen. From Table 5.3.1, we find that the 1s orbital of H (-13.6 eV) is higher in energy than both fluorine orbitals (-18.7 and -40.2 eV, respectively for $2p$ and $2s$). The energies of hydrogen $1s$ and fluorine $2p$ are a good match for combination; however, the fluorine $2s$ orbital is much too different to create a productive interaction. Therefore, we expect that the fluorine $2s$ will create a non-bonding molecular orbital, while the $1s$ and $2p_z$ orbitals combine to make σ bonding and σ^* antibonding molecular orbitals. The remaining $2p_x$ and $2p_y$ orbitals do not have compatible symmetry for bonding with hydrogen, and they will form non-bonding π molecular orbitals. The non-bonding orbitals will have similar energy and character as their component atomic orbitals.

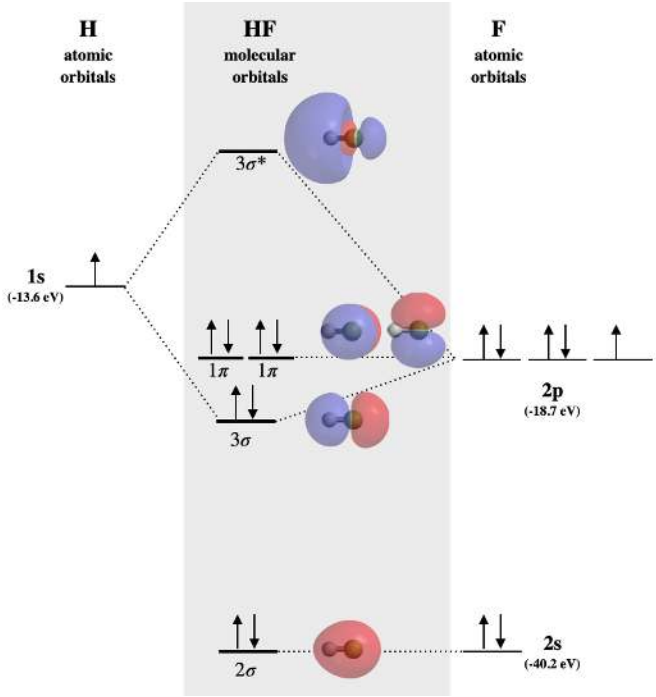


Figure 10.6.2: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

Chemical reactions take place at the HOMO and LUMO orbitals

Knowledge of molecular orbital diagrams, and the shapes of molecular orbitals, can be used to accurately explain and predict chemical reactivity. Chemical reactions take place using the highest occupied molecular orbitals (HOMO) of a nucleophile or Lewis base, and the lowest unoccupied molecular orbital (LUMO) of an electrophile or Lewis acid.

> *Lewis bases react using electrons in the HOMO, while Lewis acids react using the empty LUMO.*

Example: Reactivity of CO with metal ions

CO is an excellent ligand for many metal ions. In fact, the strong affinity between CO and the heme iron (Fe) ions in hemoglobin can explain the mechanism of carbon monoxide poisoning. When CO binds in place of O_2 to hemoglobin, that hemoglobin can no longer carry O_2 to tissue cells. CO binding to hemoglobin is strong and practically irreversible. When CO binds to metal ions, it does so through the carbon atom. This is contrary to expectations based on the Lewis structure and the known bond polarity, where electron density is polarized toward oxygen. The distribution of the electron density of the HOMO of CO can explain this observation!

? Exercise 10.6.2

Refer to the MO diagram for CO. Identify the HOMO and explain why CO bonds to metal ions through the carbon atom rather than through the oxygen atom.

Answer

In the interaction between CO and a metal ion, CO would act as a Lewis base; thus it will react using electrons in its HOMO. The MO diagram for CO is shown in Figure 10.6.1: the HOMO is the 3σ orbital (also discussed in ? Exercise 10.6.1). The electron density of that MO is centered around the carbon atom, thus the carbon atom will be a better Lewis base than the O atom.

This page titled 10.6: Polar Diatomic Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.3.2: Polar bonds** by Kathryn Haas is licensed CC BY-SA 4.0.

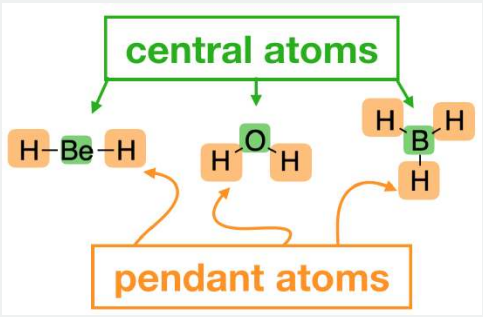
SECTION OVERVIEW

10.7: Polyatomic Molecules

We can extend the method we used for diatomic molecules to draw the molecular orbitals of more complicated, polyatomic molecules (molecules with more than two atoms). To combine several different atoms in a molecular orbital diagram, we will group orbitals from different atoms into sets that match the symmetry of a central atom. These **group orbitals** are also referred to as **symmetry adapted linear combinations (SALCs)**. We'll use a stepwise approach to do this as summarized below.

Symmetry adapted linear combinations (SALCs)

We need SALCs (aka group orbitals) to draw molecular orbital (MO) diagrams of *polyatomic* molecules. SALCs are groups of orbitals on **pendant atoms**. These groups of orbitals much match the symmetry of valence orbitals on the **central atom** in order to create a productive interaction. When we combine SALCs with the atomic orbitals on the central atom, we can generate an MO diagram that gives us information about the molecule's bonding and electronic states.



Below is a set of steps you can follow to find SALCs and draw an MO Diagram. Each step will be illustrated in detail through the examples in the subsections that follow this page.

1. Find the **point group** of the molecule and assign Cartesian coordinates so that z is the principal axis.
   Sometimes we can simplify things by looking only at the point group of the relevant orbitals. Only simplify when instructed to do so.*
2. Identify and count the pendant atoms' valence orbitals.
   Is there more than 1 type for each atom (ex. just s, or s and p?) We expect 1 SALC for each ligand orbital.
3. Generate a **reducible representation (Γ)** for the group of pendant atom orbitals using the appropriate character table.
   You have to do this for each set of orbital types. If you only have s orbitals for each ligand, you only need to generate 1 reducible representation. If you have p orbitals, you would generate additional Γ's for p_x, p_y, and p_z.
4. Break the Γ into its component **irreducible representations** from the character table. Note the symmetry of each irreducible representation, its associated orbitals, and their degeneracy.
5. If you are asked to sketch the shapes of SALCs, determine what they "look like" using one of the following strategies.
   (a) Shortcut: if the reducible representations are listed with s, p, or d orbitals in the character table, just draw them (… and skip steps b-c)
   (b) Systematic (Projection Operator) method: Draw an expanded character table and draw your molecule with each ligand identified by letters or numbers (*a,b,c...* or *i,j,k...* or *1,2,3...*) Determine where each pendant atom/orbital ends up under each of the operations of your expanded table. Project the values for each irreducible representation onto the chart you created and then add up the values. Positive and negative values are opposite signed orbitals.
6. Draw the MO diagram by combining SALCs with AO's of like symmetry. When drawing SALC energy levels, remember that the more nodal planes in your SALC orbital drawing, the higher the energy for that SALC orbital.

** When we are focused on orbitals, as in the case for finding group orbitals and drawing molecular orbital diagrams, the symmetry of the orbitals is what we are interested in. In the case of high-symmetry point groups, like $D_{\infty h}$ and $C_{\infty v}$, even though the molecule may have a C_∞ axis, the orbitals do not necessarily retain this symmetry element. For example, the p_x orbital would not have a C_∞ axis, but rather a C_2 axis. It is sufficient and useful to substitute D_{2h} for $D_{\infty h}$ and C_{2v} for $C_{\infty v}$ to simplify the problem.*

10.7.1: Bifluoride anion

10.7.2: Carbon Dioxide

10.7.3: H_2O

10.7.4: NH_3

10.7.5: CO_2 (Revisted with Projection Operators)

10.7.6: BF_3

This page titled 10.7: Polyatomic Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

10.7.1: Bifluoride anion

Finding SALCs and drawing the MO diagram for [F-H-F]$^-$

The linear anion [F-H-F]$^-$ is a good place to start as an example to illustrate the process of generating pendant atom SALCs and then constructing a molecular orbital diagram for a polyatomic molecule. We will proceed using the steps outlined on the previous page for generating SALCs and a molecular orbital diagram.

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

We begin by assigning the appropriate point group for this molecule: $D_{\infty h}$ (Figure 10.7.1.1). As mentioned in the previous page, it is useful to substitute D_{2h} for $D_{\infty h}$ when generating SALCs and molecular orbital diagrams. The z axis is assigned to be colinear with the principal axis, and in this case is the same as the C_∞ axis (Figure 10.7.1.1).

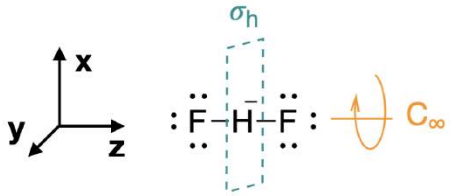


Figure 10.7.1.1: The [FHF]$^-$ anion belongs to the $D\infty_h$ point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

The next step is to identify the valence orbitals on the pendant F atoms that will form SALCs. In most cases, you should consider all of the valence orbitals. In this case, each of the fluorine atoms has four valence orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$). From these eight fluorine valence orbitals, we should expect eight group orbitals (SALCs).

3. - 5. Generate SALCS (shortcut)

To draw these SALCs for this molecule is rather simple, and we don't need to follow all the steps of finding the Γ's and reducing them. Rather, you can proceed as if you are creating bonding and antibonding molecular orbitals between the two F atoms, except that the F orbitals are separated by the H atom. Approximate sketches of the eight SALCs from F valence orbitals are shown in Figure 10.7.1.2.

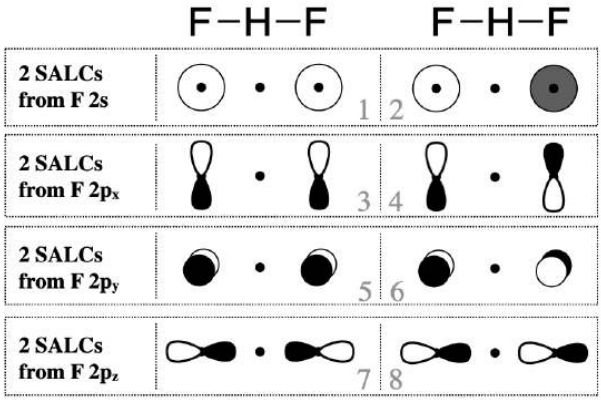


Figure 10.7.1.2: Eight SALCs from the valence orbitals of two fluorine atoms. (CC-BY-NC-SA; Kathryn Haas)

6. Draw the MO diagram by combining SALCs with AO's of like symmetry.

SALCs can productively interact with the central atom only when symmetry is compatible. Just some of the groups of orbitals in Figure 10.7.1.2 possess appropriate symmetry to combine with the hydrogen atom valence orbital (the H $1s$). In this simple case, you can decide whether orbitals have compatible symmetry by visually inspecting the shapes of the group orbitals. The F $2p_y$ and $2p_x$ orbitals do not have appropriate symmetry to bond to the H $1s$ orbital because the nodes of these orbitals run through the center of the H $1s$ orbital, thus we can eliminate all SALCs composed from F $2p_x$ and $2p_y$ (*these are SALCs numbered 3-6 in Figure* 10.7.1.2). On the other hand, the F $2s$ and $2p_z$ orbitals individually do have appropriate shape and direction in space for productive

interaction with an H $1s$ orbital. However only SALCs where the *entire group* has appropriate symmetry will combine with H $1s$ to produce bonding or antibonding molecular orbitals. Only the SALCs labeled with numbers 1 and 7 can combine with an s orbital in the center of the group. The ways in which these SALCs are able to combine with H $1s$ are illustrated in Figure 10.7.1.3.

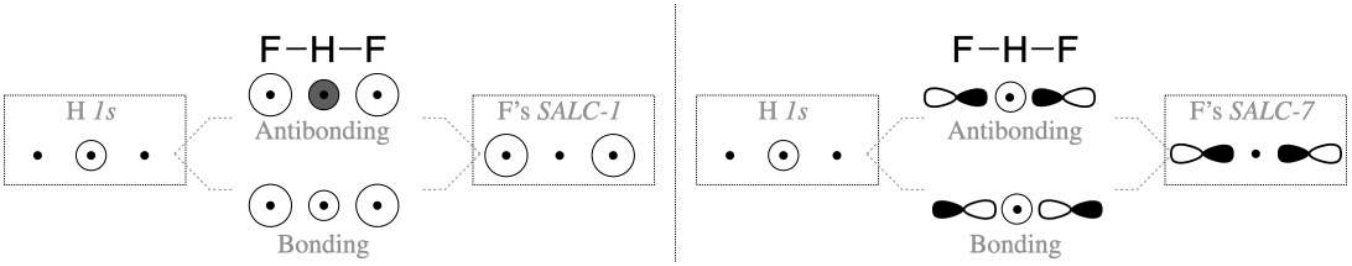
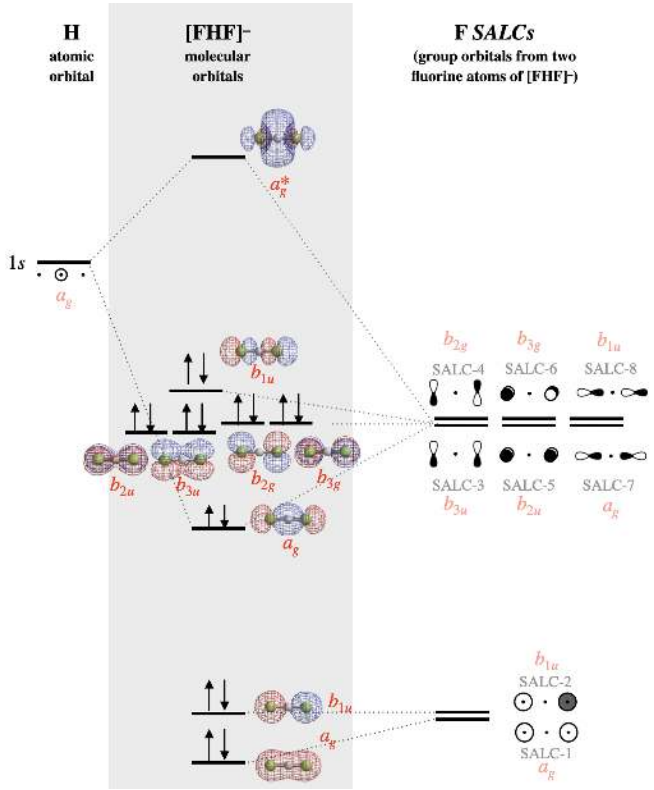


Figure 10.7.1.3: Combinations of a central H $1s$ orbital with the group orbitals, SALC-1 and SALC-7 from Figure 10.7.1.2, to create bonding and antibonding interactions. (CC-BY-NC-SA; Kathryn Haas)

Before we assume that both SALC-1 and SALC-7 will combine with the H $1s$ orbital, we must consider the energies of all atomic orbitals. The F $2p_z$ orbital has a potential energy of -18.7 eV (see Table 5.3.1). This is a good match for the H $1s$ orbital (-13.6 eV). However, the F $2s$ orbital has a much lower energy of -46.37 eV and would have weak interaction with the H $1s$.

The molecular orbital diagram for $[F\text{-}H\text{-}F]^-$ is shown in Figure 10.7.1.4. Notice that all atomic orbitals, group orbitals (SALCs), and molecular orbitals in Figure 10.7.1.4 are assigned a symmetry label that corresponds to each element's symmetry under the D_{2h} point group. The molecular orbital labels correspond to **lower-case Mulliken Labels** of individual reducible representations from the D_{2h} character table. Upper-case symbols are used to indicate symmetry and irreducible representations, while lower-case symbols are used to indicate the identity of an orbital with that symmetry. The labeling methods described for simple diatomic linear molecules (σ, π) are not sufficient to indicate the more complex symmetries of the molecular orbitals in polyatomic molecules. The use of lower-case Mulliken symbols is the most rigorous way to label the orbitals. Refer to your instructor for how you should label orbitals for any graded work.

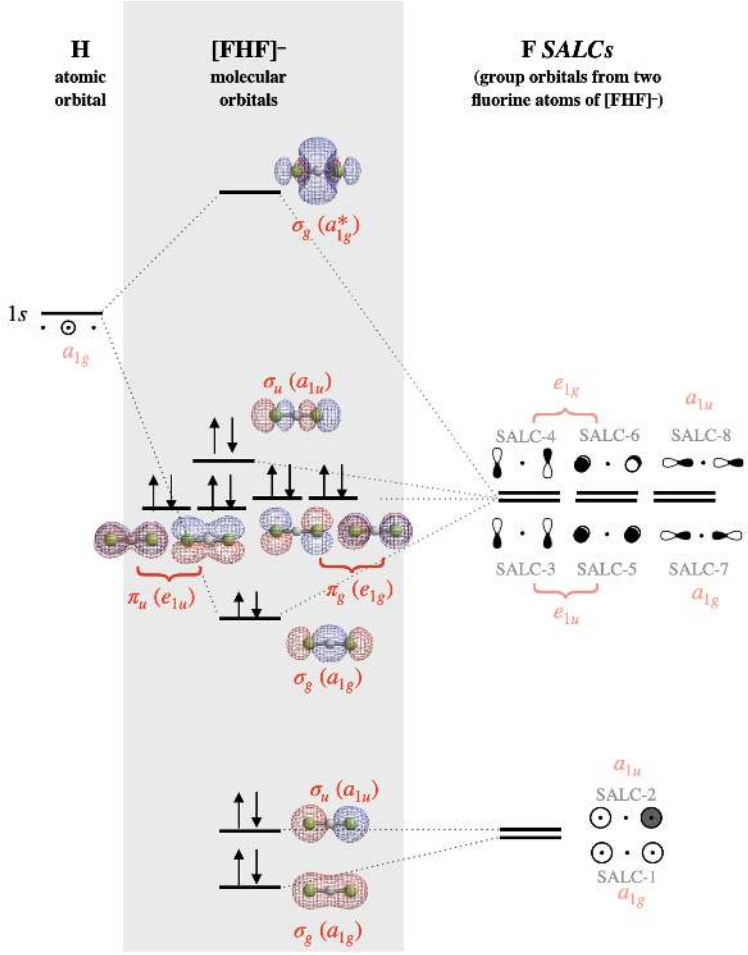


https://chem.libretexts.org/@go/page/537877

Figure 10.7.1.4:The molecular orbital diagram for [F-H-F]⁻. The molecular orbital surfaces and relative energy levels were calculated using Spartan software. SALCs are labeled according to numbers assigned in Figure 10.7.1.2. The symmetry of each SALC and orbital under the D_{2h} **point group** is shown in red font. (CC-BY-NC-SA; Kathryn Haas)

Click here for a version of Figure 10.7.1.4 **using** $D_{\infty h}$ **labeling:**

For high-symmetry groups, a shortcut is to use a lower-symmetry group that maintains the critical symmetry elements. In the case of the $D_{\infty h}$ point group, it is often sufficient to use the approximation of the D_{2h} point group and character table. This is the same MO diagram as shown above, but using the symmetry labels appropriate for the D_{2h} approximation.



Alternate Figure 10.7.1.4: The molecular orbital diagram for [F-H-F]⁻. The molecular orbital surfaces and relative energy levels were calculated using Spartan software. SALCs are labeled according to numbers assigned in Figure 10.7.1.2. The symmetry of each SALC and orbital under the D_{2h} **point group** is shown in red font. (CC-BY-NC-SA; Kathryn Haas)

Constructing the MO diagram

After identifying the atomic orbitals and constructing SALCs, place the atomic orbitals of H on one side of the diagram and all SALCs from F on the other side. Molecular orbitals are in the center.

The lowest-energy fluorine SALCs will be those composed of the lowest-energy atomic orbitals of fluorine; these would be SALC-1 (a_{1g}) and SALC-2 (a_{1u}) that are constructed from fluorine s atomic orbitals. Of these two orbitals, the one with zero nodes would be slightly lower in energy than the one with one node. When these two orbitals form molecular orbitals, the completely symmetric SALC-1 will be mostly non-bonding with slight bonding character from minor combination with the hydrogen $1s$ orbital. SALC-2, however is symmetrically incompatible with hydrogen $1s$ and will be a truly non-bonding orbital distributed over both F atoms.

The six SALCs constructed of fluorine p orbitals will have higher energy since the fluorine p atomic orbitals are higher in energy than the s orbitals (SALC-3 through SALC-8). Again, we expect SALCs with more nodes (SALC-4, -6, -8) to have slightly higher

energy than those with fewer nodes (SALC-3, -5, -7). SALC-7 will form a bonding and antibonding interaction with the hydrogen $1s$ orbital. All other SALCS are truly non-bonding, but are non-degenerate non-bonding orbitals.

In bifluoride, there is an important distinction between the Lewis structure and molecular orbital description of lone pairs. In Lewis theory, the lone pairs are localized to individual fluorine atoms, while in the molecular orbital description each lone pair is distributed over both fluorine atoms at once (see surface depiction of each molecular orbital in Figure 10.7.1.4).

This page titled 10.7.1: Bifluoride anion is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.4.1: Bifluoride anion** is licensed CC BY-SA 4.0.

10.7.2: Carbon Dioxide

Construct SALCs and the molecular orbital diagram for CO_2

Carbon dioxide is another linear molecule. This example is slightly more complex than the previous example of the bifluoride anion. While bifluoride had only one valence orbital to consider in its central H atom (the $1s$ orbital), carbon dioxide has a larger central atom, and thus more valence orbitals that will interact with SALCs.

Preliminary Steps

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The CO_2 molecule is linear and its point group is $D_{\infty h}$. The z axis is collinear with the C_∞ axis. We will use the D_{2h} point group as a substitute since the orbital symmetries are retained in the D_{2h} point group.

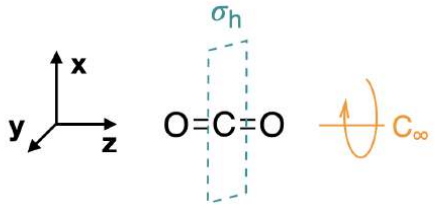


Figure 10.7.2.1: CO_2 belongs to the $D_{\infty h}$ point group. (CC_BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the two pendant oxygen atoms has four valence orbitals; $2s$, $2p_x$, $2p_y$, and $2p_z$. Thus, we can expect a total of eight SALCs.

Generate SALCs

The SALCs for CO_2 are identical in shape and symmetry to those described in the previous example for the bifluoride anion. But instead of cutting to the shortcut, we will systematically derive the SALCs here to demonstrate the process.

Step 3. Generate the Γ's

Use the D_{2h} character table to generate four reducible representations ($\Gamma's$); one for each of the four types of pendant atom orbitals ($s,\ p_x,\ p_y,\ p_z$). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. For each p orbital, assign 1 if there is no change, -1 if it remains in place but is inverted, and 0 if it moves out of its original position. The four Γ's are given below:

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\mathbf{\Gamma_{2s}}$	2	2	0	0	0	0	2	2
$\mathbf{\Gamma_{2p_x}}$	2	−2	0	0	0	0	2	−2
$\mathbf{\Gamma_{2p_y}}$	2	−2	0	0	0	0	−2	2
$\mathbf{\Gamma_{2p_z}}$	2	2	0	0	0	0	2	2

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. There are two strategies that can be used to do this. The quick and easy way is to do it "by inspection", but this only works well for simple cases. The other is by using the systematic approach for breaking a Γ into reducible representations described previously in section 4.4.2 using the following formula:

$$\text{number of } i = \frac{1}{h}\sum(\text{number of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \tag{10.7.2.1}$$

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

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

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\mathbf{\Gamma_{2s} = A_g + B_{1u}}$	$\mathbf{\Gamma_{2s}}$	**2**	**2**	**0**	**0**	**0**	**0**	**2**	**2**
	A_g	1	1	1	1	1	1	1	1
	B_{1u}	1	1	−1	−1	−1	−1	1	1
$\mathbf{\Gamma_{2p_x} = B_{2g} + B_{3u}}$	$\mathbf{\Gamma_{2p_x}}$	**2**	**−2**	**0**	**0**	**0**	**0**	**2**	**−2**
	B_{2g}	1	−1	1	−1	1	−1	1	−1
	B_{3u}	1	−1	−1	1	−1	1	1	−1
$\mathbf{\Gamma_{2p_y} = B_{3g} + B_{2u}}$	$\mathbf{\Gamma_{2p_y}}$	**2**	**−2**	**0**	**0**	**0**	**0**	**−2**	**2**
	B_{3g}	1	−1	−1	1	1	−1	−1	1
	B_{2u}	1	−1	1	−1	−1	1	−1	1
$\mathbf{\Gamma_{2p_z} = A_g + B_{1u}}$	$\mathbf{\Gamma_{2p_z}}$	**2**	**2**	**0**	**0**	**0**	**0**	**2**	**2**
	A_g	1	1	1	1	1	1	1	1
	B_{1u}	1	1	−1	−1	−1	−1	1	1

Step 5. Sketch the SALCs

From the systematic process above, you have found the symmetries (the irreducible representations) of all eight SALCs under the D_{2h} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the D_{2h} character table, and specifically the functions listed on the right side columns of the table.

Two A_g SALCs (one from s and one from p_z): The A_g SALCs are each singly degenerate and symmetric with respect to both the principal axis (z) and the inversion center (i) (based on its Mulliken Label). We can look at the functions in the D_{2h} character table that correspond to A_g and see that it is completely symmetric under the group (because the combination of x^2, y^2, z^2 shows that it is totally symmetric). This would be the same symmetry as an s orbital on the central atom. From this information, we know that these SALCs must have symmetry compatible with an s orbital on the central atom, and we can draw the two A_g SALCs shown in Figure 10.7.2.2.

Two B_{1u} SALCs (one from s and one from p_z): The Mulliken Label tells us that the B_{1u} SALCs are each antisymmetric with respect to both the principal axis and the inversion center. The function, z, appearing with B_{1u} in the character table tells us that these SALCs have the same symmetry as the z axis, or a p_z orbital on the central atom. From this information, we know that these two SALCs should be compatible with a p_z orbital on the central atom, and we can draw the two B_{1u} SALCs shown in Figure 10.7.2.2.

All other SALCs shown below are derived using a strategy similar to the one in the two cases described above.

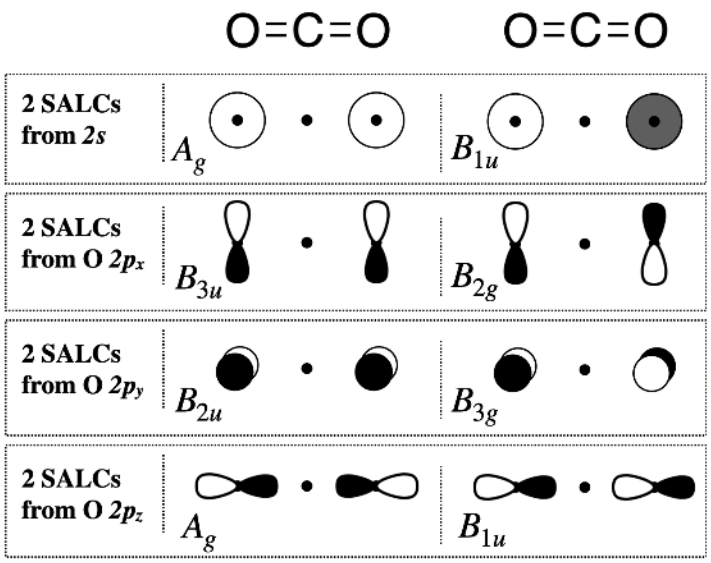


Figure 10.7.2.2: SALCs from the valence orbitals of oxygen atoms in CO_2. (CC-BY-NC-SA; Kathryn Haas)

Draw the MO diagram for CO_2

Step 6. Combine SALCs with AO's of like symmetry.

First we identify the valence orbitals on carbon: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the D_{2h} character table. The symmetry of a central s orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_g. The p_z orbital corresponds to the symmetry of the linear function z in the character table; this is B_{1u}. And so on... The symmetries of the C valence orbitals are listed below.

$$2s = A_g$$
$$2p_x = B_{3u}$$
$$2p_y = B_{2u}$$
$$2p_z = B_{1u}$$

Now that we have identified the symmetries of the eight oxygen SALCs and the four valence orbitals on carbon, we know which atomic orbitals and SALCs may combine based on compatible symmetries. We also need to know the relative orbital energy levels so that we can predict the relative strength of orbital interactions. The orbital ionization energies are listed in Section 5.3.

With knowledge of both orbital symmetries and energies, we can construct the molecular orbital diagram. The carbon atom goes on one side of the diagram while the oxygen SALCs are drawn on the opposite side. Molecular orbitals are drawn in the center column of the diagram:

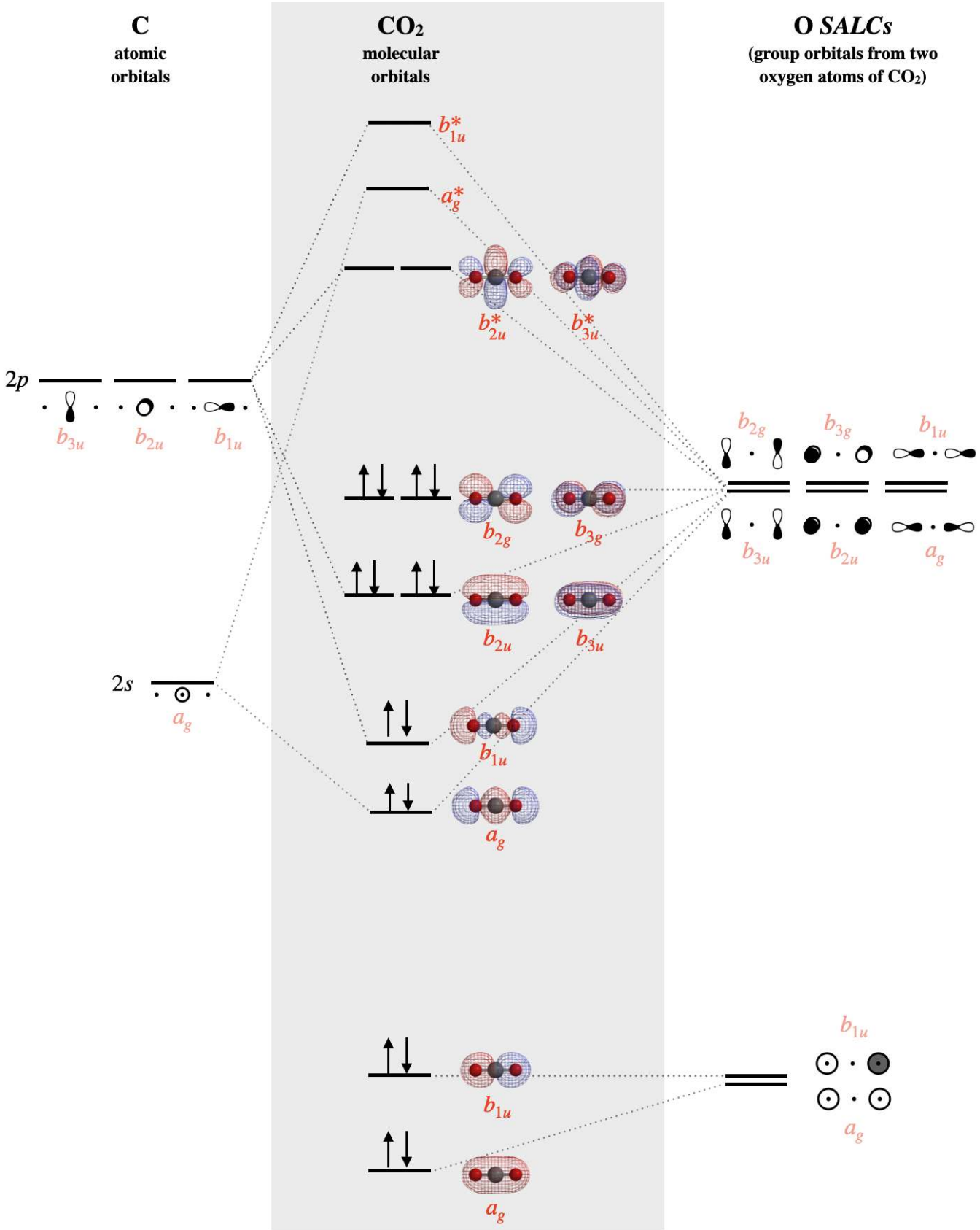


Figure 10.7.2.3: Molecular orbital diagram for carbon dioxide. (CC-BY-NC-SA; Kathryn Haas)

The SALCs on the right side of the diagram above are constructed from groups of either the $2s$ atomic orbitals of oxygen, or the $2p$ atomic orbitals of oxygen. Each SALC will combine with the atomic orbitals of carbon that have compatible symmetry; but the strength of the interaction depends on their relative energies. The individual valence atomic orbitals of oxygen have energies of $-32.36eV$ ($2s$) and $-15.87eV$ ($2p$), while the valence orbitals of carbon have energies of $-19.47eV$ ($2s$) and $-10.66eV$ ($2p$). The $2s$ orbitals of the oxygen are far lower in energy ($-32.36eV$) than all other valence orbitals, and so we should expect that molecular orbitals that are constructed from these oxygen $2s$ will be mostly non-bonding. These mostly non-bonding orbitals are the a_{1g} and b_{1g} orbitals shown at the bottom of Figure 10.7.2.3. The a_g orbital is lower in energy than the b_{1u} due to slight mixing with other orbitals of a_g symmetry.

The bonding orbitals of CO_2 include two $sigma$ molecular orbitals of a_g and b_{1u} symmetry and two π molecular orbitals of b_{2u} and b_{3u} symmetry. Each of these bonding molecular orbitals possesses a higher-energy antibonding partner. The b_{2g} and b_{3g} SALCs that are formed from oxygen $2p_x$ and $2p_y$ orbitals have no compatible match with carbon valence orbitals; thus they form two b_{2g} and b_{3g} molecular orbitals, which are truly non-bonding and mostly oxygen in character. Still, notice that each orbital is spread across both oxygen atoms at once, and again we see that each non-bonding electron pair in the HOMO is very different in molecular orbital theory compared to Lewis theory. Each non-bonding pair is distributed over both oxygen atoms at once in molecular orbital theory, while in Lewis theory each lone pair is isolated to one atom or to localized bonds attached to that atom.

This page titled 10.7.2: Carbon Dioxide is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.4.2: Carbon Dioxide** by Kathryn Haas is licensed CC BY-SA 4.0.

10.7.3: H_2O

Construct SALCs and the molecular orbital diagram for H_2O.

This is the first example so far that is not a linear molecule. Water is a bent molecule, and so it is important to remember that interactions of pendant ligands are dependent on their positions in space. You should consider the positions of the three atoms in water to be essentially fixed in relation to each other. The process for constructing the molecular orbital diagram *for a non-linear molecule*, like water, is similar to the process for linear molecules. We will walk through the steps below to construct the molecular orbital diagram of water.

Preliminary Steps

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The H_2O molecule is bent and its point group is C_{2v}. The z axis is collinear with the principal axis, the C_2 axis. There is no need to simplify this problem, as we had done for previous examples. The C_{2v} point group is simple enough.

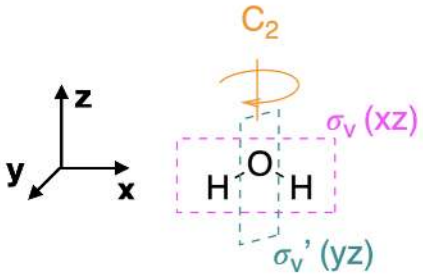


Figure 10.7.3.1: The water molecular is in the C_{2v} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the two pendant hydrogen atoms has one valence orbital, the $1s$. Thus, we can expect a total of two SALCs from these two atoms.

Generate SALCs

The SALCs for H_2O are quite simple, yet we will systematically derive the SALCs here to demonstrate the process.

Step 3. Generate the Γ's

Use the C_{2v} character table to generate one reducible representation (Γ); in this case we need only one Γ because there is only one type of valence orbital (the $1s$). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. The Γ is given below:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
$\mathbf{\Gamma_{1s}}$	2	0	2	0

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. Using either of the processes described previously, we find that the Γ reduces to the two irreducible representations A_1 and B_1 under the C_{2v} point group.

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
$\mathbf{\Gamma_{1s}}$	**2**	**0**	**2**	**0**
A_1	1	1	1	1
B_1	1	−1	1	−1

Step 5. Sketch the SALCs

From the systematic process above, you have found the symmetries (the irreducible representations) of both SALCs under the C_{2v} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the C_{2v} character table, and

specifically the functions listed on the right side columns of the table.

One A_1 SALC: The A_1 SALC is singly degenerate and symmetric with respect to both the principle axis (z) and the inversion center (i) (based on its Mulliken Label). We can look at the functions in the C_{2v} character table that correspond to A_1 and see that it is completely symmetric under the group (because the combination of x^2, y^2, z^2 shows that it is totally symmetric). This would be the same symmetry as an s orbital on the central oxygen atom. From this information, we know that this SALC must have symmetry compatible with an s orbital on the central atom. We can also see from the character table that the z axis, and thus a p_z orbital on oxygen, also possesses A_1 symmetry. This tells us that in addition to being compatible with the oxygen s orbital, it should also be compatible with the oxygen p_z orbital. From this information we can draw the A_1 SALC shown in Figure 10.7.3.2. *If it is not obvious how the A_1 sketch in Fig. 10.7.3.2 is compatible with the s and p_z orbitals of oxygen, inspect the drawings corresponding to molecular orbitals $2a_1$ and $3a_1$ in Fig. 10.7.3.3.*

One B_1 SALC: The Mulliken Label tells us that the B_1 SALC is singly degenerate and antisymmetric with respect to both the principal axis and the inversion center. The function, x, appearing with B_1 in the character table tells us that this SALC has the same symmetry as the x axis, or a p_x orbital on the central oxygen atom. From this information, we know that this SALC should be compatible with a p_x orbital on the central atom, and we can draw the B_1 SALCs shown in Figure 10.7.3.2. *If it is not obvious how the B_1 sketch in Fig. 10.7.3.2 is compatible with the p_x orbital of oxygen, inspect the drawing corresponding to molecular orbital $1b_1$ in Fig. 10.7.3.3.*

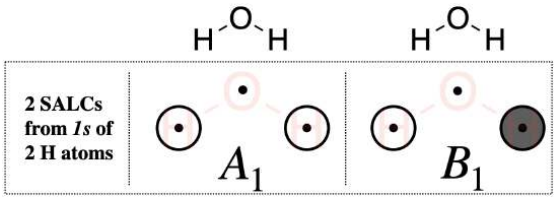


Figure 10.7.3.2: Sketch of the A_1 and B_1 hydrogen SALCs of water. (CC-BY-NC-SA; Kathryn Haas)

Not convinced about the sketches of these SALCs? You can convince yourself by putting them to the test. Try the exercise below.

? Exercise 10.7.3.1

Perform all operations of the C_{2v} point group on the two sketches of H SALCs shown in Figure 10.7.3.2, and convince yourself that each sketch does possess the A_1 and B_1 symmetries assigned to them, respectively, under the C_{2v} point group.

Answer

Add texts here. Do not delete this text first.

Draw the MO diagram for H_2O

Step 6. Combine SALCs with AO's of like symmetry.

First we must identify the valence orbitals on the central oxygen: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the C_{2v} character table. The symmetry of a central $2s$ orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_1. The p_z orbital also corresponds to A_1. And so on... The symmetries of oxygen valence orbitals are listed below.

$$2s = A_1$$
$$2p_x = B_1$$
$$2p_y = B_2$$
$$2p_z = A_1$$

Now that we have identified the symmetries of the two hydrogen SALCs and the four valence orbitals on oxygen, we know which atomic orbitals and SALCs may combine based on compatible symmetries. We also need to know the relative orbital energy levels so that we can predict the relative strength of orbital interactions. The orbital ionization energies are listed in Section 5.3.1.

With knowledge of both orbital symmetries and energies, we can construct the molecular orbital diagram. The valence orbitals of oxygen go on one side of the diagram while the hydrogen group orbitals are drawn on the opposite side. Molecular orbitals are

drawn in the center column of the diagram, as shown in Figure 10.7.3.3:

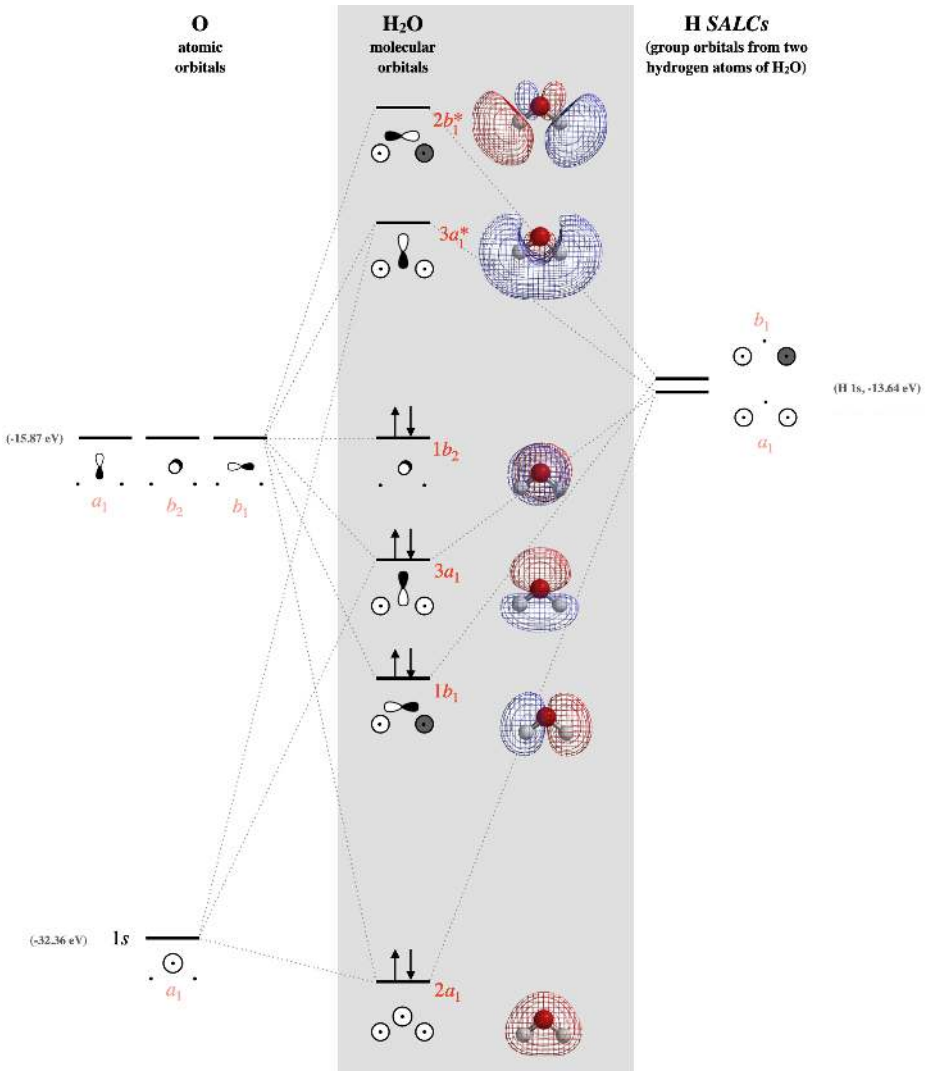


Figure 10.7.3.3: The molecular orbital diagram of water. Molecular orbital surfaces calculated using Spartan software. The surface of the $3a_1^*$ orbital has been trimmed. (CC-BY-NC-SA; Kathryn Haas)

Example 10.7.3.1

In the previous examples shown for the molecular orbital diagrams of the bifluoride anion and carbon dioxide, we discussed differences in the understanding of those molecules from molecular orbital theory compared to Lewis structures. Water contains two lone pairs in its Lewis structure. Compare the predictions about water's lone pairs of electrons and its reactivity based on (1) the combination of elementary models (Lewis, Valence Bond, and Hybridized Orbital theories) and (2) Molecular Orbital theory. Specifically address and explain how the elementary models differ from molecular orbital theory in the following respects:

a. Where are the lone pairs in water?
b. Are the two lone pairs equivalent or are they different?
c. Where are sites on the molecule that will undergo reaction with electrophiles and nucleophiles?

Solution

1) Elementary models: The Lewis structure predicts that two lone pairs are (a) localized on the oxygen atom of water and that (b) both lone pairs are equivalent. The Lewis structure, combined with Valence Bond Theory, would predict that lone pairs occupy two equivalent hybridized sp^3 atomic orbitals on oxygen. (c) Lewis theory would predict that the oxygen lone pairs are

nucleophiles; thus an electrophile would react with the oxygen atom lone pairs. The polarized O-H bond leaves the H atoms as the most electrophilic locations on the water molecule; thus nucleophiles would react at the H atoms of water.

2) Molecular orbital theory: The molecular orbitals predict that (a) the two lone pairs of water are not equivalent, and that (b) each is distributed over the entire molecule. One lone pair is in the truly non-bonding $1b_2$ orbital (Figure 10.7.3.3), which is also the HOMO. There is not another truly non-bonding orbital in the molecule, but the lowest-energy $2a_1$ orbital could be considered mostly non-bonding due to the large energy difference between it and other valence orbitals. (c) Although the $2a_1$ orbital can be considered mostly non-bonding, we cannot expect the electrons in $2a_1$ to react readily, as they are in the lowest-energy molecular orbital. Molecular orbital theory predicts that reactions occur at the HOMO and LUMO orbitals. The HOMO reacts with electrophiles, and in this case, the HOMO is distributed over the top and bottom faces of the molecule, and is centered on the oxygen atom. The LUMO would react with nucleophiles. The LUMO is the orbital labeled $3a_1^*$ in Figure 10.7.3.3, and has a major lobe that is distributed more heavily over the H atoms, and from this we should predict H atoms to be the preferred site of reaction for nucleophiles.

Expressing molecular orbitals in terms of Ψ

The general expression for a molecular orbital, or the linear combination of atomic orbitals (LCAO), was given previously as $\Psi = c_a\psi_a + c_b\psi_b$. In this expression, the wavefunction of two atoms (ψ_a and ψ_b) is combined to form the wavefunction of the molecular orbital. The coefficients c_a and c_b quantify the contribution of each atomic ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

In the case of polyatomic orbitals, each LCAO is constructed of atomic orbitals from a central atom and group orbitals (SALCs) from the pendent atoms. In the case of water, the expression above could be modified to give the expression below.

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

N represents the normalizing requirement that was mentioned previously in reference to the requirements for electron wavefunctions and probability functions. The normalizing requirement simply stated is the requirement that the probability of finding the electron in any orbital, including group orbitals, is 1. In general, the value of N for a group orbital is...

$$N = \frac{1}{\sum c_i^2}$$

...where c_i is the coefficient of each unique atomic orbital that contributes to the group. For the hydrogen SALCs of water, there are two atomic orbitals that contribute to equally to each SALC, and so the coefficient on each of the two orbitals is 1. This gives $N = \left(\frac{1}{\sqrt{1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$ for the H SALCs of water.

There are only two hydrogen SALCs: the one in which the hydrogen wavefunctions are added ($N(\psi_{H_a} + \psi_{H_b})$) has A_1 symmetry, and the one in which the hydrogen wavefunctions are subtracted ($N(\psi_{H_a} - \psi_{H_b})$) has B_1 symmetry.

The molecular orbitals from Figure 10.7.3.3 are expressed below in terms of their LCAO of individual wavefunctions. Yet, note that these expressions are simplifications that ignore orbital mixing. For example, as expressed below, they ignore contributions of oxygen $2s$ to the higher energy moelcular orbitals with A_1 symmetry (the $3a_1$ and $3a_1^*$ in Figure 10.7.3.3).

MO		*OxygenAO*		*HydrogenSALC*	*Description*
Ψ_{2a_1}	=	$c_{(ox1)}\psi_{(2s)}$	+	$c_{(hy1)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy1)}$ is positive; bonding, slightly nonbonding
Ψ_{1b_1}	=	$c_{(ox2)}\psi_{(2p_x)}$	+	$c_{(hy2)}[N(\psi_{H_a} - \psi_{H_b})]$	$c_{(hy2)}$ is positive; bonding
Ψ_{3a_1}	=	$c_{(ox3)}\psi_{(2p_z)}$	+	$c_{(hy3)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy3)}$ is positive; bonding
Ψ_{1b_2}	=	$\psi_{(2p_y)}$			nonbonding
$\Psi^*_{3a_1}$	=	$c_{(ox4)}\psi_{(2p_z)}$	+	$c_{(hy4)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy4)}$ is negative; antibonding
$\Psi^*_{1b_1}$	=	$c_{(ox5)}\psi_{(2p_x)}$	+	$c_{(hy5)}[N(\psi_{H_a} - \psi_{H_b})]$	$c_{(hy5)}$ is negative; antibonding

This page titled 10.7.3: H2O is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.4.3: H2O** is licensed CC BY-SA 4.0.

10.7.4: NH_3

Construct SALCs and the molecular orbital diagram for NH_3

This is the first example so far that has more than two pendant atoms and the first example in which the molecule has atoms that lie in three dimensions (i.e., it is not flat). Ammonia is a trigonal pyramidal molecule, with three pendant hydrogen atoms. The three-dimensional shape and the odd number of pendant atoms makes this example more complicated than the previous cases of water, carbon dioxide, and bifluoride. In this case, sketching the shapes (step 5) of pendant atom SALCs is less straightforward; rather, an alternative method, the **projection operator method**, is preferred for generating pictorial representations of the SALCs.

As in previous examples, it is important to remember that interactions of pendant ligands are dependent on their positions in three-dimensional space. You should consider the positions of the four atoms in ammonia to be essentially fixed in relation to each other. We will walk through the steps used to construct the molecular orbital diagram of ammonia. The first few steps are the same as you've seen before:

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The NH_3 molecule is trigonal pyramidal and its point group is C_{3v}. The z axis is collinear with the principal axis, the C_3 axis.

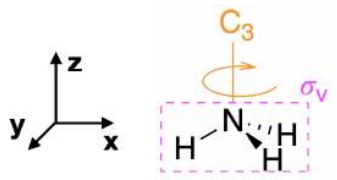


Figure 10.7.4.1: The ammonia molecule is in the C_{3v} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the three pendant hydrogen atoms has one valence orbital; the $1s$. Thus, we can expect a total of three SALCs from these three atoms.

Step 3. Generate the Γ's

Use the C_{3v} character table to generate one reducible representation (Γ); in this case we need only one Γ because there is only one type of valence orbital (the $1s$). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. The Γ is given below:

$\mathbf{C_{3v}}$	E	$2C_3$	$3\sigma_v$
$\mathbf{\Gamma_{1s}}$	3	0	1

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. Using either of the processes described previously, we find that the Γ reduces to the two irreducible representations A_1 and E under the C_{3v} point group.

$\mathbf{C_{3v}}$	E	$2C_3$	$3\sigma_v$
$\mathbf{\Gamma_{1s}}$	**3**	**0**	**2**
A_1	1	1	1
E	2	−1	0

Notice that we only found TWO irreducible representations. But, in fact we have THREE different SALCs. The E irreducible representation is doubly degenerate, which in this context means that it corresponds to two degenerate SALCs. Thus, we have already found the symmetries of the three SALCs for ammonia: Two of the SALCs are degenerate with E symmetry under the C_{3v} point group, while the third SALC has A_1 symmetry.

Step 5. Sketch the SALCs using the PROJECTION OPERATOR METHOD

From the first four steps (described above), you have found the symmetries (the irreducible representations) of all three SALCs under the C_{3v} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the C_{3v} character

table. But now we will introduce the **projection operator method** to derive the surface representation of each SALC.

Step 5.1: Label the pendent atoms

In the projection operator method, first **label each of the pendant atoms so that we can distinguish identical atoms from one another**; for example, identify the three hydrogen atoms on ammonia as H_a, H_b, and H_c (Figure 10.7.4.2).

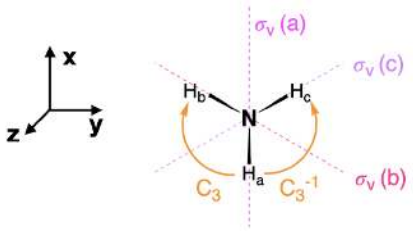


Figure 10.7.4.2: The three H's in NH_3 are chemically identical, but we can distinguish them using labels for the purpose of applying the projection operator method. In this figure, we have placed the z axis along the principal C_3 axis and placed the x axis colinear with one H. Each of the three H atoms has been labeled as H_a, H_b, or H_c. The σ_v that is coplanar with each H is labeled similarly (a, b, c) to keep account of each individual plane of symmetry. (CC-BY-NC-SA; Kathryn Haas)

Step 5.2: Create an expanded character table with one pendant atom's projected position after each operation

We will **perform each operation of the C_{3v} point group on this labeled molecule** and follow where one of the atoms is projected after the operation is complete. We will arbitrarily choose H_a. For example, upon performing the identity operation, E, the H_a atom is projected onto itself. On the other hand, H_a is projected onto H_b upon a clockwise C_3 rotation (as drawn in Figure 10.7.4.2). We take into account the result of each operation using an expanded character table (refer to the table below, 10.7.4.1). In the expanded character table, each operation within each class is written separately (i.e., $2C_3$ is accounted for separately as C_3 and C_3^{-1}).

Table 10.7.4.1: The expanded character table, and the projection of H_a by each operation is shown below.

$\mathbf{C_{3v}}$	E	C_3	C_3^{-1}	$\sigma_v(a)$	$\sigma_v(b)$	$\sigma_v(c)$
Projection of $\mathbf{H_a}$	H_a	H_b	H_c	H_a	H_c	H_b

(10.7.4.1)

Step 5.3: Find the contribution of each pendant atom to each SALC

Next, **create a linear combination of the projections for each of the SALCs** (the irreducible representations found in step 4). For each of the irreducible representations, multiply the projection by the respective character of the operation.

$$\text{Contribution of each atom to the SALC } = \sum(\text{Projection of } H_a \times \chi)$$

The linear combination for all irreducible representations of C_3v is shown below.

Table 10.7.4.2: The symmetry adapted linear combination (SALC) for each irreducible representation of C_3v is shown.

$\mathbf{C_{3v}}$	E	C_3	C_3^{-1}	$\sigma_v(a)$	$\sigma_v(b)$	$\sigma_v(c)$	Linear Combination
Projection of $\mathbf{H_a}$	$\mathbf{H_a}$	$\mathbf{H_b}$	$\mathbf{H_c}$	$\mathbf{H_a}$	$\mathbf{H_c}$	$\mathbf{H_b}$	
A_1	1	1	1	1	1	1	$= \mathbf{2H_a + 2H_b + 2H_c}$
A_2	1	1	1	−1	−1	−1	$= 0$
E	2	−1	−1	0	0	0	$= \mathbf{2H_a - H_b - H_c}$

(10.7.4.2)

Notice that there are only two irreducible representations that produce SALCs, and these are the same that were found in Step 4, above. This illustrates the fact that only the irreducible representations found through the reduction of the Γ will produce SALCs. We can ignore any irreducible representations that were not found in Step 4. Or, you can check your work in Step 4 by applying the projection operator to any irreducible representations not found in Step 4, and finding that they produce a sum of zero.

Step 5.4: Sketch the SALCs

The meaning of the linear combinations found in Table 10.7.4.2 is as follows:

- **Sketch the SALC with A_1 symmetry:** The linear combination $2H_a + 2H_b + 2H_c$ indicates all contributions to this SALC are of the same sign (of the wavefunction). Qualitatively, this means there is no node in this SALC. We can take this SALC almost literally to assume that all three H 1s wavefunctions contribute equally to the SALC. We can also use the fact that the A_1 representation possesses the full symmetry of the C_3v point group, is compatible with an s orbital on N, and thus is a totally symmetric SALC.

  Quantitatively, we can apply the normalizing factor, N, for this SALC. The linear combination for the A_1 SALC in Table 10.7.4.2 shows us that the coefficient for each orbital is 1. Thus, the normalizing factor for the A_1 SALC is $N = \left(\frac{1}{\sqrt{1^2+1^2+1^2}}\right) = \frac{1}{\sqrt{3}}$. This tells us that H_a, H_b, and H_c each contribute $\frac{1}{\sqrt{3}}$ to the normalized A_1 group orbital:

  $$A_1 \text{ group orbital } = \frac{1}{\sqrt{3}}\left[\psi_{H_a} + \psi_{H_b} + \psi_{H_c}\right]$$

  This is shown visually in Figure 10.7.4.3.
- **Sketch two SALCs with E symmetry:** The linear combination $2H_a - H_b - H_c$ indicates that there are contributions with both positive and negative sign to the wavefunction for each of the E group orbitals. Qualitatively, this tells us that there is a node within each of these two SALCs, and that the total contribution of the positive portion of the wavefunction is equal to the contribution of the negative portion.
  - **Finding the first E SALC:**
    For one of the SALCs, we can take the linear combination from Table 10.7.4.2 almost literally: The contribution from H_a is equal and opposite to the sum of the contributions from $H_b + H_c$. This would result in a SALC as shown in Figure 10.7.4.3 (E, left), that would have symmetry of the x axis and that would be compatible with the p_x orbital on N. The node exists in the yz plane and there is an equal contribution of positive and negative parts of the total wavefunction.

    We can also apply the normalizing factor, N, to find this SALC. The linear combination for the E SALC in Table 10.7.4.2 shows us that the coefficients for orbital contributions are 2, -1, and -1. Thus, the normalizing factor for the first E SALC is $N = \left(\frac{1}{\sqrt{2^2+(-1)^2+(-1)^2}}\right) = \frac{1}{\sqrt{6}}$. This normalized E group orbital is:

    $$\text{First } E \text{ group orbital } = \frac{1}{\sqrt{6}}\left[2\psi_{H_a} - \psi_{H_b} - \psi_{H_c}\right]$$

    This is shown visually in Figure 10.7.4.3 (E, left).
  - **Finding the second E SALC:**
    The second SALC is less obvious at first glance. We must use clues from the character table to help us determine what it should "look like". Since the E representation transforms as the group, (x, y), we know that one of the SALCs will have the symmetry of the x axis and p_x orbital on the central nitrogen atom, while the other should possess the symmetry of the y axis and be compatible with the p_y orbital on nitrogen. This alone could lead you to the sketch of the second SALC with E symmetry shown in Figure 10.7.4.3 (E, right). This second E SALC must have a node in the xz plane, and because H_a lies in this node, H_a cannot contribute to this group orbital. Retaining the fact that the positive and negative contributions of the linear combination must be equal, we can arrive at a SALC that has equal but opposite contributions of H_b and H_c, and no contribution by H_c (Figure 10.7.4.3, right).

    We can also apply the normalizing factor, N, to find this SALC. But we must apply the fact that H_a cannot contribute to the SALC with "y" symmetry. We remove the contribution of H_a, leaving us with coefficients of 0 for H_a and 1 for H_b and H_c. Thus, the normalizing factor for the second E SALC is $N = \left(\frac{1}{\sqrt{0^2+1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$. To this, we must add positive and negative coefficients so that the entire wavefunction of this SALC is normalized. The result for this normalized E group orbital is:

    $$\text{Second } E \text{ group orbital } = \frac{1}{\sqrt{2}}\left[\psi_{H_b} - \psi_{H_c}\right]$$

    This is shown visually in Figure 10.7.4.3.

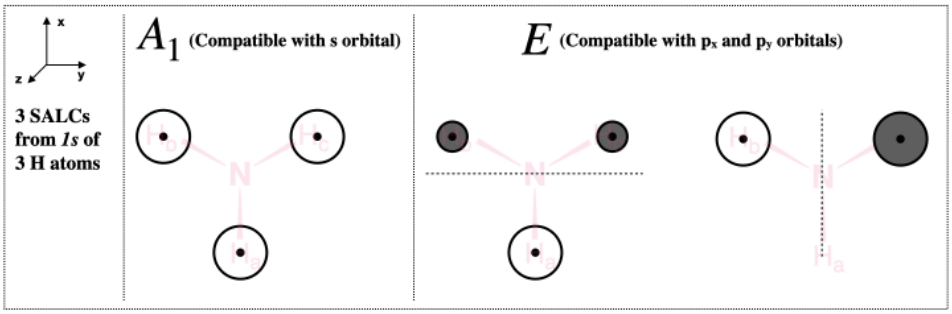


Figure 10.7.4.3: Sketches of H SALCs of ammonia from the perspective of the C_3 axiz (z axis). The A_1 SALC is shown at the left, while two degenerate SALCs with E symmetry are shown on the right. Nodes for E group orbitals are shown as dashed lines. (CC-BY-NC-SA; Kathryn Haas)

Step 6. Combine SALCs with AO's of like symmetry to draw the MO diagram for NH_3

First we must identify the valence orbitals on the central nitrogen: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the C_{3v} character table. The symmetry of a central $2s$ orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_1. The p_z orbital also corresponds to A_1. And so on... The symmetries of nitrogen valence orbitals are listed below.

$$2s = A_1$$
$$(2p_x,\ 2p_y) = E$$
$$2p_z = A_1$$

The next step is to get a sense of the relative energies of valence atomic orbitals for nitrogen and hydrogen, and then construct the molecular orbital diagram. The nitrogen $2s$ orbital is about 12 eV lower in energy than a H $1s$. This difference is an acceptable energy-match for the H orbitals to interact, but would not usually result in a strong interaction. On the other hand, the nitrogen 2p orbitals have an energy very close to the hydrogen 1s, different by only 0.5 eV. Knowledge of the relative energies of the atomic orbitals tells us that, when constructing a diagram, we can place the H SALCs at an energy similar to that of the N $2p$ orbitals, while the N $2s$ is much lower (Figure 10.7.4.4).

The $2s$ and $2p_z$ orbitals have A_1 symmetry and can combine with the A_1 SALC. These orbitals will give three molecular orbitals. The $2s$ orbital will not have strong interactions with the other orbitals of A_1 symmetry due to the large energy difference. The $2p_z$ orbital will not have good overlap with the wavefunctions for the three hydrogen orbitals due to their positions in space: The $2p_z$ orbital has half of its angular distribution pointed away from the hydrogen orbitals, and half pointed toward the center of a triangle formed by the three hydrogen atoms. The nitrogen $2s$ and $2p_z$ will combine with the hydrogen SALC of A_1 symmetry to give three molecular orbitals; one low-energy bonding orbital, one mid-energy non-bonding orbital, and one high-energy antibonding orbital. The mid-level non-bonding a_1 molecular orbital is close in energy to, and resembles, the nitrogen $2p_z$ orbital. The lowest energy a_1 molecular orbital will be lower in energy, but be similar to the nitrogen $2s$.

The remaining two $2p$ orbitals are degenerate and possess E symmetry under the C_{3v} point group. Although these orbitals are a good energy match, again, their orientation and positions in space do not allow for good orbital overlap, and their bonding and antibonding interactions are relatively weak compared to what we might otherwise expect from such a good energy match. The e atomic orbitals of nitrogen will combine with the e SALCs to give a set of two degenerate bonding molecular orbitals and a set of two degenerate antibonding orbitals (four total molecular orbitals of e symmetry). The MO diagram for NH_3 is shown in Figure 10.7.4.4, with calculated electron density surfaces of each MO shown.

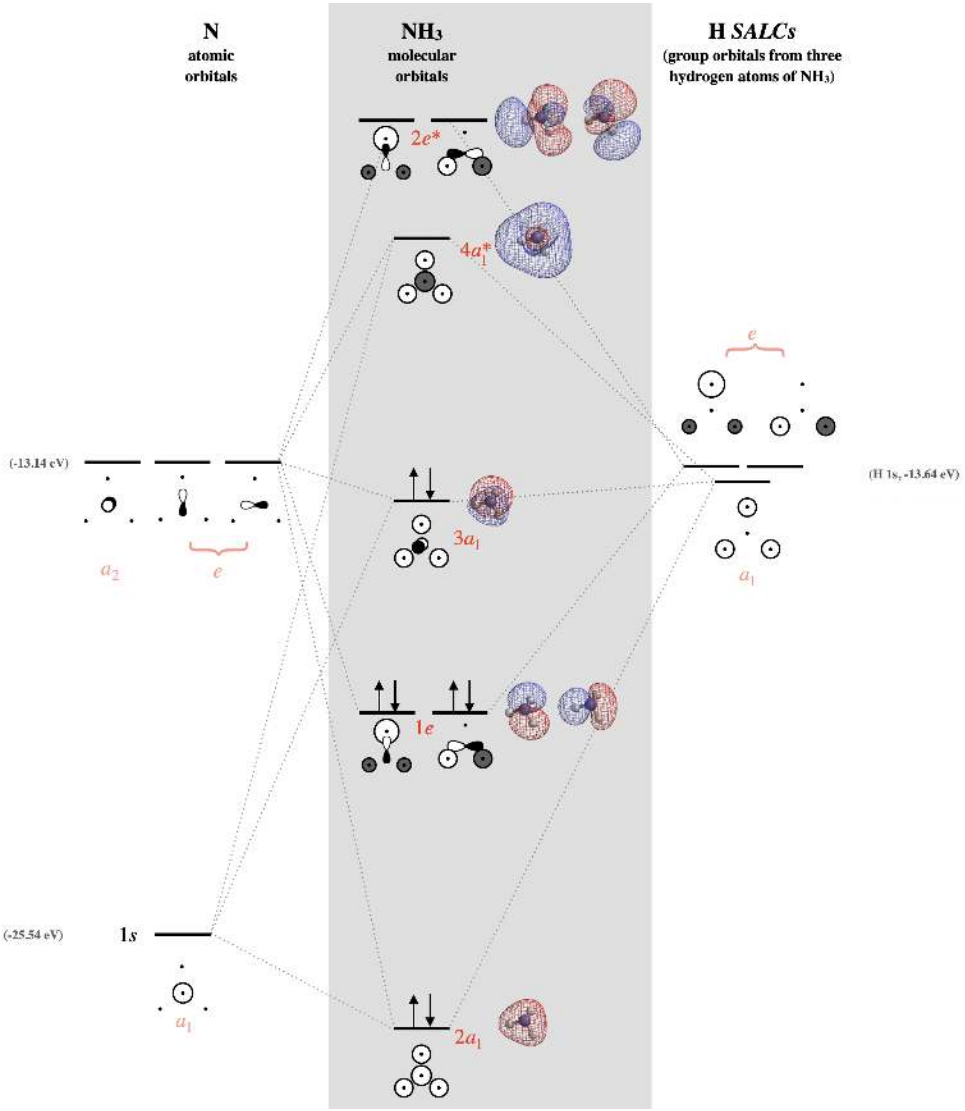


Figure 10.7.4.4: The molecular orbital diagram of ammonia. Molecular orbitals surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

This page titled 10.7.4: NH3 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.4.4: NH3** by Kathryn Haas is licensed CC BY-SA 4.0.

10.7.5: CO_2 (Revisted with Projection Operators)

The process for finding SALCs and constructing the molecular orbital diagram for carbon dioxide was described in a previous section (Section 5.4.2). However, we also just presented an alternative strategy, the projection operator method, to finding the shapes of SALCs in Section 5.4.4. Let's revisit carbon dioxide and demonstrate how you can use the projection operator method to find SALCs for carbon dioxide.

Just as before, we can simplify the problem by approximating the $D_{\infty h}$point group using D_{2h}. The first four steps for constructing the MO diagram would be the same as described in Section 5.4.2. and we will pick up from that point (with Step 5) to find what the SALCs look like using the projection operator method.

The projection operator method applied to CO_2

Step 5.1: Label the pendent atoms.

We can label the pendant atoms as O_a and O_b, as in Figure 10.7.5.1.

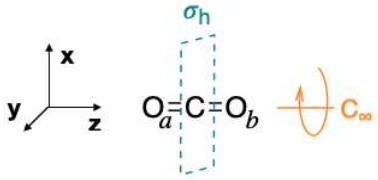


Figure 10.7.5.1: The structure of carbon dioxide with pendant oxygen atoms distinguished with labels a and b. Note that we will approximate the C_∞ axis as a C_2 axis to simplify the process of finding the SALCs. (CC-BY-SA; Kathryn Haas)

Step 5.2: Create an expanded character table with one pendant atom's projected position for each operation

The D_{2h} character table needs no expansion because each operation is in its own class. We will arbitrarily choose to determine the new position of O_a after each operation.

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Projection of O_a	O_a	O_a	O_b	O_b	O_b	O_b	O_a	O_a

Step 5.3: Find the contribution of each pendant atom to each SALC

Create a linear combination of the projections for each or the SALCs. The irreducible representations were found in step 4 in Section 5.4.2. Eight irreducible representations were found to be: $2A_g + 2B_{1u} + B_{2g} + B_{3u} + B_{3g} + B_{2u}$. For each of the irreducible representations, multiply the projection by the respective character of the operation.

$$\text{Contribution of each atom to the SALC } = \sum(\text{Projection of } H_a \times \chi)$$

The linear combination for all irreducible representations of D_{2h} are shown below.

Table 10.7.5.1: The symmetry adapted linear combination (SALC) for each irreducible representations of C_3v are shown.

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Linear Combination
Projection of O_a	O_a	O_a	O_b	O_b	O_b	O_b	O_a	O_a	
A_g	1	1	1	1	1	1	1	1	$= 4O_a + 4O_b$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= 4O_a - 4O_b$
B_{2g}	1	−1	1	−1	1	−1	1	−1	$= 0$
B_{3u}	1	−1	−1	1	−1	1	1	−1	$= 0$
B_{3g}	1	−1	−1	1	1	−1	−1	1	$= 0$
B_{2u}	1	−1	1	−1	−1	1	−1	1	$= 0$

(10.7.5.1)

Notice that there are only two irreducible representations that produce SALCs, the A_g and the B_{1u}. Since we found two of each ($2A_g + 2B_{1u}$) when we found the irreducible representations, we know that there will be two SALCs of A_g symmetry and two of B_{1u}

symmetry; that is four total SALCs from the pendant oxygens. This is the same as what we found in Section 5.4.2 using a different method.

Step 5.4: Sketch the SALCs

The SALCs with A_g symmetry: Quantitatively, we can apply the normalizing factor, N, for these SALCs. Each atom contributes equally to the SALCs, thus the normalizing factor for the A_g SALC is $N = \left(\frac{1}{\sqrt{1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$. This tells us that each oxygen contributes $\frac{1}{\sqrt{2}}$ to each of the normalized A_g group orbitals:

$$A_g \text{ group orbital } = \frac{1}{\sqrt{2}}\left[\psi_{O_a} + \psi_{O_b}\right]$$

The linear combination $4\mathrm{O}_a + 4\mathrm{O}_b$ indicates that wavefunctions from each oxygen atom contribute equally to each of the two SALCs, with the same sign of the wavefunction for each. Because we know that A_g is totally symmetric (all 1's in the characters), we can assume that the SALC's will look like a symmetric arrangement of oxygen orbitals. But which orbitals contribute? We could peek at the character table to get a hint. But we'll treat this problem systematically.

The SALCs with B_{1u} symmetry: The linear combination $4\mathrm{O}_a - 4\mathrm{O}_b$ indicates that each oxygen atom contributes equally, but that they have opposite wavefunctions. Application of the normalizing factor would give us:

$$B_{1u} \text{ group orbital } = \frac{1}{\sqrt{2}}\left[\psi_{O_a} + \psi_{O_b}\right]$$

But how do we know what the SALCs look like? Again, the character table can give us some hints, but we'll use a systematic process, below.

What do the SALCs look like? One way to systematically derive the SALC shapes is to perform the projection (Step 5.3) on specific groups of orbitals on the oxygen atom. For example, if we replicate Table 10.7.5.1 using just the group of oxygen 2s orbitals and the A_g and B_{1u} representations, we get the following:

$\mathbf{D_{2h}}$	E	$C_2(z)$	C_2 (y)	C_2 (x)	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Linear Combination
Projection of 2s orbital of $\mathrm{O_a}$	$\mathbf{O1s_a}$	$\mathbf{O1s_a}$	$\mathbf{O1}$ $\mathbf{s_b}$	$\mathbf{O1}$ $\mathbf{s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_a}$	$\mathbf{O1s_a}$	
A_g	1	1	1	1	1	1	1	1	$= \mathbf{4O1s_a}$ $+ \mathbf{4O1s_b}$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= \mathbf{4O1s_a}$ $- \mathbf{4O1s_b}$

(10.7.5.2)

This tells us that one of the A_g SALCs looks like two oxygen 1s orbitals with equal signs and contributions. It also tells us that one of the B_{1u} SALCs looks like two s orbitals with opposite signs and equal magnitudes. These two SALCs are shown in Figure 10.7.5.2.

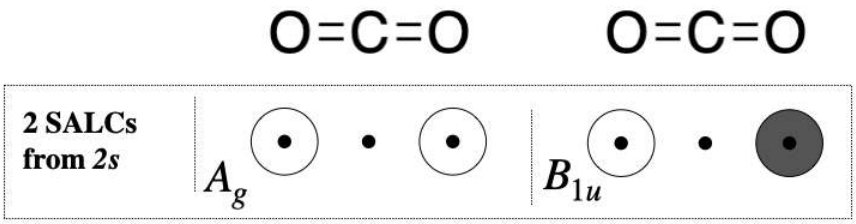


Figure 10.7.5.2: SALCs derived from two oxygen $2s$ orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

If we do the same for the $2p_z$ orbitals, we need to pay attention to the orientation of the p orbital lobes. If the orbital is moved into the opposite orientation, it would get a negative sign in the projection (see below).

$\mathbf{D_{2h}}$	E	C_2 (z)	C_2 (y)	C_2 (x)	i	$\sigma(x$ $y)$	$\sigma(x$ $z)$	$\sigma(yz)$	Linear Combination
Projection of 2px orbital of $\mathrm{O_a}$	$+\mathbf{O2}$ $\mathbf{pz_a}$	$+\mathbf{O2}$ $\mathbf{pz_a}$	$-\mathbf{O2}$ $\mathbf{pz_b}$	$+\mathbf{O2}$ $\mathbf{pz_b}$	$-\mathbf{O2}$ $\mathbf{pz_b}$	$-\mathbf{O2}$ $\mathbf{pz_b}$	$+\mathbf{O2}$ $\mathbf{pz_a}$	$+\mathbf{O2}$ $\mathbf{pz_a}$	
A_g	1	1	1	1	1	1	1	1	$= \mathbf{4O2pz_a}$ $- \mathbf{4O2pz_b}$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= \mathbf{4O2pz_a}$ $+ \mathbf{4O2pz_b}$

(10.7.5.3)

This tells us that one of the A_g SALCs is derived from two $2p_z$ orbitals of opposite sign but equal magnitude. In other words, the two p orbitals are pointing in opposite directions, but the lobes that are facing one another are of the same sign (see Figure 10.7.5.3, left). This also tells us that one of the B_{1u} orbitals is derived from two p_z orbitals of equal magnitude and equal sign (pointing in the same directions, with lobes facing one another of opposite sign!) (see Figure 10.7.5.3, right).

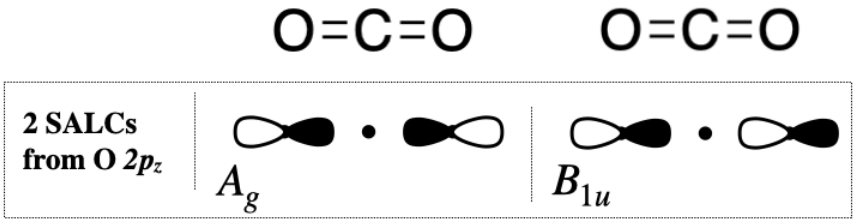


Figure 10.7.5.3: SALCs derived from two oxygen $2p_z$ orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

Now we have reached the same SALCs that we found previously in Section 5.4.2, but by an alternate method.

This page titled 10.7.5: CO_2 (Revisted with Projection Operators) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.4.4: NH_3** by Kathryn Haas is licensed CC BY-SA 4.0.

10.7.6: BF_3

The case of boron trifluoride (BF_3) is an example of a molecule with one more layer of complexity than the other examples we have seen in previous sections in this chapter. (BF_3) is more complex than previous examples because it is the first case in which there are multiple types of valence orbitals on the pendant atoms. (BF_3) possesses s and p orbitals on *both* the central atom and all of the pendant atoms. We can follow the same steps that we have previously to derive other molecular orbital diagrams; however, there is one important difference: we will treat each type of pendant orbital as an individual set of SALCs.

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The BH_3 molecule is trigonal planar, and its point group is D_{3h}. The z axis is colinear with the principle axis, the C_3 axis.

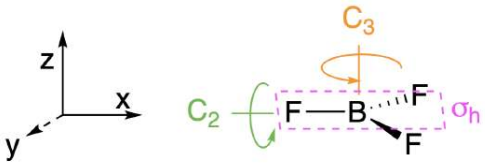


Figure 10.7.6.1: The molecule is in the D_{3h} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the three pendant fluorine atoms has four valence orbitals: one $2s$ and three $2p$ orbitals. Thus, we can expect a total of twelve SALCs from the three atoms. However, we will treat each type of orbital from the F atoms as its own set; each will have its own set of coordinates, with the y axis along the M-L bond. Thus we expect the following:

- One set of $2s$ SALCs: there is one 2s orbital on each of three atoms. This set will have three SALCs.
- One set of $2p_x$ SALCs: there is one $2p_x$ orbital on each of three atoms. Each of these individual orbitals is perpendicular to the M-L bond and coplanar with the molecule. This set will have three SALCs.
- One set of $2p_y$ SALCs: there is one $2p_y$ orbital on each of three atoms. Each of these individual orbitals is colinear with the M-L bond. This set will have three SALCs.
- One set of $2p_z$ SALCs: there is one $2p_z$ orbital on each of three atoms. Each of these individual orbitals is perpendicular to the M-L bond and parallel with the principal axis of the molecule. This set will have three SALCs.

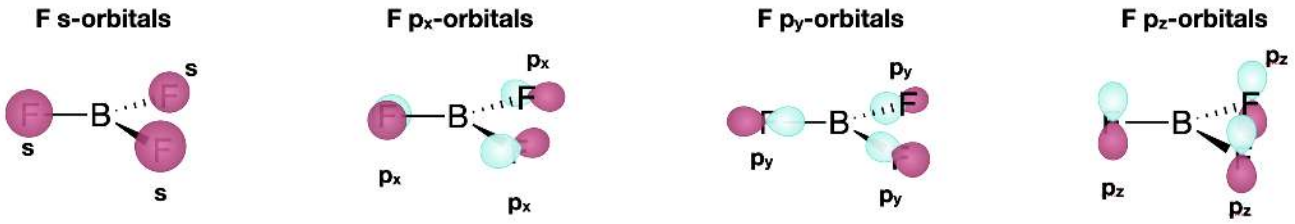


Figure 10.7.6.2: Individual sets of pendant fluorine atomic orbitals will create separate sets of SALCs. (CC-BY-SA; Kathryn Haas)

Step 3. Generate the Γ's for each set of SALCs

Use the D_{3h} character table to generate one reducible representation (Γ) for each of the four sets of pendant atomic orbitals shown in Figure 10.7.6.2; in this case we need four Γ because there are four types of valence orbital (the s, p_x, p_y, p_z).

- For the set of s orbitals: perform the operation for each class in the character table. Each s orbital is assigned a value depending on whether it moves or not: assign a value of 1 if it remains in place during the operation, or 0 (zero) if it moves out of its original place.
- for each set of p orbitals: Now there are phases (signs of the wavefunction), so a negative value is possible. Assign a value of 1 to each p orbital if it remains in place and in phase during the operation; assign a -1 if the atom's position remains, while the phase of the orbital is inverted (the positive lobe moves to the position of the negative lobe and vice versa); assign a 0 if it moves out of its original position.

The Γ for each type is given below:

$\mathbf{D_{3h}}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2s}}$	3	0	1	3	0	1
$\mathbf{\Gamma_{2p_x}}$	3	0	−1	3	0	−1
$\mathbf{\Gamma_{2p_y}}$	3	0	1	3	0	1
$\mathbf{\Gamma_{2p_z}}$	3	0	−1	−3	0	1

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. Using either of the processes described previously, we find that each of the Γ reduces to two irreducible representations under the D_{3h} point group; in each case one is singly degenerate (A) and the other doubly degenerate (E). This equates to three SALCs for each Γ (orbital type) and a total of twelve SALCs. This should give us confidence! We were in fact expecting 12 SALCs because we found that there were twelve pendant atomic orbitals to start with.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2s}}$	**3**	**0**	**1**	**3**	**0**	**1**
A_1'	1	1	1	1	1	1
E'	2	−1	0	2	−1	0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2p_x}}$	**3**	**0**	**−1**	**3**	**0**	**−1**
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2p_y}}$	**3**	**0**	**1**	**3**	**0**	**1**
A_1'	1	1	1	1	1	1
E'	2	−1	0	2	−1	0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2p_z}}$	**3**	**0**	**−1**	**−3**	**0**	**1**
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0

Step 5: Sketch the SALCs

We'll skip this step for now to make this problem simpler.

Step 6: Draw the MO diagram by combining SALCs with AO's of like symmetry.

We now know the symmetries of different pendant orbital SALCs - and it is helpful if we also know their relative energies, and the energies of the valence orbitals on the central boron atom. We can make predictions based on periodic trends, or we can use a table of ionization energies as a guide. The symmetries of the boron $2s$ and $2p$ orbitals can be found from the D_{3h} character table.

This page titled 10.7.6: BF_3 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **5.4.4: NH_3** by Kathryn Haas is licensed CC BY-SA 4.0.

CHAPTER OVERVIEW

11: Coordination Compound Bonding

11.1: Crystal Field Theory
11.2: Crystal Field Stabilization Energy
11.3: Crystal Field Splitting
11.4: Ligand Field Theory
11.5: Metal-Metal Bonding
11.6: Spectrochemical Series
11.7: Colors of Coordination Compounds
11.8: Magnetic Moments

This page titled 11: Coordination Compound Bonding is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

11.1: Crystal Field Theory

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 in the late 1920's. Crystal field theory is a purely electrostatic theory and uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

$$E \propto \frac{q_1 q_2}{r} \tag{11.1.1}$$

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.

For this simple approach to work, CFT makes some assumptions and simplifications. All ligands are modeled as negative point charges with no orbitals and the metal orbitals are modeled as clouds of negative charge. 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 shape and occupation of these d-orbitals then becomes important in an accurate description of the bond energy and properties of the transition metal compound.

Orientation of *d*-Orbitals

To understand CFT, one must first understand the shape and orientation of the d orbitals:

- 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.

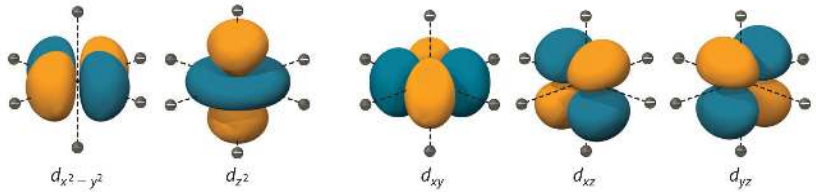


Figure 11.1.1: Spatial arrangement of ligands in the an octahedral ligand field with respect to the five d-orbitals.

Octahedral Crystal Field

When examining a single transition metal ion in free space, the five d-orbitals have the same energy (Figure 11.1.2). When ligands approach the metal ion, the ligand negative point charges destabilize the metal d-orbital based on the geometric structure of the molecule. Since ligands approach from different directions, not all d-orbitals interact equally. These interactions, however, create a splitting due to the electrostatic environment, orbitals with more interaction are higher in energy and orbitals with less interaction are lower in energy.

Definition: Barycenter

In crystal field theory the barycenter is the energy of the d orbitals in a spherical crystal field, where the negative lignad charges are evenly distributed around the metal ion in a sphere. The splitting of the d orbitals in other crystal fields will be symmetric around the barycenter (i.e. the total amount of stabalization will always be equal to the total amount of destabalization)

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 and are therefore at higher energy. Compared to a spherical field, where ligands are evenly distributed around the metal center, the d orbitals that lie between the axes (d_{xy}, d_{xz}, and d_{yz} experience less repulsion when the ligands are in an octahedral arrangement and are stabilized. This causes a splitting in the energy levels of the d-orbitals, known as crystal field splitting. For octahedral complexes, crystal field splitting is denoted by Δ_o (or Δ_{oct}) (in older texts and papers it may also be labeled as 10Dq). Any orbital that has a lobe on the axes moves to a higher energy level. The energies of the e_g symmetry orbitals (d_{z^2} and $d_{x^2-y^2}$) increase due to greater interactions with the ligands. The t_{2g} symmetry orbitals (d_{xy}, d_{xz}, and d_{yz}) decrease in energy with respect to the spherical energy level and become

more stable. This splitting is symmetric around the barycenter (the theoretical energy of the d orbitals with spherical charge distribution) which means that the energy levels of e_g are higher (by $0.6\Delta_o$) while t_{2g} are lower (by $0.4\Delta_o$). It should be noted that the labels t_{2g} and e_g come from group theory and the octahedral point group. The energy difference between the t_{2g} and e_g orbitals dictates the energy that the complex will absorb causing electrons to move from one level to the next. For transition metal complexes, the absorbed energy is typically in the visible part of the spectrum and thus this will determine the color of the complex. 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.

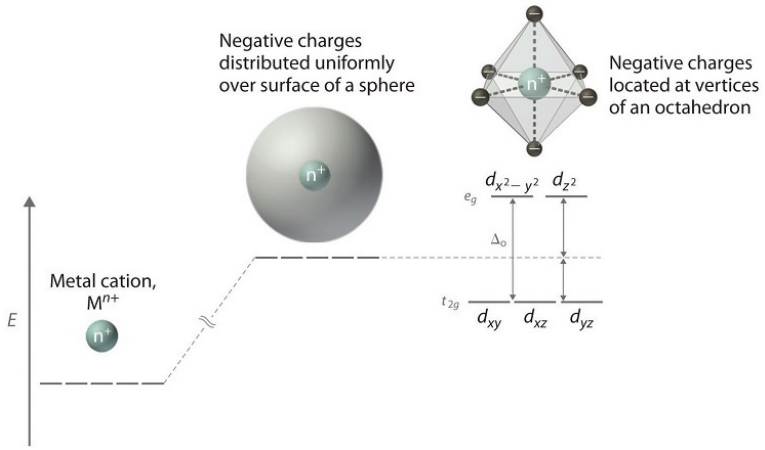


Figure 11.1.2: (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the 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. (b) The two e_g orbitals (left) 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 (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

Filling Electrons in Orbitals

d^1 - d^3

For one, two, or three d electrons the filling is straightforward. According to the Aufbau principle, electrons are filled from lower to higher energy orbitals. In an octahedral crystal field, 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. Therefore, each electron occupies one of the t_{2g} symmetry orbitals d_{xy}, d_{xz}, or d_{yz}) and all the electrons are orientated in the same direction to maximize spin multiplicity as shown in Figure 11.1.3.

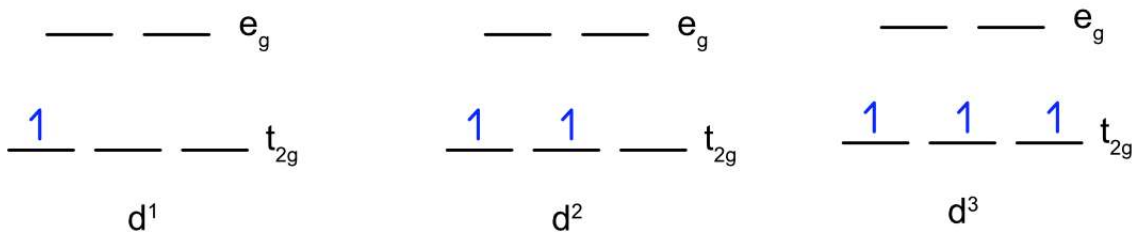


Figure 11.1.3: Arrangement of the d electrons in a octahedral crystal field for 1, 2, and 3 d electrons. (CC-BY-NC-SA; Catherine McCusker)

d^4 - d^7

When a complex has between 4 and 7 d electrons there are two ways the electrons can be arranged into the d orbitals. As an example, in d^4 the first three electrons are placed one in each of the t_{2g} symmetry orbitals. The fourth electron can either be placed in one of the empty e_g symmetry orbitals or it can be paired in one or the t_{2g} symmetry orbitals, as shown in Figure 11.1.4. The first configuration is called high spin because it maximizes the number of unpaired electrons and the second is called low spin. Whether a complex will have the high spin or low configuration depends on the relative magnitude of the spin pairing energy (the energy required to place two negatively charged electrons in the same orbital) and the crystal field splitting (Δ_o). In cases where the spin pairing energy is larger than Δ_o the complex will adopt the high spin configuration because it requires less energy to place an electron in a higher energy e_g orbital than is does to pair two electrons in the same t_{2g} orbital. In cases where Δ_o is larger than the spin pairing energy the complex will adopt a low spin configuration because it requires less energy to place a second electron in a t_{2g} orbital than it does to place one in the higher energy e_g orbitals.

Definition: Spin Pairing Energy

The spin pairing energy is the energy required to pair two electrons in an orbital. It is based on the Coulombic repulsion between the two negative charges. Larger, more diffuse orbitals will have lower spin pairing energy because the two electrons can be further apart

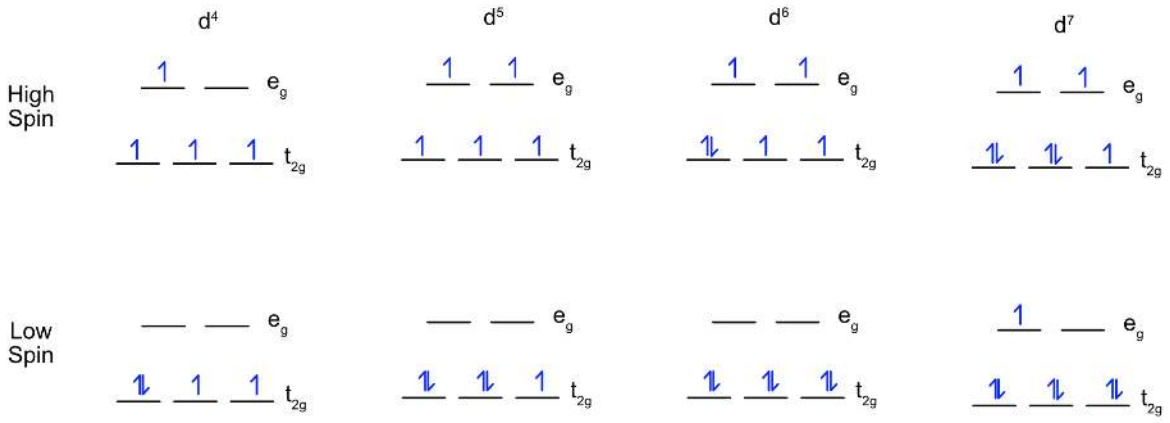


Figure 11.1.4: High spin and low spin arrangements of electrons for d^4 - d^7. (CC-BY-NC-SA; Catherine McCusker)

d^8 - d^{10}

For complexes with 8 - 10 d electrons there is again only one way to arrange the electrons. Whether or not the e_g orbitals are filled before electrons are paired in the t_{2g} orbitals the final electron configurations are as shown in Figure 11.1.5.

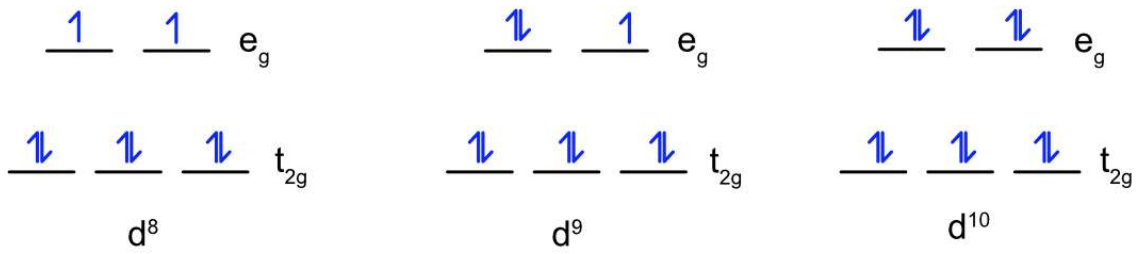


Figure 11.1.5: Arrangement of the d electrons in a octahedral crystal field for 8, 9, and 10 d electrons. (CC-BY-NC-SA; Catherine McCusker)

Tetrahedral Crystal Field

In a tetrahedral complex, the four ligands are orientated at opposite corners of a cube as shown in Figure 11.1.6*a* rather than along the axes. With the ligands between the axes, the three d orbitals which lie between the axes, d_{xy}, d_{xz}, and d_{yz} (t_2 symmetry in tetrahedral), now interact more with the ligands and are destabilized relative to the spherical crystal field. Conversely, the two d orbitals that lie along the axes, $d_{x^2-y^2}$ and d_{z^2} (e symmetry in tetrahedral), now interact less with the d orbitals and are stabilized relative to the spherical crystal field. As shown in Figure 11.1.6*b* the splitting of the d orbitals in a tetrahedral crystal field is essentially the inverse of the octahedral crystal field. The crystal field splitting energy in a tetrahedral crystal field is Δ_t. Because a tetrahedral complex has fewer ligands than an octahedral complex, and those ligands are not ideally orientated to overlap with the d orbitals Δ_t is less than Δ_o for the same metal and ligands:

$$\Delta_t \approx \frac{4}{9}\,\Delta_o \tag{11.1.2}$$

Consequentially, Δ_t is typically smaller than the spin pairing energy, so tetrahedral complexes are usually high spin. As seen with octahedral compounds, the labels for the groups of orbitals, t_2 and e in this case, come from group theory and the tetrahedral point group.

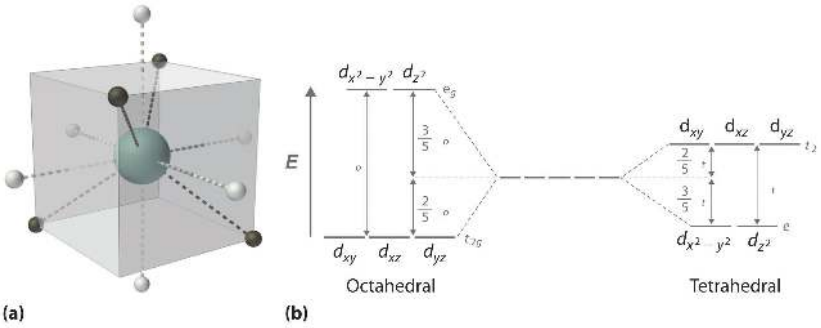


Figure 11.1.6: (a) Tetrahedral ligand field surrounding a central transition metal (teal sphere). (b) Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field (left diagram) and the tetrahedral field (right diagram).

Square Planar Crystal Field

In a complex with four ligands, the other possible arrangement of ligands is square planar. The easiest way to visualize the square planar geometry is to start with an octahedral complex and remove the two ligands that are along the z axis. The four remaining ligands are in the xy plane, along the x and y axes. From a crystal field splitting perspective, when the z ligands are removed the d orbitals split further. In an octahedral crystal field both $d_{x^2-y^2}$ and d_{z^2} are destabilized. When the z ligands are removed the d_{z^2} orbital is stabilized because it no longer interacts with ligands on the z axis. Conversely the $d_{x^2-y^2}$ orbital is further destabilized because all of the ligand negative charges are concentrated in the xy plane. Removing the z ligand has a similar effect on the d_{xy}, d_{xz}, and d_{yz} orbitals, although the magnitude of the stabilization and destabilization is less because those orbitals do not directly interact with the ligands. The d_{xy} orbital is destabilized because it also lies in the xy plane and the d_{xz} and d_{yz} orbitals are stabilized because they have lost the (indirect) interaction with the ligands on the z axis. Overall the $d_{x^2-y^2}$ orbital is significantly more destabilized than the other d orbitals, meaning the square planar geometry is most favored in complexes with 8 electrons where the $d_{x^2-y^2}$ is empty and the other more stabilized d orbitals are filled.

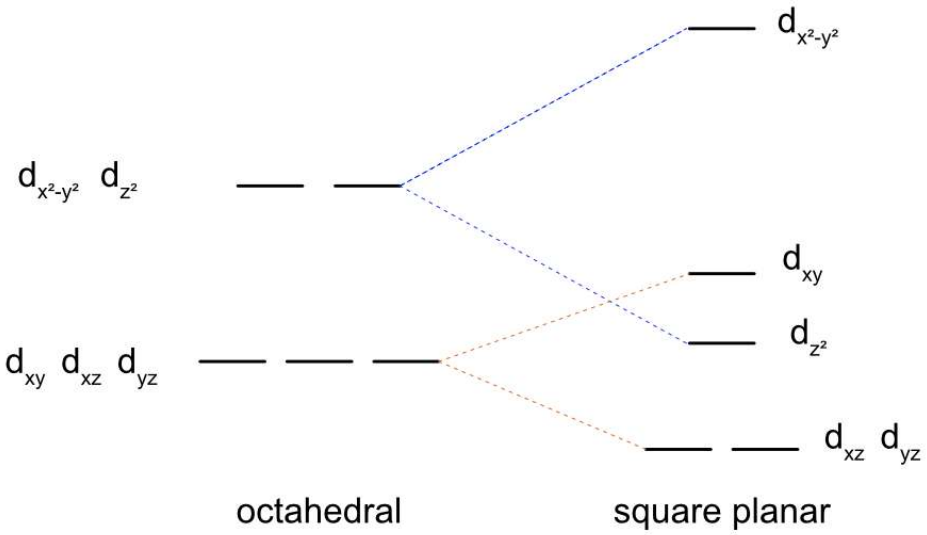
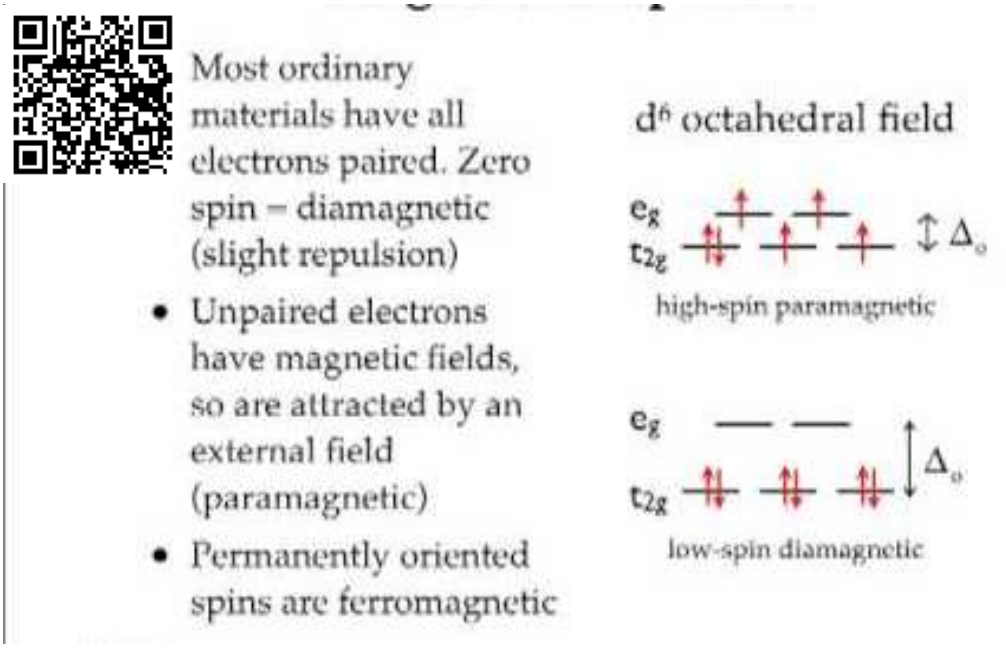


Figure 11.1.7: Comparison between octahedral and square planar crystal field splittings, showing how the energies of the d orbitals change when the two z ligands are removed from an octahedral complex to form a square planar complex. (CC-BY-NC-SA; Catherine McCusker)

Video:



Tetrahedral vs Square Planar

From VSEPR theory we know that sterically the most favorable way to arrange four ligands around a metal ion is in the tetrahedral arrangement. That puts the most possible space between the four ligands. Because of this, a four coordinate metal complex will prefer a tetrahedral geometry UNLESS there is a larger crystal field stabilization energy (CFSE) for the square planar arrangement. As discussed above, this means square planar is the preferred geometry for most metal complexes with 8 d electrons, especially when the crystal field splitting (Δ) is large. While not every d^8 complex is square planar, almost all square planar complexes are d^8 (there are examples of d^7 and d^9 square planar complexes but they are less common)

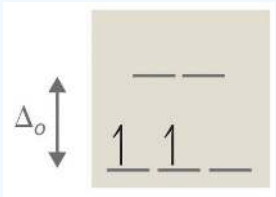
Exercise 11.1.3

For each of the following, sketch the d-orbital splitting diagram, fill the diagram with the correct number of d-electrons, list the number of unpaired electrons, and label whether they are paramagnetic or diamagnetic:

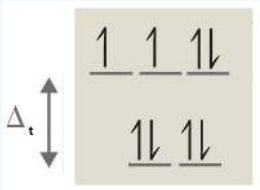
1. $[Ti(H_2O)_6]^{2+}$
2. $[NiCl_4]^{2-}$ (tetrahedral)
3. $[CoF_6]^{3-}$ (high spin)
4. $[Co(NH_3)_6]^{3+}$ (low spin)

Answer

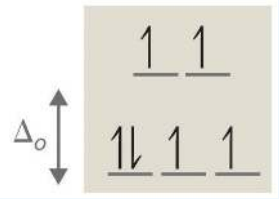
1. 2 unpaired electrons, paramagnetic



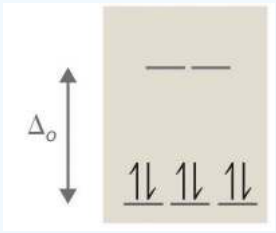
2. 2 unpaired electrons, paramagnetic



3. 4 unpaired electrons, paramagnetic



4. 0 unpaired electrons, diamagnetic



Contributors and Attributions

- Asadullah Awan (UCD), Hong Truong (UCD)
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)
- Modified by Catherine McCusker (East Tennessee State University)

This page titled 11.1: Crystal Field Theory is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **9.1: Crystal Field Theory** is licensed CC BY-NC-SA 4.0.

11.2: Crystal Field Stabilization Energy

Crystal Field Stabilization Energy

A consequence of crystal field theory is that the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand geometry and metal d-electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration and knowledge of the splitting patterns.

Definition: Crystal Field Stabilization Energy (CFSE)

The crystal field stabilization energy is defined as the energy of the electron configuration in the crystal field minus the energy of the electronic configuration in the spherical field.

$$CFSE = \Delta E = E_{\text{crystal field}} - E_{\text{spherical field}} \tag{11.2.1}$$

The CSFE will depend on multiple factors including:

- Geometry (crystal field splitting pattern)
- Number of d-electrons
- Spin Pairing Energy (the contribution of spin pairing energy is often negligible in comparison to other contributions and is omitted at times)

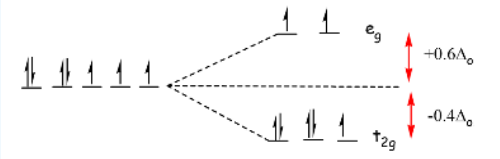
For an octahedral complex, each of the more stable t_{2g} orbitals are stabilized by $-0.4\Delta_o$ relative to spherical field whereas the higher energy e_g orbitals are destabilized by $+0.6\Delta_o$. For a complex the stabilization or destabilization of each electron is summed. Any electrons that are paired within a single orbital, also contribute spin pairing energy (+P). The overall CFSE for a complex is expressed as a multiple of the crystal field splitting parameter Δ_o.

Example 11.2.1: CFSE for a high Spin d^7 complex

What is the CFSE for a high spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both spherical and octahedral ligand fields are compared below.



The energy of the spherical field ($E_{\text{spherical field}}$) is

$$E_{\text{spherical field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral crystal field $E_{\text{oct field}}$ is

$$E_{\text{oct field}} = (5 \times -0.4\Delta_o) + (2 \times 0.6\Delta_o) + 2P = -0.8\Delta_o + 2P$$

So via Equation 11.2.1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{oct field}} - E_{\text{spherical field}} \\ &= (-0.8\Delta_o + 2P) - 2P \\ &= -0.8\Delta_o \end{aligned}$$

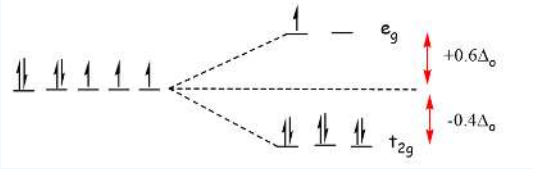
Notice that the spin pairing energy cancels out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the octahedral field is the same as that in spherical field of the free metal ion.

Exercise 11.2.1

What is the CFSE for a low spin d^7 octahedral complex?

Answer

The splitting pattern and electron configuration for both spherical and octahedral ligand fields are compared below.



The energy of the spherical field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{spherical}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand\) field $E_{\text{oct field}}$ is

$$\begin{aligned} E_{\text{oct field}} &= (6 \times -0.4\Delta_o) + (1 \times 0.6\Delta_o) + 3P \\ &= -1.8\Delta_o + 3P \end{aligned}$$

So via Equation 11.2.1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{oct field}} - E_{\text{spherical field}} \\ &= (-9/5\Delta_o + 3P) - 2P \\ &= -9/5\Delta_o + P \end{aligned}$$

This appears more a more stable configuration than the high spin d^7 configuration in Example 11.2.1, but we have then to take into consideration the pairing energy P to know definitely, which varies between $200 - 400\ kJ\ mol^{-1}$ depending on the metal.

Table 11.2.1**:** Crystal field stabilization energies (CFSE) for high and low spin octahedral complexes

Total d-electrons	Spherical Field	Octahedral Field				Crystal Field Stabilization Energy	
		High Spin		Low Spin			
	$E_{\text{spherical field}}$	Configuration	$E_{\text{crystal field}}$	Configuration	$E_{\text{crystal field}}$	High Spin	Low Spin
d^0	0	$t_{2g}^0\ e_g^0$	0	${t_{2g}}^0{e_g}^0$	0	0	0
d^1	0	$t_{2g}^1\ e_g^0$	-2/5 Δ_o	${t_{2g}}^1{e_g}^0$	-2/5 Δ_o	-2/5 Δ_o	-2/5 Δ_o
d^2	0	$t_{2g}^2\ e_g^0$	-4/5 Δ_o	${t_{2g}}^2{e_g}^0$	-4/5 Δ_o	-4/5 Δ_o	-4/5 Δ_o
d^3	0	$t_{2g}^3\ e_g^0$	-6/5 Δ_o	${t_{2g}}^3{e_g}^0$	-6/5 Δ_o	-6/5 Δ_o	-6/5 Δ_o
d^4	0	$t_{2g}^3\ e_g^1$	-3/5 Δ_o	${t_{2g}}^4{e_g}^0$	-8/5 Δ_o + P	-3/5 Δ_o	-8/5 Δ_o + P
d^5	0	$t_{2g}^3\ e_g^2$	0 Δ_o	${t_{2g}}^5{e_g}^0$	-10/5 Δ_o + 2P	0 Δ_o	-10/5 Δ_o + 2P
d^6	P	$t_{2g}^4\ e_g^2$	-2/5 Δ_o + P	${t_{2g}}^6{e_g}^0$	-12/5 Δ_o + 3P	-2/5 Δ_o	-12/5 Δ_o + P
d^7	2P	$t_{2g}^5\ e_g^2$	-4/5 Δ_o + 2P	${t_{2g}}^6{e_g}^1$	-9/5 Δ_o + 3P	-4/5 Δ_o	-9/5 Δ_o + P
d^8	3P	$t_{2g}^6\ e_g^2$	-6/5 Δ_o + 3P	${t_{2g}}^6{e_g}^2$	-6/5 Δ_o + 3P	-6/5 Δ_o	-6/5 Δ_o
d^9	4P	$t_{2g}^6\ e_g^3$	-3/5 Δ_o + 4P	${t_{2g}}^6{e_g}^3$	-3/5 Δ_o + 4P	-3/5 Δ_o	-3/5 Δ_o
d^{10}	5P	$t_{2g}^6\ e_g^4$	0 Δ_o + 5P	${t_{2g}}^6{e_g}^4$	0 Δ_o + 5P	0	0

P is the spin pairing energy and represents the energy required to pair up electrons within the same orbital. For a given metal ion P (pairing energy) is constant, but it does not vary with ligand and oxidation state of the metal ion).

Octahedral Preference

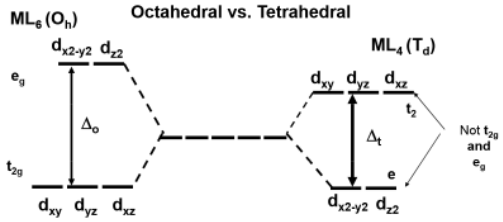
Similar CFSE values can be constructed for non-octahedral ligand field geometries once the knowledge of the d-orbital splitting is known and the electron configuration within those orbitals known, e.g., the tetrahedral complexes in Table 11.2.2. These energies geoemtries can then be contrasted to the octahedral CFSE to calculate a thermodynamic preference for a metal-ligand combination to favor the octahedral geometry. This is quantified via an octahedral site preference energy defined below.

Definition: Octahedral Site Preference Energies (OSPE)

The octahedral site preference energy (OSPE) is defined as the difference of CFSE energies for a non-octahedral complex and the octahedral complex. For comparing the preference of forming an octahedral ligand field vs. a tetrahedral ligand field, the OSPE is thus:

$$OSPE = CFSE_{(oct)} - CFSE_{(tet)} \tag{11.2.2}$$

The OSPE quantifies the preference of a complex to exhibit an octahedral geometry vs. another geometry. The OSPE for octahedral vs tetrahedral geometries is illustrated below.



Note: the conversion between Δ_o and Δ_t used for these calculations is:

$$\Delta_t \approx \frac{4}{9}\Delta_o \tag{11.2.3}$$

which is applicable for comparing octahedral and tetrahedral complexes that involve same ligands only.

Table 11.2.2: Octahedral Site Preference Energies (OSPE)

Total d-electrons	CFSE(Octahedral)	CFSE(Tetrahedral)	OSPE (for high spin complexes)**

Total d-electrons	CFSE(Octahedral)		CFSE(Tetrahedral)		OSPE (for high spin complexes)**
	High Spin	Low Spin	Configuration	**Always High Spin***	
d^0	0 Δ_o	0 Δ_o	e^0	0 Δ_t	0 Δ_o
d^1	-2/5 Δ_o	-2/5 Δ_o	e^1	-3/5 Δ_t	-6/45 Δ_o
d^2	-4/5 Δ_o	-4/5 Δ_o	e^2	-6/5 Δ_t	-12/45 Δ_o
d^3	-6/5 Δ_o	-6/5 Δ_o	$e^2t_2^1$	-4/5 Δ_t	-38/45 Δ_o
d^4	-3/5 Δ_o	-8/5 Δ_o + P	$e^2t_2^2$	-2/5 Δ_t	-19/45 Δ_o
d^5	0 Δ_o	-10/5 Δ_o + 2P	$e^2t_2^3$	0 Δ_t	0 Δ_o
d^6	-2/5 Δ_o	-12/5 Δ_o + P	$e^3t_2^3$	-3/5 Δ_t	-6/45 Δ_o
d^7	-4/5 Δ_o	-9/5 Δ_o + P	$e^4t_2^3$	-6/5 Δ_t	-12/45 Δ_o
d^8	-6/5 Δ_o	-6/5 Δ_o	$e^4t_2^4$	-4/5 Δ_t	-38/45 Δ_o
d^9	-3/5 Δ_o	-3/5 Δ_o	$e^4t_2^5$	-2/5 Δ_t	-19/45 Δ_o
d^{10}	0	0	$e^4t_2^6$	0 Δ_t	0 Δ_o

P is the spin pairing energy and represents the energy required to pair up electrons within the same orbital.

Note

Tetrahedral complexes are always high spin since the splitting is appreciably smaller than P (Equation 11.2.3).

After conversion with Equation 11.2.3. The data in Tables 11.2.1 and 11.2.2 are represented graphically by the curves in Figure 11.2.1 below for the high spin complexes only. The low spin complexes require knowledge of P to graph, which will vary depending on the identiy of the metal ion.

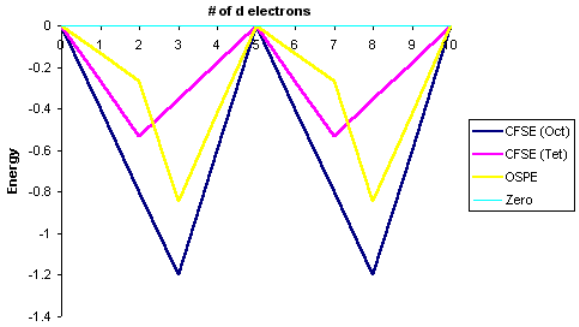


Figure 11.2.1: Crystal Field Stabilization Energies for both high spin octahedral fields ($CFSE_{oct}$) and tetrahedral fields ($CFSE_{tet}$). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes only.

From a simple inspection of Figure 11.2.1, the following observations can be made:

- The OSPE is *small* in d^1, d^2, d^5, d^6, d^7 high spin complexes and other factors influence the stability of the complexes including steric factors
- The OSPE is *large* in d^3 and d^8 high spin complexes which strongly favor octahedral geometries

Applications

The "double-humped" curve in Figure 11.2.1 is found for various properties of the first-row transition metals, including hydration and lattice energies of the M(II) ions, ionic radii as well as the stability of M(II) complexes. This suggests that these properties are somehow related to crystal field effects.

In the case of hydration energies describing the complexation of water ligands to a bare metal ion:

$$M^{2+}(g) + H_2O \rightarrow [M(OH_2)_6]^{2+}(aq) \tag{11.2.4}$$

Table 11.2.3 and Figure 11.2.2 shows this type of curve. Note that in any series of this type not all the data are available since a number of ions are not very stable in the M(II) state in water.

Table 11.2.3: Hydration energies of M^{2+} ions

M	ΔH°/kJmol^{-1}	M	ΔH°/kJmol^{-1}
Ca	-2469	Fe	-2840
Sc	no stable 2+ ion	Co	-2910
Ti	-2729	Ni	-2993
V	-2777	Cu	-2996
Cr	-2792	Zn	-2928
Mn	-2733		

Graphically the data in Table 2 can be represented by:

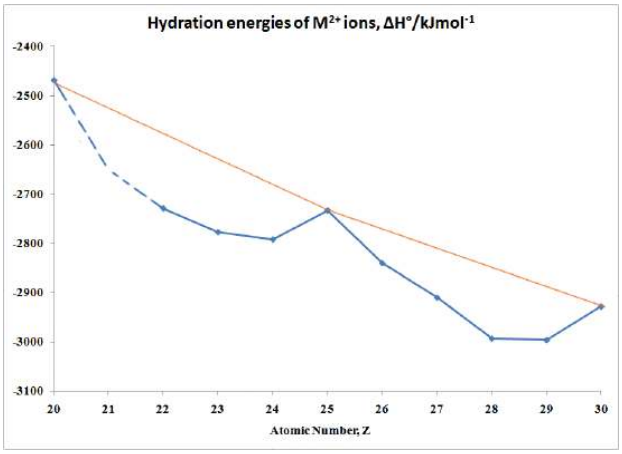


Figure 11.2.2: Hydration energies of M^{2+} ions

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

This page titled 11.2: Crystal Field Stabilization Energy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **9.2: Crystal Field Stabilization Energy** is licensed CC BY-NC-SA 4.0.

11.3: Crystal Field Splitting

Magnitude of Crystal Field Splitting

The magnitude of the crystal field splitting (Δ) dictates whether a complex with four, five, six, or seven d electrons (in an octahedral complex) is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ (i.e., Δ > P) yield a low-spin complex, whereas small values of Δ (i.e., Δ < P) produce a high-spin complex. The magnitude of Δ depends on four factors: the valence of the metal, the principal quantum number of the metal (and thus its location in the periodic table), the geometry, and the nature of the ligand(s). Values of Δ for some representative transition metal complexes are given in Table 11.3.1.

Table 11.3.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Valence of the metal

Increasing the valence of a metal ion has two effects: the radius of the metal decreases and ligands are more strongly attracted to it due to Coulombic attraction. Both factors decrease the metal–ligand distance, which in turn causes the ligands to interact more strongly with the d-orbitals. Consequently, the magnitude of Δ_o increases as the valence of the metal increases. Typically, Δ_o for a M(III) is about 50% greater than for the M(II) of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal quantum number of the metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ (3d) < Δ (4d) < Δ (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ with increasing principal quantum number is due to the larger radial extension of the d orbitals as n increases. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions. The increase in Δ going from 3d to 4d and 5d is so large that all 4d and 5d metals will form low spin complexes.

Geometry of the complex

The number of ligands in a complex as well as how well the ligand geometry overlaps with the d orbitals is also a factor in the magnitude of the crystal field splitting. For example, comparing octahedral and tetrahedral geometries the octahedral geometry has 6 ligands, and those 6 ligands overlap directly with the two d orbitals that lie along the axes, $d_{x^2-y^2}$ and d_{z^2}. The tetrahedral geometry has fewer ligands than octahedral, and those ligands overlap less ideally with the ligands that lie between the axes, d_{xy}, d_{xz}, and d_{yz}. Because of this the crystal field splitting of a tetrahedral complex is generally less than half ($\frac{4}{9}$ than an octahedral complex with the same metal and ligands. For example $[FeCl_4]^-$ has a $\Delta_t = 5{,}200\ cm^{-1}$ and $[FeCl_6]^{3-}$ has a $\Delta_o = 11{,}600\ cm^{-1}$.

Nature of the ligands

In crystal field theory ligands are all modeled as negative point charges, which means that all ligands should behave identically. Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order F > Cl > Br > I because smaller, more localized charges, such as we see for F, interact more strongly with the d-orbitals of the metal. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series.

Ligands are classified as strong field or weak field based on the spectrochemical series:

weak field $I^- < Br^- < Cl^- < \underline{S}CN^- < F^- < OH^- < ox^{-2} < \underline{O}NO < H_2O < SC\underline{N}^- < NH_3 <$ en $< \underline{N}O_2 < CN^-$, CO strong field

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 bond to a metal). The specific atom that binds in such ligands is underlined. Ligands on the weak field end of the series (halogens, OH, H_2O) will tend to form high spin complexes and ligands on the strong field end of the series (CN, CO, NO_2) will tend to form low spin complexes. Intermediate ligands in the midle of the series could form high or low spin complexes depending on other factors.

How to determine if a complex is high or low spin

1. How many d electrons does the complex have?
   - Only complexes with 4-7 d electrons have high spin and low spin configurations
2. What period is the metal?
   - 3d metals could either be high or low spin
   - 4d and 5d metals will ALWAYS be low spin
3. What is the geometry of the complex?
   - Tetrahedral complexes with 3d metals will almost always be high spin because Δt is generally less than spin pairing energy

- Square planar complexes will almost always be low spin because they are favored over tetrahedral when crystal field splitting is large
- Octahedral complexes could be either high or low spin

4. What are the ligands?
   - Strong field ligands will form low spin complexes
   - Weak field ligands will form high spin complexes
   - Intermediate field ligands could form high or low spin complexes. Additional information (like number of unpaired electrons) is needed

- Adapted by Catherine McCusker (East Tennessee State University)

This page titled 11.3: Crystal Field Splitting is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **9.4: Factors That Affect Crystal Field Splitting** is licensed CC BY-NC-SA 4.0.

11.4: Ligand Field Theory

Extension of Crystal Field Theory

Experimentally it is known that the nature of the ligand plays an important role in the magnitude of the crystal field splitting in metal complexes and can determine whether a complex is high or low spin. Empirically ligands can be ordered in the spectrochemical series, but using crystal field theory we cannot rationalize where ligands fall in the series. For example, why is the neutral CO one of the strongest field ligands in the series while the anionic halogens are weak field ligands? To understand why ligands behave differently we have to consider how ligand orbitals interact with the metal d orbitals. Ligand field theory is essentially a combination between crystal field theory and molecular orbital theory where we focus only on the orbital overlap between the metal d orbitals and select ligand orbitals (rather than considering all of the valence orbitals on both the metal and ligand)

Metal-Ligand σ Bonding

The bond between a metal and a ligand is primarily a Lewis acid-base interaction where the ligand is a Lewis base and donates a pair of electron to the metal, the Lewis acid. This interaction forms a coordinate covalent bond. As with molecular orbital theory we have to decide how (or if) the ligand lone pairs will overlap with each of the d orbitals, and what type of bonding will be formed In an octahedral complex the ligands and their lone pairs lie along the x, y, and z axes. As shown in Figure 11.4.1, the two on axis d orbitals ($d_{x^2-y^2}$ and d_{z^2}) have to correct orientation to form sigma bonds with the ligands. With the three off axis d orbitals (d_{xy}, d_{xz}, and d_{yz}) the ligand lone pair overlaps with a node in these orbitals (Figure 11.4.1c). This means there is no net overlap and no bonding (or antibonding) molecular orbital can be formed.

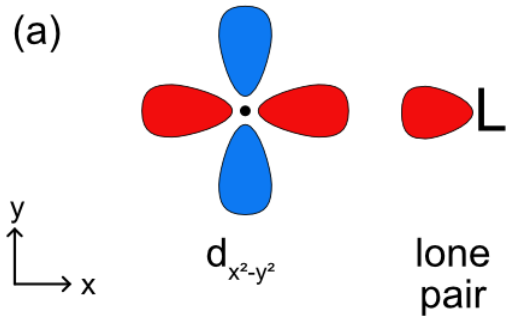


Figure 11.4.1a: Overlap between a ligand lone pair orbital and the metal $d_{x^2-y^2}$ orbital to form a sigma bond (CC BY-NC-SA, Catherine McCusker)

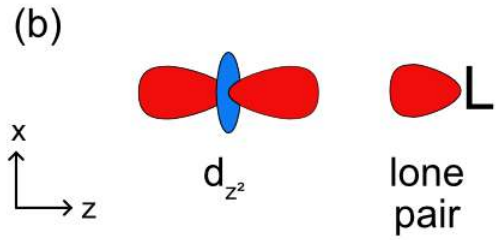


Figure 11.4.1b: Overlap between a ligand lone pair orbital and the metal d_{z^2} orbital to form a sigma bond (CC BY-NC-SA, Catherine McCusker)

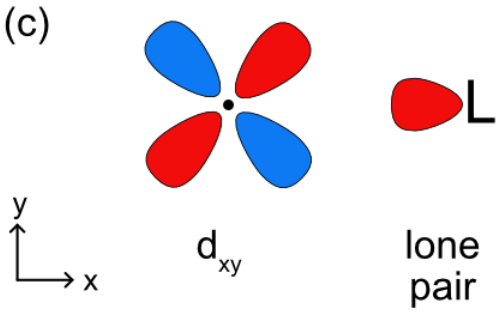


Figure 11.4.1c: There is no net overlap between the ligand lone pair orbital and the d_{xy} metal orbital, so this is a non bonding interaction (CC BY-NC-SA, Catherine McCusker)

Knowing this, we can construct a ligand field splitting diagram (a simplified molecular orbital diagram) (Figure 11.4.2). In the free metal ion all 5 of the d orbitals are degenerate and before they interact with the metal all 6 of the ligand lone pair orbitals are at the same energy as well. Generally, based on electronegativity the ligand lone pair orbitals will be lower in energy than the metal d orbitals. When the ligand lone pairs interact with metal d orbitals the on axis set of d orbitals ($d_{x^2-y^2}$ and d_{z^2}) will form sigma bonding (e_g) and sigma antibonding (e_g*) molecular orbitals. The off axis set of d orbitals are nonbonding and are not stabilized or destabilized by the ligand lone pairs. Unlike a complete molecular orbital diagrams, a ligand field diagram won't necessarily have the same number of molecular orbitals as atomic orbitals becuse not every possible bonding interaction is included (for example, any overlap between the ligand orbitals and the metal s and p orbitals are not included). As in crystal field theory we can define an octahedral ligand field splitting energy (Δ_o), which will be the difference between the two molecular orbitals with the most metal d orbital character. In Figure 11.4.2 the t_{2g} set of d orbitals are nonbonding and therefore 100% metal character. The e_g bonding orbital is closer in energy to the ligand lone pairs and will have a higher % contribution from the ligands, and the e_g* antibonding orbital is closer in energy to the metal d orbitals and will have a higher % contribution from the metal. The relevant energy difference is between the t_{2g} and e_g* orbitals, as highlighted in green in Figure 11.4.2. The splitting energy will increase as there is a stronger interaction between the metal and ligand orbitals (based on the criteria discussed previously) and the e_g* is more destabilized.

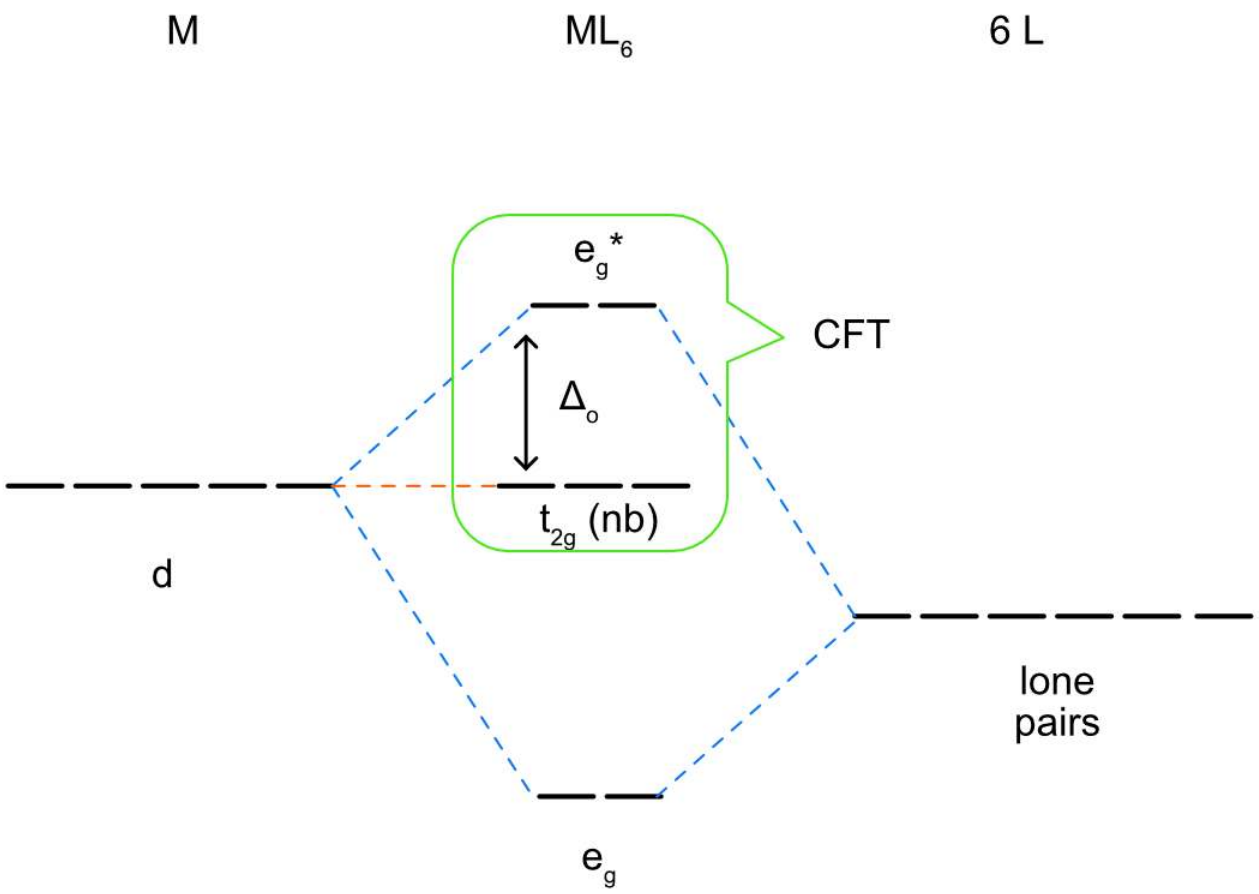


Figure 11.4.2: Octahedral ligand field splitting diagram for only sigma bonding. The $d_{x^2-y^2}$ and d_{z^2} metal orbitals form sigma bonding (e_g) and antibonding molecular orbitals (e_g*). The d_{xy}, d_{xz}, and d_{yz} orbital are nonbonding (t_{2g} (nb)). The green outline highlights the portion of the diagram that is equivalent to the crystal field splitting diagram. (CC BY-NC-SA; Catherine McCusker)

Metal-Ligand π Bonding

In addition to sigma bonding, some ligands have orbitals available which can form π bonds with metals as well. These could include p orbitals on a single donor atom such as a halogen ion or π bonding or antibonding molecular orbitals on a molecular ligand. To determine how π bonding will change the ligand field splitting picture in Figure 11.4.2, we will visualize how a ligand p orbital will interact with the metal d orbitals. The $d_{x^2-y^2}$ and d_{z^2} orbitals do not have the correct symmetry to form any type of bond with a ligand p orbital as shown in Figures $11.4.3a-b$ The d_{xy}, d_{xz}, and d_{yz} orbitals all have the correct symmetry to form π bonds with a ligand p orbital (Figure $11.4.3c$).

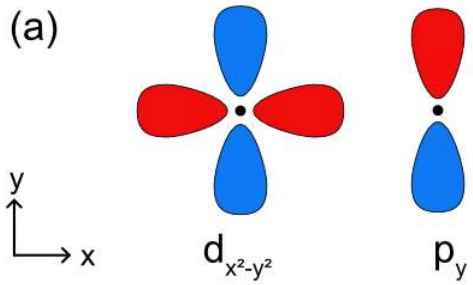


Figure 11.4.3*a*: There is no net overlap between the ligand p orbital and the $d_{x^2-y^2}$ metal orbital, so this is a non bonding interaction (CC BY-NC-SA, Catherine McCusker)

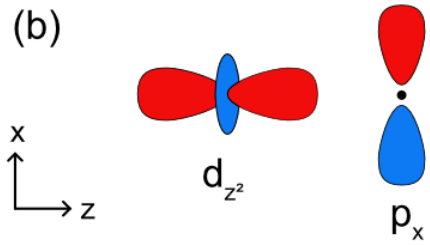


Figure 11.4.3*b*: There is no net overlap between the ligand p orbital and the d_{z^2} metal orbital, so this is a non bonding interaction (CC BY-NC-SA, Catherine McCusker)

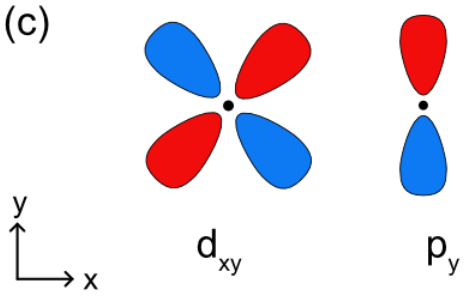


Figure 11.4.3*c*: Overlap between a ligand p orbital and the metal d_{xy} orbital to form a π bond (CC BY-NC-SA, Catherine McCusker)

Unlike metal-ligand σ bonding, where electrons are always donated from the ligand to the metal, electrons in metal-ligand π bonding can be donated from either the metal or the ligand depending on the nature of the orbitals involved. In cases where ligands have empty p or π symmetry orbitals that are close in energy to the metal d orbitals, they can accept electrons from a filled metal orbital. This is also known as π backbonding because the direction of electron donation is opposite of that found in sigma metal ligand bonding. These ligands are called π acceptor ligands. In cases where ligands have filled p or π symmetry orbitals that are close in energy to the metal d orbitals, they can donate electrons to an empty metal orbital. These ligands are called π donor ligands.

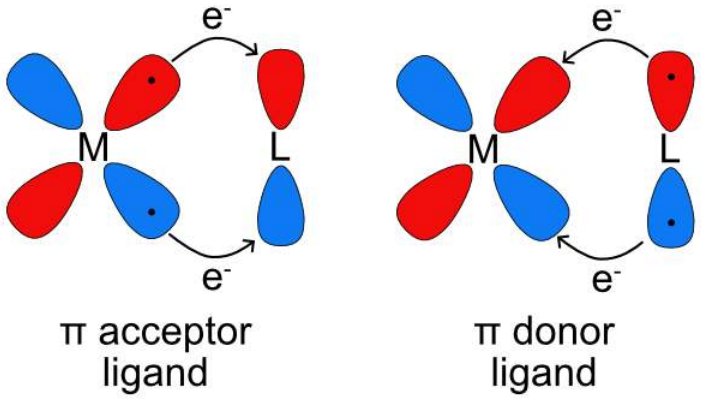


Figure 11.4.4: Illustration of metal-ligand π bonding with π acceptor and donor ligands. Filled orbitals are represented with black dots. (CC BY-NC-SA, Catherine McCusker)

π Acceptors

Ligands that are π acceptors have empty, low energy π symmetry orbitals available to accept electrons from the metal center. Most often this is a π* antibonding molecular orbital but it could also be an empty p orbital. Due to the aufbau principle, these empty orbitals will be higher in energy than any filled lone pairs on the ligands and will also generally be higher energy than the metal d orbitals. Similar to multiple bonding in main group compounds π bonding always occurs in combination with sigma bonding so in the ligand field splitting diagram of metal-ligand bonding with a π acceptor ligand the lone pairs for sigma bonding must be included as well as the empty orbitals for π bonding. As seen in Figure 11.4.3, the $d_{x^2-y^2}$ and d_{z^2} orbitals do not overlap with the ligand p orbitals. The on axis d orbitals will form sigma bonding (e_g) and sigma antibonding (e_g*) molecular orbitals. Unlike the sigma bonding only diagram, the off axis d orbitals (d_{xy}, d_{xz}, and d_{yz}) overlap with the ligand p orbitals to form π bonding (t_{2g}) and π antibonding (t_{2g}*) molecular orbitals as seen in Figure 11.4.5. Rather than being nonbonding, like in the sigma bonding only picture, the metal based t_{2g} molecular orbital is bonding. This increases the energy difference between the t_{2g} and e_g* and therefore increases Δ_o.

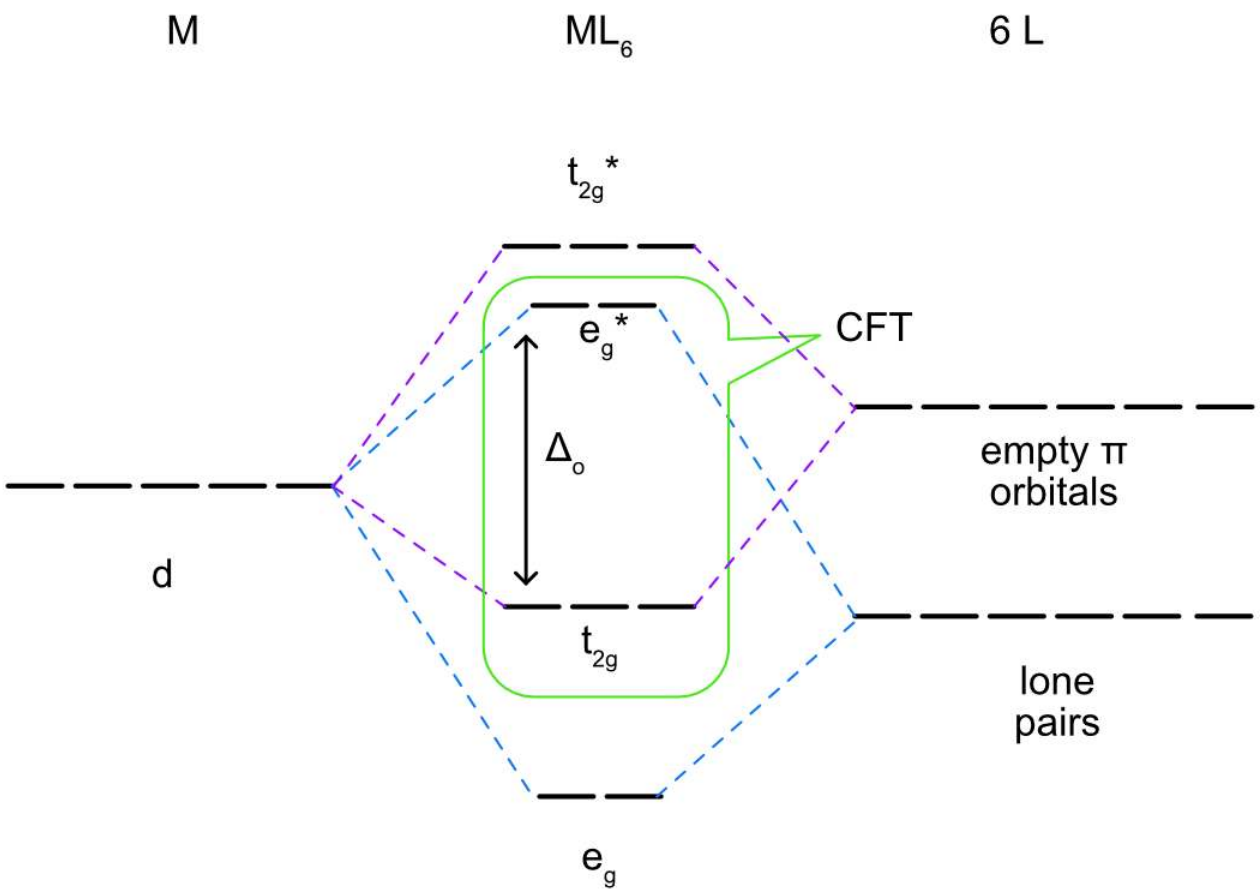


Figure 11.4.5: Octahedral ligand field splitting diagram with a π acceptor ligand. The $d_{x^2-y^2}$ and d_{z^2} metal orbitals form sigma bonding (e_g) and antibonding molecular orbitals (e_g*) with the ligand lone pairs. The d_{xy}, d_{xz}, and d_{yz} orbital form pi bonding (t_{2g}) and pi antibonding molecular orbitals (t_{2g}*) with the empty π symmetry orbitals. The green outline highlights the portion of the diagram that is equivalent to the crystal field splitting diagram. (CC BY-NC-SA; Catherine McCusker)

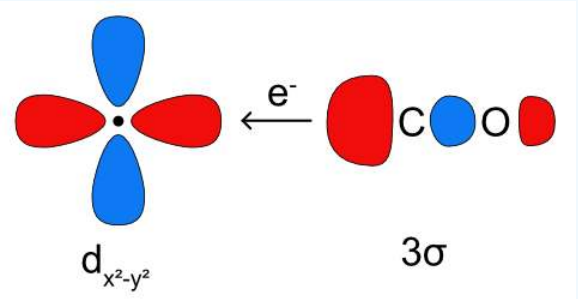
Exercise 11.4.1

Carbon monoxide is one of the most common, and strongest π acceptor ligands in inorganic chemistry. Refer to the molecular orbital diagram of CO and sketch likely metal-ligand orbital interactions for both sigma and pi bonding in a metal-CO complex. Indicate the direction of electron donation in both cases.

Answer

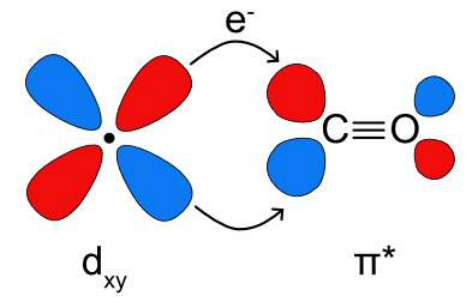
Sigma bonding:

Sigma bonding between a metal ion and a CO ligand involves overlap between the HOMO of CO (3σ) and the metal $d_{x^2-y^2}$ or d_{z^2} orbitals. Electrons are donated from the ligand to the metal.



Pi bonding:

Pi bonding between a metal ion and CO ligand involves overlap between the LUMO of CO (π*) and the metal d_{xy}, d_{xz}, or d_{yz} orbitals. Electrons are donated from the metal to the ligand.



π Donor Ligands

Ligands that are π donors have filled π symmetry orbitals that are high enough in energy to donate electrons to the metal center. Most often this is a filled p orbital, but it could also be a π bonding molecular orbital. As lone pairs are generally the highest occupied orbitals is a molecule, the filled π orbitals will be lower in energy as seen in Figure 11.4.6. The sigma interaction between the ligand lone pairs and the metal $d_{x^2-y^2}$ and d_{z^2} remain the same as previously described, forming the e_g bonding and e_g* antibonding molecular orbitals. The d_{xy}, d_{xz}, and d_{yz} overlap with the filled π orbitals to form π bonding (t_{2g}) and π antibonding (t_{2g}*) molecular orbitals. The difference between the *pi* acceptor and donor ligands is the energy and character of the t_{2g} and t_{2g}* molecular orbitals. In the π acceptor case above, the t_{2g} orbital is above the e_g and has a higher contribution from the metal and the t_{2g}* is above the e_g* and has a higher contribution from the ligand. In the π donor case the opposite is true. The t_{2g} orbital is below the e_g and has a higher contribution from the ligand and the t_{2g}* is below the e_g* and has a higher contribution from the metal. In this case Δ_o is smaller than in the sigma only picture because the t_{2g} symmetry molecular orbital has gone from nonbonding to antibonding and the energy difference between t_{2g}* and e_g* is smaller.

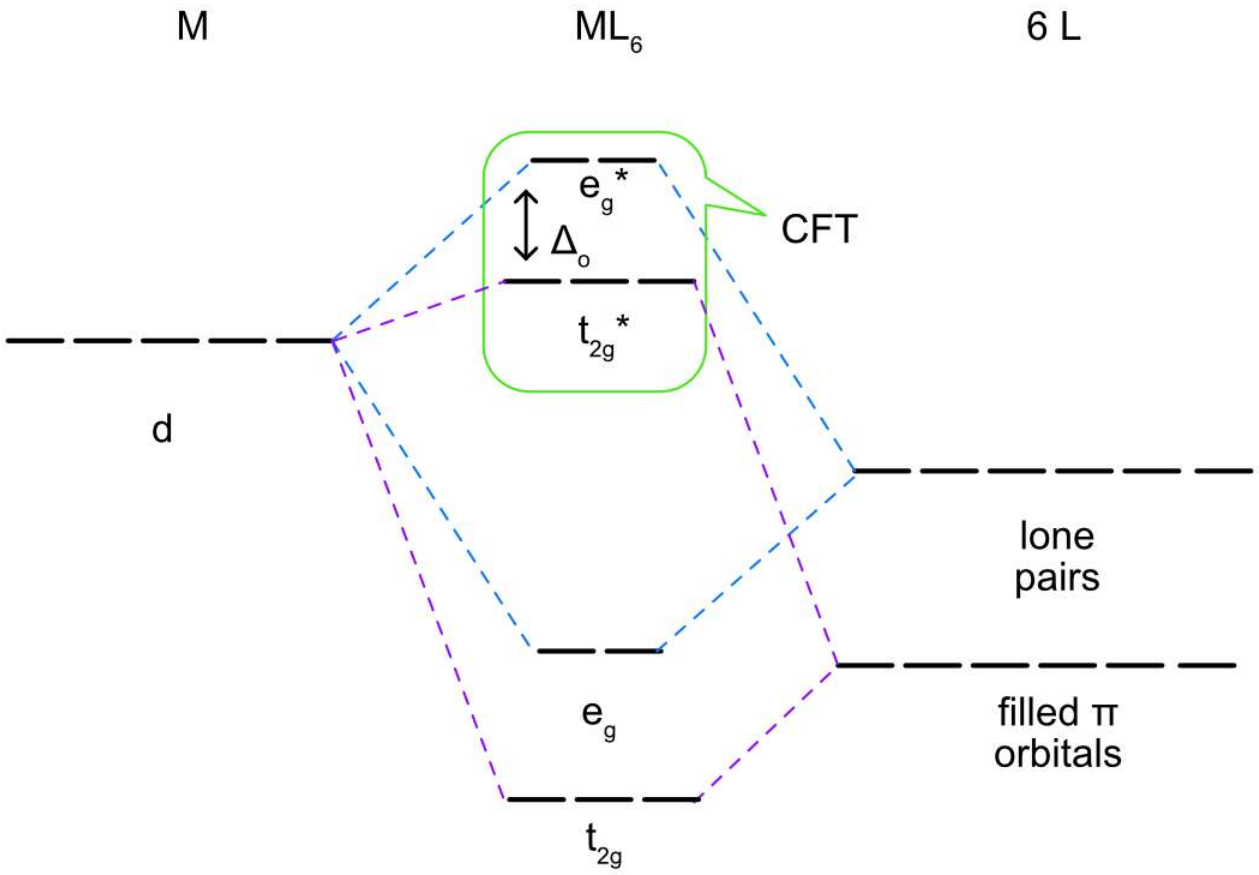


Figure 11.4.6: Octahedral ligand field splitting diagram with a π donor ligand. The $d_{x^2-y^2}$ and d_{z^2} metal orbitals form sigma bonding (e_g) and antibonding molecular orbitals (e_g*) with the ligand lone pairs. The d_{xy}, d_{xz}, and d_{yz} orbital form pi bonding (t_{2g}) and pi antibonding molecular orbitals (t_{2g}*) with the filled π symmetry orbitals. The green outline highlights the portion of the diagram that is equivalent to the crystal field splitting diagram. (CC BY-NC-SA; Catherine McCusker)

The Spectrochemical Series

As discussed above, crystal field theory alone can't distinguish the behaviors of different ligands or explain why some ligands inherently produce larger splittings than others. Armed with ligand field theory we can now revisit the spectrochemical series and explain why ligands fall where they do within the series.

Strong field ligands

Strong field ligands are ones that produce large splittings between the d orbitals and form low spin complexes. Examples of strong field ligands include CO, CN^-, and NO_2. From a ligand field theory perspective all three of these ligands have strong π bonds (either double or triple bonds) and have empty π* molecular orbitals available for backbonding. Strong field ligands are both sigma donors (all ligands are sigma donors) and π acceptors. π backbonding between a metal and a ligand stabilizes the metal based t_{2g} molecular orbital and increases Δ_o.

Weak field ligands

Weak field ligands are ones that produce small splittings between the d orbitals and form high spin complexes. Examples of weak field ligands include the halogens, OH^- and H_2O. From a ligand field perspective these ions or molecules all have filled orbitals

which can π bond with the metal d orbitals. In the case of the halogens these are filled p orbitals and in the case of OH^- and H_2O these are lone pairs which are perpendicular to the metal-ligand bond. Weak field ligands are both sigma donors and π donors. The π donation from the ligand to the metal destabilizes the metal based t_{2g} molecular orbital and decreases Δ_o.

Intermediate field ligands

Intermediate field ligands produce intermediate splittings between the d orbitals and could form high or low spin complexes. Examples of intermediate field ligands include NH_3 or ethylenediamine (en). From a ligand field perspective these ligands only have a single lone pair available for sigma bonding. All of the other orbitals on nitrogen are used for sigma bonding to the H or C atoms within the molecule. Intermediate ligands are those which are only sigma donors, and are not π donors or π acceptors. In this case the t_{2g} symmetry d orbitals are nonbonding and the Δ_o is determined by the strength of the metal ligand sigma interaction (and amount of destabilization of the e_g* molecular orbital)

This page titled 11.4: Ligand Field Theory is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **9.5: Ligand Field Theory** by Catherine McCusker is licensed CC BY-NC-SA 4.0.

11.5: Metal-Metal Bonding

Molecular orbital considerations in Dinuclear Metal Complexes with Multiple M-M Bonds

Let us begin a new chapter and think about dinuclear transition metal complexes with multiple metal-metal bonds. What is the maximum bond order that we could expect? The transition metals have five d-orbitals available, and in order to determine the maximum possible bond order we need to see how they overlap to form molecular orbitals (Fig. 11.1.1).

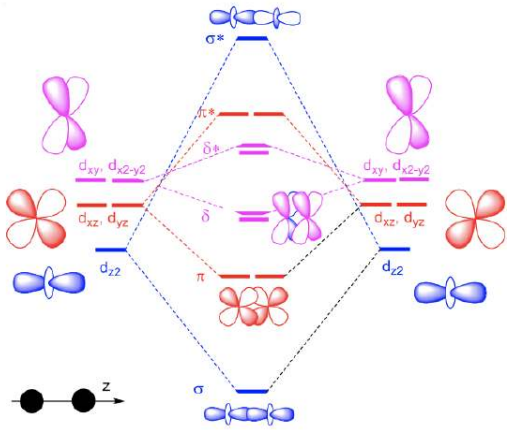


Figure 11.1.1 Molecular orbital overlap of metal d-orbitals forming M-M bonds

If we define the M-M bond axis as the z-axis, then two d_{z^2}-orbitals can overlap in σ-fashion to form a bonding and an anti-bonding σ-molecular orbital. A d_{xz}, and a d_{yz} can overlap with another d_{xz} and another d_{yz} in π-fashion to form two degenerated bonding π and two degenerated anti-bonding π*-orbitals. π-overlap is smaller than σ-overlap, therefore the split in energy between the bonding and the anti-bonding π-orbitals is smaller than the split between the bonding and the anti-bonding σ-orbitals. The d_{xy} orbital can overlap with another d_{xy} orbital in *δ*-fashion, and so can the $d_{x^2-y^2}$ with another $d_{x^2-y^2}$. This gives two bonding *δ*-orbitals and two anti-bonding *δ*-orbitals. The *δ*-overlap is even smaller than the π-overlap, therefore the energy split between the bonding and the anti-bonding *δ*-orbitals is even smaller than those for the π and π*-orbitals. So what would be the maximum bond order that could be achieved? The maximum bond order would be achieved when all bonding MOs were full, and all anti-bonding MOs were empty. We have overall five bonding MOs that we could fill with ten electrons from two metal atoms with d^5-electron configuration. The maximum bond order BO would therefore be BO=5. However, in practice only bond orders up to 4 are well known. This is because the $d_{x^2-y^2}$ orbital is usually too involved in the bonding with the ligands thereby becoming unavailable for metal-metal interactions. The $d_{x^2-y^2}$ orbital makes the strongest interactions with the ligands because most ligands approach on or near the x and the y-axes.

Electron Configurations and Multiple M-M Bonds

We can easily predict now which electron configuration leads to which metal-metal bond order. The bond order increases from 1 to 4 with the electron configuration changing from d^1 to d^4. At d^4 all bonding MOs are full with eight electrons.

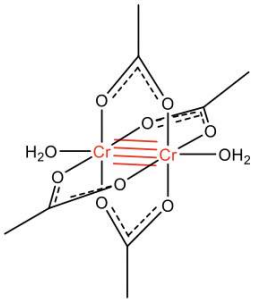


Figure 11.1.2 Tetraacetatodiaquadichromium complex

An example of a complex with a bond order of 4 is the tetraacetatodiaquadichromium complex shown (Fig. 11.1.2). Cr is in the oxidation state +2, which makes the chromium a d^4 species. We can quickly show this by counting the valence electrons. A neutral

Cr atom has 6 VE, and an electron configuration $3d^5 4s^1$. There are four acetate ligands having a 1- charge each which gives four negative charges overall. The complex is overall neutral which means that each Cr must have formally a 2+ charge, and the electron configuration is $3d^4$.

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
1	2	3	4	3	2	1	0

Figure 11.1.3 Relationship between metal-metal bond order and electron configuration

With even more electrons in the metal d-orbitals the bond order begins to decrease again as anti-bonding MOs need to be filled (Fig. 11.1.3). The combination of two metals with d^5 electron configuration leads to a triple bond, two d^6-metals give a double bond, and two d^7 metals give a single bond. A metal-metal bond should not exist for two d^8-metals because then the bond order is zero.

Evidence for M-M Multiple Bonds

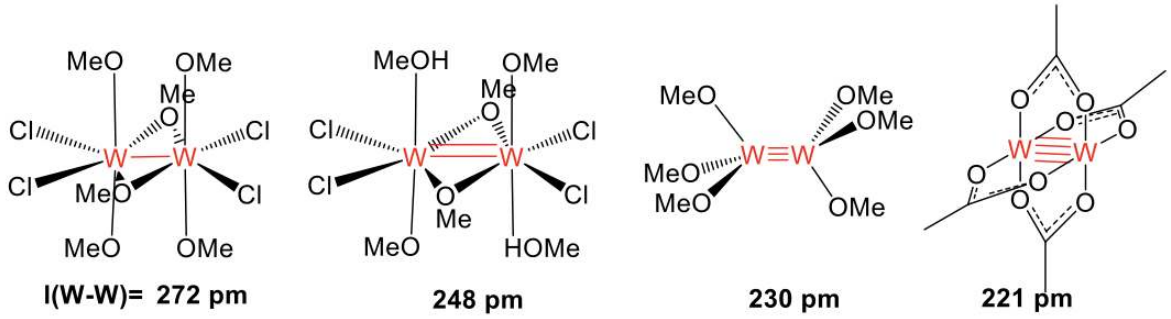


Figure 11.1.4 M-M bond length in four tungsten complexes

What experimental evidence can support the existence of a particular bond order (Fig. 11.1.4)? One argument is the bond length which can be obtained through the crystal structure determination of the complex. The shorter the bond, the higher the bond order. For instance, in the four tungsten complexes shown the bond lengths decrease from 272 pm, to 248 pm, to 230 pm to 221 pm corresponding to a single, double, triple, and quadruple bond, respectively.

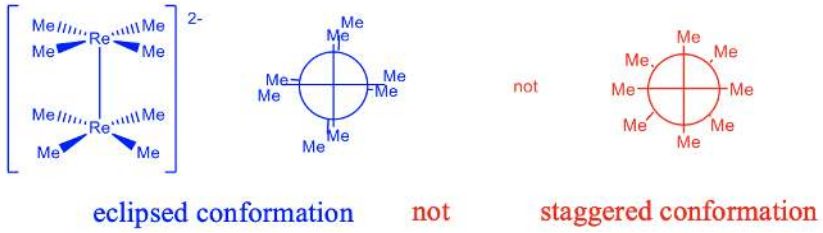


Figure 11.1.5 $ReMe_4$ confirmations

Another hint can be the conformation of a molecule (Fig. 11.1.5). For instance, the two square-planar units of the $Re_2Me_8^{2-}$ complex anion show eclipsed conformation. Steric repulsion arguments would favor the staggered conformation, so there must be a reason why the two $ReMe_4$ units are eclipsed. The rhenium is in the oxidation state +3, thus it is a d^4 species, and we would argue that there may be a Re-Re quadruple bond. This quadruple bond can only form when the d_{xy} orbitals are in eclipsed conformation, and this is only possible when the two $ReMe_4$ fragments are in eclipsed conformation. The very short bond length of 218 pm further supports the existence of the quadruple bond.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 11.5: Metal-Metal Bonding is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **11.1: Complexes with Multiple Metal-Metal Bonds** by Kai Landskron is licensed CC BY 4.0.

11.6: Spectrochemical Series

Strong and weak field ligands. The spectrochemical series ranks ligands according the **energy difference Δ_O** between the t_{2g} and e_g orbitals in their octahedral complexes. This energy difference is measured in the spectral transition between these levels, which often lies in the visible part of the spectrum and is responsible for the colors of complexes with partially filled d-orbitals. Ligands that produce a large splitting are called **strong field** ligands, and those that produce a small splitting are called **weak field** ligands.



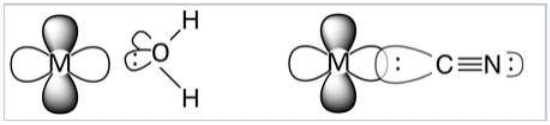
An abbreviated spectrochemical series is:

Weak field $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < H_2O <$ Pyridine $< NH_3 < NO_2^- < CN^- <$ CO **Strong field**

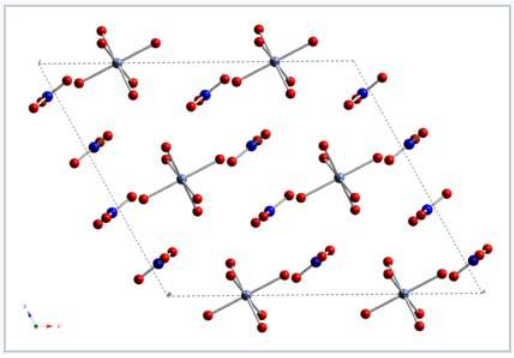
Orbital overlap

Referring to the molecular orbital diagram above, we see that the splitting between d-electron levels reflects the antibonding interaction between the e_g metal orbitals and the ligands. Thus, we expect ligand field strength to correlate with metal-ligand orbital overlap. Ligands that bind through very electronegative atoms such as **O and halogens** are thus expected to be **weak field**, and

ligands that bind through **C or P** are typically **strong field**. Ligands that bind through **N** are **intermediate** in strength. Another way to put this is that hard bases tend to be weak field ligands and soft bases are strong field ligands.



Water is a weak field ligand. The electronegative O atom is strongly electron-withdrawing, so there is poor orbital overlap between the electron pair on O and a metal d-orbital. The more electropositive C atom in the strong field ligand CN^- allows better orbital overlap and sharing of the electron pair. Note that CN^- typically coordinates metal ions through the C atom rather than the N atom.



Cobalt (II) complexes have different colors depending on the nature of the ligand. In crystals of the red compound cobalt(II) nitrate dihydrate, each cobalt ion is coordinated by six water molecules. The $[Co(H_2O)_6]^{2+}$ cations and NO_3^- anions crystallize to make a salt. When the complex is dissolved in water, Co(II) retains its coordination shell of six water molecules and the solution has the same red color as the crystal.

Energy units

Energy can be calculated in a number of ways and it is useful to try to relate the splitting energy Δ_O to more familiar quantities like bond energies.

$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu} \tag{11.6.1}$$

Here ν is the frequency of the electromagnetic radiation, h is Planck's constant (6.626×10^{-34} J*s), and c is the speed of light. $\tilde{\nu}$ is called the "wavenumber" and is the inverse of the wavelength, usually measured in cm^{-1}. Energy gaps are often expressed by spectroscopists in terms of wavenumbers.

For example, a red photon has a wavelength of about 620 nm and a wavenumber of about 16,000 cm^{-1}. In other energy units, the same red photon has an energy of 2.0 eV (1 eV = 1240 nm) or 193 kJ/mol (1 eV = 96.5 kJ/mol). If we compare this to the dissociation energy of a carbon-carbon single bond (350 kJ/mol), we see that the C-C bond has about twice the energy of a red photon. We would need an ultraviolet photon (E > 350 kJ/mol = 3.6 eV = 345 nm = 29,000cm^{-1}) to break a C-C bond.

We will see that Δ_O varies widely for transition metal complexes, from near-infrared to ultraviolet wavelengths. Thus the energy difference between the t_{2g} and e_g orbitals can range between the energy of a rather weak to a rather strong covalent bond.

Δ_O depends on both the metal and the ligand. We can learn something about trends in Δ_O by comparing a series of d^6 metal complexes

Complex	Δ_O (cm^{-1})
$[Co(H_2O)_6]^{2+}$	9,300
$[Co(H_2O)_6]^{3+}$	18,200
$[Co(CN)_6]^{3-}$	33,500
$[Rh(H_2O)_6]^{3+}$	27,000
$[Rh(CN)_6]^{3-}$	45,500

Important trends in Δ_O:

- **Co^{3+}** complexes have larger Δ_O than **Co^{2+}** complexes with the same ligand. This reflects the **electrostatic** nature of the crystal field splitting.
- **Rh^{3+}** complexes have larger Δ_O than **Co^{3+}** complexes. In general, elements in the 2nd and 3rd transition series (the **4d and 5d elements)** have **larger splitting** than those in the 3d series.

For a given metal in one oxidation state (e.g., Co^{3+}), the trend in Δ_O follows the **spectrochemical series**. Thus Δ_O is larger for $[Co(CN)_6]^{3-}$, which contains the strong field CN^- ligand, than it is for $[Co(H_2O)_6]^{3+}$ with the weak field ligand H_2O.

The 4d and 5d elements are similar in their size and their chemistry. In comparing Δ_O values for complexes in the 3d, 4d, and 5d series (e.g., comparing elements in the triads Co,Rh,Ir or Fe,Ru,Os), we always find 3d << 4d $\lesssim$ 5d. This trend reflects the spatial extent of the d-orbitals and thus their overlap with ligand orbitals. The 3d orbitals are smaller, and they are less effective in bonding than the 4d or 5d. The 4d and 5d orbitals are similar to each other because of the lanthanide contraction. At the beginning of the 5d series (between ^{56}Ba and ^{72}Hf) are the fourteen lanthanide elements (^{57}La - ^{71}Lu).

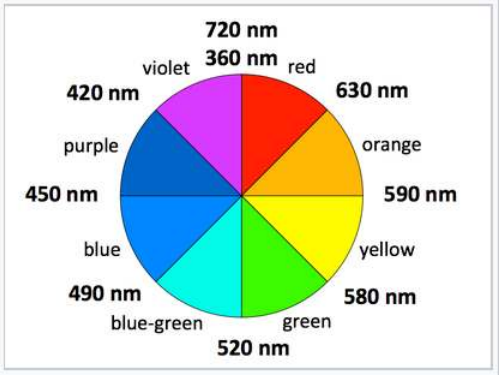
Although the valence orbitals of the 5d elements are in a higher principal quantum shell than those of the 4d elements, the addition of 14 protons to the nucleus in crossing the lanthanide series contracts the sizes of the atomic orbitals. The important result is that the **valence orbitals of the 4d and 5d elements have similar sizes** and thus the elements resemble each other in their chemistry much more than they resemble their cousins in the 3d series. For example, the chemistry of Ru is very similar to that of Os, as illustrated below, but quite different from that of Fe.



Both Os and Ru form volatile, molecular tetroxides MO_4. OsO_4 is used in epoxidation reactions and as a stain in electron microscopy. In contrast, the highest binary oxide of iron is Fe_2O_3.

Colors of transition metal complexes

A simple, qualitative way to see the relative crystal field splitting energy, Δ_O, is to observe the color of a transition metal complex. The higher the energy of the absorbed photon, the larger the energy gap. However, the color a complex absorbs is **complementary** to the color it appears (i.e., the color of light it reflects), which is **opposite** the absorbed color on the color wheel.



Complementary colors are across the color wheel from each other

Examples: (all d^7 Co^{2+} complexes)

$[Co(H_2O)_6]^{2+}$ looks purple in its salts and in concentrated solution because it absorbs in the green range.

$[Co(NH_3)_6]^{2+}$ is straw-colored because it absorbs in the blue range.

$[Co(CN)_6]^{4-}$, looks red, absorbs in the violet and ultra-violet part of the spectrum. This is consistent with the idea that CN^- is a stronger field ligand than NH_3, because the energy of a UV photon is higher than that of a red-orange photon.

This method is applicable to most transition metal complexes, as the majority of them absorb somewhere in the visible range (400-700 nm = 25,000 to 14,300 cm^{-1}), or have UV transitions that tail into the visible, making them appear yellow; however there are complexes such as $[Rh(CN)_6]^{3-}$ that appear colorless because their d-d transitions are in the ultraviolet. Other complexes such as $[Mn(H_2O)]_6^{2+}$ are weakly colored because their d-d transitions involve a change in the spin state of the complex.

This page titled 11.6: Spectrochemical Series is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **5.4: Spectrochemical Series** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

11.7: Colors of Coordination Compounds

The color for a coordination complex can be predicted using the Crystal Field Theory (CFT). Knowing the color can have a number of useful applications, such as the creation of pigments for dyes in the textile industry. The tendency for coordination complexes to display such a wide array of colors is merely coincidental; their absorption energies happen to fall within range of the visible light spectrum. Chemists and physicists often study the color of a substance not to understand its sheer appearance, but because color is an indicator of a chemical's physical proprieties on the atomic level.

The Electromagnetic Spectrum

The electromagnetic spectrum (EM) spectrum is made up of photons of different wavelengths. Photons, unique in displaying the properties of both waves and particles, create visible light and colors in a small portion of the EM spectrum. This visible light portion has wavelengths in approximately the 400-700 nanometer range (a nanometer, “nm,” is 10^{-9} meters). Each specific wavelength corresponds to a different color (Figure 11.7.1), and when all the wavelengths are present, it appears as white light.

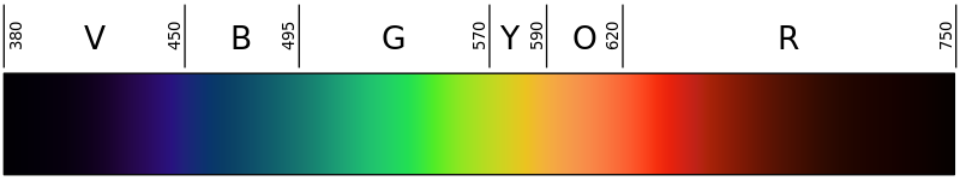


Figure 11.7.1: A linear representation of the visible light spectrum. (Public Domain; Gringer via Wikipedia)

The wavelength and frequency of a wave are inversely proportional: as one increases, the other decreases; this is a consequence of all light traveling at the same speed.

$$\lambda \propto \nu^{-1}$$

Because of this relationship, blue light has a much higher frequency and more energy than red light.

Perceiving Color

Color is perceived in two ways, through additive mixing, where different colors are made by combining different colors of light, and through subtractive mixing, where different wavelengths of light are taken out so that the light is no longer pure white. For colors of coordination complexes, subtractive mixing is considered. As shown in Figure 11.7.2, the idea behind subtractive mixing is that white light (which is made from all the colors mixed together) interacts with an object. The object absorbs some of the light, and then reflects or transmits (or both, depending on the object) the rest of the light, which contacts the eye. The object is perceived as whichever color is not absorbed. In Figure 11.7.2, white light (simplified as green, red, and blue bands) is shone through a solution. The solution absorbs the red and green wavelengths; however, the blue light is reflected and passes through, so the solution appears blue. This procedure takes place whenever an object displays visible color. If none of the light is absorbed, and all is reflected back off, the object appears white; if all of the light is absorbed, and there is none left to reflect or transmit through, the object appears black.

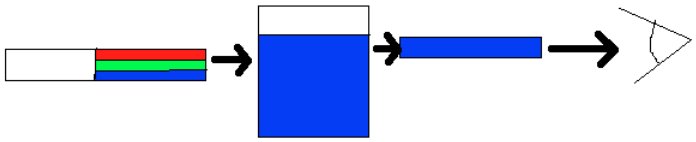


Figure 11.7.2: Subtractive mixing

Colors of Coordination Complexes: Crystal Field Splitting

When ligands attach to a transition metal to form a coordination complex, electrons in the d orbital split into high energy and low energy orbitals. The difference in energy of the two levels is denoted as Δ, and it is a characteristic a property both of the metal and the ligands. This is illustrated in Figure 11.7.3; the "o" subscript on the Δ indicates that the complex has octahedral geometry.

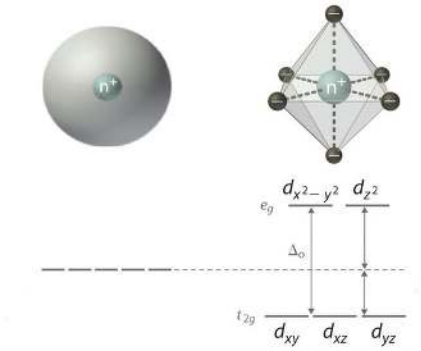


Figure 11.7.3: d-Orbitals Splitting in an octahedral ligand field. (CC BY-SA-NC; anonymous by request)

If Δ_o is large, and much energy is required to promote electrons into the high energy orbitals, the electrons will instead pair in the lower energy orbitals, resulting in a "low spin" complex (Figure 11.7.4*A*); however, if Δ_o is small, and it takes little energy to occupy the higher orbitals, the electrons will do so, and remain unpaired (until there are more than five electrons), resulting in a “high spin” complex (Figure 11.7.4*B*). Different ligands are associated with either high or low spin —a "strong field" ligand results in a large Δ_o and a low spin configuration, while a "weak field" ligand results in a small Δ_o and a high spin configuration. For more details, see the Crystal Field Theory (CFT) page.

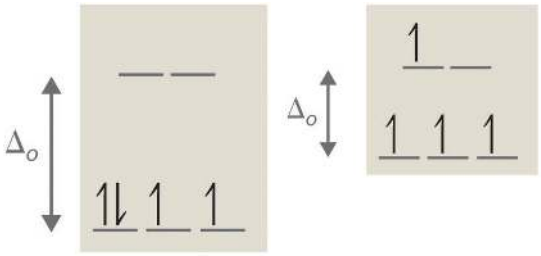


Figure 11.7.4: (a) Low Spin, Strong Field ($\Delta_o > P$). (b): High Spin, Weak Field ($\Delta_o < P$). (CC BY-SA-NC; anonymous)

A photon equal to the energy difference Δ_o can be absorbed, promoting an electron to the higher energy level. As certain wavelengths are absorbed in this process, subtractive color mixing occurs and the coordination complex solution becomes colored. If the ions have a noble gas configuration, and have no unpaired electrons, the solutions appear colorless; in reality, they still have a measured energy and absorb certain wavelengths of light, but these wavelengths are not in the visible portion of the EM spectrum and no color is perceived by the eye.

In general, a larger Δ_o indicates that higher energy photons are absorbed, and the solution appears further to the left on the EM spectrum shown in Figure 11.7.1. This relationship is described in the equation

$$\Delta_o = hc/\lambda$$

where h and c are constants, and λ is the wavelength of light absorbed.

Using a color wheel can be useful for determining what color a solution will appear based on what wavelengths it absorbs (Figure 11.7.6). If a complex absorbs a particular color, it will have the appearance of whatever color is directly opposite it on the wheel. For example, if a complex is known to absorb photons in the orange range, it can be concluded that the solution will look blue. This concept can be used in reverse to determine Δ for a complex from the color of its solution.

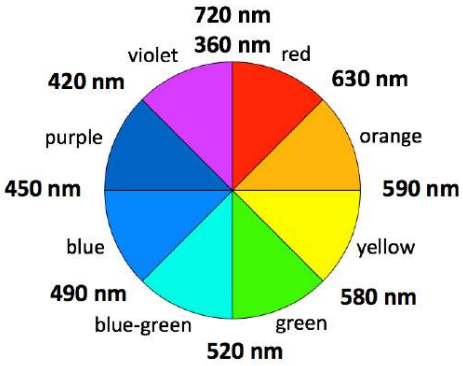


Figure 11.7.5: Color wheel with wavelengths marked (CC BY-SA 4.0 International; Tem5psu via source)

Relating the Colors of Coordination Complexes to the Spectrochemical Series

According to the Crystal Field Theory, ligands that have smaller Δ) values are considered "weak field" and will absorb lower-energy light with longer λ values (ie a "red shift"). Ligands that have larger Δ) values are considered "strong field" and will absorb higher-energy light with shorter λ values (ie a "blue shift"). This relates to the colors seen in a coordination complex. Weaker-field ligands induce the absorption of longer wavelength (lower frequency=lower energy) light than stronger-field ligands since their respective Δ_o values are **smaller** than the electron pairing energy.

The energy difference, Δ_o, determines the color of the coordination complex. According to the **spectrochemical series**, the high spin ligands are considered "weak field," and absorb longer wavelengths of light (weak Δ_o), while complexes with low spin ligands absorb light of greater frequency (high Δ_o). The color seen is the complementary color of the color associated with the absorbed wavelength. To predict which possible colors and their corresponding wavelengths are absorbed, the spectrochemical series can be used:

(Strong field/large Δ_0/low spin) (weak field/ small Δ_0/high spin)

CO^-, NO^-, CN^->NO_2^->en>py≈NH_3>$EDTA^{4-}$>NCS^->H_2O>ONO^->ox^{2-}>OH^->F^->SCN^->Cl^->Br^->I^-

Example 11.7.1

If a solution with a dissolved octahedral complex appears yellow to the eye, what wavelength of light does it absorb? Is this complex expected to be low spin or high spin?

Solution

A solution that looks yellow absorbs light that is violet, which is roughly 410 nm from the color wheel. Since it absorbs high energy, the electrons must be raised to a higher level, and Δ_o is high, so the complex is likely to be low spin.

Example 11.7.2

An octahedral metal complex absorbs light with wavelength 535 nm. What is the crystal field splitting Δ_o for the complex? What color is it to the eye?

Solution

To solve this question, we need to use the equation

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

with

- h is Planck's constant and is $6.625 \times 10^{-34} J \cdot s$ and
- c is the speed of light and is $2.998 \times 10^8 \, m/s$.

It is also important to remember that 1 nm is equal to 1×10^{-9} meters. With all this information, the final equation looks like this:

$$\Delta_o = \frac{(6.625 \times 10^{-34}\, J \cdot s)(2.998 \times 10^{8}\, m/s)}{(535nm)\left(\frac{1\, m}{1 \times 10^{9}\, nm}\right)} = 3.712\, J/molecule$$

It is not necessary to use any equations to solve the second part of the problem. Light that is 535 nm is green, and because green light is absorbed, the complex appears red (refer to Figures 11.7.1 and 11.7.6 for this information).

Note: the fact that the complex is octahedral makes no impact when solving this problem. Although the splitting is different for complexes of different structures, the mechanics of solving the problem are identical.

Example 11.7.3

There are two solutions, one orange and one blue. Both solutions are known to be made up of a cobalt complex; however, one has chloride ions as ligands, while the other has ammonia ligands. Which solution is expected to be orange?

Solution

In order to solve this problem, it is necessary to know the relative strengths of the ligands involved. A sample ligand strength list is given here, but see Crystal Field Splitting for a more complete list:

$$CN^- > en > NH_3 > H_2O > F^- > SCN^- > Cl^-$$

From this information, it is clear that NH_3 is a stronger ligand than Cl^-, which means that the complex involving NH_3 has a greater Δ, and the complex will be low spin. Because of the larger Δ, the electrons absorb higher energy photons, and the solution will have the appearance of a lower energy color. Since orange light is less energetic than blue light, the NH_3 containing solution is predicted to be orange

References

1. Cox, P. A. Instant Notes Inorganic Chemistry. Second ed. Grand Rapids: Garland, Incorporated, 2004.
2. Nassau, Kurt. The Physics and Chemistry of Color : The Fifteen Causes of Color. Second ed. New York: Wiley-Interscience, 2001.
3. Petrucci, Ralph H., William S. Harwood, and Geoff E. Herring. General Chemistry : Principles and Modern Applications. Ninth ed. Upper Saddle River: Prentice Hall PTR, 2006.
4. Petrucci, Ralph H., Carey Bissonnette, F. Geoffrey Herring, Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. Tenth Ed. Upper Saddle River: Pearson Education, Inc. 2011.

Problems

1. What color will a complex be that absorbs light that is 600 nm be?
2. What color will a complex an octahedral complex appear if it has a Δ_o of $3.75 \times 10^{-19}\, J$?
3. Would you expect a violet solution to be high spin or low spin? What about a red solution?
4. There are two solutions, one which is yellow and another which is violet. The solutions are $[Co(H_2O)_6]^{3+}$and $[Co(CN^-)_6]^{3-}$. What are the colors of each solution?

Answers

1. Blue. The color absorbed is orange.
2. It is red. Using Δ=hc/λ, h=6.626*10^{-34}J*s, c=2.998*10^{8}m/s, wavelength would equal 530 nm. So green is absorbed, and the complementary color of green is red, so red is the color of the complex.
3. It would be high spin. The complementary color of violet is yellow, which has a wavelength of 570 nm. For a red solution, the complementary color absorbed is green, with a wavelength of 530 nm, so it would be considered low spin.
4. $[Co(H_2O)_6]^{3+}$ is violet and $[Co(CN^-)_6]^{3-}$ is yellow. Looking at the spectrochemical series, H_2O is a weak field ligand, so it absorbs colors of long wavelengths—in this case, the longer wavelength is yellow, so the color reflected is violet. CN^- is a strong field ligand, so it absorbs colors of shorter wavelengths-in this case, the shorter wavelength is violet, so the color reflected is yellow.

Contributors and Attributions

- Deyu Wang (UCD)

This page titled 11.7: Colors of Coordination Compounds is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

- **Colors of Coordination Complexes** is licensed CC BY 4.0.

11.8: Magnetic Moments

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation number and stereochemistry of the central metal ion in coordination complexes. A common laboratory procedure for the determination of the magnetic moment for a complex is the Gouy method which involves weighing a sample of the complex in the presence and absence of a magnetic field and observing the difference in weight. A template is provided for the calculations involved.

For first row transition metal ions in the free ion state, i.e. isolated ions in a vacuum, all 5 of the 3d orbitals are degenerate.

A simple crystal field theory approach to the bonding in these ions assumes that when they form octahedral complexes, the energy of the d orbitals are no longer degenerate but are split such that two orbitals, the d_{x2-y2} and the d_{z2} (e_g subset) are at higher energy than the d_{xy}, d_{xz}, d_{yz} orbitals (the t_{2g} subset).

For octahedral ions with between 4 and 7 d electrons, this gives rise to 2 possible arrangements called either high spin/weak field or low spin/strong field respectively. The energy gap is dependent on the position of the coordinated ligands in the SPECTROCHEMICAL SERIES.

Note

A good starting point is to assume that all Co(III), d^6 complexes are octahedral and LOW spin, i.e. t_{2g}^6.

In tetrahedral complexes, the energy levels of the orbitals are again split, such that the energy of two orbitals, the $d_{x^2-y^2}$ and the d_{z^2} (e subset) are now at lower energy (more favored) than the remaining three d_{xy}, d_{xz}, d_{yz} (the t_2 subset) which are destabilized.

> *Tetrahedral complexes are ALL high spin since the difference between the 2 subsets of energies of the orbitals is much smaller than is found in octahedral complexes.*

The usual relationship quoted between them is:

$$\Delta_{tet} \approx \frac{4}{9}\Delta_{oct}$$

Square planar complexes are less common than tetrahedral and d^8 e.g. Ni(II), Pd(II), Pt(II), etc, have a strong propensity to form square planar complexes. As with octahedral complexes, the energy gap between the d_{xy} and $d_{x^2-y^2}$ is Δ_{oct} and these are considered strong field / low spin hence they are all diamagnetic, μ=0 Bohr Magneton (B.M.)

The formula used to calculate the spin-only magnetic moment can be written in two forms; the first based on the number of unpaired electrons, n, and the second based on the electron spin quantum number, S. Since for each unpaired electron, $n = 1$ and $S = 1/2$ then the two formulae are clearly related and the answer obtained must be identical.

$$\mu_{so} = \sqrt{n(n+2)}$$

$$\mu_{so} = \sqrt{4S(S+1)}$$

Comparison of calculated spin-only magnetic moments with experimental data for some octahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d^1 (t_{2g}^1)	√3 = 1.73	1.6-1.7
V(III)	d^2 (t_{2g}^2)	√8 = 2.83	2.7-2.9
Cr(III)	d^3 (t_{2g}^3)	√15 = 3.88	3.7-3.9
Cr(II)	d^4 high spin (t_{2g}^3 e_g^1)	√24 = 4.90	4.7-4.9
Cr(II)	d^4 low spin (t_{2g}^4)	√8 = 2.83	3.2-3.3
Mn(II)/ Fe(III)	d^5 high spin (t_{2g}^3 e_g^2)	√35 = 5.92	5.6-6.1
Mn(II)/ Fe(III)	d^5 low spin (t_{2g}^5)	√3 = 1.73	1.8-2.1
Fe(II)	d^6 high spin (t_{2g}^4 e_g^2)	√24 = 4.90	5.1-5.7
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin (t_{2g}^5 e_g^2)	√15 = 3.88	4.3-5.2
Co(II)	d^7 low spin (t_{2g}^6 e_g^1)	√3 = 1.73	1.8
Ni(II)	d^8 (t_{2g}^6 e_g^2)	√8 = 2.83	2.9-3.3
Cu(II)	d^9 (t_{2g}^6 e_g^3)	√3 = 1.73	1.7-2.2

Comparison of calculated spin-only magnetic moments with experimental data for some tetahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Cr(V)	d^1 (e^1)	√3 = 1.73	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	√8 = 2.83	2.6 - 2.8
Fe(V)	d^3 (e^2 t_2^1)	√15 = 3.88	3.6-3.7
-	d^4 (e^2 t_2^2)	√24 = 4.90	-
Mn(II)	d^5 (e^2 t_2^3)	√35 = 5.92	5.9-6.2
Fe(II)	d^6 (e^3 t_2^3)	√24 = 4.90	5.3-5.5
Co(II)	d^7 (e^4 t_2^3)	√15 = 3.88	4.2-4.8
Ni(II)	d^8 (e^4 t_2^4)	√8 = 2.83	3.7-4.0
Cu(II)	d^9 (e^4 t_2^5)	√3 = 1.73	-

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

This page titled 11.8: Magnetic Moments is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **Magnetic Moments of Transition Metals** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

12: Coordination Compound Spectroscopy

12.1: Molecular Vibrations

12.2: Identifying Active Vibrations

12.3: Carbonyl Vibrational Modes

This page titled 12: Coordination Compound Spectroscopy is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

12.1: Molecular Vibrations

The Heisenberg uncertainty principle argues that all atoms in a molecule are constantly in motion (otherwise we would know position and momentum accurately). For molecules, they exhibit three general types of motions: translations (external), rotations (internal) and vibrations (internal). A diatomic molecule contains only a single motion., while polyatomic molecules exhibit more complex vibrations, known as normal modes.

Molecular Vibrations

A molecule has translational and rotational motion as a whole while each atom has it's own motion. The vibrational modes can be IR or Raman active. For a mode to be observed in the IR spectrum, changes must occur in the permanent dipole (i.e. not diatomic molecules). Diatomic molecules are observed in the Raman spectra but not in the IR spectra. This is due to the fact that diatomic molecules have one band and no permanent dipole, and therefore one single vibration. An example of this would be O_2 or N_2. However, unsymmetric diatomic molecules (i.e. CN) do absorb in the IR spectra. Polyatomic molecules undergo more complex vibrations that can be summed or resolved into normal modes of vibration.

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

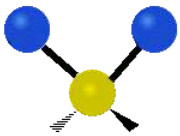
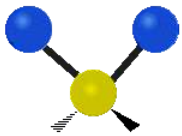
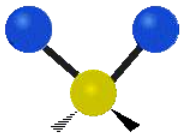
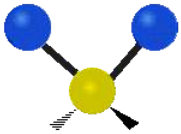
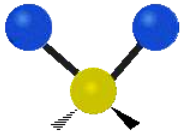
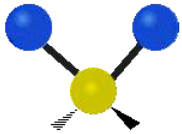
Symmetric Stretching	Asymmetric Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

Figure 12.1.1***:*** *Six types of Vibrational Modes. Images used with permission (Public Domain; Tiago Becerra Paolini).*

Calculate Number of Vibrational Modes

Degree of freedom is the number of variables required to describe the motion of a particle completely. For an atom moving in 3-dimensional space, three coordinates are adequate so its degree of freedom is three. Its motion is purely translational. If we have a molecule made of N atoms (or ions), the degree of freedom becomes 3N, because each atom has 3 degrees of freedom. Furthermore, since these atoms are bonded together, all motions are not translational; some become rotational, some others vibration. For non-linear molecules, all rotational motions can be described in terms of rotations around 3 axes, the rotational degree of freedom is 3 and the remaining 3N-6 degrees of freedom constitute vibrational motion. For a linear molecule however, rotation around its own axis is no rotation because it leave the molecule unchanged. So there are only 2 rotational degrees of freedom for any linear molecule leaving 3N-5 degrees of freedom for vibration.

The degrees of vibrational modes for **linear molecules** can be calculated using the formula:

$$3N - 5 \tag{12.1.1}$$

The degrees of freedom for **nonlinear molecules** can be calculated using the formula:

$$3N - 6 \tag{12.1.2}$$

n is equal to the number of atoms within the molecule of interest. The following procedure should be followed when trying to calculate the number of vibrational modes:

1. Determine if the molecule is linear or nonlinear (i.e. Draw out molecule using VSEPR). If linear, use Equation 12.1.1. If nonlinear, use Equation 12.1.2
2. Calculate how many atoms are in your molecule. This is your N value.
3. Plug in your N value and solve.

Example 12.1.1: Carbon dioxide

How many vibrational modes are there in the linear CO_2 molecule ?

Answer

There are a total of 3 atoms in this molecule. It is a linear molecule so we use Equation 12.1.1. There are

$$3(3) - 5 = 4$$

vibrational modes in CO_2.

Would CO_2 and SO_2 have a different number for degrees of vibrational freedom? Following the procedure above, it is clear that CO_2 is a linear molecule while SO_2 is nonlinear. SO_2 contains a lone pair which causes the molecule to be bent in shape, whereas, CO_2 has no lone pairs. It is key to have an understanding of how the molecule is shaped. Therefore, CO_2 has 4 vibrational modes and SO_2 has 3 modes of freedom.

Followup (SO_2)

Would CO_2 and SO_2 have a different number for degrees of vibrational freedom? Following the procedure above, it is clear that CO_2 is a linear molecule while SO_2 is nonlinear. SO_2 contains a lone pair which causes the molecule to be bent in shape, whereas, CO_2 has no lone pairs. It is key to have an understanding of how the molecule is shaped. Therefore, CO_2 has 4 vibrational modes and SO_2 has 3 modes of freedom.

Example 12.1.2: Methane

How many vibrational modes are there in the tetrahedral CH_4 molecule ?

Answer

In this molecule, there are a total of 5 atoms. It is a nonlinear molecule so we use Equation 12.1.2. There are

$$3(5) - 6 = 9$$

vibrational modes in CH_4.

Example 12.1.3: Buckyballs

How many vibrational modes are there in the nonlinear C_{60} molecule ?

Answer

In this molecule, there are a total of 60 carbon atoms. It is a nonlinear molecule so we use Equation 12.1.2. There are

$$3(60) - 6 = 174$$

vibrational modes in C_{60}.

References

1. Harris, Daniel C., and Michael D. Bertolucci. *Symmetry and Spectroscopy: an Introduction to Vibrational and Electronic Spectroscopy*. New York: Dover Publications, 1989. Print.
2. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. Harlow: Pearson Education, 2008. Print.

This page titled 12.1: Molecular Vibrations is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

- **Number of Vibrational Modes in a Molecule** is licensed CC BY 4.0.

12.2: Identifying Active Vibrations

Symmetry and group theory can be applied to understand molecular vibrations. This is particularly useful in the contexts 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 12.2.1).

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

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

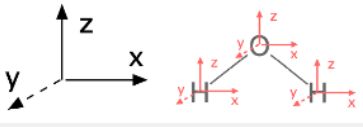


Figure 12.2.1: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom.

Now that we know the molecule's point group, we can use group theory to determine the symmetry of all motions in the molecule; the symmetry of each of its degrees of freedom. Then we will subtract rotational and translational degrees of freedom to find the vibrational degress 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:

$$\begin{aligned} \text{Linear Molecule Degrees of Freedom} &= 3N-5 \\ \text{Non-Linear Molecule Degrees of Freedom} &= 3N-6 \end{aligned} \tag{12.2.1}$$

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 12.2.1).

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

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

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

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

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

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

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

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

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

(12.2.2)

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

Now that we've found the Γ_{modes} (12.2.2), 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:

$$\#\ of\ i = \frac{1}{h}\sum(\#\ \ of\ operations\ in\ class) \times (\chi_\Gamma) \times (\chi_i) \tag{12.2.3}$$

In other words, the number of irreducible representations of type i is equal to the sum of the number of operations in the class $\times$ the character of the \

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

Using equation 12.2.3, we find that for all normal modes of H_2O:

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2 \tag{12.2.4}$$

Notice their are 9 irreducible representations in equation 12.2.4. These irreducible representations represent the symmetries of all 9 motions of the molecule: vibrations, rotations, and translations.

Exercise 12.2.1: Derive the irreducible representation in equation 12.2.4.

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 12.2.4.

Hint

To find the number of each irreducible representation that combine to form the Γ_{modes}, we need the characters of $\Gamma modes$ that we found above (12.2.2), the C_{2v} character table (below), and equation 12.2.3.

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 12.2.3) 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.

$$\text{Vibrations} = \Gamma_{modes} - \text{Rotations} - \text{Translations} \tag{12.2.5}$$

In the example of H_2O, the total degrees of freedom are given above in equation 12.2.4, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{12.2.6}$$

But which of the irreducible representations are ones that represent rotations and translations? The symmetry of rotational and translational degrees 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 translations irreducible representations from the total Γ_{modes}.

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

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

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

$$\begin{aligned} H_2O \text{ vibrations} &= \Gamma_{modes} - \text{ Rotations } - \text{ Translations} \\ &= (3A_1 + 1A_2 + 3B_1 + 2B_2) - (A_1 - B_1 - B_2) - (A_2 - B_1 - B_2) \\ &= 2A_1 + 1B_1 \end{aligned} \tag{12.2.7}$$

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. 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 by completely symmetric, while the B_1 vibration is antisymmetric with respect to the principle C_2 axis.

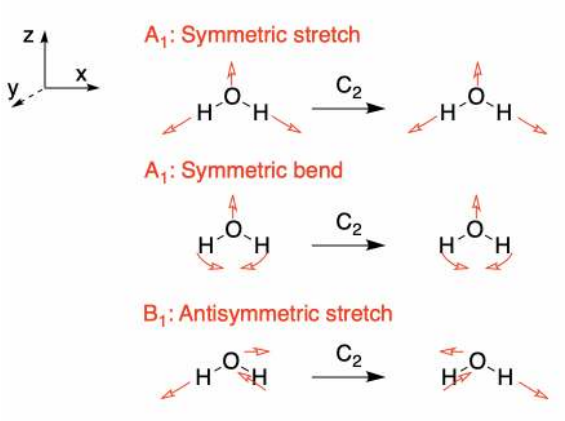


Figure 12.2.2: Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

Table 12.2.1: Summary of the Symmetry of Molecular Motions for Water

All Motions (step 2 above)	Translations (x,y,z)	Rotations (R_x, R_y, R_z)	**Remaining Vibrations**	Description of Vibration
$3A_1$	$1A_1$		$2A_1$	One is a symmetric stretch. The other is a symmetric bend. Both are *IR-active* and *Raman-active*
A_2		$1A_2$		
$3B_1$	$1B_1$	$1B_1$	$1B_1$	Antisymmetric stretch that is *IR-active* and *Raman-active*.
$2B_2$	$1B_2$	$1B_2$		

Exercise 12.2.1

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

Add texts here. Do not delete this text first.

Acknowledgements

Curated or created by Kathryn Haas

This page titled 12.2: Identifying Active Vibrations is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

12.3: Carbonyl 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 structures, and their isomers are shown in Figure 12.3.1. The isomers in each case can be distinguished using vibrational spectroscopy.

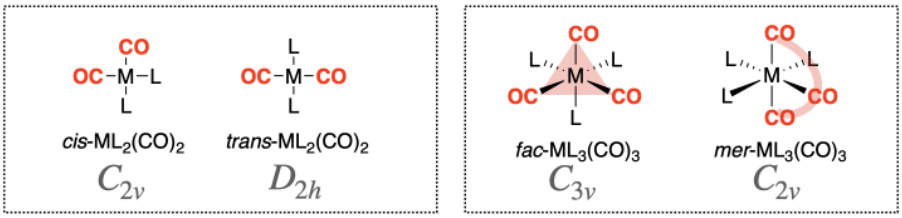


Figure 12.3.1: *Cis*- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box. *Mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$) are shown in the right box. The point groups for each of the general structures is also shown. (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 12.3.1. 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 12.3.2 will be used here.



Figure 12.3.2: *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 12.3.2 (red arrows →). These vectors are used to produce a \reducible representation (Γ) for the C—O stretching motions in each molecule. Using the symmetry operations under the appropriate character table, assign a value of 1 to each vector that remains in place during the operation, and a value of 0 if the vector moves out of place. There will be no occasion where a vector remains in place but is inverted, so a value of -1 will not occur.

cis- $ML_2(CO)_2$:

For *cis*- $ML_2(CO)_2$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{cis-CO}.

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0

(12.3.1)

trans- $ML_2(CO)_2$:

For trans- $ML_2(CO)_2$, the point group is D_{2h} and so we use the operations under the D_{2h} character table to create the $\Gamma_{trans-CO}$.

$\mathbf{C_{2v}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0

(12.3.2)

Step 3: Break each Γ into its component irreducible representations

Each Γ can be reduced using inspection or by the systematic method described previously.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

(12.3.3)

In the case of *trans*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_{3u} irreducible representations:

$\mathbf{C_{2v}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0	
A_g	1	1	1	1	1	1	1	1	$x^2,\ y^2,\ z^2$
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

(12.3.4)

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 12.3.3 (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 is 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 12.3.3 (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 is 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 12.3.1

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 12.3.1) in both IR and Raman spectra. Could either of these vibrational spectroscopies be used to distinguish the two isomers?

Answer

Add texts here. Do not delete this text first.

This page titled 12.3: Carbonyl Vibrational Modes is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

CHAPTER OVERVIEW

13: Substitution Reactivity

13.1: Reactions of Metal Complexes
13.2: Substitution Reactions
13.3: Inert and Labile Complexes
13.4: Chelate Effects
13.5: Substitution Mechanisms
13.5.1: Dissociative Mechanism
13.5.2: Interchange Mechanism
13.5.3: Associative Mechanism
13.6: Activation Parameters
13.7: Dissociation
13.8: Association
13.9: The Trans Effect

This page titled 13: Substitution Reactivity is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

13.1: Reactions of Metal Complexes

Although there are a vast array of reactions that occur at transition metal centers, we will touch on only a subset of the possibilities. This chapter will focus on the reactions of octahedral and square planar metal complexes, and the reactions will be divided into three types:

1. **Substitution reactions at the metal center**: these are reactions in which one ligand is replaced with another ligand within the metal's inner coordination sphere.
2. **Redox**: these are reactions in which the metal oxidation state formally changes by gaining or loosing electrons.
3. **Ligand reactions**: these are reactions that occur primarily on the ligands that are bound to metal ions.

Review of reaction coordinate diagrams and terms

Before we begin our discussion of reactions, let's review some of the vocabulary and models that chemists use to understand reactions.

A chemical reaction can be represented with a reaction coordinate diagram in which the total potential energy of a state is plotted in the vertical y axis, and the "**reaction coordinate**" (sometimes also referred to as "reaction progress", or "extent of reaction") is plotted on the horizontal x axis. The reaction coordinate is often drawn as the progress of a reaction from reactants (R) on the left to products (P) on the right.* Examples of reaction coordinate diagrams for a one-step and a two-step reaction are shown in Figure 13.1.1. Notice the difference in the reaction profile that depends on the number of reaction steps. A one-step reaction has one "hill" shape, while a two step reaction takes on a "saddle" shape.

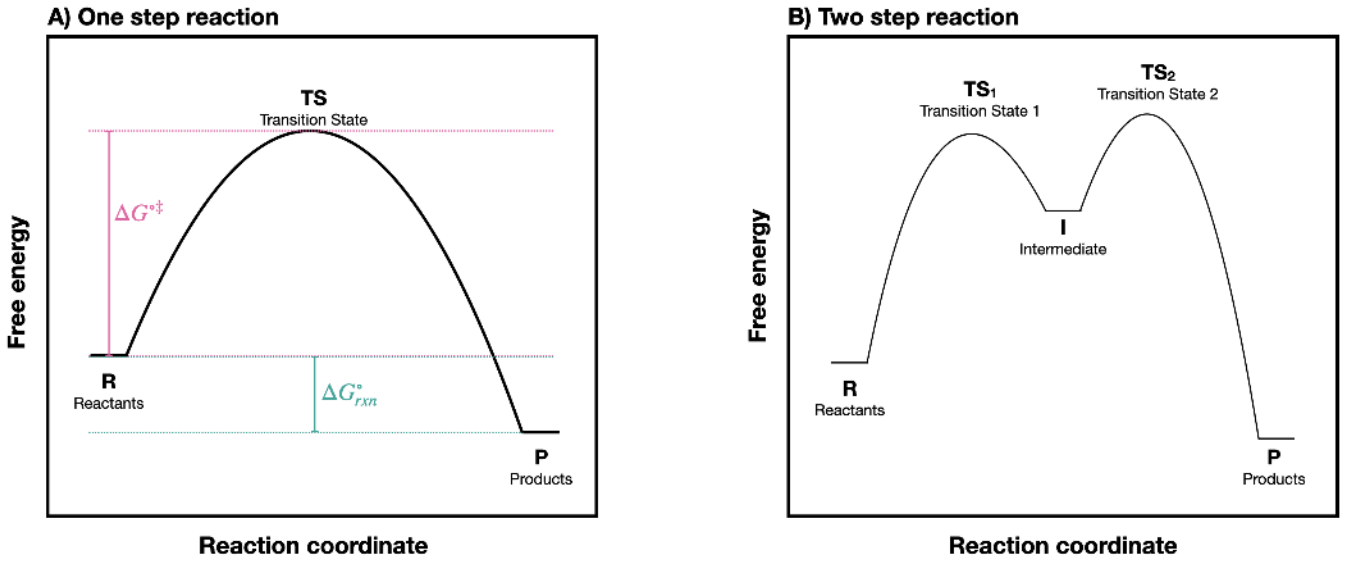


Figure 13.1.1: Examples of a reaction coordinate diagram for a one-step reaction (left), and a two-step reaction (right). (CC-BY-SA; Kathryn Haas)
*Many students find it helpful to envision the horizontal axis in an reaction coordinate diagram as being analogous to the progress bar at the bottom of a youtube video.

Thermodynamics

The difference in energy between reactants (R) and products (P) indicates whether reactants or products will dominate at thermodynamic equilibrium. At standard conditions, this difference is the standard Gibbs Free Energy of the reaction (ΔG°_{rxn} or ΔG°). The Gibbs free-energy change is a combination of enthalpy change (ΔH°) and entropy change (ΔS°):

$$\Delta G^{\circ} = \Delta H^{o} - T\Delta S^{o}$$

where

- T is the temperature in Kelvin (recall that the Kelvin temperature is simply the Celsius temperature plus 273.15).
- Enthalpy change (ΔH°) is the heat released or absorbed by the reaction.

- Entropy change (ΔS°) is the change in disorder from reactants to products. In a reaction in which one molecule cleaves into two smaller molecules, for example, disorder increases, so ΔS° is positive.

The standard Gibbs free energy change for a reaction can be related to the reaction's equilibrium constant K_{eq} by the equation:

$$\Delta G^\circ = -RT \ln K_{eq}$$

where R is the gas constant (8.314 J/mol×K) and T is the temperature in Kelvin (K).

A negative value for ΔG_{rnx}° (an exergonic reaction) corresponds to K_{eq} being greater than 1, an equilibrium constant which favors product formation. Conversely, an endergonic reaction has a positive value of ΔG°, and a K_{eq} between 0 and 1.

Kinetics

The highest point between two energy minima is a transition state (TS). The difference in energies of the reactant and the highest-energy TS is the standard free energy of activation ($\Delta G^{\circ\ddagger}$). The activation energy, in combination with the temperature at which the reaction is being run, determines the rate of a reaction: the higher the activation energy, the slower the reaction. The rate constant (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. The relationship between activation energy and the rate constant, k, is given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{or} \qquad \ln k = \ln A - \frac{E_A}{RT}$$

A rate law is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The rate is defined as the change in reactants or products over time. For example, in a reaction of two reactants (R_1 and R_2) to form product (P), a rate law could be written as follows:

$$\frac{d[\mathrm{P}]}{dT} = \mathrm{k}[\mathrm{R}_1][\mathrm{R}_2]$$

The rate law above is second order overall, and first order with respect to both R_1 and R_2. The order indcates the power of reactant concentrations for individual reactants or overall for the reaction.

In a one-step reaction, the product is formed in one step. There is an energy barrier to overcome so that this process can happen. At the height of that energy barrier is the TS. In a one-step reaction, there is one transition state. In contrast, in a two-step reaction, there are two transition states and an intermediate (denoted by the letter I). The first step from R to I, passes over transition state TS_1, is endergonic. The second step passing through transition state TS_2 is exergonic. The intermediate (I) is thus depicted as an energy 'valley' (a local energy minimum) situated between the two energy maxima; TS_1 and TS_2.

In Figure 13.1.1B, notice that the energy barrier for the first step is larger than the energy barrier for the second step. This means that the first step is slower than the second. In a multi-step reaction, the slowest step - the step with the largest energy barrier - is referred to as the rate-limiting or rate-determining step. The rate-determining step can be thought of as the 'bottleneck' of the reaction: a factor which affects the rate-determining step will affect the overall rate of the reaction. Conversely, a factor which affects only a much faster step will not significantly affect the rate of the overall reaction.

Summary and Key Terms

Reaction coordinate diagrams convey some very important ideas about how the reaction can proceed, and about the thermodynamics and kinetics of the reaction. In the sections that follow, the following key terms will be used:

Description of Key Terms

Reactants (R): The molecular species that are the starting materials for a chemical reaction. These are often written at the left side of a reaction coordinate diagram.

Products (P): The molecular species that result from a chemical reaction. These are often written at the right side of a reaction coordinate diagram.

Transition State (TS): a transition state is the transient species that exists at an energy maximum. In other words, TS's are highest-energy structures along a reaction pathway. Hammond's postulate suggests that the structure of a transition state should

resemble the lower-energy species (R, P, or I) adjacent to it along the reaction coordinate, and most closely resembles the structure of the species closest in energy.

Intermediate (I): an intermediate is a high-energy structure at a local minimum. Intermediates are sometimes thought of as long-lived transition states. Unlike transition states, intermediates sometimes exist long enough and in high enough concentration to be detectable experimentally.

Microscopic reversibility: if a reaction can proceed in the forward direction from R to P, then in principle, it can also proceed in the reverse direction from P to R. There may be many possibilities for how a reaction *could* happen, but the lowest-energy pathway in the forward direction is also the lowest energy pathway in the reverse direction. In other words, the reactions passes through the same lowest-energy I and TS in the forward and reverse directions.

Steady-State Approximation: the concentration of an intermediate is assumed to react as quickly as it forms. This approximation allows us to assume that concentration of an intermediate remains "steady" throughout the reaction progress. This approximation is useful for analysis of reaction kinetics.

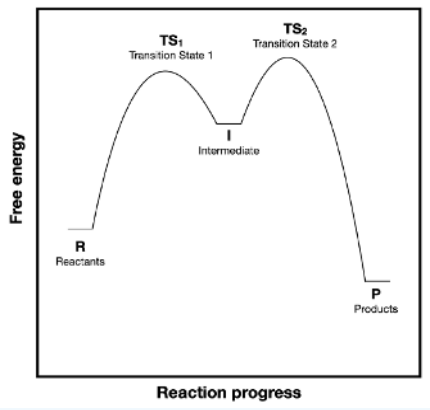
Order: The order of a reaction indicates the power of total reactant concentration in a kinetic rate law. The order of a reactant indicates that reactant's power in the rate law. For example, is a rate law that is $\mathrm{Rate} = \mathrm{k}\ [\mathrm{A}]^2[\mathrm{B}]$, the reaction is second order in A, first order in B and third order overall. If there were also a reactant, C, that was not part of the rate law, the reaction would be zero order with respect to C.

Exercise 13.1.1

Figure 13.1.1 is replicated below for convenience. This figure shows a reaction coordinate diagram for a two-step reaction.

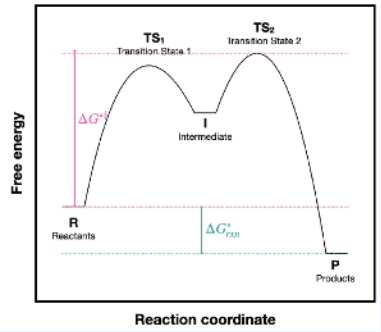
a. (ΔG°) and $\Delta G^{\circ\ddagger}$) are labeled on Figure 13.1.1A, but not on Figure 13.1.1B. Add the appropriate labels to diagram B. (copied below for convenience).

b. Consider the energy barriers for the first and second steps and explain why the steady-state approximation is a valid assumption.

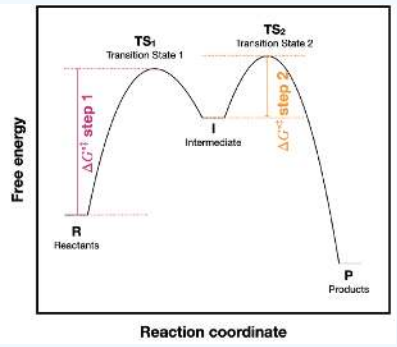


Answer

a) The activation energy for this reaction is the difference between R and TS_2 because TS_2 is the highest energy along the reaction pathway.



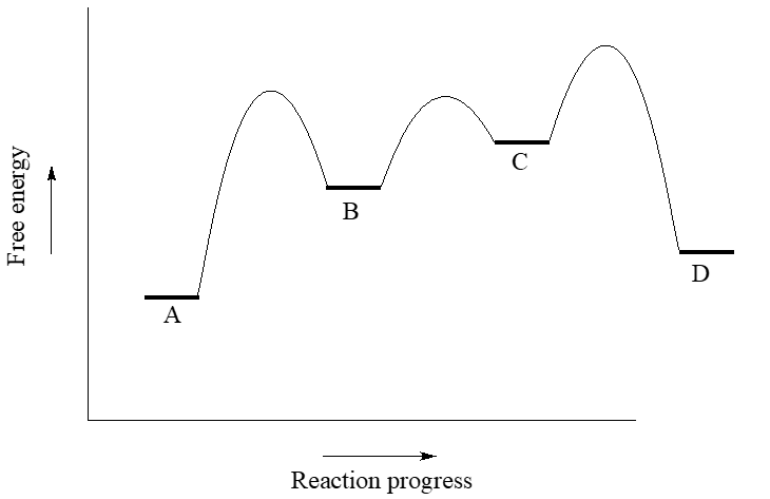
b) The activation energy for step 2 is much smaller than for step 1. This tells us that step 2 occurs faster than step 1. So, the concentration of intermediate should not increase over the course of the reaction, and it should react at least as fast as it is formed. The fact that the activation barrier for step 2 is less than for step one allows us to assume that [I] does not change over the course of the reaction. This should generally be true for all intermediates.



Exercise 13.1.1

Use the reaction coordinate diagram below to answer the questions.

a. Is the overall reaction endergonic or exergonic in the forward (A to D) direction?
b. How many steps does the reaction mechanism have?
c. How many intermediates does the reaction mechanism have?
d. Redraw the diagram if necessary. Add a label showing the energy barrier for the rate-determining step of the forward reaction.
e. Add a label showing ΔG°_{rxn} for the reverse reaction (D to A).
f. What is the fastest reaction step, considering both the forward and reverse directions?



Answer

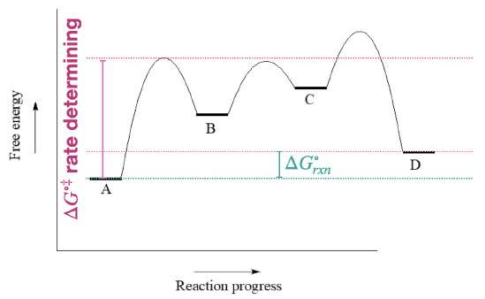
a. D is higher energy than A, so the reaction is endergonic

b. Three steps

c. Two: B and C are intermediates.

d. The first step is rate determining since it has the largest activation barrier.

e. ΔG°_{rxn} for the reverse reaction (D to A) is the same as for the froward direction, with a reverse of its sign.



f. The fastest step has the lowest barriers: this would be the step to/from B and C.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

Curated or created by Kathryn Haas

This page titled 13.1: Reactions of Metal Complexes is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **6.3: A Quick Review of Thermodynamics and Kinetics** by Tim Soderberg is licensed CC BY-NC-SA 4.0. Original source: https://digitalcommons.morris.umn.edu/chem_facpubs/1/.

13.2: Substitution Reactions

Ligand substitution refers to the replacement of one ligand in a coordination complex with another ligand.



Figure 13.2.1: Substitution of one ligand for another in a coordination complex.

Remember, a ligand in coordination chemistry is just a Lewis base that binds to a metal atom or ion. It does so by donating a lone pair (or other pair of electrons). Generallly, this donation is reversible. The donor can always take its electrons back. Typically, there may be some balance between the metal's need for more electrons and the donor's attraction for its own electrons; donor atoms are frequently more electronegative than the metal.

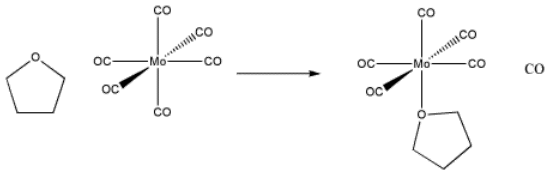


Figure 13.2.2: An example of ligand substitution. THF replaces a carbon monoxide in this molybdenum complex.

Even though the reaction is pretty simple, it can occur in different ways.

That is, the elementary steps involved in the reaction can occur in different orders. The elementary reactions are the individual bond-making or bond-breaking events that lead to an overall change. Sometimes the order of steps is referred to as the mechanism or the mechanistic pathway.

- The mechanism is the order of elementary reaction steps.
- Elementary reaction steps are individual bond-making and breaking steps.

You may have seen reaction mechanisms before. For example, carbonyl addition chemistry can involve lengthy mechanisms, in which a number of proton transfers and other bond-making and bond-breaking steps must occur to get from one state to another. Because ligand substitution is simpler than that, it is a good place to study mechanism in a little more depth, without getting overwhelmed by the details.

The sequence of steps in the mechanism influences how different factors will impact the reaction. For example, changing concentrations of different components in a reaction mixture can affect the time it takes for a reaction to finish.

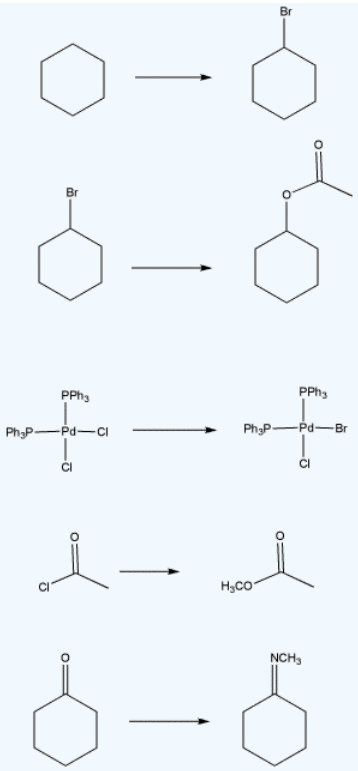
- The mechanism can have a dramatic impact on the outcome of the reaction under different circumstances.

These kinds of considerations have a dramatic impact on industrial processes such as pharmaceutical production. In that setting, chemical engineers need to make decisions about how much of each reactant must be admitted to a reaction mixture and how long they should be allowed to react together. If they allow the reaction to proceed for too, long, there may be “side-reactions” that start to occur, interfering with the quality of the product, and they will waste valuable time in the production pipeline. If they don’t allow it to react long enough, the reaction may not finish, and the product will be contaminated with leftover starting materials.

In this chapter, we will look at how this simple reaction can occur in different ways. We will see some different methods that are used to tell which way the reaction occurs (i.e. evidence of what is really happening). We will also look at some different factors that may influence whether the reaction is likely to occur one way or the other (i.e. reasons it is happening that way, or reasons we expect it will happen that way).

? Exercise 13.2.1

Some kind of substitution occurs in each of the following reactions: an atom or group replaces another. In each case, identify what is being replaced, and what replaces it.



Answer a

a bromine atom replaces a hydrogen atom

Answer b

an acetate group (ethanoyl ester) replaces a bromine atom

Answer c

a bromine atom replaces a chlorine atom (or ions)

Answer d

a methoxy group replaces a chlorine atom

Answer e

a methylamino group replaces an oxygen atom

This page titled 13.2: Substitution Reactions is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

- **3.1: Introduction to Substitution** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

13.3: Inert and Labile Complexes

Kinetics of Substitution Reactions

Kinetics is a branch of chemistry that is concerned with the rates of chemical reactions. In this section, we will discuss the rates of metal-ligand (M-L) substitution reactions.

Let's start with some examples. In the table below are three examples of ligand substitution reactions of hexaaquo metal complexes to form hexaammine complexes. These reactions are nearly identical with the exception of the metal ion. The products are thermodynamically favored in all cases.

Reaction	Rate constant (k)	Labile or Inert
$[Ni(OH_2)]^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	$k = 10^4 s^{-1}$ (1 ns)	Labile (happens in < 1 min)
$[Cr(OH_2)]^{3+} + 6\,NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+}$	$k = 10^{-3} s^{-1}$ (6 days)	Inert (slow, takes hours)
$[Cu(OH_2)]^{2+} + 6\,NH_3 \rightleftharpoons [Cu(NH_3)_6]^{2+}$	$k = 10^8 s^{-1}$	Very Labile (happens in seconds)

Definitions

- **Kinetically Labile** - Metal complexes that undergo "kinetically fast" substitution reactions are **kinetically labile**. Taube suggested that these are reactions in which half of the reactant is consumed in one minute or less ($t_{1/2}$ <1 min).
- **Kinetically Inert** - Metal complexes that undergo "kinetically slow" substitution reactions are **kinetically inert** or **non-labile**. Taube suggested that these are reactions in which $t_{1/2}$ >1 min.

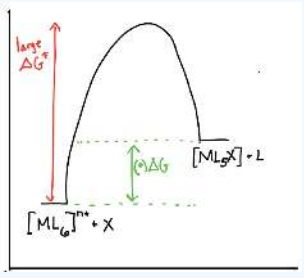
A common pitfall is to confuse the meaning of kinetic terms, like *labile* and *inert*, with thermodynamic terms, like *stable* and *unstable*. It is important to distinguish between kinetics and thermodynamics. For example, the complex $[Fe(H_2O)Cl]^{2+}$ has a large formation constant and is thermodynamically stable; yet it is also labile. On the other hand, the complex $[Co(NH_3)_6]^{3+}$ is unstable in acidic aqueous solution and decomposes spontaneously to $[Co(H_2O)_6]^{3+}$; yet it decomposes slowly because it is inert. It is good practice to use clear terms such as "*kinetically* labile" or "*kinetically* inert" and "*thermodynamically* stable" and "*thermodynamically* unstable".

Exercise 13.3.1

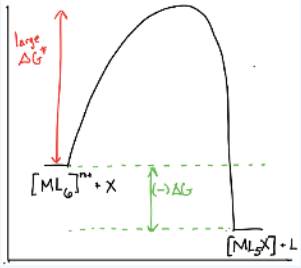
Draw the reaction coordinate diagrams for a reaction of the form $[ML_6]^{n+} + X \rightleftharpoons [ML_5X]^{n+} + L$ in the following scenarios:

a. $[ML_6]^{n+}$ is theromdynamically stable and kinetically inert.
b. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically inert.
c. $[ML_6]^{n+}$ is theromdynamically stable and kinetically labile.
d. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically labile.

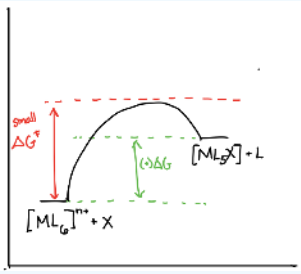
Answer a)



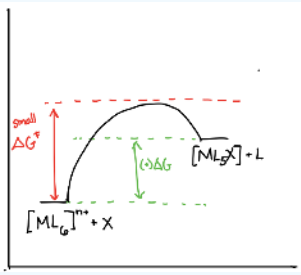
Answer b)



Answer c)



Answer d)



Factors that affect rates of substitution reactions:

Some of the factors that affect the kinetic rates of ligand substitution are the same factors that affect thermodynamic stability (see Chapter 10). The same factors that make a complex stable can also make it more inert. Why are kinetic factors related to thermodynamic stability? It is because the structure and stability of the reactant complex is related to the structure and stability of the transition state. The reactant complex must change its geometry to form an intermediate or transition state. When the reactant is particularly stable, it can result in a higher activation energy associated with moving away from the stable configuration. However, it is incorrect to assume that stability is *always* correlated with reaction rates. Kinetic and thermodynamic factors are related, yet separate.

There are three important factors that influence kinetic rate of substitution:

1. Ligand Field Stabilization Energy (LFSE): Electron configurations that place electrons in higher-energy orbitals (particularly antibonding orbitals) result in more labile complexes. As long as there are not electrons in higher-energy orbitals, the lability correlates roughly with LFSE. The more negative the LFSE, the more inert.
2. Coulombic attraction between the metal and ligand: In general, higher charge density on the metal ion or on the ligand(s) leads to stronger electrostatic attraction between metal and ligand. Stronger Coulombic attraction generally leads to slower dissociation steps and faster association steps. The effect that these have on the reaction rate depends on elementary steps that take part in the rate-determine step(s).
3. Denticity: Multi-dentate ligands create particularly inert complexes as a result of the kinetic chelate effect.

All three considerations are described in more detail below.

? Exercise 13.3.2

In which compound from each pair would you expect the strongest ionic bonds? Why?

a) LiF vs KBr
b) $CaCl_2$ vs. KCl

Answer a

The ions in LiF are both smaller than in KBr, so the force of attraction between the ions in LiF is greater because of the smaller separation between the charges.

Answer b

Calcium has a 2+ charge in $CaCl_2$, whereas potassium has only a + charge, so the chloride ions are more strongly attracted to the calcium than to the potassium.

Taube's observations of metal complex substitution rates

Henry Taube (Nobel Prize, 1983) tried to understand kinetic lability by comparing the factors that govern bond strengths to observations about the rates of reaction of coordination complexes. He saw some things that were unsurprising. He also drew some new conclusions based on ligand field theory.

Taube observed that **many M^{+1} ions (M = metal) are more labile than many M^{+3} ions**, in general. That isn't too surprising, since metal ions function as electrophiles (Lewis acids) and ligands function as nucleophiles (Lewis bases) in forming coordination complexes. In other words, *metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly*. However, there were exceptions to that general rule. For example, Taube also observed that Mo_5^+ compounds are more labile than Mo_3^+ compounds. So, there must be more going on here than *just* the effects of electrostatic attraction.

Another factor that governs ionic bond strengths is the *size of the ion*. Typically, **ions with smaller atomic radii form stronger bonds** than ions with larger radii. Taube observed that Al^{3+}, V^{3+}, Fe^{3+} and Ga^{3+} ions are all about the same size. All these ions exchange ligands at about the same rate. That isn't surprising, because they have the same charge and the same radius. However, Cr^{3+} is also about the same size as those ions and it also has the same charge, but it is much less labile. Once again, there are exceptions to our regular expectations based on simple electrostatic considerations. Furthermore, 4d and 5d transition metals (Y→Cd, and Ac→Hg) are much more inert than 3d transition metals (Sc→Zn). This is unexpected when we consider size; the 4d and 5d metals are much larger than the 3d metals. This unexpected behavior tells us that electrostatics alone cannot predict lability.

Taube came up with a hypothesis that could explain the seeming contradictory oservations described above: *kinetic lability must be affected by d-electron configuration*. This idea forms the basis of Taube's rules about lability.

For example, metals like Ni^{2+} and Cu^{2+} are very labile. The d orbital splitting diagrams for those compounds would have d electrons in the e_g set. Remember, the e_g set arises from interaction with the ligand donor orbitals; this set corresponds to a σ antibonding level.

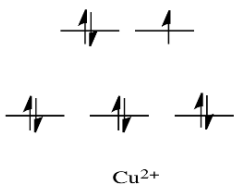


Figure 13.3.1: d^9-electron configuration assuming octahedral geometry.

By comparison, V^{2+} is rather inert. The d orbital splitting diagram in this case has electrons in the t_{2g} set, but none in the e_g set.

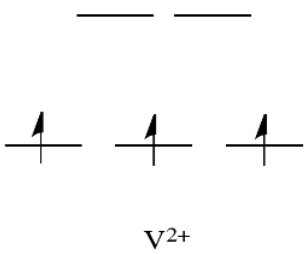


Figure 13.3.2: d^3-electron configuration assuming octahedral geometry.

So, having electrons in the higher energy, antibonding e_g level weakens the bond to the ligand, so the ligand can be replaced more easily. In the absence of those higher energy electrons, the bond to the ligand is stronger, and the ligand isn't replaced as easily.

On the other hand, metals like Ca^{2+}, Sc^{3+} and Ti^{4+} are pretty labile. The d orbital splitting diagrams in those cases are pretty simple: there are no d-electrons at all in these ions.

That means having no electrons in these mostly non-bonding levels leaves the complex susceptible to ligand replacement. But it's hard to see why population of an orbital that is mostly non-bonding would have an effect on ligand bond strength.

Instead, this factor probably has something to do with the part of ligand substitution that we have ignored so far. Not only does one ligand need to leave, but a second one needs to bond in its place. So, having an empty orbital for the ligand to donate electrons into (or, put another way, not having electrons in the way that may complicate donation from the ligand) makes that part of the reaction easier.

? Exercise 13.3.3

Consider all possible electron configurations for octahedral complexes (d^0 to d^{10}, high spin and low spin cases): predict whether each case would be inert, intermediate, or labile.

Answer

	Kinetically Inert (Slow)	Kinetically Labile (Fast)
d^n electron count and ligand field strength	Octahedral configurations with empty e_g orbitals: • d^3 • low-spin d^4, d^5, d^6 Strong-field d^8 (square planar)	Octahedral configurations with occupied e_g orbitals: • d^1, d^2, d^7, d^9, d^10 • high-spin d^4, d^5, d^6 Weak-field d^8 (usually tetrahedral)

? Exercise 13.3.4

Put the metal ions in order of decreasing reaction rate (from labile to inert):

a) Al^{3+}, Na^+, Mg^{2+}

b) $Ca^{2+}, Mg^{2+}, Sr^{2+}$

Answer (a)

Most Labile to most inert: $Na^+ > Mg^{2+} > Al^{3+}$

These are metal ions with similar size and varying charge. They are in order of increasing charge and increasing density from left to right.

Answer (b)

Most labile to most inert: $Sr^{2+} > Ca^{2+} > Mg^{2+}$

These metal ions have the same charge, and vary in size. They are in order of decreasing charge and increasing charge density from left to right.

? Exercise 13.3.5

Some metals, like Mn^{2+}, can be either labile or inert, depending on whether they are high spin or low spin. Explain why using d orbital splitting diagrams.

Answer

Add texts here. Do not delete this text first.

? Exercise 13.3.6

Predict whether the following metals, in octahedral complexes, are labile or not.

a) Co^{3+} (high spin)

b) Co^{3+} (low spin)

c) Fe^{2+} (low spin)

d) Fe^{2+} (high spin)

e) Zn^{2+}

Answer

Answer a

labile (electrons in higher energy d orbital set)

Answer b

not labile (all electrons in lower energy d orbitals)

Answer c

not labile (all electrons in lower energy d orbitals)

Answer d

labile (electrons in higher energy d orbital set)

Answer e

labile (electrons in higher energy d orbital set)

Generalizations for how metal ion affects kinetics:

These are some generalizations about how the kinetics of substitution is affected by the metal ion identity and the d^n electron configuration.

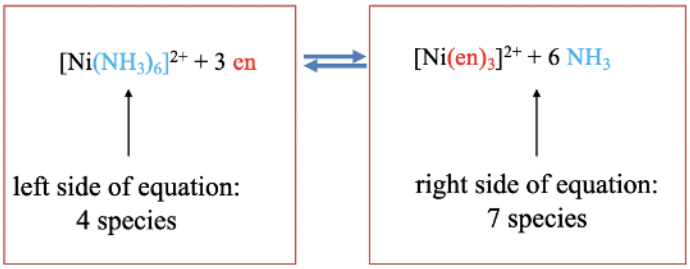
1. s-block metals are very labile, except for those with very high charge density (eg. $Mg^{2+}\ is\ inert$)
2. d^{10} metals are labile (eg: Zn^{2+}, Cu^{+}, Hg^{2+})
3. Other ions with a full shell are labile (eg: Ln^{3+} of f-block)
4. 3d M^{2+}, *when high spin*, are generally labile (eg. $Cu^{2+} is\ very\ labile$)
5. 4d and 5d are usually inert due to higher LFSE (low spin, high LFSE)
6. M^{2+} is more labile than the same metal as M^{3+}
7. d^3 and low spin d^6 are inert (eg. Cr^{3+}, Co^{3+}, low spin Fe^{2+})

Chelate Complexes

In addition to considering factors related to the metal ion and charge or covalent character of metal-ligand bonds, an important consideration is the effect a chelate ligand on reaction kinetics. This effect is also discussed in more detail later in this chapter (Section 12.4.5).

Recall the Thermodynamic Chelate Effect

Chelating complexes tend to be more stable than complexes with monodentate ligands. This is called the "thermodynamic chelate effect". The effect deserves an explanation. The explanation is the increase of entropy that occurs when two or more monodentate ligands are replaced by a chelating ligand. The entropy increases because the overall number of particles increases as the substitution takes place.



$$\Delta S^\circ = +88 \text{ J K}^{-1} \text{ mol}^{-1}$$

Figure 13.3.3: Example of the thermodynamic chelate effect

For example, the substitution of six ammine ligands in the hexaammine nickel (2+) complex by three ethylenediamine chelating ligands increases the number of molecules from four to seven, and hence the entropy increases, in this case by 88 J K^{-1} and mol^{-1} (Figure 13.3.3)

The Kinetic Chelate Effect

In addition to the thermodynamic chelate effect, there is the kinetic chelate effect. Chelate complexes are frequently more inert than complexes with monodentate ligands. Chelate complexes are more inert for two reasons (Figure 13.3.4).

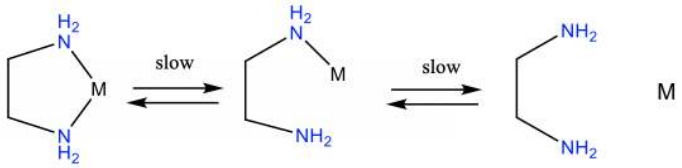


Figure 13.3.4: Illustration of the kinetic chelate effect

Firstly, the whole ligands needs to rotate and bend in order to cleave the first metal-ligand bond. This requires time and slows the kinetics of the bond cleavage. The second reason is that the detached donor atom cannot leave the proximity of the complex because the ligand is still attached via the other donor atom. This increases the probability of the re-formation of the metal-ligand bond which decreases the probability of both bonds being cleaved.

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

Curated or created by Kathryn Haas

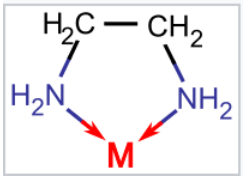
Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 13.3: Inert and Labile Complexes is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

- **9.1: Substitution Reactions and their Mechanisms** by Kai Landskron is licensed CC BY 4.0.

13.4: Chelate Effects

Ligands that contain more than one binding site for a metal ion are called **chelating** ligands (from the Greek word χηλή, chēlē, meaning "claw"). As the name implies, chelating ligands have **high affinity** for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands.



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

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

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

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

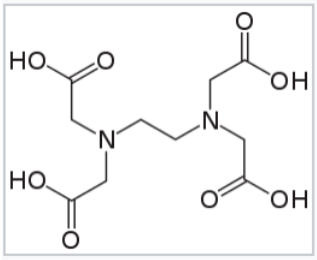
Electronically, the ammonia and en ligands are very similar, since both bind through N and since the Lewis base strengths of their nitrogen atoms are similar. This means that ΔH° must be very similar for the two reactions, since six Co-N bonds are formed in each case. Interestingly however, we observe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

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

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

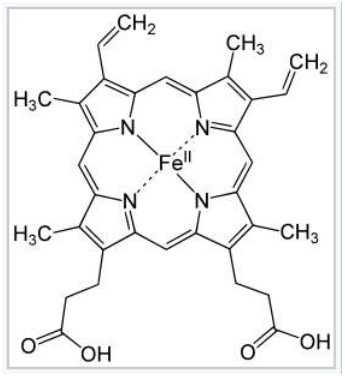
$$\frac{K_f(en)}{K_f(NH_3)} = e^{\frac{-\Delta\Delta G^o}{RT}} \approx e^{\frac{+\Delta\Delta S^o}{R}} \approx e^{12} \approx 10^5 \qquad (13.4.1)$$

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



Ethylenediaminetetraaceticacid acid (EDTA), a hexadentate ligand

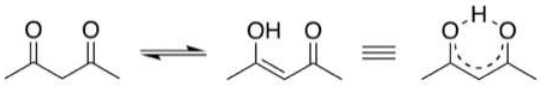
The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "**pre-organized**" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand which is strongly complexes transition metal ions, including (in biological systems) Fe^{+2}.



Heme b

Some other common chelating and cyclic ligands are shown below:

Acetylacetonate ($acac^-$, right) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$ forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



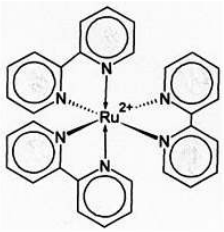
2,2'-Bipyridine and related bidentate ligands such as 1,10-phenanthroline (below, center left) form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex (below left) is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for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

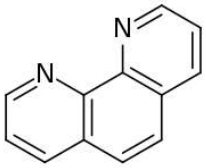


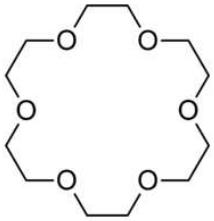
Prof. Jacqueline Barton (Caltech) has used metal polypyridyl complexes to study electron transfer reactions that are implicated in the biological sensing and repair of damage in DNA molecules.

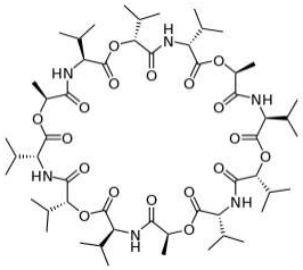
Crown ethers such as 18-crown-6 (below, center right) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.

The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (below right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.









This page titled 13.4: Chelate Effects is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Amanda Bowman via source content that was edited to the style and standards of the LibreTexts platform.

- **5.11: Chelate and Macrocyclic Effects** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

13.5: Substitution Mechanisms

A mechanism is the sequence of elementary steps by which a reaction proceeds. There are two aspects that describe the mechanism of a substitution reaction. One is called the **stoichiometric mechanism**, and the other one is called the **intimate mechanism**. The *stoichiometric* part of the mechanism is defined by the identity of the intermediate, or lack thereof. The *intimate* part of the mechanism is defined by the rate limiting step, and how the rate is dependent on the identity of the incoming ligand.

Stoichiometric Mechanisms

The *stoichiometric* part of the mechanism is **defined by the identity of the intermediate, or lack thereof**. There are three classes of stoichiometric mechanisms based on the type of intermediates that can be characterized. If the intermediate can be isolated it is either an Associative (higher-coordination number intermediate) or Dissociative (lower-coordination number intermediate) reaction. On the other hand, if the intermediate cannot be isolated because it is short-lived (or does not exist) the reaction is classified as Interchange.

Associative (A) Mechanism

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating **an intermediate with a higher coordination number**. The leaving group leaves in a second step to form the product. The generic reaction below illustrates the steps of an associative mechanism. Note that the intermediate, $\mathrm{ML}_n\mathrm{XY}$, has a higher coordination number than that of the reactant, $\mathrm{ML}_n\mathrm{X}$.

$$\begin{array}{rc} \text{Overall Reaction:} & \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X} \\ \hline \text{Step 1 (Association):} & \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{XY} \\ \text{Step 2 (Dissociation):} & \mathrm{ML}_n\mathrm{XY} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X} \end{array}$$

Associative mechanisms are typical of square planar, d^8 complexes. The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **higher coordination number** than the reactant complex.

Dissociative (D) Mechanism

Dissociative (D) mechanisms involve a first step where a bond between the metal ion and the leaving group breaks, creating **an intermediate with a lower coordination number.** The entering group enters in a second step to form the product. The generic reaction below illustrates the steps of a dissociative mechanism. Note that the intermediate, ML_n, has a lower coordination number than that of the reactant, $\mathrm{ML}_n\mathrm{X}$.

$$\begin{array}{rc} \text{Overall Reaction:} & \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X} \\ \hline \text{Step 1 (Dissociation):} & \mathrm{ML}_n\mathrm{X} \rightleftharpoons \mathrm{ML}_n + \mathrm{X} \\ \text{Step 2 (Association):} & \mathrm{ML}_n + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} \end{array}$$

The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **lower coordination number** than the reactant complex.

Interchange (I) Mechanism

Interchange (I) Mechanisms take place in one concerted step where the entering group enters as the leaving group leaves. Bond formation and bond breaking occur simultaneously. In the case of an interchange mechanism, no intermediate is detectable. This means that either there is no intermediate, or that the intermediate is too high-energy and short-lived to be detected. The generic reaction below illustrates the single step of an interchange mechanism. Note that the species, $[\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger}$, can be defined as either a transition state or a very short-lived intermediate. The distinction between these two possibilities is difficult; *when the intermediate is undetectable it is not considered a true intermediate*.

$$\begin{array}{rc} \text{Overall Reaction:} & \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X} \\ \hline \text{Step 1 (Concerted):} & \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons [\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger} + \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X} \end{array}$$

The interchange mechanism is common for many six-coordinate (octahedral) metal complexes. The hallmark feature that distinguishes the interchange mechanism from other possible mechanisms is the **absence of a detectable intermediate**. If an intermediate is detected, the mechanism is considered associative (A). Another piece of evidence that can indicate an interchange mechanism is stereochemical changes from reactant to product. If specific sterochemistry (ie cis or trans relationships) is changed, it may be taken as evidence that an intermediate exists long enough to allow rearrangement to occur.

Distinguishing A, D, and I Mechanisms

Figure 13.5.1 shows examples of possible reaction profiles for each of the stoichiometric mechanisms described above. The profile of A and D mechanisms can be similar; they each require an intermediate, and the primary difference between A and D is the sequence of steps. An I mechanism lacks a true intermediate. These three cases can be difficult to distinguish experimentally, and especially if characterization of an intermediate is difficult. Notice that the reaction coordinate diagram for A and D pathways, shown in Figure 13.5.1, are similar. The only necessary difference between them is in the identity of the intermediate species.

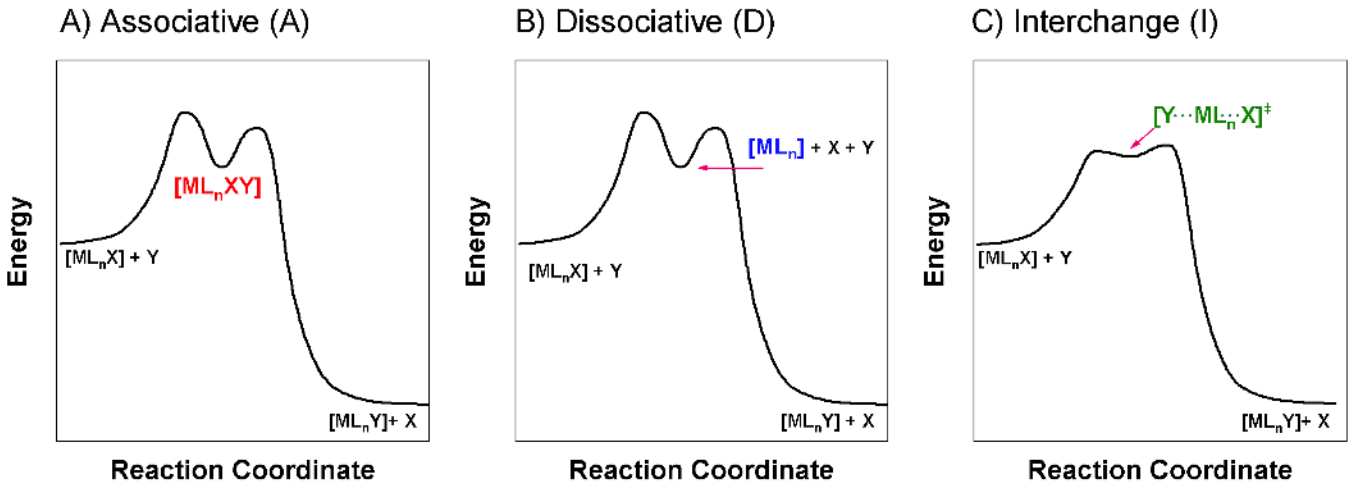


Figure 13.5.1: Example reaction coordinate diagrams for generic reactions that proceed through associative, dissociative, or interchange mechanisms. (Panel A) A reaction proceeds through an Associative pathway if it forms an intermediate with higher coordination number than its reactant complex. Here, an exergonic reaction is shown, where intermediate Extra close brace or missing open brace has a higher coordination number than reactant Extra close brace or missing open brace. (Panel B) A reaction proceeds through a Dissociative pathway if it forms an intermediate of lower coordination number than its reactant. Here, an exergonic reaction is shown where intermediate, Extra close brace or missing open brace, has lower coordination number than the reactant complex, Extra close brace or missing open brace. (Panel C) A reaction proceeds through an Interchange pathway if there is no true intermediate and the reaction proceeds in one step where bonds are broken and formed simultaneously. Shown here is an exergonic reaction where there is a high-energy species that is too unstable to be isolated; thus it is not a true intermediate and is considered equivalent to a transition state. (CC-BY-SA; Kathryn Haas).

Intimate Mechanisms

The intimate mechanism is defined by characteristics of the rate-limiting step. The reaction is classified as associatively-activated (using a subscript, a) if the rate changes by more than 10-fold as the entering group is varied. The reaction is classified as dissociatively-activated (using a subscript, d) if the rate changes by less than 10-fold as the entering group is varied.

Associatively-Activated Mechanisms

The rate-limiting step of an associatively activated pathway is formation of a bond between the entering group and the central metal ion. These reactions also require formation of an encounter complex in a pre-equilibrium step prior to bond forming or bond

breaking steps discussed here (see Eigen-Wilkins Mechanism).

Associatively-activated A and I (A_a and I_a)

In the case of an associatively-activated associative pathway (A_a) or an associatively-activated interchange pathway (I_a), the rate-limiting step is the association of the entering group (Y) with the reactant, ML_nX. In the case of the A_a pathway, it is the first step (bolded) below.

A_a Mechanism

Step 1 (Association): $ML_nX + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_nXY$ **$\Longleftarrow$ RATE LIMITING ASSOCIATION**

Step 2 (Dissociation): $ML_nXY \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY + X$

In the case of A_a, the first step shown above is slower than the second step ($k_1 < k_2$). In this case, an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between A_a and I_a mechanisms is often impossible.

Associatively-activated D (D_a)

In the case of an associatively-activated dissociative reaction (D_a), the rate limiting step is the association of the entering group (Y) with the intermediate ML_n; the second step (bolded) in the mechanism shown below:

D_a Mechanism

Step 1 (Dissociation): $ML_nX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_n + X$

Step 2 (Association): $ML_nX + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY$ **$\Longleftarrow$ RATE LIMITING ASSOCIATION**

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$).

? Exercise 13.5.1

Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_a, I_a, and D_a pathways. Use these diagrams to explain why it is impossible to distinguish between A_a and I_a.

Hint

Notice that the reaction coordinate diagrams for A and D pathways, shown in Figure 13.5.1, are similar. The only necessary difference between them is the identity of the intermediate. These diagrams can be modified to represent associatively-activated pathways by altering the relative energy of the transition state for the associative step; the energy barrier for the associative step must be greater than that of the dissociative step. In other words, the difference between A_a, D_a is in the relative energies of the first and second transition states. In the case of I_a, the diagram could be similar to the I profile shown in Figure 13.5.1, with the exception that the energy barrier for making the M-Y bond is greater than the energy barrier for breaking the M-X bond.

Answer

The three reaction coordinate diagrams shown in the figure below represent A_a, I_a, and D_a mechanisms respectively. If your diagram does not match this perfectly, that may be OK. The important features are:

- A_a: This reaction profile should show an intermediate with higher coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for formation of this intermediate is the associative step, and therefore it should also be the rate-limiting step for an A_a mechanism; in other words, the first step should have the highest energy barrier.
- I_a: This reaction profile should lack a stable intermediate. The energy barrier for creating of the M-Y bond must be rater-limiting. The diagram shown below is an acceptable solution, but a diagram like shown in Panel C of Figure 13.5.1 is also correct. It is not clear from the diagram alone whether bond breaking or bond making are rate-limiting; this

nuance would lie primarily in the identity of the transition state, and whether the M-Y bond is stronger or weaker than the M-X bond in the transition state.

- D_a: This reaction profile should show an intermediate with lower coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for association of the entering group with the intermediate (the second step) must be rate-limiting in a D_a mechanism. In other words, the second step should have the highest energy barrier.

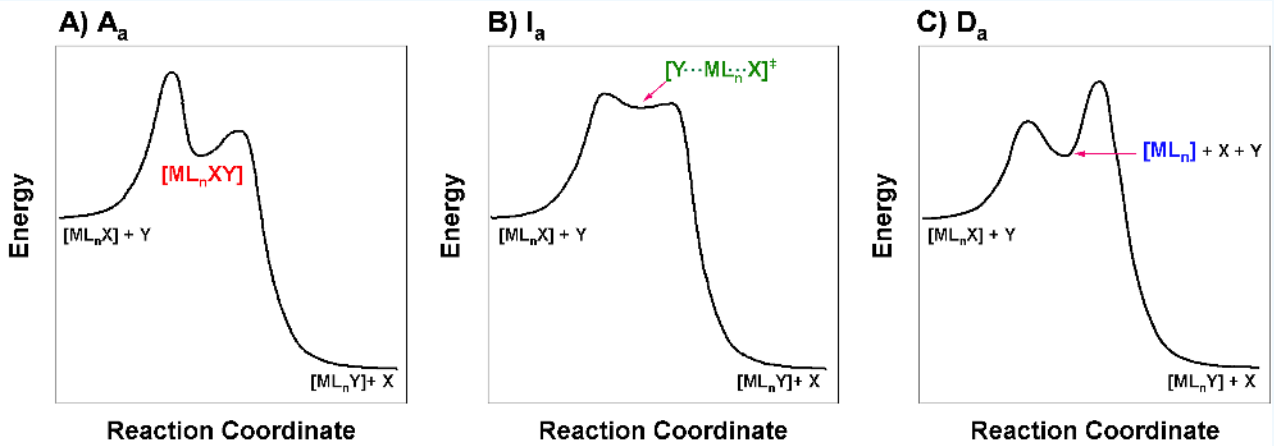


Figure for Excercise 13.5.1: Reaction coordinate diagrams for associatively-activated mechanisms. (A) Associatively-activated associative, A_a. (B) Associatively-activated interchange, I_a. (C) Associatively-activated dissociative, D_a. (CC-BY-SA; Kathryn Haas)

The A_a and I_a mechanisms have different reaction profiles while still the rate-limiting step is the initial association of the incoming ligand to the metal center. These two types of mechanisms are difficult to distinguish because in the case of A_a, there is a relatively small energy barrier for reaction of the intermediate to form product; thus this intermediate is not long-lived and would be difficult to detect. Experimental distinction between A_a and I_a lies in the detection and characterization of this intermediate, and since it may be elusive in A_a, it is difficult to unambiguously determine whether an associatively-activated mechanism is A_a or I_a.

Dissociatively-Activated Mechanisms

When the rate-determining step is the breaking of a bond between the central metal ion and the leaving group, it is considered a dissociatively-activated (subscript d) mechanism. The rates of these reactions are largely independent of the identity of the incoming ligand.

Dissociatively-activated A (A_d)

In the case of a dissociatively-activated associative pathway ($\mathrm{A_d}$), the rate-limiting step is the dissociation of the leaving group (X) from the intermediate, $\mathrm{ML}_n\mathrm{XY}$; the second step (bolded) below.

A_d Mechanism

Step 1 (Association): $\mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{XY}$

Step 2 (Dissociation): $\mathrm{ML_nXY} \underset{\mathrm{k}_{-2}}{\overset{\mathrm{k}_2}{\rightleftharpoons}} \mathrm{ML_nY} + \mathrm{X}$ $\Longleftarrow$ **RATE LIMITING DISSOCIATION**

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$.

Dissociatively-activated D and I (D_a and I_a)

In the case of a dissociatively-activated dissociative reaction ($\mathrm{D_d}$), or a dissociatively-activated interchange pathway ($\mathrm{I_d}$), the rate limiting step is the dissociation of the leaving group (X) from the reactant, $\mathrm{ML}_n\mathrm{X}$. For D_d the rate limiting step is the first step (bolded) in the mechanism shown below:

D_d Mechanism		
Step 1 (Dissociation):	$ML_nX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_n + X$	$\Longleftarrow$ **RATE LIMITING DISSOCIATION**
Step 2 (Association):	$ML_nX + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY$	

In the case of D_d, the first step shown above is slower than the second step ($k_1 < k_2$ and an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between D_d and I_d mechanisms is often impossible.

Exercise 13.5.2

You should complete Excercise 13.5.1 before attempting this excercise.

Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_d, I_d, and D_d pathways.

Answer

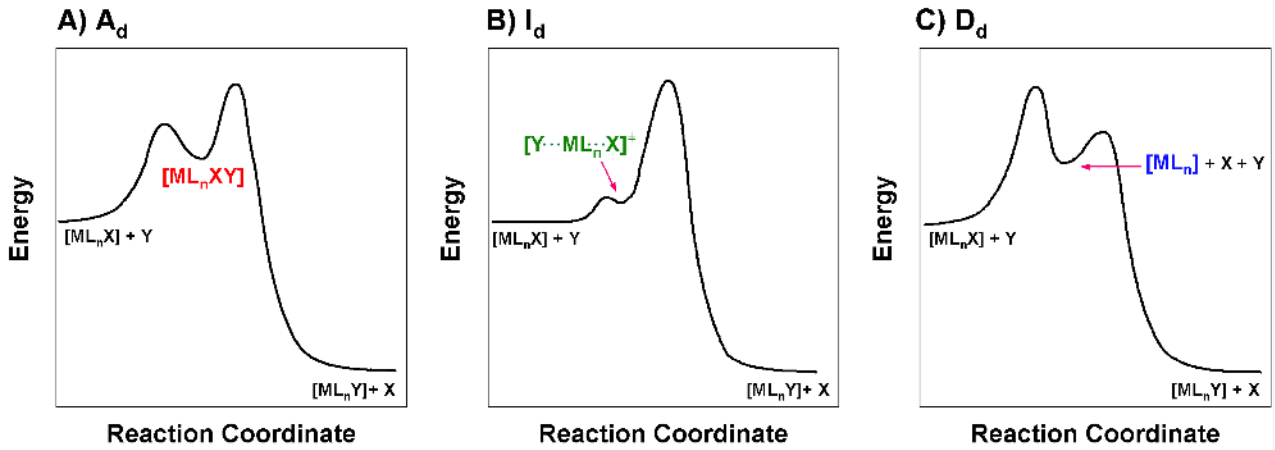


Figure for Excercise 13.5.2: Reaction coordinate diagrams for dissociatively-activated mechanisms. (A) Dissociatively-activated associative, A_d. (B) Dissociatively-activated interchange, I_d. (C) Dissociatively-activated dissociative, D_d. (CC-BY-SA; Kathryn Haas)

Curated or created by Kathryn Haas

This page titled 13.5: Substitution Mechanisms is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

13.5.1: Dissociative Mechanism

Derrivation of the Rate Law

A Dissociative (D) mechanism is two steps in which the first step is the dissociation of a ligand. The intermediate, ML_n, has a lower coordination number than that of the reactant, ML_nX.

$$\begin{array}{rl} \text{Step 1 (Dissociation):} & ML_nX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_n + X \\ \text{Step 2 (Association):} & ML_n + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY \\ \hline \text{Overall Reaction:} & ML_nX + Y \rightleftharpoons ML_nY + X \end{array}$$

If we assume that $k_{-2} << k_2$, the rate law for the formation of products is the rate law of the second step.

$$\frac{d\,[ML_n]}{dt} = k_2[ML_n][Y]$$

We can assume that the concentration of the intermediate is small enough that it would be difficult or impossible to measure its concentration. Here, we can evoke the steady-state approximation and assume that the concentration, $[ML_n]$, is approximately unchanging over the course of reaction. The $[ML_n]$ depends on k_1, k_{-1} and k_2. These assumption are expressed mathematically as follows.

$$\frac{d\,[ML_n]}{dt} = k_1\,[ML_nX] - k_{-1}\,[ML_n]\,[X] - k_2\,[ML_n]\,[Y] = 0$$

We can then use the equation above to solve for $[ML_n]$.

$$ML_n = \frac{k_1\,[ML_nX]}{k_{-1}[X] + k_2[Y]}$$

Then substitution this into the rate law given above for the second step of the mechanism. This would yield a rate law that depends only on species with measurable concentrations.

$$\frac{d\,[ML_nY]}{dt} = \frac{k_2 k_1\,[ML_nX]\,[Y]}{k_{-1}[X] + k_2[Y]}$$

The rate law above suggests that the rate of product formation has an inverse relationship to the concentration of the outgoing ligand, X. This is one piece of evidence that can be used to distinguish a Dissociative mechanism; that is if the rate of reaction decreases as [X] in solution is increased it is evidence of a D mechanism. This rate law also suggests that ther is a complicated dependence of the reaction rate on the concentration of incoming ligand, Y. The importance of [Y] compared to [X] depends mathmatically on the weight of the two values in the demoninator of the rate law. If [X] >> [Y], then a valid approximation is to assume that the $k_2[Y]$ term is relatively small and simplify the rate law by dropping it out completely.

$$\text{If X >> Y, then simplify: } \frac{d\,[ML_nY]}{dt} = \frac{k_2 k_1\,[ML_nX]\,[Y]}{k_{-1}[X]}$$

The resulting rate law (above) has a simpler dependence on [Y]; that is when [X] is large, the reaction rate is directly related to [Y].

The opposite extreme is under conditions of high [Y]. This yields a rate law that is first order in its dependence on the reactant metal complex. When [Y] is large, and the $k_{-1}[X]$ term is relatively insignificant, the rate law can be simplified to the pseudo-first order rate law as follows.

$$\text{If Y >> X, then simplify: } \frac{d\,[ML_nY]}{dt} = k_1[ML_nX]$$

The best type of experimental evidence to determine a dissociative mechanism would be a systematic study of the dependence of rate on both [X] and [Y]. However, the dissociative reaction is unique in that it displays this type of saturation kinetics at high concnetration of the incoming ligand, and so the study of how a reaction rate behaves under high [Y] is common.

First-order reactions

Under conditions of high [Y], the a reaction following a D mechanism is said to follow "first order" kinetics. This type of reaction is sometimes called a first order reaction. That means the rate law depends on only one concentration term.

Why does the dissociative mechanism depend on concentrations in this specific way?

The rate depends on one molecule losing a ligand. Once it does so, a second ligand can replace the one that left. However, losing a ligand may be harder to do than gaining a new one. To lose a ligand, a bond must be broken, which costs energy. To gain a new ligand, a bond is made, releasing energy. That first step is harder to do, so it takes longer. It is a bottleneck that slows the reaction down. It is called the rate-determining step.

- The rate-determining step is the slow step of the reaction.
- The rate-determining step controls the rate of the overall reaction; everything else has to wait for that step to happen.
- Once the rate-determining step has occurred, everything else follows very quickly.

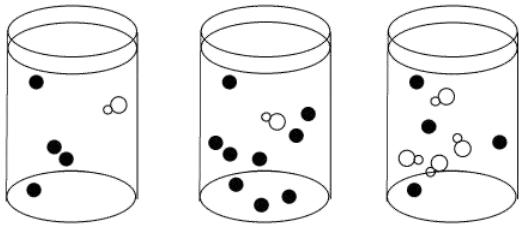


Figure 13.5.1.1: A bottleneck in a reaction. If the reaction must wait for the white molecule to dissociate, it doesn't matter how many black molecules there are; the reaction still goes just as slow. However, the more white molecules there are, the more frequently they will be able to react with the black molecules as dissociation occurs.

No collision is necessary for the metal complex to lose a ligand. Instead, a bond in the metal complex has to break. That just takes time and energy. As a result, concentration of the incoming ligand matters very little.

We should think a little more about energy requirements, available energy and reaction rate. It takes a certain amount of energy to break a bond. Over any given period of time, a specific amount of energy is available in the surroundings to use. That energy is not available uniformly. Some molecules will get more energy from their surroundings and others will get less. There will be a statistical distribution, like a bell curve, of energy available in different molecules. That means bond-breaking events are governed by statistics.

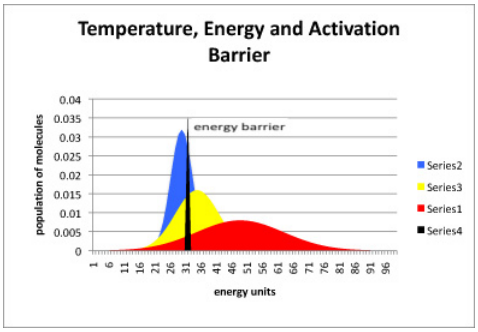


Figure 13.5.1.2: The relationship between temperature, energy available, and energy barrier. The black line represents energy needed to start the reaction, also called the energy barrier or the activation barrier. The blue curve is the distribution of available energy in a group of molecules at a cooler temperature. The yellow curve is for a group of molecules that is a little warmer, and the red curve even warmer.

In figure 13.5.1.2, most of the molecules at the low temperature (blue) do not have enough energy to begin the reaction. A small portion do, and so the reaction will proceed, but very slowly. In the yellow curve, there is more energy available, and so a large fraction of molecules have the energy necessary to begin the reaction. In the red curve, the vast majority have sufficient energy to react. Thus, one of the factors governing how quickly a reaction will happen is the energy needed, or activation barrier. A second factor is the energy available, as indicated by the temperature.

Of course, even if there is enough energy for the reaction, the reaction might not occur yet. Energy is necessary but not sufficient to start a reaction. There are also statistical factors in terms of whether a molecule has its energy allotted into the right places, or in some cases, whether two molecules that need to react together are oriented properly.

Suppose at a given temperature it takes a specific amount of time for half the molecules to gain enough energy so that they can undergo the reaction. That amount of time is called the half life of the reaction. After one half life, half the molecules have reacted and half remain. After a second half life, half the remaining molecules (another quarter, for three quarters of the original material in all) have also reacted, and a quarter still remain. After a third half life, half the remaining ones (another eighth, making it seven eighths reacted in total) will have reacted, leaving an eighth of the original material behind.

- Exponential decay is based on a statistical distribution of energy availability.
- The concept of half life is related to exponential decay.
- It takes a fixed period of time for a half of the metal complex obtain enough energy to dissociate.

Thus, the time it takes for the reaction to happen does not really depend on the concentration of anything.

However, the change in *concentration* over time -- the quantity that we can usually measure most easily -- depends on the original concentration, and for that reason the concentration of the metal complex appears in the rate law.

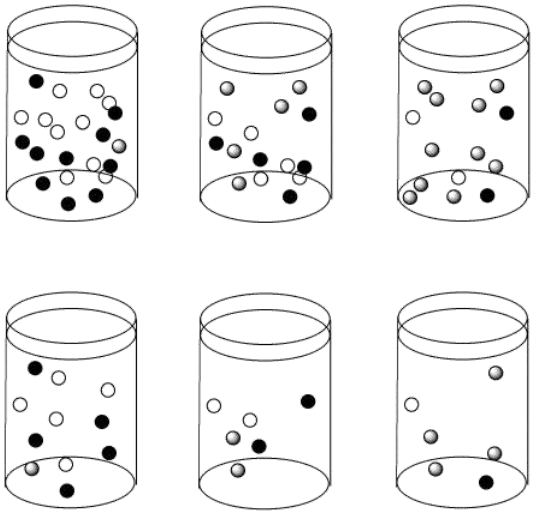


Figure 13.5.1.3: The reactions in the top row and bottom row are proceeding with the same half-life as we move from left to right. However, the top row starts out more concentrated than the bottom row. As a result, the *concentrations* in the top row are changing more quickly than in the bottom row.

Suppose the half life for a particular case of ligand substitution is one second. After a half life, a 1 M solution becomes 0.5 M, so the rate of change in concentration per time is 0.5M/s. But after the same half life, a 0.5 M solution becomes 0.25 M, so the change in concentration is 0.25 M/s.

? Exercise 13.5.1.1

If a first order reaction has a half-life of 120 seconds, how much of the original material is left after

a) four minutes? b) six minutes? c) eight minutes? d) ten minutes?

Answer a

4 minutes = 240 seconds = 2 x 120 second = 2 half lives.

Material left = 50% x 50% = 0.5 x 0.5 = 0.25 = 25% left

Answer b

6 minutes = 360 seconds = 3 x 120 second = 3 half lives.

Material left = 0.5 x 0.5 x 0.5 = 0.125 = 12.5% left

Answer c

8 minutes = 480 seconds = 4 x 120 second = 4 half lives.

Material left = 0.5 x 0.5 x 0.5 x 0.5 = 0.0625 = 6.25% left

Answer d

10 minutes = 600 seconds = 5 x 120 second = 5 half lives.

Material left = 0.5 x 0.5 x 0.5 x 0.5 x 0.5 = 0.03125 = 3.125% left

? Exercise 13.5.1.2

Given the first-order dissociative rate law above, what would happen to the reaction rate for substitution in each of the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is halved
c. the concentration of ligand is doubled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is halved

Answer a

Dissociative Rate Law: Rate = $[ML_n]$, if ML_n is the complex. There is no dependence on [X], if X is the new ligand.

Rate will double: Rate = 2 x $[ML_n]_0$, if $[ML_n]_0$ is the original concentration.

Answer b

Rate will be halved: Rate = 0.5 x $[ML_n]_0$.

Answer c

Rate will triple: Rate = 3 x $[ML_n]_0$.

Answer d

Rate will be halved: Rate = 0.5 x $[ML_n]_0$.

? Exercise 13.5.1.3

Plot graphs of initial rate vs concentration to show what you would see in dissociative substitution.

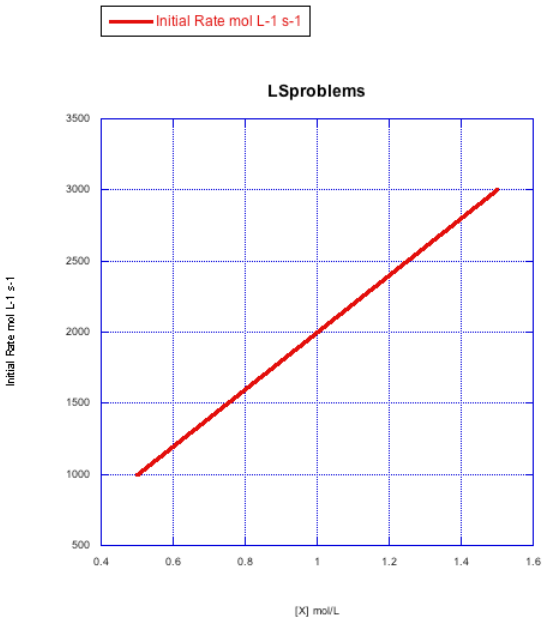
a) The concentration of metal complex, $[ML_n]$, is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

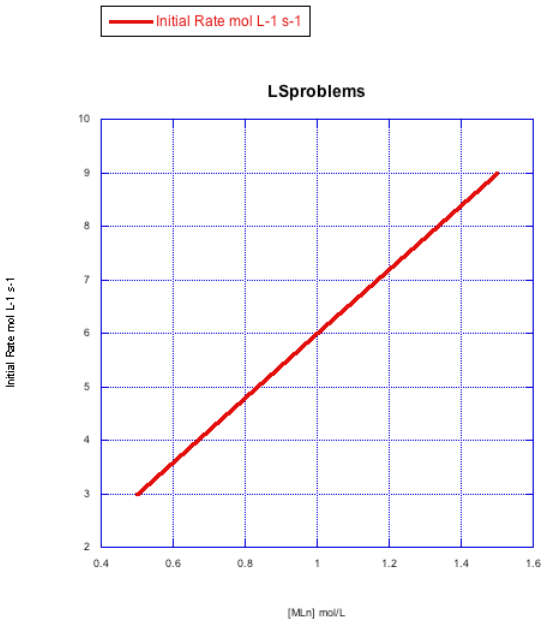
b) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L

? Exercise 13.5.1.4

Given the following sets of initial rate data, determine whether each case represents a dissociative substitution. [MLn] = concentration of the coordination complex; [X] = concentration of incoming ligand.

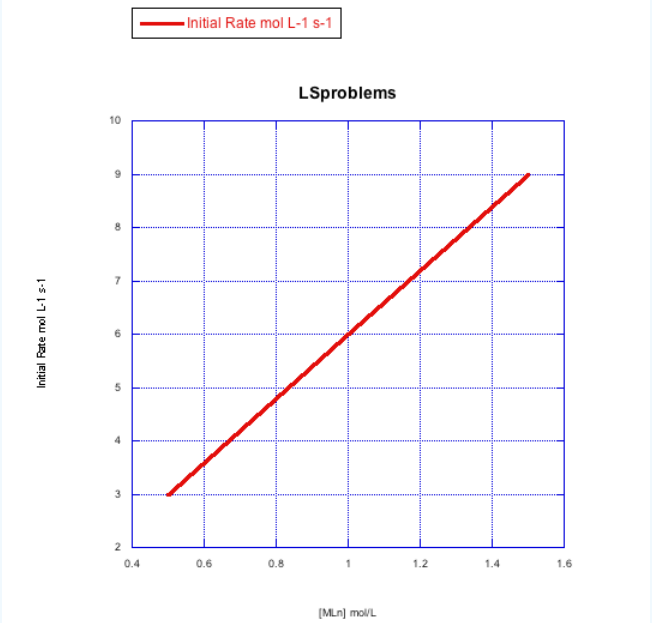
a)

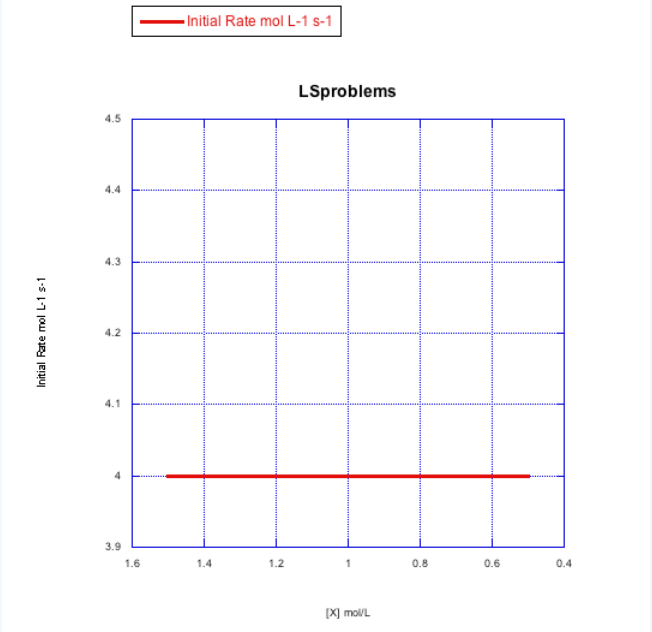




b)

https://chem.libretexts.org/@go/page/537905





Answer a

The rate increases with both concentration of metal complex and incoming ligand. This looks like an associative mechanism.

Answer b

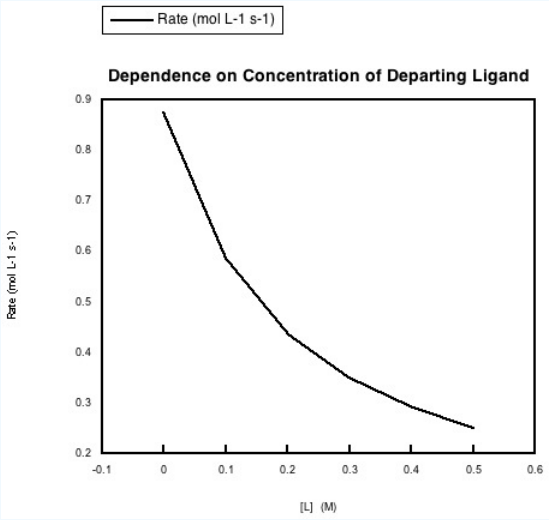
The rate depends on concentration of the metal complex, but not the incoming ligand. This looks like a dissociative mechanism.

Answer c

The rate depends on the concentration of incoming ligand, but not the metal complex. Whatever is going on here, it isn't a simple dissociative mechanism.

Exercise 13.5.1.5

In the following data, the concentration of the metal complex and the incoming ligand were held constant, but more of the departing ligand was added to the solution.



a) Explain what the data says about rate dependence on this concentration.

b) Explain this rate dependence in terms of the reaction.

Answer a

The rate of the reaction is depressed when the concentration of the departing ligand is increased.

Answer b

This dependence could indicate an equilibrium in the dissociative step. The more departing ligand is added, the more the equilibrium is pushed back towards the original metal complex. With less dissociated metal complex around, the entering ligand cannot form the new complex as quickly.

Exercise 13.5.1.6

In certain solvents, such as THF, acetonitrile and pyridine, the rate law for substitution often appears to be Rate = $k_1[ML_n] + k_2[ML_n][X]$, in which X is the incoming ligand and ML_n is the metal complex.

a) What do these solvents have in common?

b) What is a possible explanation for this rate law?

c) This rate law has been shown to be consistent with an entirely associative mechanism. How is that possible?

Answer a

These solvents all have lone pairs. They could be Lewis bases or nucleophiles.

Answer b

It looks like two competing mechanisms. On term suggests a dissociative mechanism, whereas the other term suggests a dissociative mechanism. They could be happening in competition with each other.

Answer c

On the other hand, it could be that there is one mechanism with two different nucleophiles. If the incoming ligand is the nucleophile, the term on the right shows up in the rate law. If the solvent is the nucleophile, forming a third complex, the term on the left shows up in the rate law. That's because we would typically change the amount of metal complex and the

amount of ligand that we add to the solution in order to determine the rate law, but we wouldn't normally be able to change the concentration of the solvent, so it would be a constant. (How could you confirm this explanation in an experiment?)

This page titled 13.5.1: Dissociative Mechanism is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

- **3.4: Dissociative Mechanism and Kinetics** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

13.5.2: Interchange Mechanism

Interchange (I) Mechanisms take place in one concerted step where there is no intermediate, or the intermediate is elusive. The reactio nessentially occurs in once step in which bond forming and bond breaking is concerted, as shown below. The species, $[\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger}$, can be defined as either a transition state or a very short-lived intermediate.

$$\text{Step 1 (Concerted):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons [\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger} + \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

The rate law of this one-step reaction depends on whether the relative rates of the forward and reverse reactions. When the reaction is practically irreversible, then the rate depends only on the formation of product, and not its reaction to re-form product. In this case, the rate law is a simple second-order rate law.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]$$

On the other hand, if the rate of re-formation of reactant is significant, then the rates of forward and reverse reactions must be considered in the rate law.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{X}][\mathrm{X}]$$

In the latter case where there is a dependence of rate on both [X] and [Y], an effective strategy is to employ the condition where solution concentration of both [X] and [Y] are simultaneously high so that the reaction is effectively a competition of two pseudo-first order reactions that depend primarily on the metal complex concentrations. In such a case as this, another helpful piece of information is the equilibrium constant for the reaction ($K = \frac{k_1}{k_{-1}}$). The rate law is written below.

$$\text{When [X] and [Y] are very high: } \frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{X}] = -\frac{d[\mathrm{ML}_n\mathrm{X}]}{dt}$$

One distinguishing feature of an I mechanism compared to a D mechanism can be determined from such an experiment under high concentration of X and Y. In the case of a D mechanism and sufficiently high concentration of incoming ligand, [Y], the reaction demonstrations saturation kinetics to give a pseudo-first order rate law depending only on the concentration of reactant metal complex. In the case of I, the reaction rate is not a simple first order rate law because even under high [Y] and [X], there is a dependence of rate on concentration of the product complex.

Reactions that are I_a or I_d are distinguished by the relative strength of the M-X and M-Y bond in the transition state. These reactions can be distinguished by varying the Identities of X and Y to determine how the reaction rate depends on identity of X and Y. If there is a large dependence on the incoming ligand, and less so on the outgoing ligand, it could be classified as an I_a mechanisms. The opposite is also true.

This page titled 13.5.2: Interchange Mechanism is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

13.5.3: Associative Mechanism

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating an intermediate, ML_nXY, with a higher coordination number than that of the reactant, ML_nX.

$$\begin{array}{rr} \text{Step 1 (Association):} & ML_nX + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_nXY \\ \text{Step 2 (Dissociation):} & ML_nXY \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY + X \\ \hline \text{Overall Reaction:} & ML_nX + Y \rightleftharpoons ML_nY + X \end{array}$$

To determine the rate law, we can use a similar process as we followed for D mechanisms, which are also two steps. Assuming that $k_2 >> k_{-2}$, the rate of formation of product from the second step is:

$$\frac{d[ML_nY]}{dt} = k_2[ML_nXY]$$

The steady state approximation allows us to assume that the intermediate is in low concentration (too low to be reliably measured) and that it is unchanging. We can use the rate law for the first step to find $[ML_nXY]$ in terms of species that can be reliably measured.

$$\frac{d[ML_nXY]}{dt} = k_1[ML_nX][Y] - k_{-1}[ML_nXY] - k_2[ML_nXY] = 0$$

...solving this first-step rate law for $[ML_nXY]$ gives $[ML_nXY] = \frac{k_1[ML_nX][Y]}{k_{-1} + k_2}$

And then substitution $[ML_nXY]$ into the rate law for the second step, and let $k = \frac{k_1 k_2}{k_{-1}+k_2}$ to gives the overall rate law below.

$$\frac{d[ML_nY]}{dt} = \frac{k_1 k_2[ML_nX][Y]}{k_{-1} + k_2} = k[ML_nX][Y]$$

This overall rate law is second order, and first order with respect to each of the reactants. This means that there is a direct (linear) relationship between concentration of either reactant and the rate of reaction.

Why does the associative mechanism depend on concentrations in this specific way?

This is a case of two molecules coming together. If both compounds are dissolved in solution, they must “swim around” or travel through the solution until they bump into each other and react. The more concentrated the solution is, or the more crowded it is with molecules, the more likely are the reactants to bump into each other. If we double the amount of new ligand in solution, an encounter between ligand and complex becomes twice as likely. If we double the amount of metal complex in solution, an encounter also becomes twice as likely.

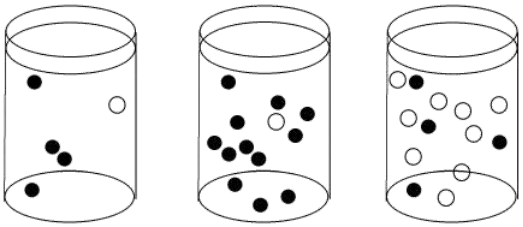


Figure 13.5.3.1: The effect of concentration on collision probability. In the first beaker, there is a chance that a black molecule and white molecule will meet and react together. The chance of a meeting is much higher in both the second beaker, where there are lots more black molecules, and in the third beaker, where there are many more white molecules.

? Exercise 13.5.3.1

Given the associative rate law above, what would happen to the reaction rate for an associative substitution in the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled

b. the concentration of ligand is tripled, and the concentration of metal complex is doubled
c. the concentration of ligand is tripled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is doubled

Answer a

Associative Rate Law: $Rate = [ML_n][X]$, if ML_n is the complex and X is the new ligand.

Rate will quadruple: $Rate = (2 \times [ML_n]_0) \times (2 \times [X]_0) = 4 \times [ML_n]_0[X]_0$, if $[X]_0$ and $[ML_n]_0$ are the original concentrations.

Answer b

Rate will sextuple: $Rate = (3 \times [ML_n]_0) \times (2 \times [X]_0) = 6 \times [ML_n]_0[X]_0$.

Answer c

Rate will nonuple: $Rate = (3 \times [ML_n]_0) \times (3 \times [X]_0) = 9 \times [ML_n]_0[X]_0$.

Answer d

Rate will stay the same: $Rate = (0.5 \times [ML_n]_0) \times (2 \times [X]_0) = 1 \times [ML_n]_0[X]_0$.

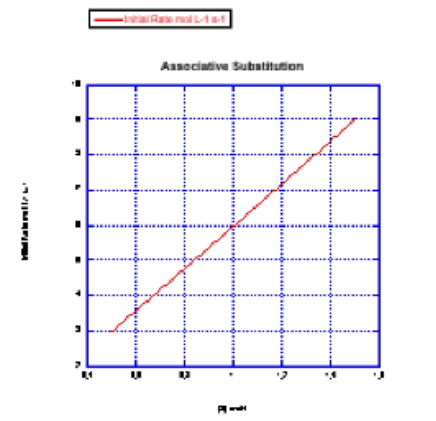
Exercise 13.5.3.2

Plot graphs of initial rate vs. concentration to show what you would see in associative substitution.

a) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

b) The concentration of metal complex, $[ML_n]$, is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

Answer



Exercise 13.5.3.3

In the previous problem, the experiment was run in a particular way for particular reasons.

a) Why was one concentration held constant while the other one was changed? Why not change both?

b) Why does the graph report "initial rate" -- just the rate at the very beginning of the reaction?

Answer a

Changing both concentrations at once would leave some doubt about whether one concentration had affected the rate, or the other concentration, or both. In practice, one concentration is usually held constant while the other is kept in excess and varied.

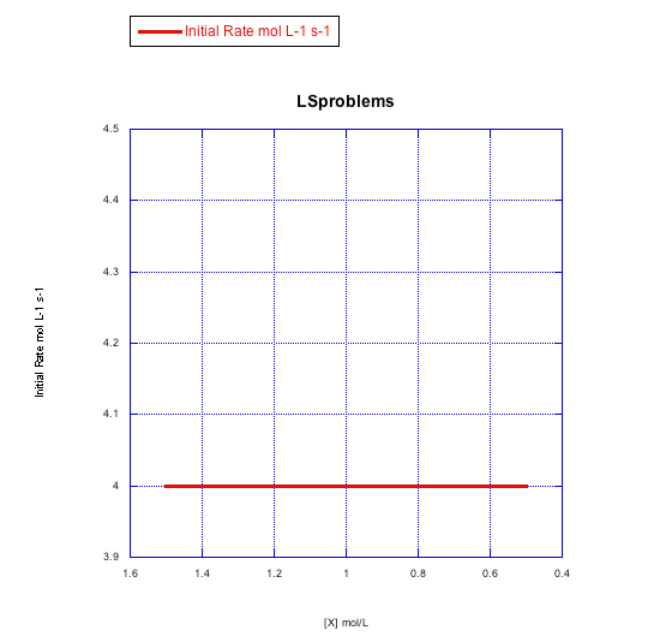
Answer b

Rate changes over time because the concentrations of reactants change as they are consumed. By reporting only the initial rate (usually meaning less than 5% or 10% complete, but possibly even less than that if a lot of data can be gathered very quickly), the concentrations are still about what you started with. That means you can report a rate that corresponds to a given concentration with confidence.

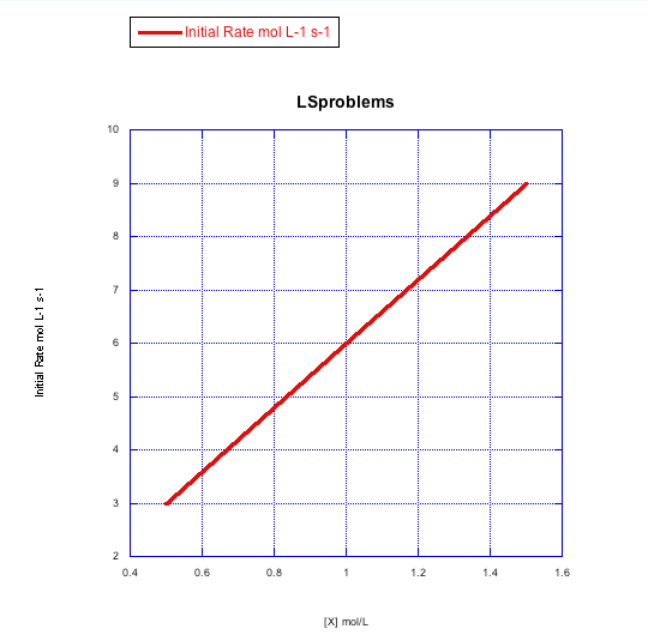
Exercise 13.5.3.4

Given the following sets of initial rate data (rates measured at the beginning of a reaction), determine whether each case represents an associative substitution.

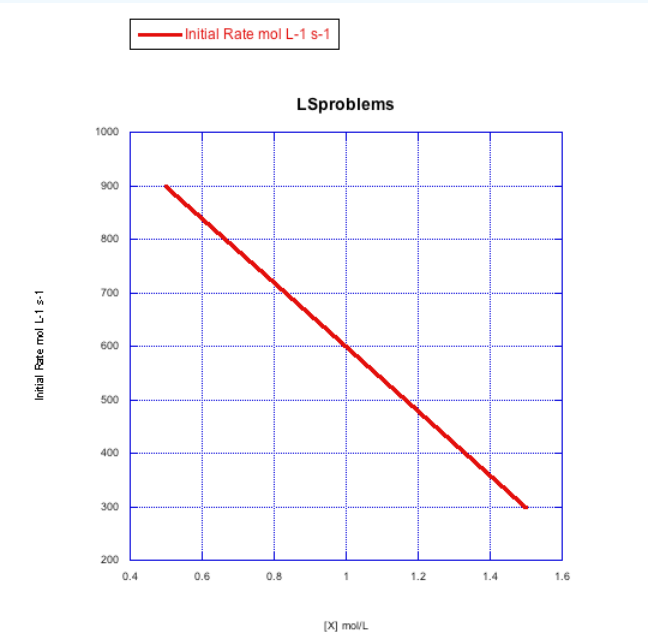
a)



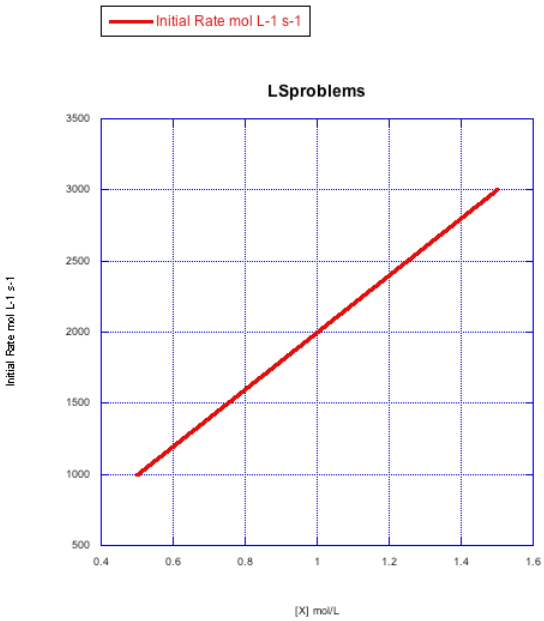
b)


Initial Rate mol L-1 s-1
LSproblems
Initial Rate mol L-1 s-1
[X] mol/L
10
9
8
7
6
5
4
3
2
0.4
0.6
0.8
1
1.2
1.4
1.6

c)


Initial Rate mol L-1 s-1
LSproblems
Initial Rate mol L-1 s-1
[X] mol/L
1000
900
800
700
600
500
400
300
200
0.4
0.6
0.8
1
1.2
1.4
1.6

d)



Answer a

The rate would change with the ligand concentration if associative. This rate is constant over a range of ligand concentrations, so the reaction is not associative.

Answer b

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

Answer c

The rate changes over the concentration range, but it decreases. This is the opposite of what should happen. This reaction does not follow a simple associative pathway.

Answer d

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

? Exercise 13.5.3.5

What information can be gained from the slopes of lines in Exercise 13.5.3.4 ?

Answer

Because $Rate = k[ML_n][L]$ is held constant while [L] is varied, then the slope of the line is k [ML_n]. Since you would know the value of [ML_n], you could obtain the rate constant from the quantity (slope/ [ML_n]).

Note that the rate law for an A mechanism, and a reversible I mechanism are of the same form: they are each first order with respect to each reactant. Thus, an unambiguous determination between the two is difficult because it would require detection of the intermediate, which exists only at a very low concentration.

This page titled 13.5.3: Associative Mechanism is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **3.3: Associative Mechanism and Kinetics** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

13.6: Activation Parameters

The rate law shows how the rate of a reaction depends on concentrations of different species in solution. The proportionality constant, k, is called the rate constant. It contains other information about the energetic requirements of the reaction.

All reactions must overcome activation barriers in order to occur. The activation barrier is the sum of the energy that must be expended to get the reaction going. An activation barrier is often thought of, cartoonishly, as a hill the molecule has to climb over during the reaction. Once, there, it can just slide down the other side of the hill to become products. At the top of the hill, the molecule exists in what is called the "transition state". At the transition state, the structure is somewhere between its original form and the structure of the products.

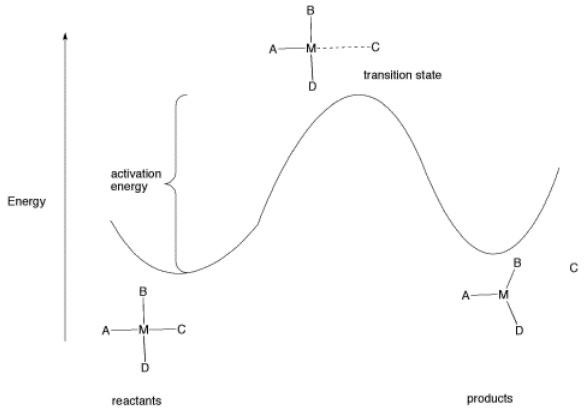


Figure 13.6.1: The activation barrier for a ligand dissociation step.

The type of diagram shown in figure LS6.1 is sometimes called a "reaction progress diagram". It shows energy changes in the system as a reaction proceeds. One or more activation barriers may occur along the reaction pathways, as various elementary steps occur in the reaction. In the above case, it is easy to imagine the source of the energy barrier, because some energy must be expended to break the bond to ligand C.

However, after that barrier is passed, energy is lowered again. This can happen for several reasons. Once C has separated from the metal complex, it is free to vibrate, tumble, roll and zip around all on its own. That means it can put its energy into any of those modes, independently of the metal complex. As a result, the entropy of the system increases. That lowers the overall "free energy" of the system. In addition, there may be some relief of crowding as the molecule changes from a four-coordinate complex to a three-coordinate complex, so strain energy is also lowered.

? Exercise 13.6.1

Make drawings depicting the relationship between reaction progress and energy for the following cases:

a) a new ligand binds to a four-coordinate complex, forming a five coordinate complex.

b) a two-step process in which a new ligand binds to a four-coordinate complex, forming a five coordinate complex, and then an old ligand dissociates to form a new, four-coordinate complex.

The rate constant gives direct insight into what is happening at the transition state, because it gives us the energy difference between the reactants and the transition state. Based on that information, we get some ideas of what is happening on the way to the transition state.

The rate constant can be broken down into pieces. Mathematically, it is often expressed as

$$k = (\frac{RT}{Nh})e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

In which R = the ideal gas constant, T = temperature, N = Avogadro's number, h = Planck's constant and $\Delta G^{\ddagger}$ = the free energy of activation.

The ideal gas constant, Planck's constant and Avogadro's number are all typical constants used in modeling the behaviour of molecules or large groups of molecules. The free energy of activation is essentially the energy requirement to get a molecule (or a mole of them) to undergo the reaction.

Note that k depends on just two variables:

- $\Delta G^{\ddagger}$ or the energy required for the reaction
- T or the temperature of the surroundings, which is an index of the available energy

The ratio of activation free energy to temperature compares the energy needs to the energy available. The more energy available compared to the energy needed, the lower this ratio becomes. As a result, the exponential part of the function becomes larger (since the power has a minus sign). That makes the rate constant bigger, and the reaction becomes faster.

The activation free energy is constant for a given reaction. It can be broken down in turn to:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

in which $\Delta H^{\ddagger}$ = activation enthalpy and $\Delta S^{\ddagger}$ = activation entropy.

The activation enthalpy is the energy required for the reaction. The activation entropy deals with how the energy within the molecule must be redistributed for the reaction to occur. These two parameters can be useful in understanding events leading to the transition state.

For example, in ligand substitution, an associative pathway is marked by low enthalpy of activation but a negative entropy of activation. The low enthalpy of activation results because bonds don't need to be broken before the transition state, so it doesn't cost much to get there. That's favorable and makes the reaction easier. However, a decrease in entropy means that energy must be partitioned into fewer states. That's not favorable and makes the reaction harder. The reason the energy must be redistributed this way is that two molecules (the metal complex and the new ligand) are coming together to make one bigger molecule. They can no longer move independently of each other, and all of their combined energy must be reapportioned together, with a more limited range of vibrational, rotational and translational states to use for that purpose.

- Associative pathway: more bond making than bond breaking; lower enthalpy needs
- Associative pathway: two molecules must be aligned and come together; fewer degrees of freedom for energy distribution; decrease in entropy

On the other hand, the dissociative pathway is marked by a higher enthalpy of activation but a positive entropy of activation. The higher enthalpy of activation results because a bond must be broken in the rate determining step. That's not favorable. However, the molecule breaks into two molecules in the rate determining step. these two molecules have more degrees of freedom in which to partition their energy than they did as one molecule. That's favorable.

- Dissociative pathway: more bond breaking in rate determining step, higher enthalpy needs
- Dissociative pathway: one molecule converts to two molecules in rate determining step, greater degrees of freedom in two independently moving molecules, entropy increases

Thus, looking at the activation parameters can reveal a lot about what is going on in the transition state.

? Exercise 13.6.2

What factor(s) other than entropy might raise the free energy of the transition state going into an associative step between a metal complex and an incoming ligand? (What factor might make the first, associative step slower than the second, dissociative step?)

Answer

The metal centre is becoming more crowded as the new ligand arrives, so an increase in energy owing to steric hindrance may also play a role in the transition state energetics.

Exercise 13.6.3

Other mechanisms for ligand substitution are also possible. The following case is referred to as an associative interchange (I_A).



a) Describe in words what happens in an associative interchange.

b) Predict the rate law for the reaction.

c) Qualitatively predict the activation entropy and enthalpy, compared with

i) an associative mechanism and

ii) a dissociative mechanism.

Answer a

The new ligand, B, is arriving at the same time as the old ligand, A, is departing. We might also describe it as new ligand B pushing old ligand A out of the complex.

Answer b

$Rate = k[ML_5A][B]$, which looks like an associative rate law.

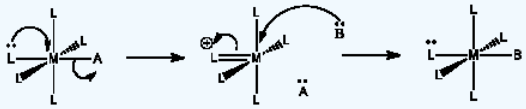
Answer c

This is a thought-provoking question without a definite answer. Associative mechanisms typically have lower activation enthalpy than dissociative mechanisms, because there has also been some bond-making prior to the bond-breaking in the rate determining step. The associative interchange would be a little more like the associative mechanism than dissociative. The mix of bond-making and bond-breaking at the transition state would make the enthalpy of activation relatively low.

Associative mechanisms have negative activation entropies, whereas dissociative mechanisms have positive activation entropies. The associative interchange could be in between the two, given that the elementary step would be close to entropically neutral overall. What happens at the transition state is a little harder to imagine, but it might reflect the small changes in entropy through the course of the reaction, producing a small entropy of activation. On the other hand, if the incoming ligand is forced to adopt some specific approach as it comes into the molecule (to stay out of the way of the departing ligand, for example) then that restriction could show up as a small negative activation entropy.

Exercise 13.6.4

For the following mechanism:



a) Describe in words what is happening.

b) Predict the rate determining step.

c) Predict the rate law for the reaction.

d) Qualitatively predict the activation entropy and enthalpy, compared with

i) both an associative mechanism and

ii) a dissociative mechanism.

e) Suggest some ligands that may be able to make this mechanism occur.

Answer a

The lone pair donation from one ligand appears to push another ligand out.

Answer b

The first step is probably rate determining, because of the bond breaking involved.

Answer c

If the first step is rate determining, $Rate = k[ML_5A]$.

Answer d

Another question without a very clear answer. Compared with an associative mechanism, the activation entropy is probably much more positive, because additional degrees of freedom are being gained as the molecule heads over the activation barrier and one of the ligands separates to be on its own. However, the activation entropy may be less positive than in a regular dissociation, because in this case the breaking of one bond has to be coordinated with the formation of another.

The enthalpy of activation has both a bond-making and bond-breaking component, a little like in an associative mechanism. However, the amount of bond making here is probably less important, because pi bonds are typically not as strong as sigma bonds. The activation enthalpy is probably higher than an associative pathway but not as high as a dissociative one.

Answer e

The donor ligand must have a lone pair. Oxygen donors would be good candidates, because even if one lone pair is already donating in a sigma bond, an additional lone pair may be available for pi donation. The same thing is true for halogen donors. It would also be true for anionic nitrogen donors but not for neutral nitrogen donors, because a neutral nitrogen has only one lone pair.

This page titled 13.6: Activation Parameters is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **3.5: Activation Parameters** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

13.7: Dissociation

Consider what must happen for the simplest case of a purely dissociative (D) reaction mechanism for an octahedral metal complex. The first step, and the rate-limiting step must be dissociation of one ligand to form an intermediate with a lower coordination number. Such a situation, where an octahedral complex looses a ligand, X, to become a square pyramidal intermediate is shown below in Figure 13.7.1.

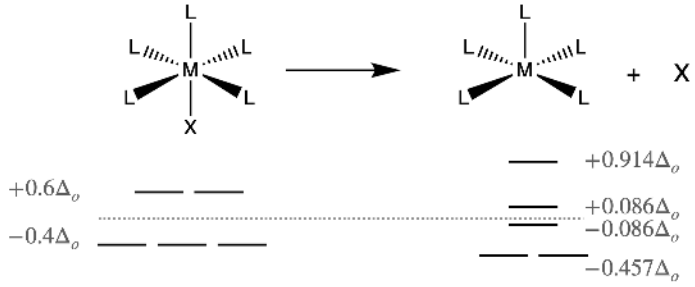


Figure 13.7.1: Dissociation of a ligand to form a square pyramidal intermediate. This would be the first step of a dissociative (D) reaction mechanism. The Ligand Field Activation Energy (LFAE) can be calculated from the splitting energies of the octahedron compared to the square planar intermediate. (CC-BY-SA; Kathryn Haas)

If the dissociation of a ligand is rate-determining, factors that lower the energy of the transition state or intermediate structures will speed the reaction rate. Here we could consider the differences in ligand-field stabilization energy (LFSE). The difference between the LFSE of the octahedral reactant and that of the intermediate is defined as the ligand field activation energy (LFAE). The LFAE can be calculated for a given d-electron count for an octahedral reactant and a square pyramidal intermediate using the information provided in Figure 13.7.1. Metal ions with particularly low (more negative) LFAE values tend to be more labile, while those with particularly high (less negative) values tend to be more inert. However, most octahedral complexes are expected to react through dissociative mechanisms due to the unfavorable steric crowding that must occur during an associative pathway.

The ease by which the M-X bond is broken will also influence rate of a dissociative reaction, and this can be probed experimentally. The following experiments can give evidence that support the argument that a reaction occurs by a dissociative pathway, or that it is dissociatively activated.

Experimental evidence that supports dissociative mechanism

1. Identity of the entering ligand has little effect on reaction rate.

If dissociation is the rate-determining step, the identity of the entering ligand, Y, should have little effect on the reaction rate. Therefore, an experiment that varies Y while holding X constant can indicate whether or not Y is involved in the rate-determining step. If the identity of Y has little effect on rate, then it must not be involved in the rate-determining step. Such experimental evidence can be taken as evidence of a dissociative mechanism. For example, the rate constants for reaction of Extra close brace or missing open brace with different incoming ligands, shown below, has rate constants of similar magnitude (they are approximately within one order of magnitude), indicating a dissociatively activated mechanism. In this case, other lines of evidence suggest this is a reaction with a I_d mechanism.

$$[Cr(NH_3)_5H_2O]^{3+} + Y^- \rightleftharpoons [Cr(NH_3)_5Y]^{2+} + H_2O$$

Table 13.7.1: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry, 5th edition*, pg 449.

Entering Ligand, Y^-	Rate Constant, k_1 $(10^{-4} M^{-1} s^{-1})$
NCS^-	4.2
Cl^-	0.7
Br^-	3.7
$CF_3CO_2^-$	1.4

2. Steric Crowding of the Metal Complex

Steric crowding of the metal complex would inhibit a dissociative pathway through steric crowding of the entering ligand. However, steric crowding can increase the stability of the intermediate after dissociation of the ligand from the crowded octahedral complex. If the reaction rate increases with steric crowding of the reactant complex, this is taken as evidence to support a dissociative mechanism.

3. Volume of Activation

One molecule generally takes up less space than two sperate molecules. This usually holds true in solution. Measurement of a rate constant's dependence on pressure can be used to determine the volume of activation (ΔV_{act}) and give insight into the mechanism of that reaction. In a dissociation mechanism, the dissociation causes one metal complex to become two separate molecules. Thus, the intermediate should, in principle, take up more space than the reactant complex. In a situation like this, we expect that the rate of reaction should decrease with increasing pressure, giving a positive value for ΔV_{act}. However, solvation of ions can influence volume, and this should be considered in interpretation of pressure-dependence data.

4. Increased coulombic attraction with the leaving group decreases reaction rate.

Couloubic (electrostatic) attraction between the dissociating ligand, X, and the metal complex should slow ligand dissociation. Coulombic attraction increases with increased magnitude of charges and with decreased distance. If the reaction rate slows with increased charge of the metal ion or the ligand itself, this is taken as evidence of a dissociative mechanism. Likewise, if rate decreases as the radius of the central metal ion is decreased, this is evidence to support a dissociative mechanism.

5. Increased strength of the M-X bond decreases reaction rate.

Free energy relationships between the formation constant of M-X and the kinetic rate constant of the reaction can provide evidence to support a dissociative mechanism (Discussed in the next section).

This page titled 13.7: Dissociation is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

13.8: Association

Associative mechanisms tend to be less common for octahedral complexes as a result of steric hindrance of the metal ion by six ligands. However, reactions of octahedral complexes with associative character are more likely if the ligands have low steric bulk and/or the central metal ion is larger with longer bonds (as in the case of $4d$ and $5d$ metal ions). Reactions of octahedrons have also been observed in cases of low d-electron count or low electron density around the central ion, presumably making nucleophilic reaction more favorable. If an octahdral complex is determined to have associative character, in most cases it is associatively-active interchange (I_a).

The evidence that supports arguments for associative mechanisms is somewhat the opposite as that which would support dissociative character. One typical piece of evidence that supports an associative pathway is **a large effect of the incoming ligand on the reaction rate constant**. For example, in the reaction of hexaaquo chromium (III) ion (Extra close brace or missing open brace) with various incoming ligands (shown below), rate constants vary by several orders of magnitude. This data is evidence of an associative mechanism (I_a). In contrast, the reaction of pentaamineaquo chromium (III) ion (Extra close brace or missing open brace) occurs by an associative mechanism (data shown in Section 12.4.1). The difference in reaction mechanisms for different chromium (III) complexes can be justified by the different electron densities around their metal ion center. The ammine ligand is a stronger sigma donor and thus the metal center is more electron rich in the case of Extra close brace or missing open brace. Nucleophilic reaction by an incoming ligand is thus more likely in the case of Extra close brace or missing open brace, which has a more electrophilic center.

$$[Cr(H_2O)_6]^{3+} + Y^- \rightleftharpoons [Cr(H_2O)_5Y]^{2+} + H_2O$$

Table 13.8.1: Rate Constants for Exchange of Aquo Ligand of hexaaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry, 5th edition*, pg 449.

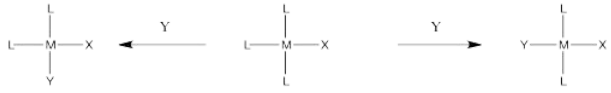
Entering Ligand, Y^-	Rate Constant, k_1 $(10^{-4}M^{-1}s^{-1})$
NCS^-	180
NO_3^-	73
Cl^-	2.9
Br^-	0.9
I^-	0.08

Another piece of evidence that can support associative mechanisms is the temperature-dependence of the rate law, which in turn can yield the entropy of activation (represented as $\Delta S^\ddagger$ or ΔS_{act}). When an incoming ligand associates with a metal complex and two molecules beome one, there would be a negative change in the entropi (entropy decreases). A negative value for the entropy of activation indicates an associative pathway. An example of this is in the substitution of the aquo ligand in $[Ru(EDTA)(H_2O)]^-$, which has a negative value of $\Delta S^\ddagger$, indicating an I_a mechanism.

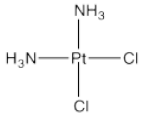
This page titled 13.8: Association is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Amanda Bowman.

13.9: The Trans Effect

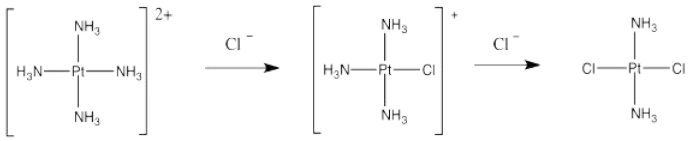
Occasionally in ligand substitution there is a situation in which there are two identical ligands that could be replaced, but two different products would result depending on which ligand left. This situation often happens in square planar complexes, for example. Replacement of one ligand would lead to a *cis* product. Replacement of the other one would lead to a *trans* product.



An important example of this issue is in the synthesis of cis-platin, an antitumour medication frequently used to treat ovarian and testicular cancer.

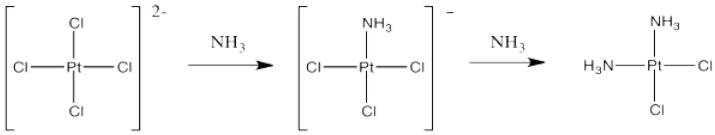


Cis-platin could be made from treatment of tetraammineplatinum(II) with chloride salts. The chloride ion could replace two of the ammonia ligands.



But that doesn't work. That synthesis results in the formation of *trans*-platin, a compound that has all of the nasty side effects of the *cis* isomer but with none of the therapeautic benefit.

If instead you were to start with tetrachloroplatinate salts and treat them with ammonia, you could replace two of the chloride ligands. That works really well, and it provides *cis*-platin, not *trans*-platin.



? Exercise 13.9.1

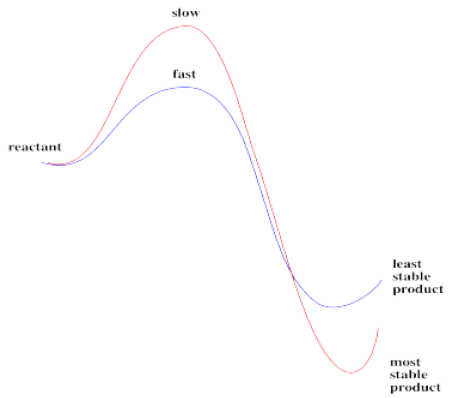
What do you think is the mechanism of substitution of the two reactions above? Why?

Answer

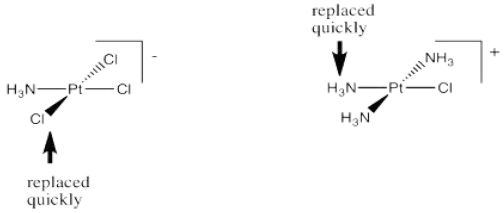
This is probably an associative mechanism because of the square planar geometry.

This reaction, if run under these conditions, is clearly not always under thermodynamic control. Two different products result, depending on how the reaction is done. One of those isomers is probably more stable than the other; if thermodynamics were in charge, it would form the same thing both times.

Instead, there may be an element of kinetic control for at least one of the pathways. A given product might be made, not because it is more stable, but simply because it forms more quickly than the other one.



Take another look at those two reactions. One of the things that they have in common is that the ligand that gets replaced is *trans* to a chloride. It is not *trans* to an ammonia. Maybe the other ligands in the complex can influence how quickly one ligand can leave.



Specifically, the "*trans* effect" is the role of *trans*-ligands in influencing substitution rates in square planar complexes.

The following kinetic data were obtained for substitutions on square planar platinum complexes, in the reaction:

$$trans-(PEt_3)_2PtLCl + py \rightarrow trans-(PEt_3)_2PtLpy^+ + Cl^-$$

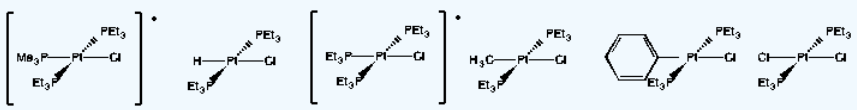
L	k_{obs} (s^{-1})	T, °C
PMe_3	0.20	0
H^-	0.047	0
PEt_3	0.041	0
CH_3^-	6.0×10^{-4}	25
$C_6H_5^-$	1.2×10^{-4}	25
Cl^-	3.5×10^{-6}	25

Ref: Cooper Langford & Harry Gray, *Ligand Substitution Processes*, W.A. Benjamin, NY, 1965, p. 25.

? Exercise 13.9.2

Draw structures for each of the complexes listed in the table.

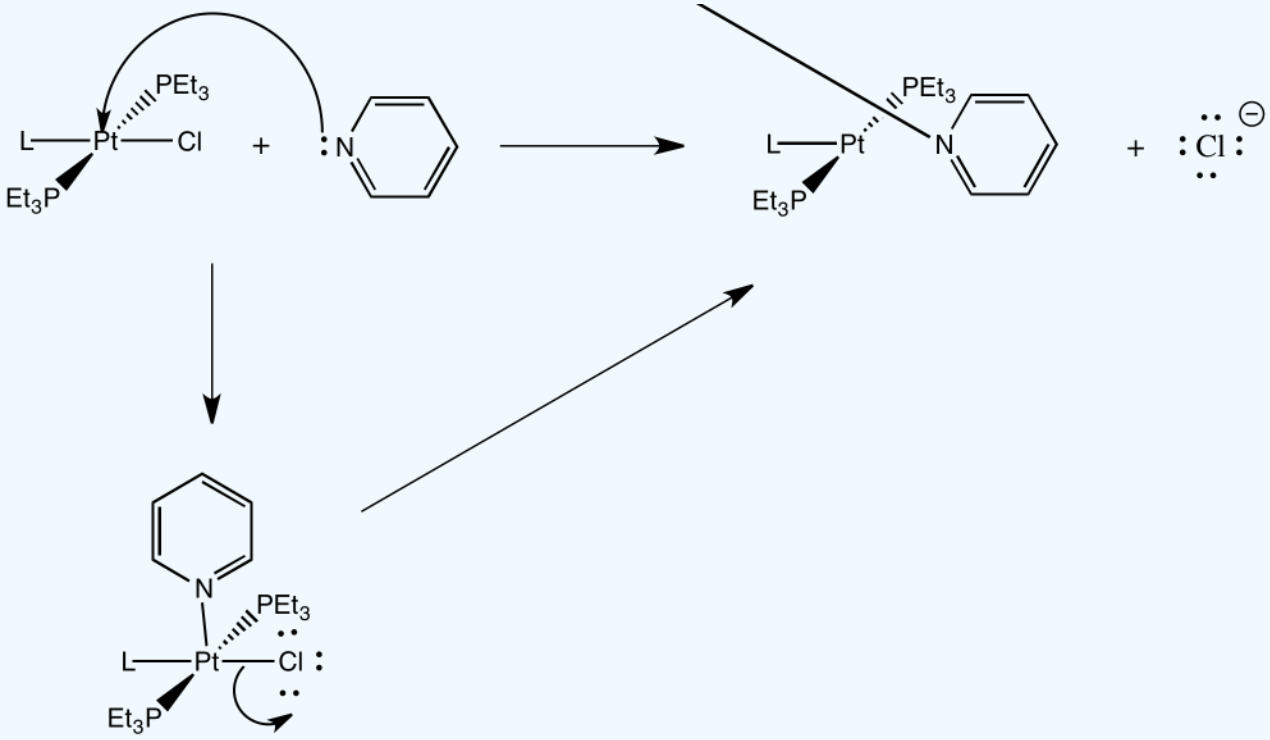
Answer



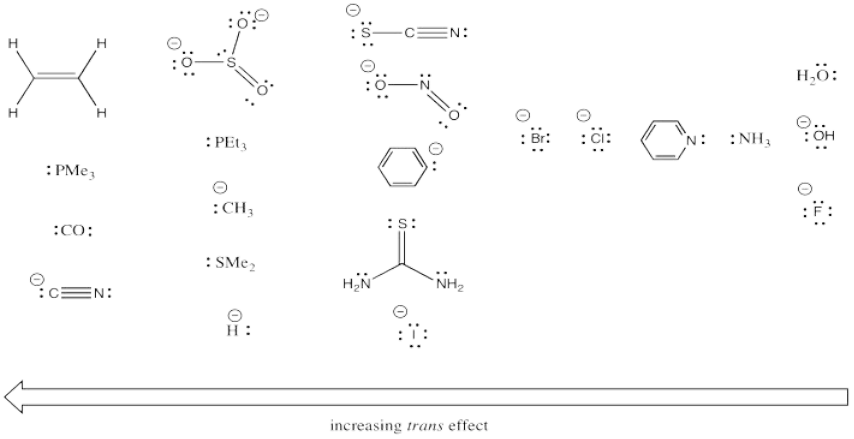
Exercise 13.9.3

Provide a mechanism with arrows for the reaction studied in the table.

Answer



Clearly that *trans* ligand has a dramatic effect on how quickly the chloride can be substituted in the above study. Additional studies like this one have led to some general trends. Below, the ligands on the left have strong *trans*-effects. Ligands *trans* to them are substituted very quickly. The ligands on the right have very modest *trans* effects. Ligands *trans* to them are substituted only slowly.



Exercise 13.9.4

Look for empirical trends in the series of ligands above. Without trying to explain exactly why, find chemically relevant factors that may be responsible for these reactivity trends.

Answer

There is an electronegativity trend: the less electronegative, the greater the *trans* effect (see the halogens, as well as the series O,N,C and also the orders within several pairings: S,P; O,S and N,P).

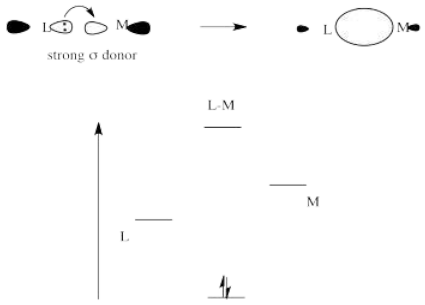
Alternatively, some of the above could be described by a polarizability trend: more polarizable atom, greater *trans* effect (for example, the halogens).

Most of the ligands containing π-bonds have strong *trans* influence (but not all).

Most of the π-donors have a weaker *trans* influence. However, these ligand cover a very broad range in this series.

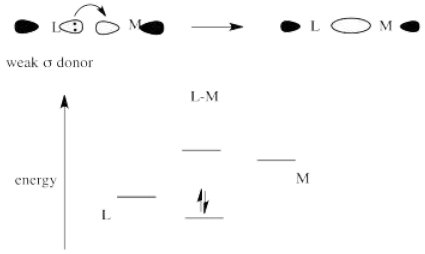
In general, explanations of the trans effect have focused on two separate types of ligands. These are strong sigma donors and strong pi acceptors.

Strong sigma donors donate electrons very effectively to the metal via a sigma bond. Because the ligand trans to this donor would be bonding via donation to the same metal p orbital, there is a competition. The metal p orbital bonds more favorably with the strong sigma donor, and the ligand trans to it is left with a weaker bond.



The strong sigma donor gets good overlap with the metal orbital and the resulting interaction goes down low in energy.

The weak sigma donor gets poorer overlap with the metal orbital and only weak stabilization of the donor electrons.



Place these two choices together, and the metal orbital will engage in a strong bonding interaction with the strong σ-donor. Doing so lowers the electronic energy significantly. It won't interact very much with the weak σ-donor, because doing that won't result in as much lowering of electronic energy. The result is a strong bond on one side of the metal and a weak bond on the other. That weak bond will break easily and that ligand will be replaced easily.



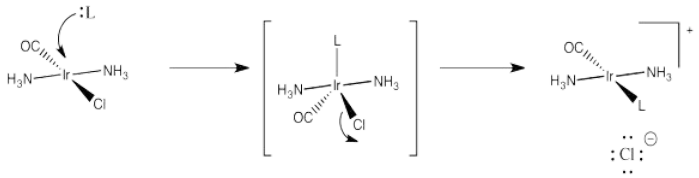
? Exercise 13.9.5

Which of the ligands in the *trans* effect series are probably strong σ-donors? Why?

Answer

The strongest σ-donors are typically those with more polarizable donor atoms (such as S, P, I) as well as those with less electronegative donor ions such as C^- and H^-.

Strong pi acceptors exert their trans effect in a different way. They are thought to stabilize a particular geometry of the five-coordinate intermediate in substitution of square planar complexes. We haven't worried too much about the geometry of that intermediate, but it is probably trigonal bipyramidal. It would have three ligands in an equatorial plane and two more directly opposite each other, in the axial positions.



Essentially, the incoming ligand pushes two of the ligands down from the square plane to form this trigonal bipyramid. When it comes time for a ligand to leave, it is probably going to be one of these ligands that is already on the move. They are already on a trajectory out of the square plane, anyway.

A strong pi acceptor like CO exerts its *trans* effect by making sure it, along with the ligand opposite it, gets into that equatorial plane. It does that by a stabilizing delocalization that happens when the π-acceptor is in the electron-rich equatorial plane. In that position, it can draw electron density via π-donation from two different donors. If it were in an axial position, it could still delocalize electrons this way, but it would draw most effectively from just one donor rather than two.



favoured

So which of those two ligands is going to keep moving and leave the complex? It certainly won't be the one that is exerting a stabilizing, delocalizing effect on the complex via its strong bonding interactions. It will be the unlucky *trans* ligand that got dragged along with it.

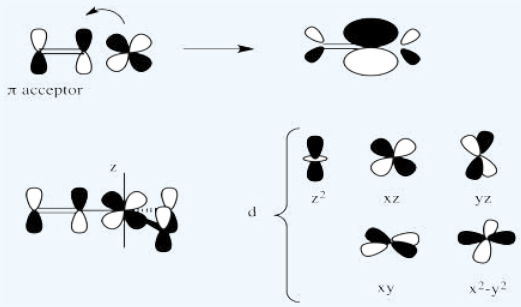
? Exercise 13.9.6

Which of the ligands in the *trans*-effect series are probably strong π-acceptors? Show why.

? Exercise 13.9.7

Draw an orbital picture showing the -delocalization described in the trigonal bipyramidal intermediate. Label the orbitals, assuming the z axis is along the axis of the trigonal bipyramid (i.e. the equatorial plane is the xy plane).

Answer



? Exercise 13.9.8

Substitution of trans ligands in μ-oxo-bis(μ-acetato)diruthenium complexes: Synthesis and kinetic studies. Hussain, Bhatt, Kumar, Thorat, Padhiyar and Shukla, *Inorganica Chemica Acta*, **2009**, *362*, 1101-1108.

Given the structure $[Ru_2O(L)_6(acetate)_2](PF_6)_2$, in which L is a neutral donor,

a) Draw the structure of the counterion, PF_6^-.

b) Provide an account of the valence electron count in the ruthenium coordination complex.

Valence electrons on metal	
Total charge on ligands	
Charge on the metal	
Revised count on metal	
Electrons donated by ligands	
Total electrons on metal in complex	

Data shows that the ligands L are *trans* to the bridging oxo ligand are labile.

c) Use orbital cartoons and words to provide an explanation for this effect.

When water is added to an acetone solution of $[Ru_2O(pyridine)_4(L)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$ is formed.

d) Draw the product of this reaction.

When pyridine is added to $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_6(acetate)_2](PF_6)_2$ is formed. The following rate constants were observed for this reaction.

[pyridine] mol L^{-1}	k_{obs} s^{-1} (x 10^{-3})
0.005	1.75
0.012	2.53
0.025	9.7
0.049	16.7
0.100	35.2

e) Use the data from this table to determine the order in pyridine. Provide an explanation for your conclusion.

f) Draw a mechanism for the reaction, consistent with the data.

g) Write a rate law for the reaction.

h) The authors studies the same reaction with different ligands instead of pyridine. They observed an increase in rate constants with increasing basicity of the incoming ligands. Provide an explanation for this observation.

Answer a



5 valence electrons - 6 bonds - 0 nonbonding = -1

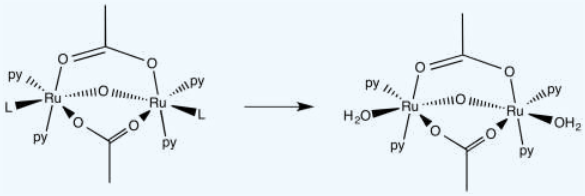
Answer b

Valence electrons on metal	8
Total charge on ligands	-4 (-2 per Ru)
Charge on the metal	+2
Revised count on metal	6
Electrons donated by ligands	12
Total electrons on metal in complex	18

Answer c

The oxo is a strong sigma donor and hogs the orbital with the metal thus leaving very little room for orbital bonding trans to the sigma donor.

Answer d



Answer e

First order. Although there is some amount of error in the data, doubling the pyridine concentration generally results in a doubling of the rate.

Answer f

The mechanism you draw would have to involve a first associative step; because the complex is already 18 electrons, associative interchange is likely.

Answer g

$$Rate = k[ML_n][py]$$

Answer h

Basic ligands have stronger attraction to the metal thus accelerating the reaction.

This page titled 13.9: The Trans Effect is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Amanda Bowman.

- **3.7: The Trans Effect** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

Index

A

acid ionization constants
3.3: Acidity of Binary Hydrides
acid strength
3.3: Acidity of Binary Hydrides
acidity
3.3: Acidity of Binary Hydrides
acidity and basicity
3.2: Brønsted-Lowry Model
alkali metals
3.3: Acidity of Binary Hydrides
alkaline earth metals
3.3: Acidity of Binary Hydrides
anion
2.1: Atomic Structure
antifluorite
6.5C: Structure - Fluorite and Antifluorite
aqua ligands
3.5: Acidity of Metal Cations
Arrhenius acid
3.1: Acid-Base Theories
Arrhenius base
3.1: Acid-Base Theories
Arrhenius definition
3.1: Acid-Base Theories
Arrhenius theory
3.2: Brønsted-Lowry Model
association constant
7.6: Complex-Ion Equilibria
atomic mass
2.1: Atomic Structure
atomic mass unit
2.1: Atomic Structure
atomic number
2.1: Atomic Structure
atomization enthalpy
6.4: Born-Haber Cycles
Aufbau principle
2.4: Electron Configurations (Atoms)

B

binary acid
2.3: Chemical Nomenclature
binary compound
2.3: Chemical Nomenclature
binary hydrides
3.3: Acidity of Binary Hydrides
body centered cubic
6.1: Unit Cells
bond energy
3.3: Acidity of Binary Hydrides
bond length
2.8: Electronegativity
bond strength
3.3: Acidity of Binary Hydrides
Brønsted acids
3.2: Brønsted-Lowry Model
3.3: Acidity of Binary Hydrides
Brønsted bases
3.2: Brønsted-Lowry Model
3.3: Acidity of Binary Hydrides

C

cathodic protection
4.5: Electrochemical Corrosion
cation
2.1: Atomic Structure
ccp
6.5D: Structure - Zinc Blende (ZnS)
chelate ring
7.5: Isomerism
Chelation Effect
7.6: Complex-Ion Equilibria
chemical equilibria
7.6: Complex-Ion Equilibria
chemical reactions
3.2: Brønsted-Lowry Model
chemical symbol
2.1: Atomic Structure
chemistry
3.3: Acidity of Binary Hydrides
chirality
9.5: Applications of Symmetry - Chirality
combustion reaction
2.6: Redox Reactions and Oxidation State
complex ion
7.2: Lewis Acids and Bases
7.6: Complex-Ion Equilibria
conjugate acids and bases
3.2: Brønsted-Lowry Model
coordinate covalent bond
7.1: Coordination Compounds
7.2: Lewis Acids and Bases
coordinate covalent bonds
7.6: Complex-Ion Equilibria
coordination complex
11.7: Colors of Coordination Compounds
coordination complexes
11.7: Colors of Coordination Compounds
coordination compounds
7.1: Coordination Compounds
core electron
2.4: Electron Configurations (Atoms)
corrosion
4.5: Electrochemical Corrosion
corrosion resistance
4.5: Electrochemical Corrosion
covalent bond
2.2: Molecular and Ionic Compounds
2.8: Electronegativity
covalent compound
2.2: Molecular and Ionic Compounds
covalent radius
2.7: Periodic Trends
crystal field splitting
11.1: Crystal Field Theory
11.2: Crystal Field Stabilization Energy
11.3: Crystal Field Splitting
crystal field stabilization energy
11.2: Crystal Field Stabilization Energy
crystal field theory
11.1: Crystal Field Theory
11.2: Crystal Field Stabilization Energy
11.7: Colors of Coordination Compounds
crystal structure
6.1: Unit Cells
cubic closest packing
6.1: Unit Cells
cubic closet packing
6.5D: Structure - Zinc Blende (ZnS)

D

Dalton unit
2.1: Atomic Structure
diamagnetic
11.1: Crystal Field Theory
dissociation constant
7.2: Lewis Acids and Bases
double bond
2.9: Electron-Dot Structures

E

effective nuclear charge
2.7: Periodic Trends
electrolysis
5.1: Electrolysis
electrolytic cell
5.1: Electrolysis
electromagnetic spectrum
11.7: Colors of Coordination Compounds
electron affinity
2.7: Periodic Trends
electron configuration
2.4: Electron Configurations (Atoms)
electronegativity
2.8: Electronegativity
3.3: Acidity of Binary Hydrides
electronegativity trends
3.3: Acidity of Binary Hydrides
electroplating
5.1: Electrolysis
enantiomers
9.5: Applications of Symmetry - Chirality
energy level
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
equilibrium
3.2: Brønsted-Lowry Model

F

Face Centered Cubic
6.5A: Structure - Rock Salt (NaCl)
fcc structure
6.5A: Structure - Rock Salt (NaCl)
formal charge
2.10: Formal Charges and Resonance
formation constant
7.2: Lewis Acids and Bases
7.6: Complex-Ion Equilibria
free radical
2.9: Electron-Dot Structures
fundamental unit of charge
2.1: Atomic Structure

G

goiter
- 2.1: Atomic Structure

Gouy balance
- 2.11: Molecular Orbitals

H

heterolytic bond cleavage
- 3.3: Acidity of Binary Hydrides

Hexagonal Closest Packed
- 6.1: Unit Cells

high spin
- 11.1: Crystal Field Theory
- 11.2: Crystal Field Stabilization Energy
- 11.3: Crystal Field Splitting

Hund's rule
- 2.4: Electron Configurations (Atoms)

hydration
- 11.2: Crystal Field Stabilization Energy

hydride ion
- 3.3: Acidity of Binary Hydrides

hydrogen ion transfer
- 3.2: Brønsted-Lowry Model

hydrogen transfer
- 3.3: Acidity of Binary Hydrides

hydron
- 3.1: Acid-Base Theories

hypervalent molecule
- 2.9: Electron-Dot Structures

I

identity operation
- 9.1: Symmetry Elements

improper rotation
- 9.1: Symmetry Elements

inert pair effect
- 2.5: Electron Configurations (Ions)

ion
- 2.1: Atomic Structure

ion product
- 6.7: Solubility Equilibria

ionic bond
- 2.2: Molecular and Ionic Compounds
- 2.5: Electron Configurations (Ions)

ionic compound
- 2.2: Molecular and Ionic Compounds

ionic salts
- 3.3: Acidity of Binary Hydrides

ionic solvent
- 5.1: Electrolysis

ionization energy
- 2.7: Periodic Trends

isoelectronic
- 2.7: Periodic Trends

isomerism
- 7.5: Isomerism

K

Kepert Model
- 7.4: Structures

L

lattice enthalpy
- 6.4: Born-Haber Cycles

Lewis acid
- 7.2: Lewis Acids and Bases

Lewis base
- 7.2: Lewis Acids and Bases
- 7.6: Complex-Ion Equilibria

Lewis structure
- 2.9: Electron-Dot Structures

Lewis symbol
- 2.9: Electron-Dot Structures

ligand
- 7.2: Lewis Acids and Bases

ligand field theory
- 11.4: Ligand Field Theory

Linear Combination of Atomic Orbitals (LCAO)
- 10.1: Molecular Orbitals

lone pair
- 2.9: Electron-Dot Structures

low spin
- 11.1: Crystal Field Theory
- 11.2: Crystal Field Stabilization Energy
- 11.3: Crystal Field Splitting

M

magnetic moments
- 11.8: Magnetic Moments

mass number
- 2.1: Atomic Structure

metal ion
- 7.6: Complex-Ion Equilibria

molecular compound
- 2.2: Molecular and Ionic Compounds

molecular orbital theory
- 2.11: Molecular Orbitals

Molecular Structure
- 2.10: Formal Charges and Resonance

molecule polarity
- 3.3: Acidity of Binary Hydrides

monatomic ion
- 2.2: Molecular and Ionic Compounds

MRI
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy

N

NMR
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy

nomenclature
- 2.3: Chemical Nomenclature

nonaqueous solvents
- 3.2: Brønsted-Lowry Model

nonmetals
- 3.3: Acidity of Binary Hydrides

nonpolar covalent bond
- 2.8: Electronegativity

Nuclear Shielding
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy

O

octahedral
- 11.1: Crystal Field Theory

Octahedral Preference
- 11.2: Crystal Field Stabilization Energy

Octahedral Site Preference Energy
- 11.2: Crystal Field Stabilization Energy

octet rule
- 2.9: Electron-Dot Structures

orbital diagram
- 2.4: Electron Configurations (Atoms)

orbital mixing
- 10.4: Orbital Mixing

overall symmetry
- 9.1: Symmetry Elements

overpotential
- 5.1: Electrolysis

oxidation
- 2.6: Redox Reactions and Oxidation State

oxidizing agent
- 2.6: Redox Reactions and Oxidation State

oxoacids
- 3.4: Acidity of Oxoacids

oxyacid
- 2.3: Chemical Nomenclature

oxyacids
- 3.4: Acidity of Oxoacids

oxyanion
- 2.2: Molecular and Ionic Compounds

P

paramagnetic
- 11.1: Crystal Field Theory

paramagnetism
- 2.11: Molecular Orbitals

Pauling's rules
- 3.4: Acidity of Oxoacids

periodic table
- 3.3: Acidity of Binary Hydrides

pi acceptor
- 11.4: Ligand Field Theory

pi donor
- 11.4: Ligand Field Theory

polar covalent bond
- 2.8: Electronegativity

polyatomic ion
- 2.2: Molecular and Ionic Compounds

Pourbaix diagrams
- 4.4: Pourbaix Diagrams

precipitate
- 2.6: Redox Reactions and Oxidation State

precipitation reaction
- 2.6: Redox Reactions and Oxidation State

proper rotation
- 9.1: Symmetry Elements

proton transfer
- 3.2: Brønsted-Lowry Model

pure covalent bond
- 2.8: Electronegativity

Q

quadrupolar nuclei
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy

R

redox reaction
4.1: Redox Reactions
reduction
2.6: Redox Reactions and Oxidation State
relaxation
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
resonance
2.10: Formal Charges and Resonance
resonance forms
2.10: Formal Charges and Resonance
resonance hybrid
2.10: Formal Charges and Resonance
rock salt structure
6.5A: Structure - Rock Salt (NaCl)
rust
4.5: Electrochemical Corrosion

S

Sabatier Principle
9.1: Symmetry Elements
Sacrificial Coatings
4.5: Electrochemical Corrosion
SALC
10.7.2: Carbon Dioxide
Schoenflies symbol
9.1: Symmetry Elements
sigma donor
11.4: Ligand Field Theory
simple cubic structure
6.1: Unit Cells
single bond
2.9: Electron-Dot Structures
Solubility Effects
7.6: Complex-Ion Equilibria
solubility product
6.7: Solubility Equilibria
spectrochemical series
11.3: Crystal Field Splitting
11.6: Spectrochemical Series
11.7: Colors of Coordination Compounds
sphalerite
6.5D: Structure - Zinc Blende (ZnS)
Spin
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
spin pairing energy
11.1: Crystal Field Theory
11.2: Crystal Field Stabilization Energy
square planar
11.1: Crystal Field Theory
stability constant
7.6: Complex-Ion Equilibria
strong and weak acids
3.2: Brønsted-Lowry Model
strong field
11.4: Ligand Field Theory
Symmetry Adapted Linear Combinations
10.7: Polyatomic Molecules
symmetry elements
9.1: Symmetry Elements
symmetry operations
9.1: Symmetry Elements

T

T1
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
T2
8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy
tetrahedral
11.1: Crystal Field Theory
trans effect
13.9: The Trans Effect
trigonal prismatic coordination
7.4: Structures
triple bond
2.9: Electron-Dot Structures

U

unified atomic mass unit
2.1: Atomic Structure

V

valence electrons
2.4: Electron Configurations (Atoms)
valence shell
2.4: Electron Configurations (Atoms)

W

weak field
11.4: Ligand Field Theory

Z

zinc blend structure
6.5D: Structure - Zinc Blende (ZnS)

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: CH275: Foundations of Inorganic Chemistry

Webpages: 119

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC-SA 4.0: 90.8% (108 pages)
- CC BY-NC-SA 3.0: 8.4% (10 pages)
- Undeclared: 0.8% (1 page)

By Page

- CH275: Foundations of Inorganic Chemistry - *CC BY-NC-SA 4.0*
  - Front Matter - *CC BY-NC-SA 4.0*
    - TitlePage - *CC BY-NC-SA 4.0*
    - InfoPage - *CC BY-NC-SA 4.0*
    - Table of Contents - *CC BY-NC-SA 4.0*
    - Licensing - *CC BY-NC-SA 4.0*
  - 1: Introduction - *CC BY-NC-SA 4.0*
  - 2: Chemical Structure and Periodic Trends (Review) - *CC BY-NC-SA 4.0*
    - 2.1: Atomic Structure - *CC BY-NC-SA 4.0*
    - 2.2: Molecular and Ionic Compounds - *CC BY-NC-SA 4.0*
    - 2.3: Chemical Nomenclature - *CC BY-NC-SA 4.0*
    - 2.4: Electron Configurations (Atoms) - *CC BY-NC-SA 4.0*
    - 2.5: Electron Configurations (Ions) - *CC BY-NC-SA 4.0*
    - 2.6: Redox Reactions and Oxidation State - *CC BY-NC-SA 4.0*
    - 2.7: Periodic Trends - *CC BY-NC-SA 4.0*
    - 2.8: Electronegativity - *CC BY-NC-SA 4.0*
    - 2.9: Electron-Dot Structures - *CC BY-NC-SA 4.0*
    - 2.10: Formal Charges and Resonance - *CC BY-NC-SA 4.0*
    - 2.11: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 3: Acid-Base Chemistry - *CC BY-NC-SA 4.0*
    - 3.1: Acid-Base Theories - *CC BY-NC-SA 4.0*
    - 3.2: Brønsted-Lowry Model - *CC BY-NC-SA 4.0*
    - 3.3: Acidity of Binary Hydrides - *CC BY-NC-SA 4.0*
    - 3.4: Acidity of Oxoacids - *CC BY-NC-SA 3.0*
    - 3.5: Acidity of Metal Cations - *CC BY-NC-SA 4.0*
  - 4: Redox Reactivity - *CC BY-NC-SA 4.0*
    - 4.1: Redox Reactions - *CC BY-NC-SA 4.0*
    - 4.2: Balancing Redox Reactions - *CC BY-NC-SA 4.0*
    - 4.3: Electrochemical Potentials - *CC BY-NC-SA 4.0*
    - 4.4: Pourbaix Diagrams - *CC BY-NC-SA 4.0*
    - 4.5: Electrochemical Corrosion - *CC BY-NC-SA 3.0*
  - 5: Electrochemistry - *CC BY-NC-SA 4.0*
    - 5.1: Electrolysis - *CC BY-NC-SA 4.0*
    - 5.2: Cyclic Voltammetry - *CC BY-NC-SA 4.0*
    - 5.3: CV Electrodes - *CC BY-NC-SA 4.0*
  - 6: Ionic Compounds - *CC BY-NC-SA 4.0*
    - 6.1: Unit Cells - *CC BY-NC-SA 4.0*
    - 6.2: Ionic Radii and Radius Ratios - *CC BY-NC-SA 4.0*
    - 6.3: Lattice Energy - *CC BY-NC-SA 4.0*
    - 6.4: Born-Haber Cycles - *CC BY-NC-SA 4.0*
    - 6.5: Ionic Lattices - Examples - *CC BY-NC-SA 4.0*
      - 6.5A: Structure - Rock Salt (NaCl) - *CC BY-NC-SA 4.0*
      - 6.5B: Structure - Caesium Chloride (CsCl) - *CC BY-NC-SA 4.0*
      - 6.5C: Structure - Fluorite and Antifluorite - *CC BY-NC-SA 4.0*
      - 6.5D: Structure - Zinc Blende (ZnS) - *CC BY-NC-SA 4.0*
    - 6.6: Lattice Energy and Solubility - *CC BY-NC-SA 4.0*
    - 6.7: Solubility Equilibria - *CC BY-NC-SA 3.0*
  - 7: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 7.1: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 7.2: Lewis Acids and Bases - *CC BY-NC-SA 4.0*
    - 7.3: Nomenclature and Ligands - *CC BY-NC-SA 4.0*
    - 7.4: Structures - *CC BY-NC-SA 4.0*
    - 7.5: Isomerism - *CC BY-NC-SA 4.0*
    - 7.6: Complex-Ion Equilibria - *CC BY-NC-SA 4.0*
    - 7.7: Hard-Soft Acid-Base Theory - *CC BY-NC-SA 4.0*
  - 8: NMR and IR Spectroscopy - *CC BY-NC-SA 4.0*

- 8.1: Infrared (IR) Spectroscopy - *CC BY-NC-SA 4.0*
- 8.2: Interpreting Infrared Spectra - *CC BY-NC-SA 4.0*
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy - *CC BY-NC-SA 4.0*
- 8.4: Chemical Shifts - *CC BY-NC-SA 4.0*
- 8.5: Proton Equivalence - *CC BY-NC-SA 4.0*
- 8.6: Chemical Shifts in \(^1H\) NMR Spectroscopy - *CC BY-NC-SA 4.0*
- 8.7: Peak Integration - *CC BY-NC-SA 4.0*
- 8.8: Peak Splitting - *CC BY-NC-SA 4.0*

9: Symmetry - *CC BY-NC-SA 4.0*

- 9.1: Symmetry Elements - *CC BY-NC-SA 4.0*
- 9.2: Point Groups - *CC BY-NC-SA 4.0*
- 9.3: Assigning Point Groups - *CC BY-NC-SA 4.0*
- 9.4: Character Tables - *CC BY-NC-SA 4.0*
- 9.5: Applications of Symmetry - Chirality - *CC BY-NC-SA 4.0*

10: Molecular Orbital Theory - *CC BY-NC-SA 4.0*

- 10.1: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 10.1.1: s-Orbital MOs - *CC BY-NC-SA 3.0*
  - 10.1.2: p-Orbital MOs - *CC BY-NC-SA 3.0*
  - 10.1.3: d-Orbital MOs - *CC BY-NC-SA 4.0*
- 10.2: Non-bonding Orbitals - *CC BY-NC-SA 4.0*
- 10.3: Molecular Orbital Diagrams - *CC BY-NC-SA 4.0*
- 10.4: Orbital Mixing - *CC BY-NC-SA 4.0*
- 10.5: Diatomic Molecules - *CC BY-NC-SA 4.0*
- 10.6: Polar Diatomic Molecules - *CC BY-NC-SA 4.0*
- 10.7: Polyatomic Molecules - *CC BY-NC-SA 4.0*
  - 10.7.1: Bifluoride anion - *CC BY-NC-SA 4.0*
  - 10.7.2: Carbon Dioxide - *CC BY-NC-SA 4.0*
  - 10.7.3: H_2O - *CC BY-NC-SA 4.0*
  - 10.7.4: NH_3 - *CC BY-NC-SA 4.0*
  - 10.7.5: CO_2 (Revisted with Projection Operators) - *CC BY-NC-SA 4.0*
  - 10.7.6: BF_3 - *CC BY-NC-SA 4.0*

11: Coordination Compound Bonding - *CC BY-NC-SA 4.0*

- 11.1: Crystal Field Theory - *CC BY-NC-SA 4.0*
- 11.2: Crystal Field Stabilization Energy - *CC BY-NC-SA 4.0*
- 11.3: Crystal Field Splitting - *CC BY-NC-SA 4.0*
- 11.4: Ligand Field Theory - *CC BY-NC-SA 4.0*
- 11.5: Metal-Metal Bonding - *CC BY-NC-SA 4.0*
- 11.6: Spectrochemical Series - *CC BY-NC-SA 4.0*
- 11.7: Colors of Coordination Compounds - *CC BY-NC-SA 4.0*
- 11.8: Magnetic Moments - *CC BY-NC-SA 4.0*

12: Coordination Compound Spectroscopy - *CC BY-NC-SA 4.0*

- 12.1: Molecular Vibrations - *CC BY-NC-SA 4.0*
- 12.2: Identifying Active Vibrations - *CC BY-NC-SA 4.0*
- 12.3: Carbonyl Vibrational Modes - *CC BY-NC-SA 4.0*

13: Substitution Reactivity - *CC BY-NC-SA 4.0*

- 13.1: Reactions of Metal Complexes - *CC BY-NC-SA 3.0*
- 13.2: Substitution Reactions - *CC BY-NC-SA 4.0*
- 13.3: Inert and Labile Complexes - *CC BY-NC-SA 4.0*
- 13.4: Chelate Effects - *CC BY-NC-SA 4.0*
- 13.5: Substitution Mechanisms - *CC BY-NC-SA 3.0*
  - 13.5.1: Dissociative Mechanism - *CC BY-NC-SA 4.0*
  - 13.5.2: Interchange Mechanism - *CC BY-NC-SA 4.0*
  - 13.5.3: Associative Mechanism - *CC BY-NC-SA 3.0*
- 13.6: Activation Parameters - *CC BY-NC-SA 3.0*
- 13.7: Dissociation - *CC BY-NC-SA 4.0*
- 13.8: Association - *CC BY-NC-SA 4.0*
- 13.9: The Trans Effect - *CC BY-NC-SA 3.0*

Back Matter - *CC BY-NC-SA 4.0*

- Index - *CC BY-NC-SA 4.0*
- Glossary - *CC BY-NC-SA 4.0*
- Detailed Licensing - *CC BY-NC-SA 4.0*
- Detailed Licensing - *CC BY-NC-SA 4.0*
- Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: CH275: Foundations of Inorganic Chemistry

Webpages: 119

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC-SA 4.0: 90.8% (108 pages)
- CC BY-NC-SA 3.0: 8.4% (10 pages)
- Undeclared: 0.8% (1 page)

By Page

- CH275: Foundations of Inorganic Chemistry - *CC BY-NC-SA 4.0*
  - Front Matter - *CC BY-NC-SA 4.0*
    - TitlePage - *CC BY-NC-SA 4.0*
    - InfoPage - *CC BY-NC-SA 4.0*
    - Table of Contents - *CC BY-NC-SA 4.0*
    - Licensing - *CC BY-NC-SA 4.0*
  - 1: Introduction - *CC BY-NC-SA 4.0*
  - 2: Chemical Structure and Periodic Trends (Review) - *CC BY-NC-SA 4.0*
    - 2.1: Atomic Structure - *CC BY-NC-SA 4.0*
    - 2.2: Molecular and Ionic Compounds - *CC BY-NC-SA 4.0*
    - 2.3: Chemical Nomenclature - *CC BY-NC-SA 4.0*
    - 2.4: Electron Configurations (Atoms) - *CC BY-NC-SA 4.0*
    - 2.5: Electron Configurations (Ions) - *CC BY-NC-SA 4.0*
    - 2.6: Redox Reactions and Oxidation State - *CC BY-NC-SA 4.0*
    - 2.7: Periodic Trends - *CC BY-NC-SA 4.0*
    - 2.8: Electronegativity - *CC BY-NC-SA 4.0*
    - 2.9: Electron-Dot Structures - *CC BY-NC-SA 4.0*
    - 2.10: Formal Charges and Resonance - *CC BY-NC-SA 4.0*
    - 2.11: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 3: Acid-Base Chemistry - *CC BY-NC-SA 4.0*
    - 3.1: Acid-Base Theories - *CC BY-NC-SA 4.0*
    - 3.2: Brønsted-Lowry Model - *CC BY-NC-SA 4.0*
    - 3.3: Acidity of Binary Hydrides - *CC BY-NC-SA 4.0*
    - 3.4: Acidity of Oxoacids - *CC BY-NC-SA 3.0*
    - 3.5: Acidity of Metal Cations - *CC BY-NC-SA 4.0*
  - 4: Redox Reactivity - *CC BY-NC-SA 4.0*
    - 4.1: Redox Reactions - *CC BY-NC-SA 4.0*
    - 4.2: Balancing Redox Reactions - *CC BY-NC-SA 4.0*
    - 4.3: Electrochemical Potentials - *CC BY-NC-SA 4.0*
    - 4.4: Pourbaix Diagrams - *CC BY-NC-SA 4.0*
    - 4.5: Electrochemical Corrosion - *CC BY-NC-SA 3.0*
  - 5: Electrochemistry - *CC BY-NC-SA 4.0*
    - 5.1: Electrolysis - *CC BY-NC-SA 4.0*
    - 5.2: Cyclic Voltammetry - *CC BY-NC-SA 4.0*
    - 5.3: CV Electrodes - *CC BY-NC-SA 4.0*
  - 6: Ionic Compounds - *CC BY-NC-SA 4.0*
    - 6.1: Unit Cells - *CC BY-NC-SA 4.0*
    - 6.2: Ionic Radii and Radius Ratios - *CC BY-NC-SA 4.0*
    - 6.3: Lattice Energy - *CC BY-NC-SA 4.0*
    - 6.4: Born-Haber Cycles - *CC BY-NC-SA 4.0*
    - 6.5: Ionic Lattices - Examples - *CC BY-NC-SA 4.0*
      - 6.5A: Structure - Rock Salt (NaCl) - *CC BY-NC-SA 4.0*
      - 6.5B: Structure - Caesium Chloride (CsCl) - *CC BY-NC-SA 4.0*
      - 6.5C: Structure - Fluorite and Antifluorite - *CC BY-NC-SA 4.0*
      - 6.5D: Structure - Zinc Blende (ZnS) - *CC BY-NC-SA 4.0*
    - 6.6: Lattice Energy and Solubility - *CC BY-NC-SA 4.0*
    - 6.7: Solubility Equilibria - *CC BY-NC-SA 3.0*
  - 7: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 7.1: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 7.2: Lewis Acids and Bases - *CC BY-NC-SA 4.0*
    - 7.3: Nomenclature and Ligands - *CC BY-NC-SA 4.0*
    - 7.4: Structures - *CC BY-NC-SA 4.0*
    - 7.5: Isomerism - *CC BY-NC-SA 4.0*
    - 7.6: Complex-Ion Equilibria - *CC BY-NC-SA 4.0*
    - 7.7: Hard-Soft Acid-Base Theory - *CC BY-NC-SA 4.0*
  - 8: NMR and IR Spectroscopy - *CC BY-NC-SA 4.0*

- 8.1: Infrared (IR) Spectroscopy - *CC BY-NC-SA 4.0*
- 8.2: Interpreting Infrared Spectra - *CC BY-NC-SA 4.0*
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy - *CC BY-NC-SA 4.0*
- 8.4: Chemical Shifts - *CC BY-NC-SA 4.0*
- 8.5: Proton Equivalence - *CC BY-NC-SA 4.0*
- 8.6: Chemical Shifts in \(^1H\) NMR Spectroscopy - *CC BY-NC-SA 4.0*
- 8.7: Peak Integration - *CC BY-NC-SA 4.0*
- 8.8: Peak Splitting - *CC BY-NC-SA 4.0*

9: Symmetry - *CC BY-NC-SA 4.0*
- 9.1: Symmetry Elements - *CC BY-NC-SA 4.0*
- 9.2: Point Groups - *CC BY-NC-SA 4.0*
- 9.3: Assigning Point Groups - *CC BY-NC-SA 4.0*
- 9.4: Character Tables - *CC BY-NC-SA 4.0*
- 9.5: Applications of Symmetry - Chirality - *CC BY-NC-SA 4.0*

10: Molecular Orbital Theory - *CC BY-NC-SA 4.0*
- 10.1: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 10.1.1: s-Orbital MOs - *CC BY-NC-SA 3.0*
  - 10.1.2: p-Orbital MOs - *CC BY-NC-SA 3.0*
  - 10.1.3: d-Orbital MOs - *CC BY-NC-SA 4.0*
- 10.2: Non-bonding Orbitals - *CC BY-NC-SA 4.0*
- 10.3: Molecular Orbital Diagrams - *CC BY-NC-SA 4.0*
- 10.4: Orbital Mixing - *CC BY-NC-SA 4.0*
- 10.5: Diatomic Molecules - *CC BY-NC-SA 4.0*
- 10.6: Polar Diatomic Molecules - *CC BY-NC-SA 4.0*
- 10.7: Polyatomic Molecules - *CC BY-NC-SA 4.0*
  - 10.7.1: Bifluoride anion - *CC BY-NC-SA 4.0*
  - 10.7.2: Carbon Dioxide - *CC BY-NC-SA 4.0*
  - 10.7.3: H_2O - *CC BY-NC-SA 4.0*
  - 10.7.4: NH_3 - *CC BY-NC-SA 4.0*
  - 10.7.5: CO_2 (Revisted with Projection Operators) - *CC BY-NC-SA 4.0*
  - 10.7.6: BF_3 - *CC BY-NC-SA 4.0*

11: Coordination Compound Bonding - *CC BY-NC-SA 4.0*
- 11.1: Crystal Field Theory - *CC BY-NC-SA 4.0*
- 11.2: Crystal Field Stabilization Energy - *CC BY-NC-SA 4.0*
- 11.3: Crystal Field Splitting - *CC BY-NC-SA 4.0*
- 11.4: Ligand Field Theory - *CC BY-NC-SA 4.0*
- 11.5: Metal-Metal Bonding - *CC BY-NC-SA 4.0*
- 11.6: Spectrochemical Series - *CC BY-NC-SA 4.0*
- 11.7: Colors of Coordination Compounds - *CC BY-NC-SA 4.0*
- 11.8: Magnetic Moments - *CC BY-NC-SA 4.0*

12: Coordination Compound Spectroscopy - *CC BY-NC-SA 4.0*
- 12.1: Molecular Vibrations - *CC BY-NC-SA 4.0*
- 12.2: Identifying Active Vibrations - *CC BY-NC-SA 4.0*
- 12.3: Carbonyl Vibrational Modes - *CC BY-NC-SA 4.0*

13: Substitution Reactivity - *CC BY-NC-SA 4.0*
- 13.1: Reactions of Metal Complexes - *CC BY-NC-SA 3.0*
- 13.2: Substitution Reactions - *CC BY-NC-SA 4.0*
- 13.3: Inert and Labile Complexes - *CC BY-NC-SA 4.0*
- 13.4: Chelate Effects - *CC BY-NC-SA 4.0*
- 13.5: Substitution Mechanisms - *CC BY-NC-SA 3.0*
  - 13.5.1: Dissociative Mechanism - *CC BY-NC-SA 4.0*
  - 13.5.2: Interchange Mechanism - *CC BY-NC-SA 4.0*
  - 13.5.3: Associative Mechanism - *CC BY-NC-SA 3.0*
- 13.6: Activation Parameters - *CC BY-NC-SA 3.0*
- 13.7: Dissociation - *CC BY-NC-SA 4.0*
- 13.8: Association - *CC BY-NC-SA 4.0*
- 13.9: The Trans Effect - *CC BY-NC-SA 3.0*

Back Matter - *CC BY-NC-SA 4.0*
- Index - *CC BY-NC-SA 4.0*
- Glossary - *CC BY-NC-SA 4.0*
- Detailed Licensing - *CC BY-NC-SA 4.0*
- Detailed Licensing - *CC BY-NC-SA 4.0*
- Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: CH275: Foundations of Inorganic Chemistry

Webpages: 119

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC-SA 4.0: 90.8% (108 pages)
- CC BY-NC-SA 3.0: 8.4% (10 pages)
- Undeclared: 0.8% (1 page)

By Page

- CH275: Foundations of Inorganic Chemistry - *CC BY-NC-SA 4.0*
  - Front Matter - *CC BY-NC-SA 4.0*
    - TitlePage - *CC BY-NC-SA 4.0*
    - InfoPage - *CC BY-NC-SA 4.0*
    - Table of Contents - *CC BY-NC-SA 4.0*
    - Licensing - *CC BY-NC-SA 4.0*
  - 1: Introduction - *CC BY-NC-SA 4.0*
  - 2: Chemical Structure and Periodic Trends (Review) - *CC BY-NC-SA 4.0*
    - 2.1: Atomic Structure - *CC BY-NC-SA 4.0*
    - 2.2: Molecular and Ionic Compounds - *CC BY-NC-SA 4.0*
    - 2.3: Chemical Nomenclature - *CC BY-NC-SA 4.0*
    - 2.4: Electron Configurations (Atoms) - *CC BY-NC-SA 4.0*
    - 2.5: Electron Configurations (Ions) - *CC BY-NC-SA 4.0*
    - 2.6: Redox Reactions and Oxidation State - *CC BY-NC-SA 4.0*
    - 2.7: Periodic Trends - *CC BY-NC-SA 4.0*
    - 2.8: Electronegativity - *CC BY-NC-SA 4.0*
    - 2.9: Electron-Dot Structures - *CC BY-NC-SA 4.0*
    - 2.10: Formal Charges and Resonance - *CC BY-NC-SA 4.0*
    - 2.11: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 3: Acid-Base Chemistry - *CC BY-NC-SA 4.0*
    - 3.1: Acid-Base Theories - *CC BY-NC-SA 4.0*
    - 3.2: Brønsted-Lowry Model - *CC BY-NC-SA 4.0*
    - 3.3: Acidity of Binary Hydrides - *CC BY-NC-SA 4.0*
    - 3.4: Acidity of Oxoacids - *CC BY-NC-SA 3.0*
    - 3.5: Acidity of Metal Cations - *CC BY-NC-SA 4.0*
  - 4: Redox Reactivity - *CC BY-NC-SA 4.0*
    - 4.1: Redox Reactions - *CC BY-NC-SA 4.0*
    - 4.2: Balancing Redox Reactions - *CC BY-NC-SA 4.0*
    - 4.3: Electrochemical Potentials - *CC BY-NC-SA 4.0*
    - 4.4: Pourbaix Diagrams - *CC BY-NC-SA 4.0*
    - 4.5: Electrochemical Corrosion - *CC BY-NC-SA 3.0*
  - 5: Electrochemistry - *CC BY-NC-SA 4.0*
    - 5.1: Electrolysis - *CC BY-NC-SA 4.0*
    - 5.2: Cyclic Voltammetry - *CC BY-NC-SA 4.0*
    - 5.3: CV Electrodes - *CC BY-NC-SA 4.0*
  - 6: Ionic Compounds - *CC BY-NC-SA 4.0*
    - 6.1: Unit Cells - *CC BY-NC-SA 4.0*
    - 6.2: Ionic Radii and Radius Ratios - *CC BY-NC-SA 4.0*
    - 6.3: Lattice Energy - *CC BY-NC-SA 4.0*
    - 6.4: Born-Haber Cycles - *CC BY-NC-SA 4.0*
    - 6.5: Ionic Lattices - Examples - *CC BY-NC-SA 4.0*
      - 6.5A: Structure - Rock Salt (NaCl) - *CC BY-NC-SA 4.0*
      - 6.5B: Structure - Caesium Chloride (CsCl) - *CC BY-NC-SA 4.0*
      - 6.5C: Structure - Fluorite and Antifluorite - *CC BY-NC-SA 4.0*
      - 6.5D: Structure - Zinc Blende (ZnS) - *CC BY-NC-SA 4.0*
    - 6.6: Lattice Energy and Solubility - *CC BY-NC-SA 4.0*
    - 6.7: Solubility Equilibria - *CC BY-NC-SA 3.0*
  - 7: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 7.1: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 7.2: Lewis Acids and Bases - *CC BY-NC-SA 4.0*
    - 7.3: Nomenclature and Ligands - *CC BY-NC-SA 4.0*
    - 7.4: Structures - *CC BY-NC-SA 4.0*
    - 7.5: Isomerism - *CC BY-NC-SA 4.0*
    - 7.6: Complex-Ion Equilibria - *CC BY-NC-SA 4.0*
    - 7.7: Hard-Soft Acid-Base Theory - *CC BY-NC-SA 4.0*
  - 8: NMR and IR Spectroscopy - *CC BY-NC-SA 4.0*

- 8.1: Infrared (IR) Spectroscopy - *CC BY-NC-SA 4.0*
- 8.2: Interpreting Infrared Spectra - *CC BY-NC-SA 4.0*
- 8.3: Nuclear Magnetic Resonance (NMR) Spectroscopy - *CC BY-NC-SA 4.0*
- 8.4: Chemical Shifts - *CC BY-NC-SA 4.0*
- 8.5: Proton Equivalence - *CC BY-NC-SA 4.0*
- 8.6: Chemical Shifts in \(^1H\) NMR Spectroscopy - *CC BY-NC-SA 4.0*
- 8.7: Peak Integration - *CC BY-NC-SA 4.0*
- 8.8: Peak Splitting - *CC BY-NC-SA 4.0*

9: Symmetry - *CC BY-NC-SA 4.0*

- 9.1: Symmetry Elements - *CC BY-NC-SA 4.0*
- 9.2: Point Groups - *CC BY-NC-SA 4.0*
- 9.3: Assigning Point Groups - *CC BY-NC-SA 4.0*
- 9.4: Character Tables - *CC BY-NC-SA 4.0*
- 9.5: Applications of Symmetry - Chirality - *CC BY-NC-SA 4.0*

10: Molecular Orbital Theory - *CC BY-NC-SA 4.0*

- 10.1: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 10.1.1: s-Orbital MOs - *CC BY-NC-SA 3.0*
  - 10.1.2: p-Orbital MOs - *CC BY-NC-SA 3.0*
  - 10.1.3: d-Orbital MOs - *CC BY-NC-SA 4.0*
- 10.2: Non-bonding Orbitals - *CC BY-NC-SA 4.0*
- 10.3: Molecular Orbital Diagrams - *CC BY-NC-SA 4.0*
- 10.4: Orbital Mixing - *CC BY-NC-SA 4.0*
- 10.5: Diatomic Molecules - *CC BY-NC-SA 4.0*
- 10.6: Polar Diatomic Molecules - *CC BY-NC-SA 4.0*
- 10.7: Polyatomic Molecules - *CC BY-NC-SA 4.0*
  - 10.7.1: Bifluoride anion - *CC BY-NC-SA 4.0*
  - 10.7.2: Carbon Dioxide - *CC BY-NC-SA 4.0*
  - 10.7.3: H_2O - *CC BY-NC-SA 4.0*
  - 10.7.4: NH_3 - *CC BY-NC-SA 4.0*
  - 10.7.5: CO_2 (Revisted with Projection Operators) - *CC BY-NC-SA 4.0*
  - 10.7.6: BF_3 - *CC BY-NC-SA 4.0*

11: Coordination Compound Bonding - *CC BY-NC-SA 4.0*

- 11.1: Crystal Field Theory - *CC BY-NC-SA 4.0*
- 11.2: Crystal Field Stabilization Energy - *CC BY-NC-SA 4.0*
- 11.3: Crystal Field Splitting - *CC BY-NC-SA 4.0*
- 11.4: Ligand Field Theory - *CC BY-NC-SA 4.0*
- 11.5: Metal-Metal Bonding - *CC BY-NC-SA 4.0*
- 11.6: Spectrochemical Series - *CC BY-NC-SA 4.0*
- 11.7: Colors of Coordination Compounds - *CC BY-NC-SA 4.0*
- 11.8: Magnetic Moments - *CC BY-NC-SA 4.0*

12: Coordination Compound Spectroscopy - *CC BY-NC-SA 4.0*

- 12.1: Molecular Vibrations - *CC BY-NC-SA 4.0*
- 12.2: Identifying Active Vibrations - *CC BY-NC-SA 4.0*
- 12.3: Carbonyl Vibrational Modes - *CC BY-NC-SA 4.0*

13: Substitution Reactivity - *CC BY-NC-SA 4.0*

- 13.1: Reactions of Metal Complexes - *CC BY-NC-SA 3.0*
- 13.2: Substitution Reactions - *CC BY-NC-SA 4.0*
- 13.3: Inert and Labile Complexes - *CC BY-NC-SA 4.0*
- 13.4: Chelate Effects - *CC BY-NC-SA 4.0*
- 13.5: Substitution Mechanisms - *CC BY-NC-SA 3.0*
  - 13.5.1: Dissociative Mechanism - *CC BY-NC-SA 4.0*
  - 13.5.2: Interchange Mechanism - *CC BY-NC-SA 4.0*
  - 13.5.3: Associative Mechanism - *CC BY-NC-SA 3.0*
- 13.6: Activation Parameters - *CC BY-NC-SA 3.0*
- 13.7: Dissociation - *CC BY-NC-SA 4.0*
- 13.8: Association - *CC BY-NC-SA 4.0*
- 13.9: The Trans Effect - *CC BY-NC-SA 3.0*

Back Matter - *CC BY-NC-SA 4.0*

- Index - *CC BY-NC-SA 4.0*
- Glossary - *CC BY-NC-SA 4.0*
- Detailed Licensing - *CC BY-NC-SA 4.0*
- Detailed Licensing - *CC BY-NC-SA 4.0*
- Detailed Licensing - *Undeclared*