CHEM 124A: FUNDAMENTALS OF INORGANIC CHEMISTRY

University of California, Davis

LibreTexts™

UCD Chem 124A: Fundamentals of Inorganic Chemistry

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 and 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 06/07/2025

TABLE OF CONTENTS

Licensing

1: Introduction to Inorganic Chemistry

- 1.1: What is inorganic chemistry?
- 1.2: Inorganic vs Organic Chemistry
- 1.3: History of Inorganic Chemistry
- 1.4: Perspectives
- 1.5: Practice problems

2: Atomic Structure

- 2.1: Historical Development of Atomic Theory
  - 2.1.1: The Periodic Table
  - 2.1.2: Discovery of Subatomic Particles and the Bohr Atom
- 2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions
  - 2.2.1: Particle in a Box
  - 2.2.2: Quantum Numbers and Atomic Wave Functions
  - 2.2.3: Aufbau Principle
  - 2.2.4: Shielding
- 2.3: Periodic Properties of Atoms
  - 2.3.1: Ionization energy
  - 2.3.2: Electron Affinity
  - 2.3.3: Covalent and Ionic Radii
- 2.4: Problems (do we want this here?)

3: Simple Bonding Theory

- 3.1: Lewis Electron-Dot Diagrams
  - 3.1.1: Resonance
  - 3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)
  - 3.1.3: Formal Charge
  - 3.1.4: Lewis fails to predict unusual cases- Boron and Beryllium
- 3.2: Valence Shell Electron-Pair Repulsion
  - 3.2.1: Lone Pair Repulsion
  - 3.2.2: Multiple Bonds
  - 3.2.3: Electronegativity and Atomic Size Effects
  - 3.2.4: Ligand Close Packing
- 3.3: Molecular Polarity
- 3.4: Hydrogen Bonding

4: Symmetry and Group Theory

- 4.1: Symmetry Elements and Operations
  - 4.1.1: Symmetry Elements
- 4.2: Molecular Point Groups
  - 4.2.1: Point Groups

        - 4.2.1.1: Groups of Low and High Symmetry
        - 4.2.1.2: Other Groups
    - 4.3: Properties and Representations of Groups
        - 4.3.1: Matrices
        - 4.3.2: Matrix
        - 4.3.3: Representations of Point Groups
        - 4.3.4: Representations
        - 4.3.5: Character Tables
    - 4.4: Character Tables
    - 4.5: Examples and Applications of Symmetry
        - 4.5.1: Chirality
        - 4.5.2: Molecular Vibrations
        - 4.5.3: Normal Modes of Vibration
        - 4.5.4: Selection Rules for IR and Raman Spectroscopy
        - 4.5.5: Stretching Frequencies and Structure Determination
    - 4.6: Problems (do we want this here?)

5: Molecular Orbitals

- 5.1: Formation of Molecular Orbitals from Atomic Orbitals
    - 5.1.1: Molecular Orbitals from s Orbitals
    - 5.1.2: Molecular Orbitals from p Orbitals
    - 5.1.3: Molecular orbitals from d orbitals
    - 5.1.4: Nonbonding Orbitals and Other Factors
- 5.2: Homonuclear Diatomic Molecules
    - 5.2.1: Molecular Orbitals
    - 5.2.2: Orbital Mixing
    - 5.2.3: Diatomic Molecules of the First and Second Periods
    - 5.2.4: Photoelectron Spectroscopy
- 5.3: Heteronuclear Diatomic Molecules
    - 5.3.1: Polar bonds
    - 5.3.2: Ionic Compounds and Molecular Orbitals
- 5.4: Diatomic Molecular Orbitals
    - 5.4.1: Molecular Orbital Theory
- 5.P: Problems

6: Larger (Polyatomic) Molecules

- 6.1: Bifluoride anion
- 6.2: CO_2
- 6.3: H_2O
- 6.4: NH_3
- 6.5: CO_2 revisted with Projection Operators
- 6.6: BF_3
- 6.7: SALCs and the projection operator technique
    - 6.7.1: NH3 Molecular Orbitals
    - 6.7.2: Td Molecular Orbitals
    - 6.7.3: D4h Molecular Orbitals
    - 6.7.4: Pi Donor and Acceptor Ligands

7: Solids

- 7.1: Crystal Lattices
  - 7.1.1: Inorganic Solids
  - 7.1.2: Lattice Basics
    - 7.1.2.1: Covalent Network Solids
    - 7.1.2.2: How to Decide What Type of Structure
    - 7.1.2.3: Ionic Structures
    - 7.1.2.4: Metallic Structures
    - 7.1.2.5: Molecular Structures
  - 7.1.3: Lattice Defects
    - 7.1.3.1: Frenkel Defect
    - 7.1.3.2: Metal Oxides
    - 7.1.3.3: Schottky Defects
    - 7.1.3.4: Solid Defects
  - 7.1.4: Metal Lattices
    - 7.1.4.1: Structure and Properties of Metals
    - 7.1.4.2: Metal Packing- Layers
    - 7.1.4.3: Metal Packing- Three Dimensions
    - 7.1.4.4: Problems
    - 7.1.4.5: Solutions to Selected Problems
  - 7.1.5: Solids
    - 7.1.5.1: Body Centered Packing
    - 7.1.5.2: Metal Structures
    - 7.1.5.3: Simple Cubic
    - 7.1.5.4: Solids
    - 7.1.5.5: Sphere Packing
    - 7.1.5.6: Tetrahedral and Octahedral Sites
  - 7.1.6: Thermodynamics of Lattices
    - 7.1.6.1: Lattice Energy
    - 7.1.6.2: Lattice Energy- The Born-Haber cycle
    - 7.1.6.3: Lattice Enthalpies and Born Haber Cycles
    - 7.1.6.4: The Born-Lande' equation
- 7.2: Solids
  - 7.2.1: Crystalline and Amorphous Solids
  - 7.2.2: Arrangement of Atoms in Crystals
  - 7.2.3: Stucture of Simple Binary Compounds
  - 7.2.4: Crystal Defects
  - 7.2.5: Bonding and Properties of Solids
  - 7.2.6: Metals and Semiconductors
  - 7.2.7: Superconductors
  - 7.2.8: Polymers
  - 7.2.9: Modern Materials
  - 7.2.10: End of Chapter Material

8: Coordination Chemistry

- 8.1: Introduction and History of Coordination Compounds
  - 8.1.1: History of Coordination Compounds
- 8.2: Structure and Nomenclature of Coordination Compounds

- 8.2.1: Intro to Coordination Chemistry
- 8.2.2: Coordination Numbers and Geometry
  - 8.2.2.1: Jahn-Teller Distortions
  - 8.2.2.2: Molecular Examples
- 8.2.3: Introduction to Coordination Chemistry
- 8.2.4: Isomers
  - 8.2.4.1: Optical Isomers in Inorganic Complexes
    - 8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
    - 8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes
    - 8.2.4.1.3: Polarimetry
  - 8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
  - 8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
  - 8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
  - 8.2.4.5: Stereoisomers of Complex Metal Complexes
  - 8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
  - 8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
  - 8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
- 8.2.5: Ligands
  - 8.2.5.1: EDTA
  - 8.2.5.2: The Irving-Williams Series
- 8.2.6: What is a Complex Ion?
- 8.2.7: Nomenclature of Coordination Complexes

- 8.3: Complex Ion Chemistry
  - 8.3.1: Acidity of the Hexaaqua Ions
  - 8.3.2: Geometry of Complex Ions
  - 8.3.3: Ligand Exchange Reactions (Introduction)
  - 8.3.4: Ligand Exchange Reactions (Thermodynamics)
  - 8.3.5: Nomenclature of Complex Ions
  - 8.3.6: Origin of Color in Complex Ions
  - 8.3.7: Reactions of the Hexaaqua Ions with Ammonia
  - 8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
  - 8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
  - 8.3.10: Stereoisomerism in complex ions
- 8.4: Complex Ion Equilibria
  - 8.4.1: Chelation
  - 8.4.2: Complex-Ion Equilibria
  - 8.4.3: Complex Equilibrium
  - 8.4.4: Hard and Soft Acids and Bases
  - 8.4.5: Stability of Metal Complexes and Chelation

9: Crystal Field Theory

- 9.1: Colors of Coordination Complexes
- 9.2: Crystal Field Stabilization Energy
- 9.3: Crystal Field Theory
- 9.4: High Spin and Low Spin Complexes
- 9.5: Introduction to Crystal Field Theory
- 9.6: Magnetic Moments of Transition Metals
- 9.7: Magnetism
- 9.8: Metals, Tetrahedral and Octahedral
- 9.9: Non-octahedral Complexes

- 9.10: Octahedral vs. Tetrahedral Geometries
- 9.11: Orgel Diagrams
  - 9.11.1: Qualitative Orgel Diagrams
- 9.12: Tanabe-Sugano Diagrams
- 9.13: Thermodynamics and Structural Consequences of d-Orbital Splitting

10: Ligand Field Theory

- 10.1: Ligand Field Theory Fundamentals

11: Spectroscopic Techniques

- 11.1: Fundamentals of Electron Absorption Spectroscopy
- 11.2: Basics of Spectroscopy
  - 11.2.1: Breakdown of EM Radiation
- 11.3: Electronic Spectroscopy
- 11.4: Vibrational Spectroscopy
- 11.5: X-ray Spectroscopy
  - 11.5.1: Extended X-ray Absorption Fine Structure (EXAFS)
  - 11.5.2: X-ray Absorption Near Edge Structure (XANES)
  - 11.5.3: X-ray Absorption Spectroscopy (XAS)
- 11.6: Magnetic Resonance Spectroscopies
  - 11.6.1: NMR Animations
    - 11.6.1.1: Basic Concepts
      - 11.6.1.1.1: Magnetic Resonance Imaging
    - 11.6.1.2: pi Pulses
    - 11.6.1.3: Pulsed NMR Introduction
    - 11.6.1.4: Spin Echo

Index

Index

Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Introduction to Inorganic Chemistry

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

1.1: What is inorganic chemistry?
1.2: Inorganic vs Organic Chemistry
1.3: History of Inorganic Chemistry
1.4: Perspectives
1.5: Practice problems

1: Introduction to Inorganic Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.1: What is inorganic chemistry?

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

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

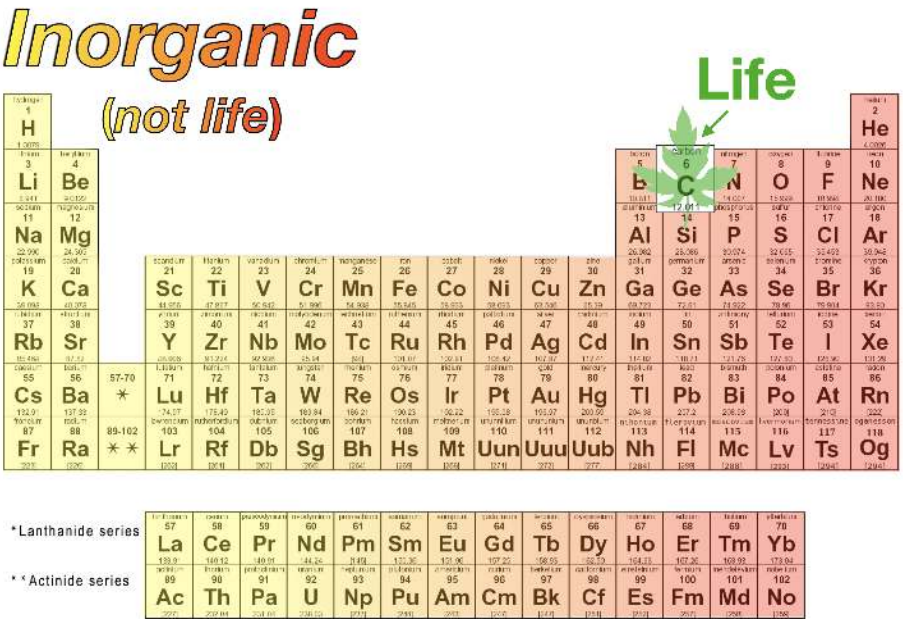


Figure 1.1.1. An illustration of the historic meaning of "organic" and "inorganic". The modern understanding of organic and inorganic chemistry is not consistent with these historical meanings.

External links:

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

Practice

What are the Sub-Fields of Inorganic Chemistry?

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

Answer

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

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

1.1: What is inorganic chemistry? is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.2: Inorganic vs Organic Chemistry

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

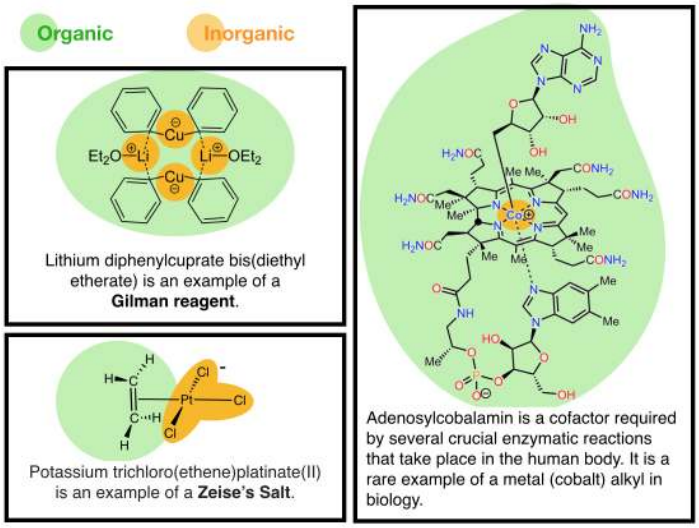


Figure 1.2.1. Some examples of organometallic catalysts. These compounds catalyze organic reactions or biochemical reactions and they are compounds that contain both carbon and metals. These compounds are examples of molecules that cannot be defined only as organic molecules or only as inorganic molecules.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

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

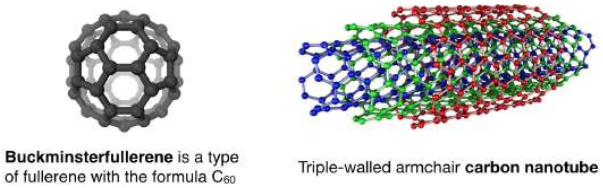


Figure 1.2.2: This figure is created from information found on the Wikipedia articles for Buckmisterfullerene and carbon nanotubes. Attribution Eric Wieser, Multi-walled Carbon Nanotube, CC BY-SA 3.0.

Although carbon nanotubes and fullerenes are allotropes of carbon, their material properties are somewhat foreign to many organic chemists, who traditionally have focused on smaller organic molecules having very different properties. However, these properties are familiar to inorganic chemists. Thus, inorganic chemists have embraced these molecules as "inorganic" due to the fact that they behave more like inorganic materials than smaller organic molecules. This class of carbon-based molecules serves as another

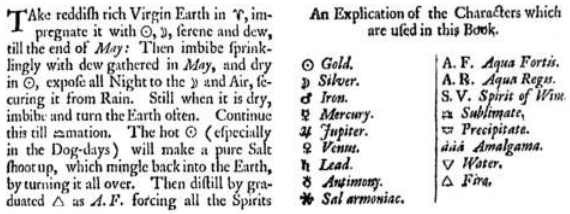
example of molecules that are not perfectly matched to the traditional definitions of "organic" and "inorganic" chemistry. Certainly, the future will hold more and more examples of molecules that do not fit into the traditional disciplines of chemistry.

This page titled 1.2: Inorganic vs Organic Chemistry is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

1.3: History of Inorganic Chemistry

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

The existence of chemistry as a field of study owes much to the fact that gold was a valuable commodity throughout our history. In both the ancient Egyptian society and during the Roman Empire, gold mines were the property of the state, not an individual or group. So there were few ways for most people to legally get any gold for themselves. The Alchemists were a varied group of scholars and charlatans who aimed to solve this problem by creating the **Philosopher's Stone** (which caused the transmutation of lead into gold). Three major streams of alchemy are known: Chinese, Indian, and European, with all three streams having some factors in common. Techniques developed in the European stream ultimately influenced the development of the science of chemistry.


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

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

☉ *Gold.*	A. F. *Aqua Fortis.*
☽ *Silver.*	A. R. *Aqua Regis.*
♂ *Iron.*	S. V. *Spirit of Wine.*
☿ *Mercury.*	♎ *Sublimate,*
♃ *Jupiter.*	♏ *Precipitate.*
♀ *Venus.*	*ȧȧȧ Amalgama.*
♄ *Lead.*	▽ *Water.*
♁ *Antimony.*	△ *Fire.*
✱ *Sal armoniac.*	

Figure 1.3.1. Alchemist recipe. Many of the specific approaches that alchemists used when they tried changing lead into gold are vague and unclear. Each alchemist had his own code for recording his data. The processes were kept secret so others could not profit from them. Different scholars developed their own set of symbols as they recorded the information they came up with. Many alchemists were not very honest, taking money from a nobleman by claiming to be able to make gold from lead, then leaving town in the middle of the night. Sometimes the nobleman would detect the fraud and have the alchemist hung. By the 1300's, several European rules had declared alchemy to be illegal and set out strict punishments for those practicing the alchemical arts.

Although alchemists were never successful in changing lead into gold, they made several contributions to modern-day chemistry. Strong acids and bases were discovered, including nitric acid ($ceHNO3$), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl), as well as sodium hydroxide ($NaOH$). Glassware for running chemical reactions was developed, as were methods for distillation, crystallization, and sublimation. Alchemy helped improve the study of metallurgy and the extraction of metals from ores. More systematic approaches to research were developed that allowed the discovery of atoms and laid the groundwork for development of the periodic table. For more about the History of Chemistry in general, try the LibreText page A Brief History of Chemistry.

Inorganic compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue ($Fe_4[Fe(CN)_6]_3$). However, the chemical nature of these substances was unknown until the late nineteenth and early twentieth century when the modern field of coordination chemistry emerged. Much of what we know about inorganic chemistry is based largely on the work of and debates between Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913) and Sophus Mads Jørgensen (1837 –1914). After Werner succeeded in these debates, the field of inorganic chemistry declined in popularity until the mid-twentieth century, when the second world war stimulated renewed interest. During the post-war era, several important discoveries and theories were developed. For example, important theories of bonding in coordination compounds were developed.

Soon after World War II, Crystal Field Theory (CFT) and Ligand Field Theory (LFT) were developed. These are two critical and complimentary theories that provide explanations of spectroscopic, chemical, and structural properties of inorganic coordination compounds, CFT being more simple, and LFT more accurate. In the 1950's, organometallic catalysts were discovered that catalyzed important organic reactions and the Haber-Bosch Process was discovered. The Haber-Bosch Process is catalyzed by an inorganic oxide catalyst and is one of the world's most important industrial reactions. It provides for the synthesis of ammonia directly from elemental nitrogen, N_2, and hydrogen, H_2.

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

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

Contributions

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

Part of this page is adapted from the following LibreTexts pages

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

1.3: History of Inorganic Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **1.3: History of Inorganic Chemistry** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

1.4: Perspectives

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

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

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

- The very first issue of Inorganic Chemistry from 1962: https://pubs.acs.org/toc/inocaj/1/1
- The latest issue of Inorganic chemistry: https://pubs.acs.org/toc/inocaj/current
- The most popular Inorganic Chemistry articles from the past month and the past year: https://pubs.acs.org/action/showMostReadArticles?journalCode=inocaj

1.4: Perspectives is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **1.4: Perspectives** by Kathryn Haas has no license indicated.

1.5: Practice problems

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

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

1.5: Practice problems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **1.5: Practice problems** by Kathryn Haas has no license indicated.

CHAPTER OVERVIEW

2: Atomic Structure

2.1: Historical Development of Atomic Theory

2.1.1: The Periodic Table

2.1.2: Discovery of Subatomic Particles and the Bohr Atom

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

2.2.1: Particle in a Box

2.2.2: Quantum Numbers and Atomic Wave Functions

2.2.3: Aufbau Principle

2.2.4: Shielding

2.3: Periodic Properties of Atoms

2.3.1: Ionization energy

2.3.2: Electron Affinity

2.3.3: Covalent and Ionic Radii

2.4: Problems (do we want this here?)

2: Atomic Structure is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.1: Historical Development of Atomic Theory

Notes about this page

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

Alternatives pages on the history of atomic theory are:

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

Skills to Develop

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

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions
- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford

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

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

Atomic Theory through the Nineteenth Century

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

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

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure 2.1.1). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.
3. Atoms of one element differ in properties from atoms of all other elements.

4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure 2.1.2).
5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure 2.1.3).

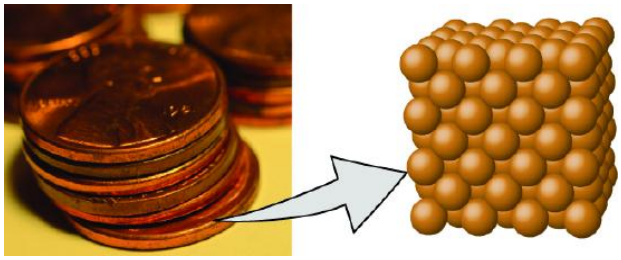


Figure 2.1.1: *A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)*

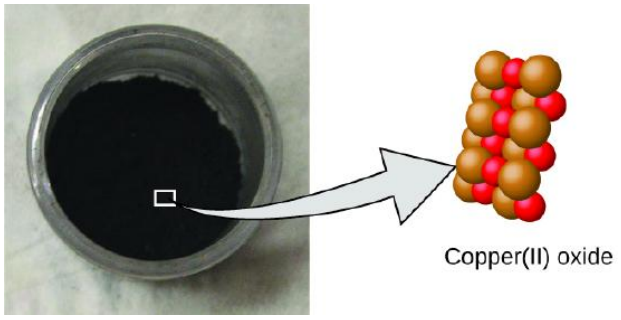


Figure 2.1.2: *Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)*

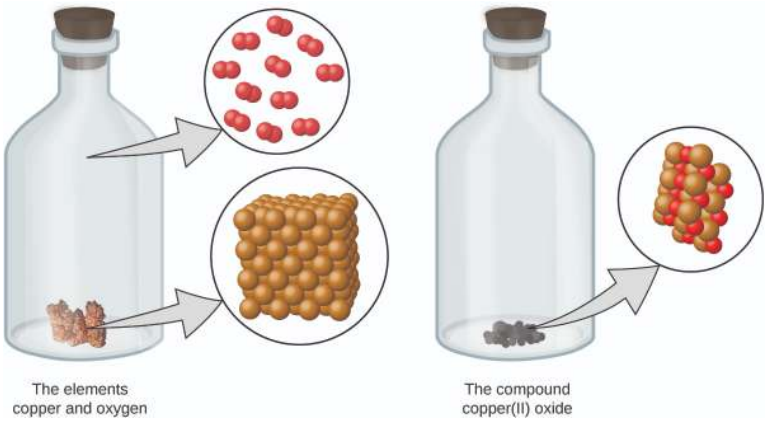


Figure 2.1.3*: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work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

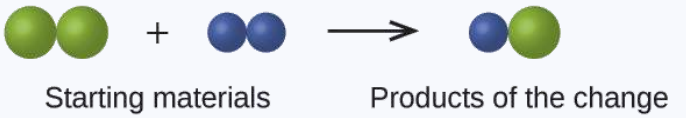
Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer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

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

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

Example 2.1.1: Testing Dalton's Atomic Theory

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

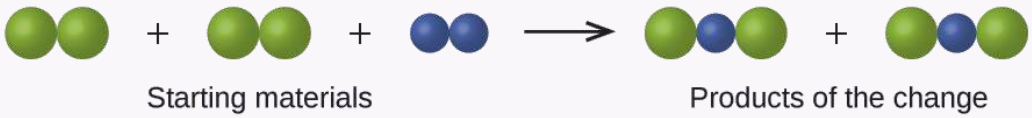


Solution

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

Exercise 2.1.1

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



Answer

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

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 2.1.1.

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

Sample	Carbon	Hydrogen	Mass Ratio

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

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

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

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

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

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 2.1.4).

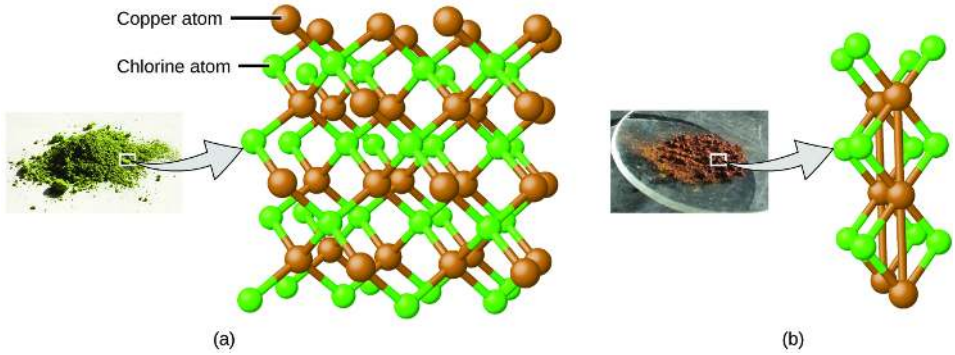


***Figure* 2.1.4**: *Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons;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

Example 2.1.2: Laws of Definite and Multiple Proportions

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

Solution

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

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

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

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

The ratio of these ratios is:

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

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

Exercise 2.1.2

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

Answer

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13\text{ g C}}{2.96\text{ g H}}$.

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

The ratio of these ratios is

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

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

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

Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 2.1.1).

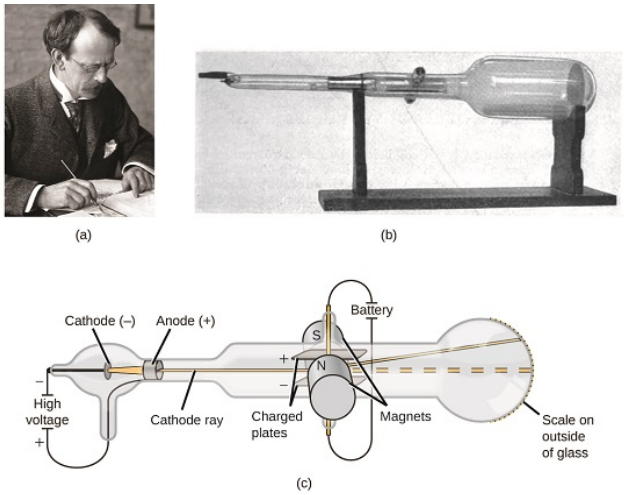
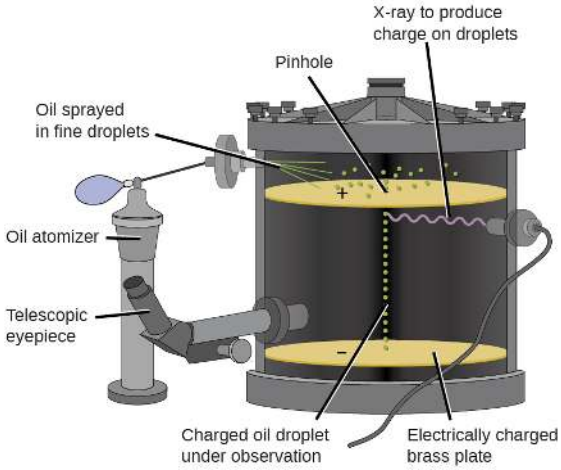


***Figure* 2.1.5**: *(a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons).*

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

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 2.1.2).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

***Figure* 2.1.6**: *Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.*

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to

Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

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

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 2.1.3).

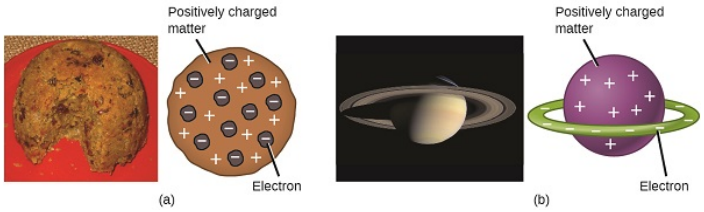


***Figure 2.1.7**: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work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

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

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 2.1.4). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"[1] (p. 68).

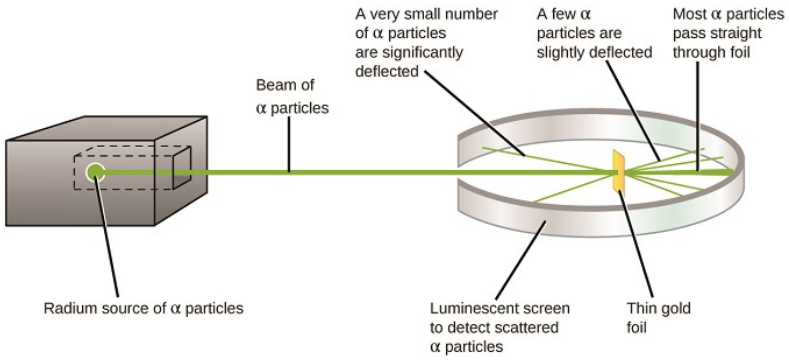


***Figure 2.1.8**: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly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

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive

charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

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

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 2.1.5).

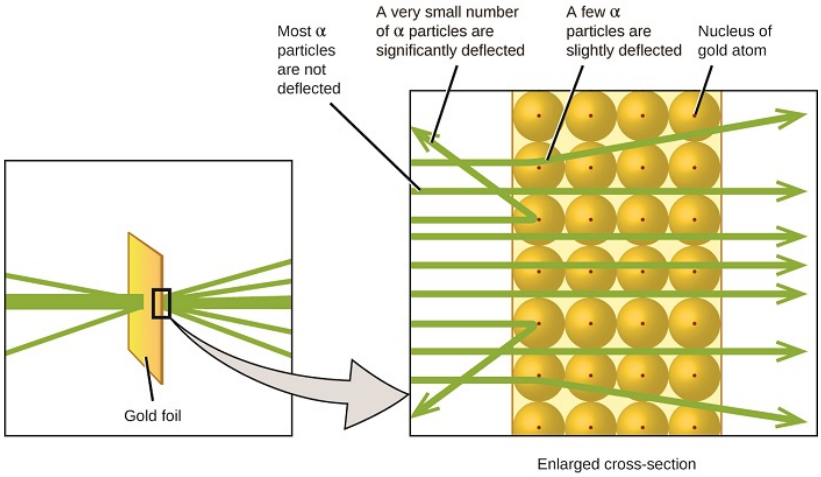
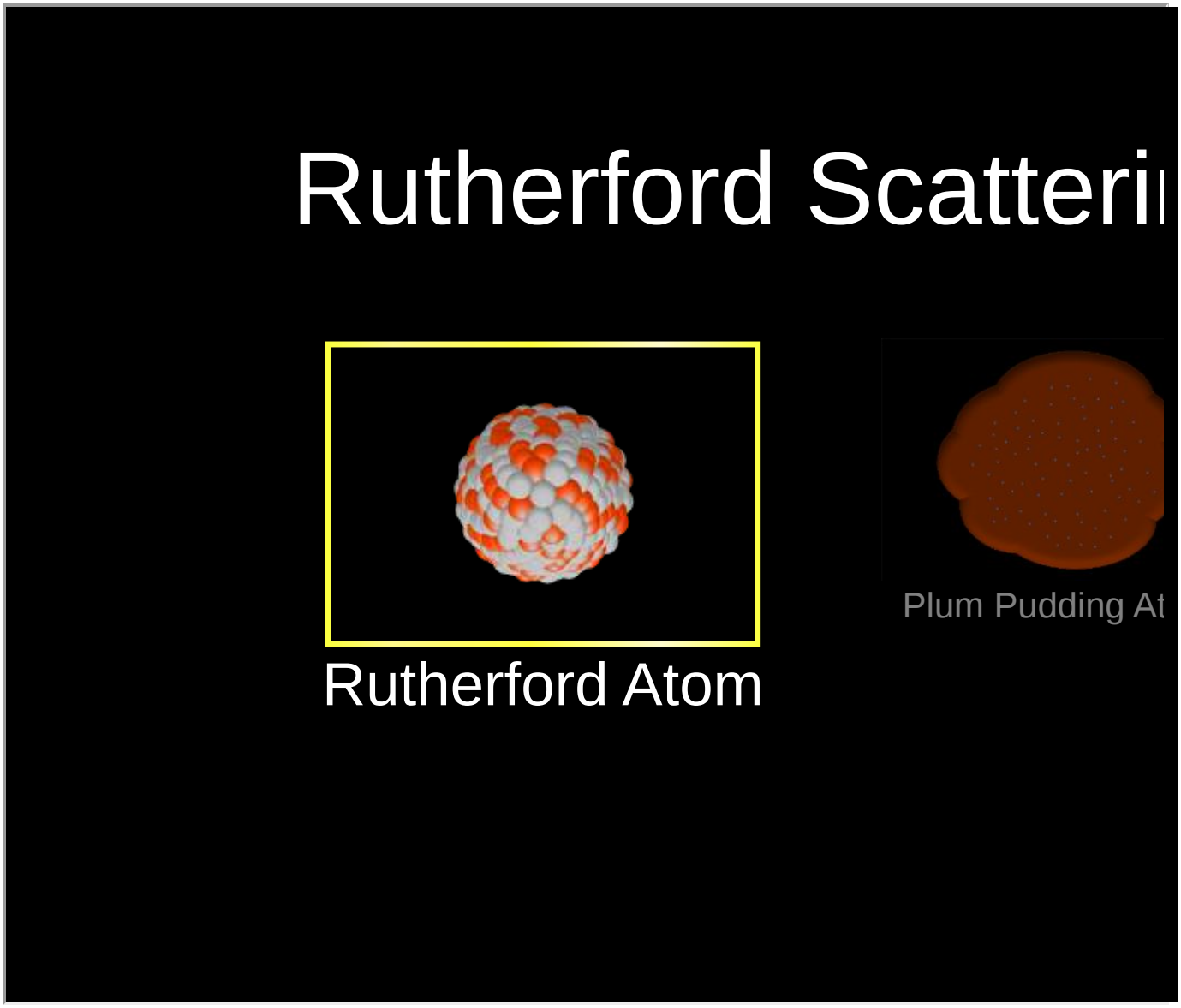


***Figure* 2.1.9**: *The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied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

After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.



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

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

Video* 2.1.2*: An Introduction to Subatomic Particles

Summary

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

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

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

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

Footnotes

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

Glossary

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

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

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

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

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

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

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

neutron
uncharged, subatomic particle located in the nucleus

proton
positively charged, subatomic particle located in the nucleus

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

Contributors

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

Feedback

Have feedback to give about this text? Click here.

Found a typo and want extra credit? Click here.

2.1: Historical Development of Atomic Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.1.1: The Periodic Table

Learning Objectives

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

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

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

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

John Newlands (1838–1898)

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

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

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

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

The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as "atomic volume" (Figure 3.4.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density of the element in grams per

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

$$\frac{molar\ mass\left(\ g/mol\right)}{density\left(\ g/cm^3\right)} = molar\ volume\left(cm^3/mol\right) \tag{3.4.1}$$

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

Dimitri Mendeleev (1834–1907)

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

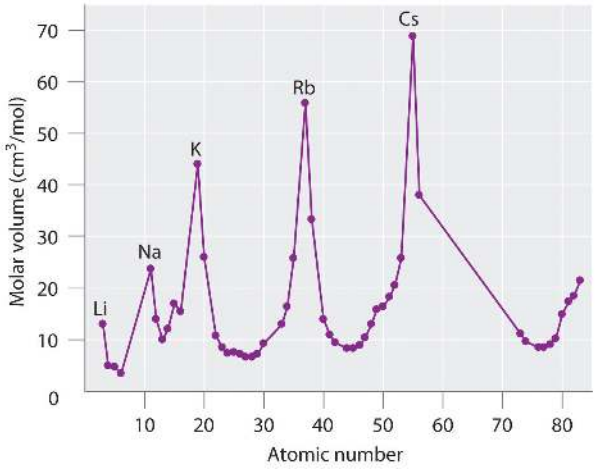


Figure 3.4.2 Variation of atomic volume with atomic number, adapted from Meyer's plot of **1870:** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Mendeleev's Periodic Table

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

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

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

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

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

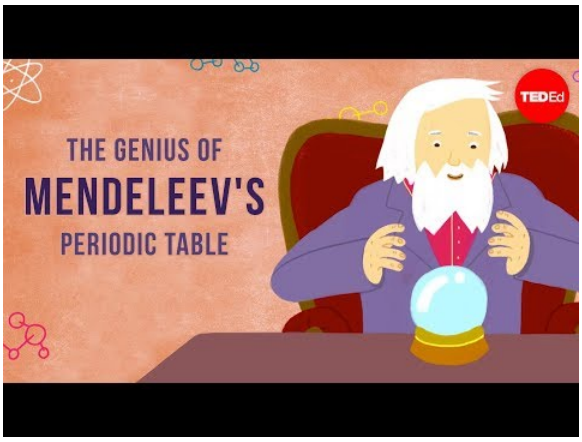


Table 3.4.1 Comparison of the properties predicted by Mendeleev in 1869 for *eka*-aluminum and *eka*-silicon with the properties of gallium (discovered in 1875) and germanium (discovered in 1886)

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

*mp = melting point; bp = boiling point.

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

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

The Role of the Atomic Number in the Periodic Table

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

atomic number *Z*, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

H. G. J. Moseley (1887–1915)

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

Example 3.4.1

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

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

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

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

Solution:

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

Exercise

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

Answer: *eka*-mercury

Summary

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

Key Takeaways

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

Conceptual Problems

1. Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.

2. Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?
3. How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
4. The *eka*- naming scheme devised by Mendeleev was used to describe undiscovered elements.
    1. Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
    2. Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

Numerical Problem

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

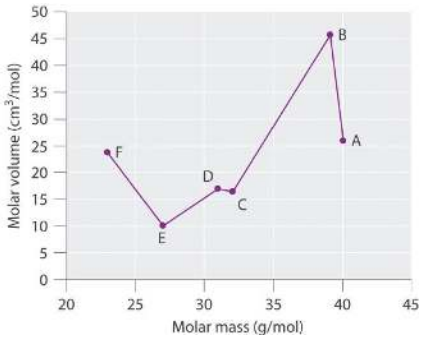
Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

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

Answer

1.

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



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

than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

Contributors and Attributions

- Anonymous

Modified by Joshua Halpern

Video from TED-Ed Lou Serocp

2.1.1: The Periodic Table is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **2.1.1: The Periodic Table** has no license indicated.

2.1.2: Discovery of Subatomic Particles and the Bohr Atom

Hydrogen Absorption and Emission Spectra

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

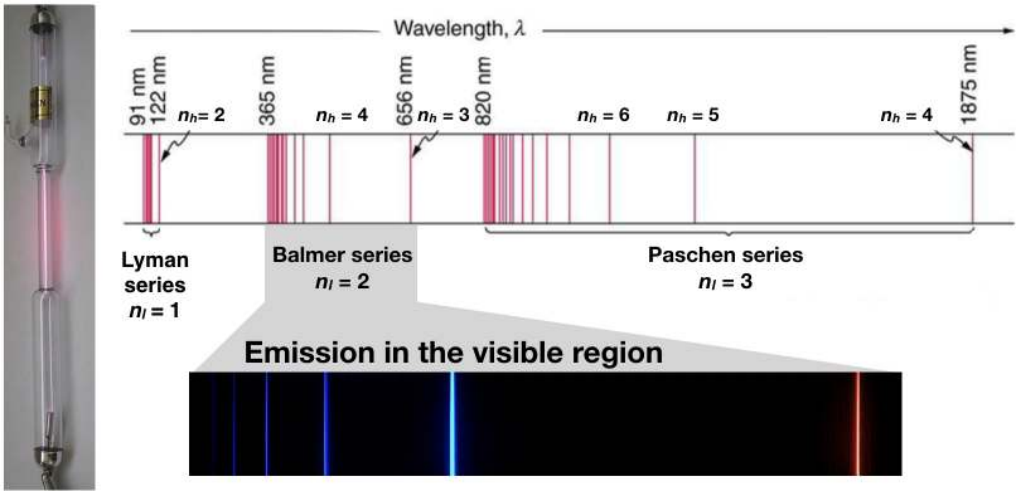


Figure 2.1.2.1: The emission of light by hydrogen atoms. (left) A sample of excited hydrogen atoms emits a characteristic red light. (bottom) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red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

The Balmer Series

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

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

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

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

,

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

Other Series

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

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

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

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

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

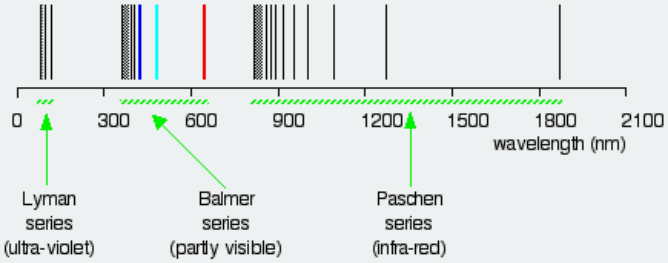
n_h	2	3	4	5
λ (nm)	121	102	97	94
$\tilde{u}$ (cm^{-1})	82,2291	97,530	102,864	105,332

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

Multiple series

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

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



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

Example 2.1.2.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

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

Solution:

We can use the Rydberg equation (Equation $Ref 2.1.2.2$ to calculate the wavelength:

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

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

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

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

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

and

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

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

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

? Exercise 2.1.2.1: The Pfund Series

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

Answer

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

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

The Bohr Model

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

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

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

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

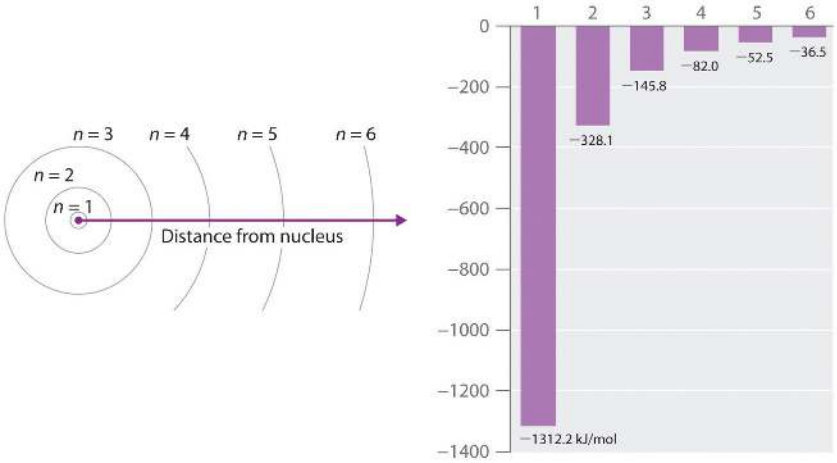
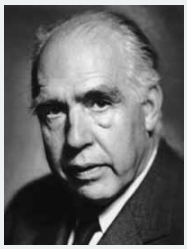


Figure 2.1.2.2*: The Bohr Model of the hydrogen atom (a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.*

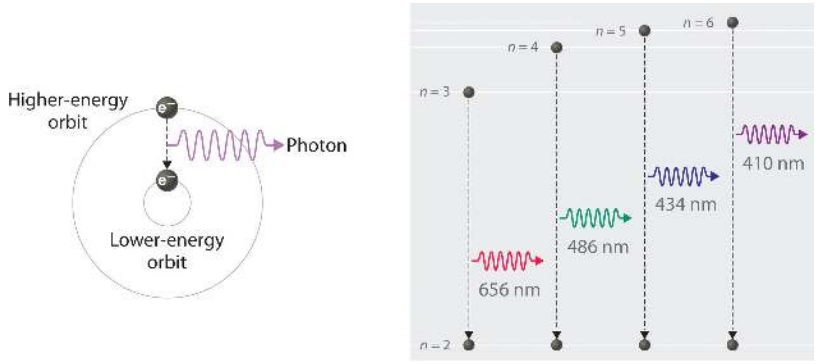
Niels Bohr (1885–1962)

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



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

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



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

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

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

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

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

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

Canceling *hc* on both sides gives

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

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

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

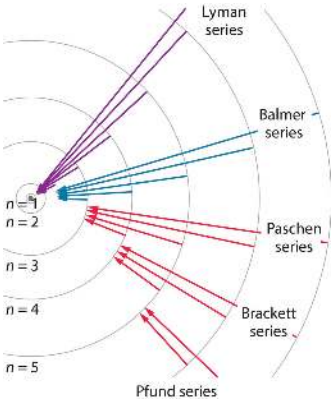


Figure 2.1.2.4: Electron transitions responsible for the various series of lines observed in the emission spectrum of hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding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

Using Atoms to Time

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

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

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

Example 2.1.2.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

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

Solution:

We can use the Rydberg equation to calculate the wavelength:

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

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

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

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

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

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

and

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

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

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

? Exercise 2.1.2.1: The Pfund Series

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

Answer

4.65 × 10^3 nm; infrared

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

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

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

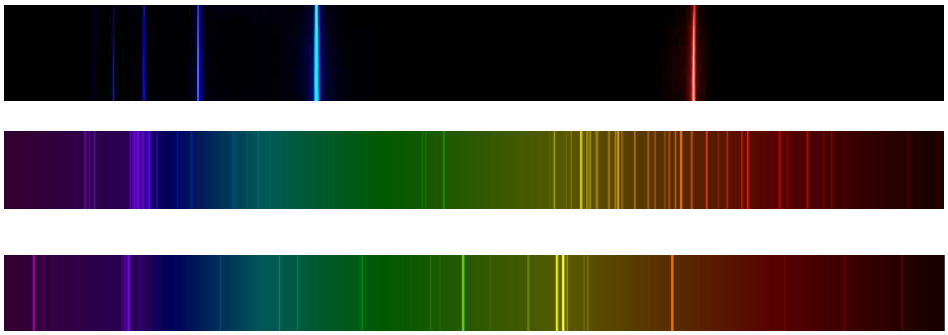


Figure 2.1.2.5: The emission spectra of elements compared to hydrogen. **Top:** hydrogen gas (atomized to hydrogen atoms in the discharge tube). **Middle:** neon. **Bottom:** mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest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

The Energy States of the Hydrogen Atom

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

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

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

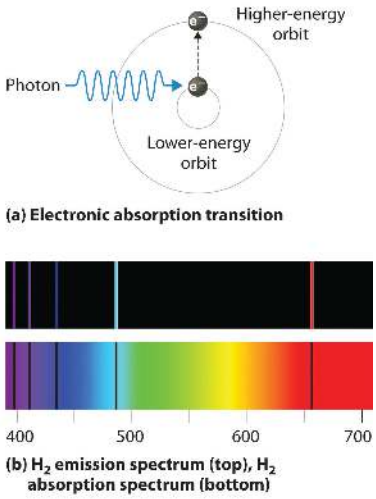


Figure 2.1.2.6: Absorption and emission spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

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

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

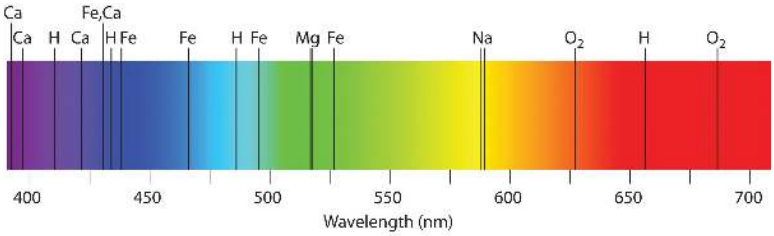


Figure 2.1.2.7: *The visible spectrum of sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the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

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

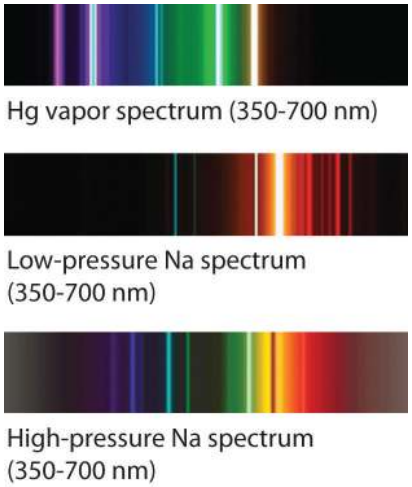


Figure 2.1.2.8: *The emission spectra of sodium and mercury. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in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

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

2.1.2: Discovery of Subatomic Particles and the Bohr Atom is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **2.1.2: Discovery of Subatomic Particles and the Bohr Atom** is licensed CC BY-NC-SA 3.0.

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

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

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

$$\hat{H}\psi = E\psi \tag{2.2.1}$$

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

The Hamiltonian, $\hat{H}$

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

$$\hat{H} = \frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{2.2.2}$$

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

Kinetic Energy

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

Potential energy

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

$$V(x,y,x) = \frac{-Ze^2}{4\pi\epsilon_0 r} = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}} \tag{2.2.3}$$

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

The Wavefunction, ψ

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

$$\psi_{n,l,m_l} = R_{n,l}(r) + Y_{l,m_l}(\theta,\phi) \tag{2.2.4}$$

Quantum Numbers define ψ

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

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

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

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

Some important considerations and limitations

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

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

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

1. There is only one possible value for ψ for any set of the three quantum numbers n, l, m_l.
2. The ψ approaches zero as r approaches infinity, and so ψ^2 also approaches zero as $r \rightarrow \infty$.
3. The total probability of finding the electron anywhere in space is 1. (Show integral)
4. Any two orbitals must not occupy the same space. (Show integral)
5. The probability of finding the electron anywhere in infinite space must be defined. This means that the wave functions and their first derivatives must be continuous (i.e. not change abruptly from one point to the next).

Awesome Sources for further reading

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

This page titled 2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

2.2.1: Particle in a Box

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

The model of a particle in a box

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

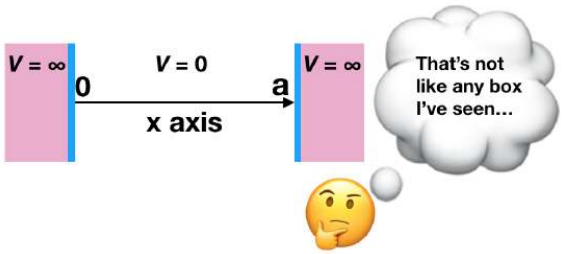


Figure 2.2.1.1. An illustration of the particle in the box model (particle not shown). The box is actually just a one-dimensional space, often assigned to the x-dimension (the x-axis). The particle has wave properties and is trapped in the box. Since no forces act on the particle inside the box, the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

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

The Schrödinger wave equation for a particle in a box

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

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

The Hamiltonian in three dimensions (from equation 2.2.2):

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

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

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

Exercise 2.2.1.1

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

Answer

Here is the Hamitlonian Equation for in three dimensions.

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

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

(1) Simplify the expression for kinetic energy

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

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

And the overall Hamiltonian is simplified:

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

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

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

The simplified Hamiltonian is now:

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

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

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

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

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

The wavefunction of a one-dimensional wave

Although we've simplified the Schrödinger Equation by considering the particle in the box, Equation 2.2.1.1 may still look mysterious to you. But it's simpler than you might realize. Let's unpack it! Here we'll go through the steps of deriving the 1-dimensional wavefunction for the particle in a box. We won't try to derive a three-dimensional wavefunction for a "real" electron,

but when you understand how to find the 1-dimensional wavefunction, and what it tells us, then you can conceptually extend this to understand what the wavefunction tells us about electrons in three dimensions.

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

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

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

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

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

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

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

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

What are r and s?

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

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

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

? Exercise 2.2.1.2: Prove that Equation 2.2.1.3 is true

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

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

Differentiation Rules for sin and cos:

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

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

Answer

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

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

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

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

The result of taking the first derivative...

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

...and the second derivative...

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

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

(3) Simplify

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

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

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

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

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

Why is this a useful exercise?

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

? Exercise 2.2.1.4

*Complete Exercise 2.2.1.2before attempting this one.

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

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

Answer

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

(1) Rearrange

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

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

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

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

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

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

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

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

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

What are A and B?

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

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

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

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

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

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

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

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

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

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

$$\sin(ra) = 0$$

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

$$ra = \pm n\pi$$

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

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

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

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

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

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

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

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

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

So, now you can see how a 1-D wavefunction can be solved. But how do we find the E of the electron from this? Well, in order to not distract you earlier, we skipped over a very simple way to do this. The E falls right out of the equations you just saw. We can set

the two expressions we found above for the constant r, (equations 2.2.1.4 and 2.2.1.6) equal to one another and then solve for E:

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

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

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

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

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

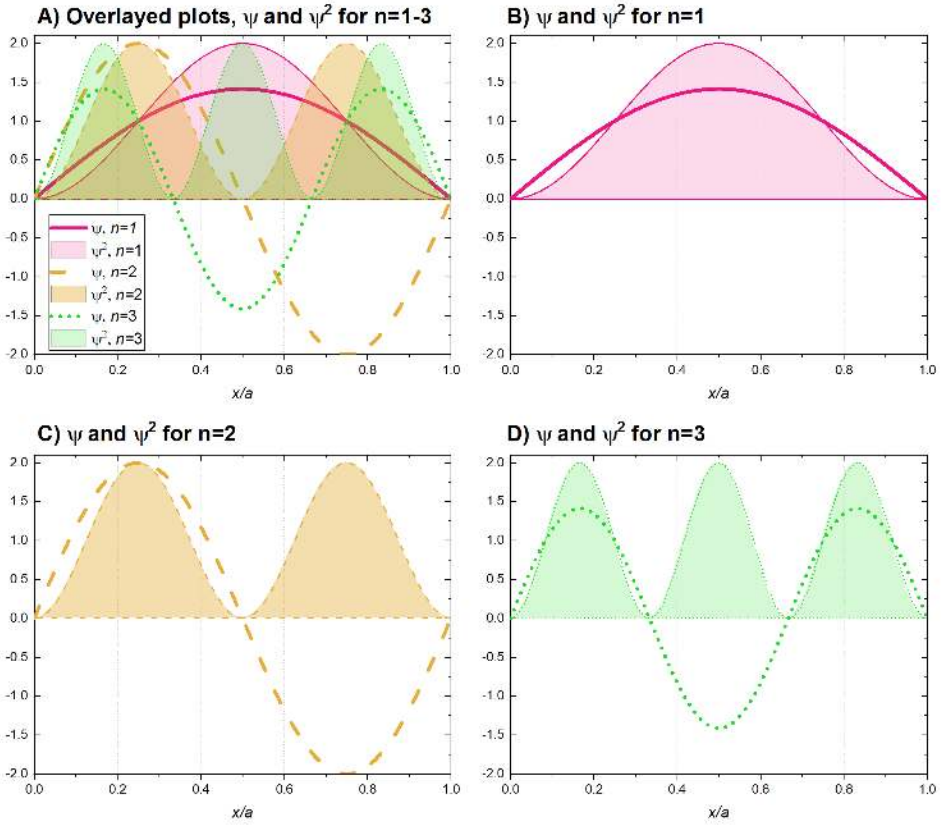


Figure 2.2.1.2. Plots of the 1-D ψ and ψ^2 for $n = 1$, $n = 2$, and $n = 3$ of a box of length a. The wavefunction (ψ) is plotted as a thick solid, dashed, or dotted line. The square of the wavefunction (ψ), which represents the probability of finding the particle at position x, is plotted as the thinner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

The graphs above represent "solutions" to the wave function. For example, the solution $n = 1$ gives the plot shown in Figure 2.2.1.2B. The solution of $n = 2$ is plotted in Figure 2.2.1.2C, and so on. These values for n are some of the possible solutions to

the 1-dimensional ψ, and they yield descriptions of the wave behavior and probability of finding a particle in 1-dimensional space.

How does this apply to atoms?

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

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

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

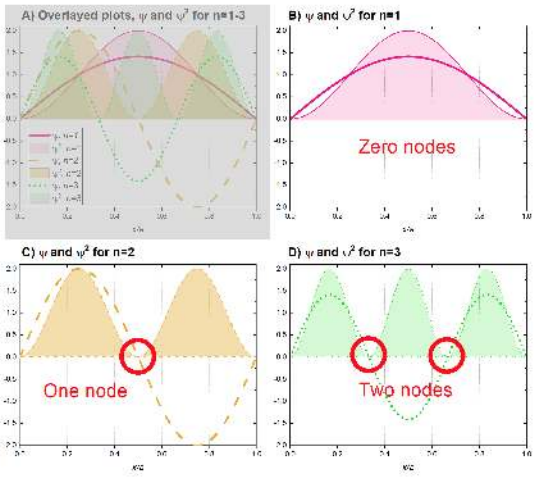
A change in sign of the ψ (and where both $psi = 0$ and $\psi^2 = 0$) is a node. In both the 1-dimensional particle in a box model and in the more realistic 3-dimensional case, a node is found where the ψ changes sign. At this point, $\psi = \psi^2 = 0$; in other words there is zero probability of finding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

? Exercise 2.2.1.4

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

Answer

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



Exercise 2.2.1.5

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

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

Answer

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

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

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

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

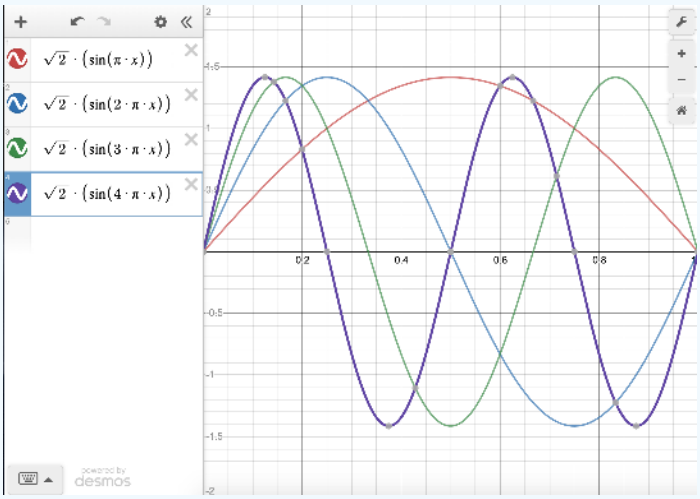
For n=2,3,4 you would repeat the process above. You will get the following functions:

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

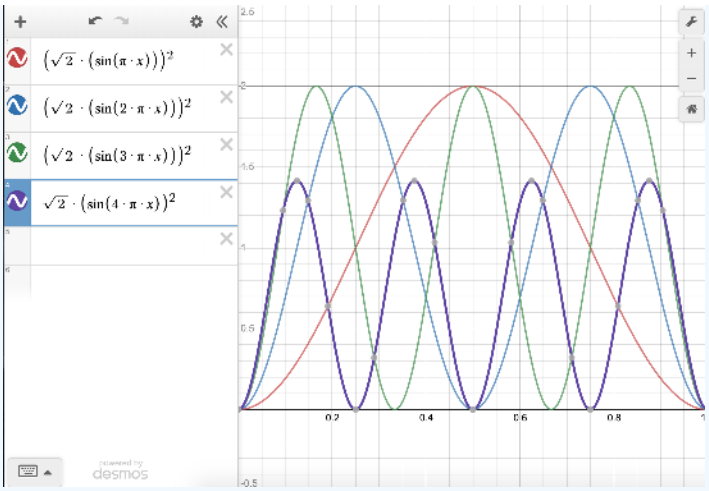
For n=3: $\psi = \sqrt{2}\left(\sin(3\pi x)\right)$

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

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



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



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

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

This page titled 2.2.1: Particle in a Box is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.2.1: Particle in a Box** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

2.2.2: Quantum Numbers and Atomic Wave Functions

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

Quantum numbers

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

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

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

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

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

Table 2.2.2.1. Quantum Numbers

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

1-Electron Wavefunctions (Atomic orbitals)

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

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

Allowed Energies

From the wavefunction, we can find the allowed energies of an electron in an atom. We have not given you the more complex form of the wavefunction where you'd need to derive 2.2.2.2from 2.2.2.1because it is outside the scope of this course. Instead, consider the process that

we used to derive the energy of a particle in a one-dimensional box in the previous section. A similar process can be used to find the energy of an electron in three dimensions, shown in 2.2.2.2

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

,

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

? Exercise 2.2.2.1

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

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

Answer (a)

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

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

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

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

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

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

Answer (b)

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

Step 1.

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

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

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

Step 2.

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

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

Exercise 2.2.2.2

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

Answer

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

Radial and Angular contributions to the wavefunction:

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

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

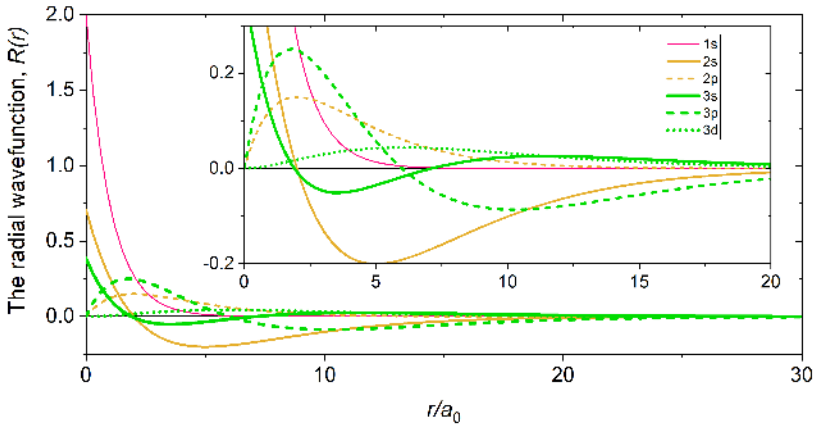


Figure 2.2.2.1. Plots of the radial wavefunction, $R_{n,l}(r)$, for the first three shells. The wavefunctions are plotted relative to $\frac{r}{a_0}$, where $a_0 = 52.9pm = 0.529$Å is the Bohr Radius (the radius of a hydrogen 1s orbital). The expressions for these radial wavefunctions ($R_{n,l}(r)$)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

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

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

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

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

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

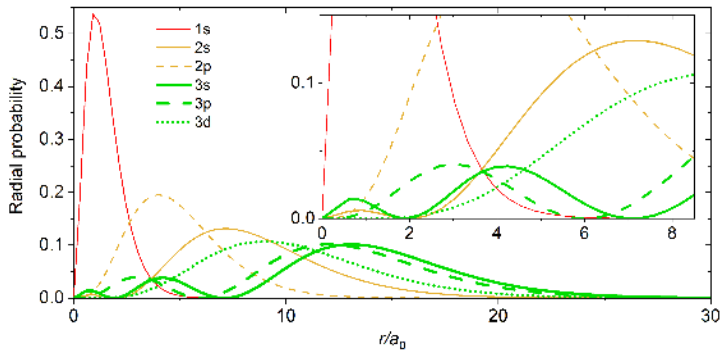


Figure 2.2.2.2: Plots of the normalized radial probability functions for the first three shells. The radial wavefunctions ($R_{n,l}(r)$) are shown in Table 2.2.2.2. (Kathryn Haas; CC-NC-BY-SA)

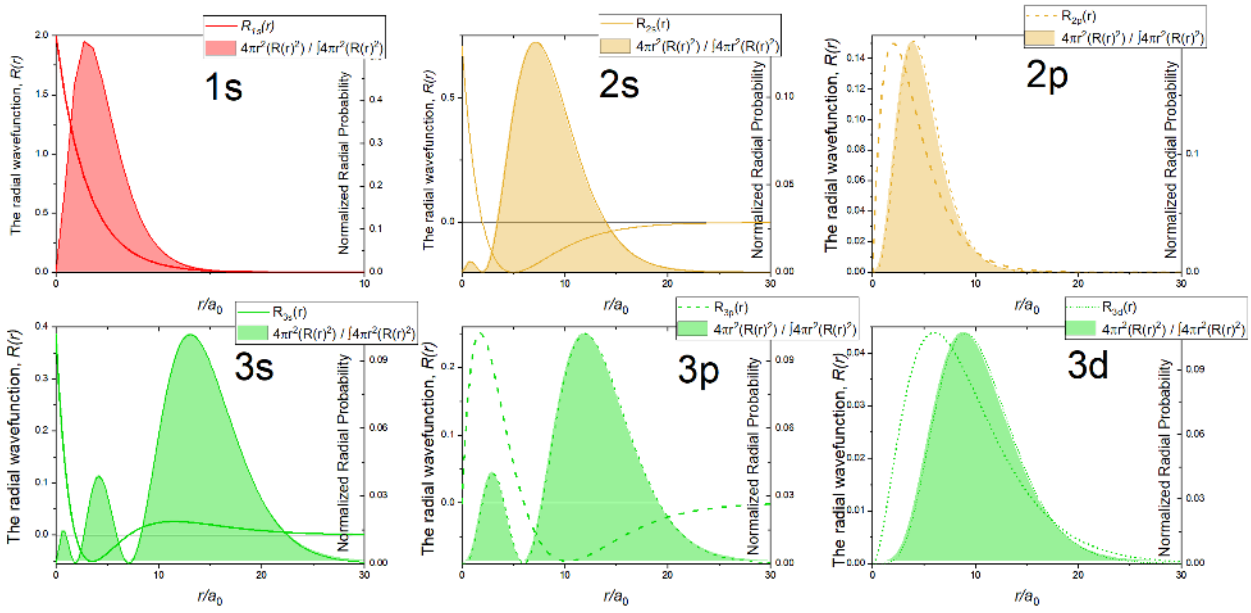


Figure 2.2.2.2. Plots of the normalized radial probability function for each orbital in the first three shells (shaded curves). The radial wavefunctions are also shown (Table 2.2.2.2). The y-axis on the left of each plot corresponds to the radial wavefunction (line); the y-axis on the right of each plot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

Radial nodes

From the discussion of the 1-dimensional particle in a box, we learned that nodes exist where $\psi = 0$. In the case of the 3-dimensional wavefunction, there are two different types of nodes: radial nodes and angular nodes. **Radial nodes occur where the radial part of the**

wavefunction is zero ($R(x) = 0$). These are easy to find by plotting the radial part of the wavefunction and finding where the radial part of the wavefunction (and the radial probability function) is zero (where $R_{n,l}(r) = 0$) and where $4\pi r^2 (R_{n,l}(r))^2 = 0$. These nodes are spherical in shape and depend on the energy level and subshell (the values of n and l). **The number of radial nodes is $n - l - 1$**. An example of a radial node is the single node that occurs in the $2s$ orbital ($2 - 0 - 1 = 1$ node). In contrast, the 1s orbital has zero radial nodes ($1 - 0 - 1 = 0$ nodes). Where there is a node, there is zero probability of finding an electron.

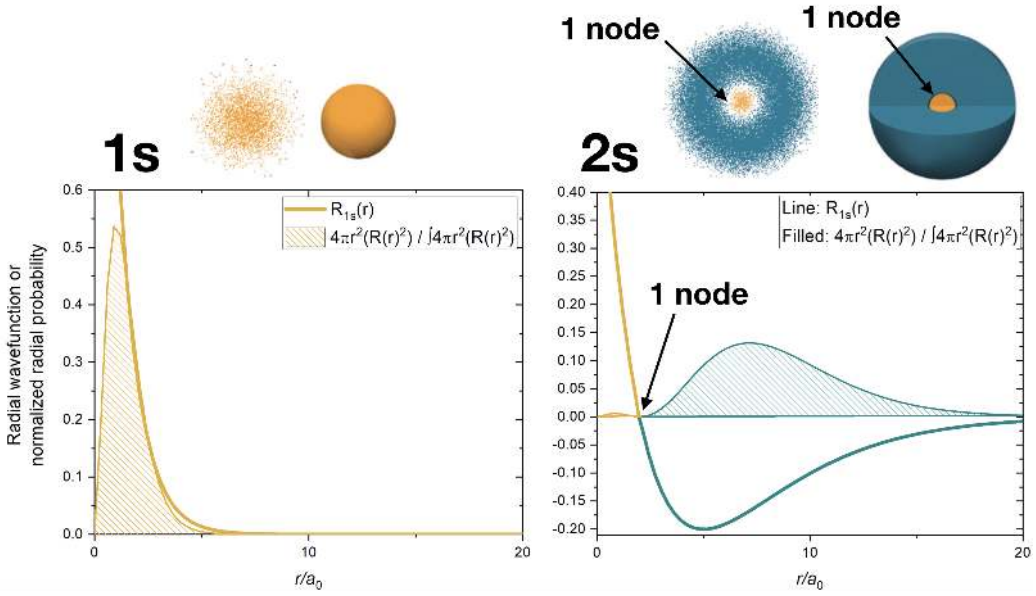


Figure 2.2.2.3: Visualization of the 1s and 2s atomic orbitals. Each orbital is shown as both an electron probability density plot and a contour plot above its wavefunction and probability density function. The 1s orbital has zero radial nodes. The 2s orbital has one radial node where its wavefunction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

Boundary surfaces

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

? Exercise 2.2.2.1

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

Answer

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

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

s-orbitals:

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

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

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

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

p-orbitals

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

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

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

d-orbitals

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

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

f-orbital

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

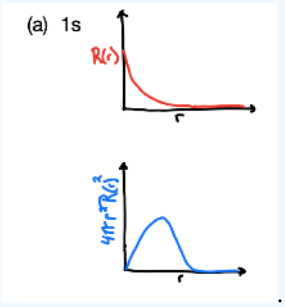
? Exercise 2.2.2.1

Draw a rough plot of the following:

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

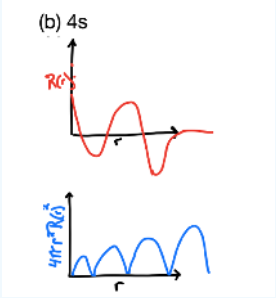
Answer, 1s

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



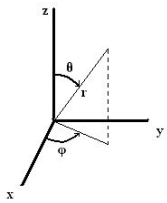
Answer, 4s

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



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

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

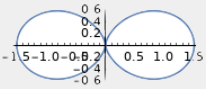
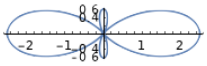
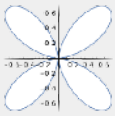
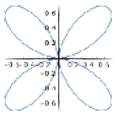


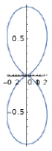
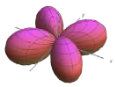
$$Y_{l,m_l}(\theta,\phi)=\left(\frac{1}{4\pi}\right)^{1/2} y\,(\theta,\phi)$$

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

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

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

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

subshell	m_l (orbital)	θ	ϕ	Plots of θ^2	orbital shapes
$l = 2$, d	$m_l = -2$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i2\phi}$		

Angular nodes

Angular nodes exist where $(Y_{l,m_l}(\theta,\phi))^2 = 0$. These nodes are planar in shape, and they depend on the value of l. The number of angular nodes in any orbital is equal to l. This means that s-orbitals ($l = 0$) have zero angular nodes, p-orbitals ($l = 1$) have one angular node, d-orbitals ($l = 2$) have two angular nodes, and so on. Planar nodes can be flat planes (like the nodes in all p orbitals) or they can have a conical shape, like the two angular nodes in the d_{Z^2} orbital. Angular nodes in some p and d orbitals are shown in Figure 2.2.2.4

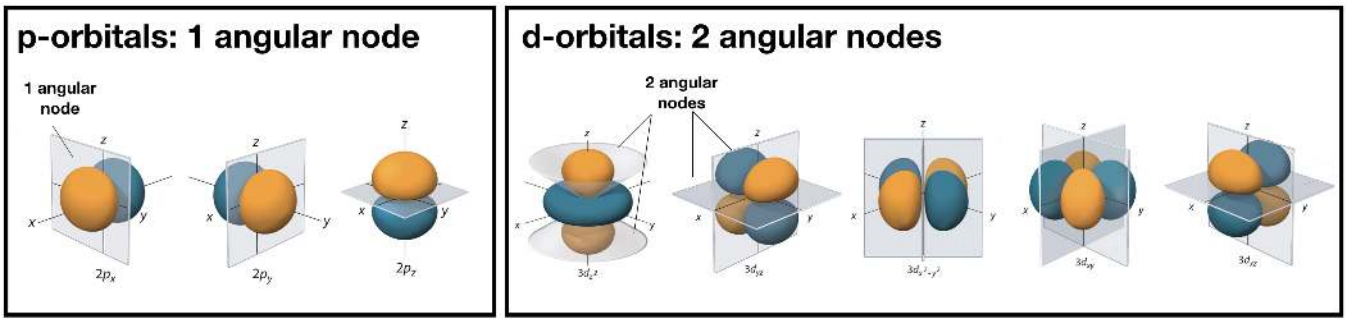
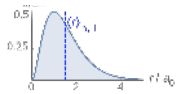
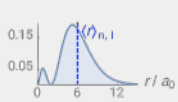
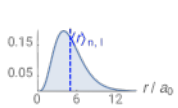
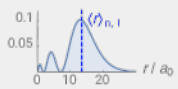
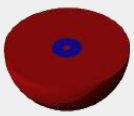


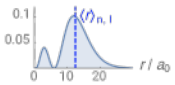
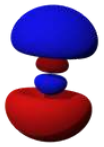
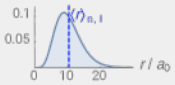
Figure 2.2.2.4: The angular nodes in p-orbitals and d-orbitals are shown. Every p orbital has one angular node, and every d orbital has two angular nodes. The number of angular nodes in any orbital is equal to the value of the quantum number, l. (CC BY-NC-SA; anonymous by request)

Atomic Orbitals

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

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

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

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

This page titled 2.2.2: Quantum Numbers and Atomic Wave Functions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.2.2: Quantum Numbers and Atomic Wave Functions** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

2.2.3: Aufbau Principle

Introduction

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

The Ground State of Hydrogenic Atoms/Ions

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

The Ground State of Multi-electron Atoms/Ions

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

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

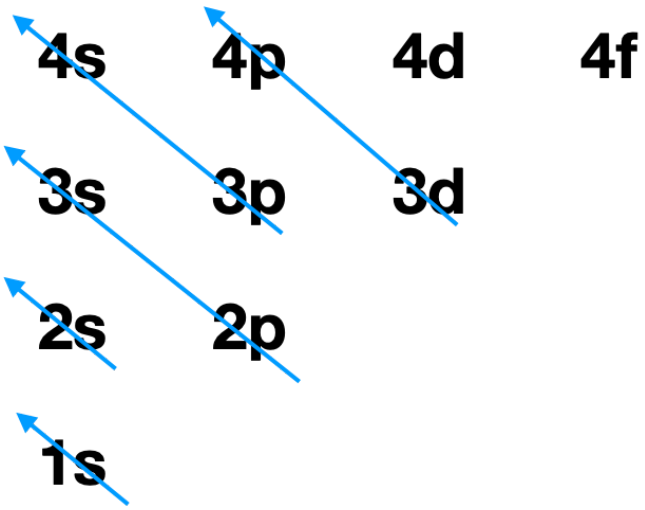


Figure 2.2.3.1. The order of filling of ground state electron orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc... (CC-BY-NC-SA; Kathryn Haas)

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

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

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

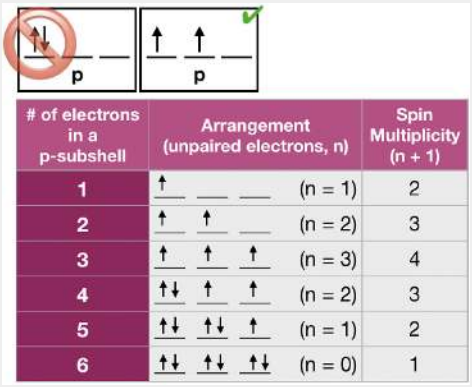


Figure 2.2.3.2 . Hund's rule is that spin multiplicity must be maximized in the ground state. (Kathryn Haas; CC-NC-BY-SA)

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

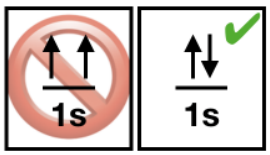


Figure 2.2.3.3 . Pauli's principle tells us that paired electrons must have opposite spin. (Kathryn Haas; CC-NC-BY-SA)

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

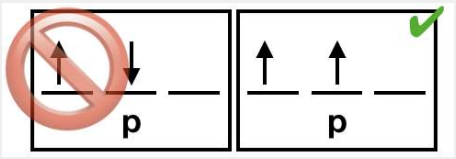


Figure 2.2.3.4. Unpaired electrons should have identical spins due to the exchange interaction. (Kathryn Haas; CC-NC-BY-SA)

Trends in Expected Electron Configuration

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

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

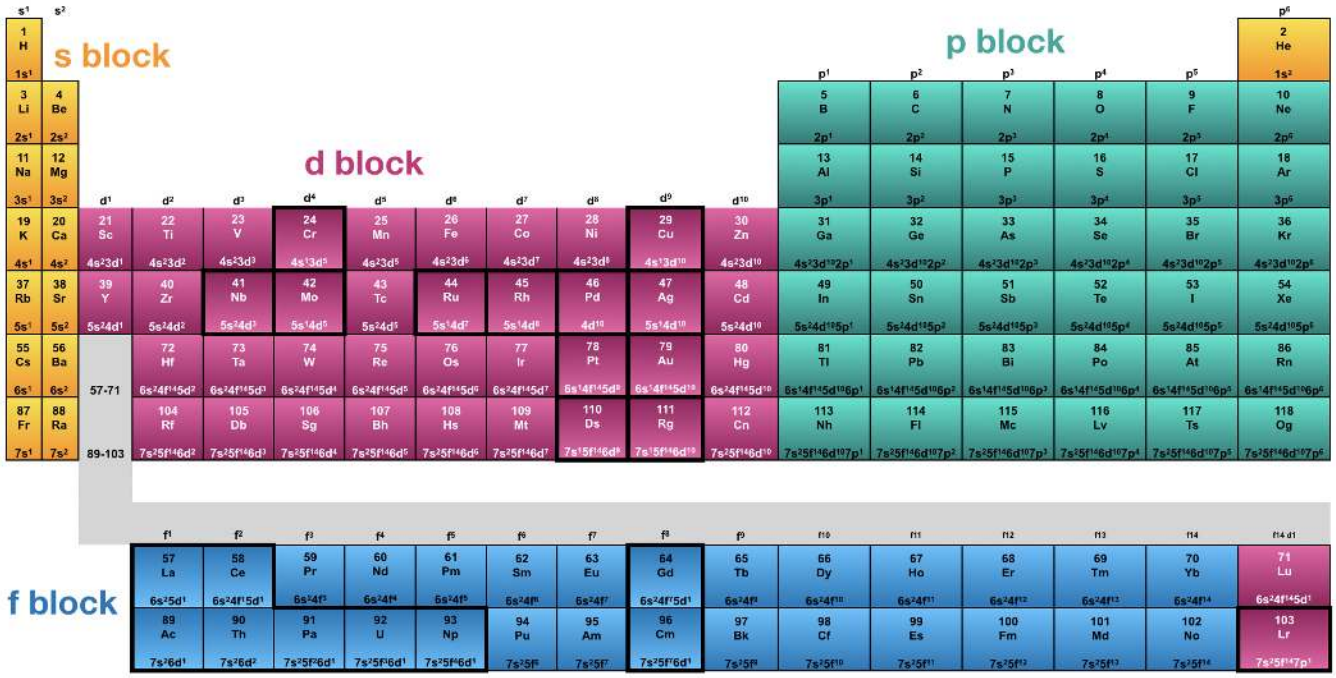


Figure 2.2.3.5. This is a depiction of the periodic table that highlights the s-, p-, d-, and f- blocks in different colors. Violations of the expected trend in electron configurations are outlined in a heavy black line. Several elements of the d block and f block violate the general trends in electron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

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

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

References

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

This page titled 2.2.3: Aufbau Principle is shared under a Public Domain license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.2.3: Aufbau Principle** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

2.2.4: Shielding

Introduction

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

Effective Nuclear Charge (Z*)

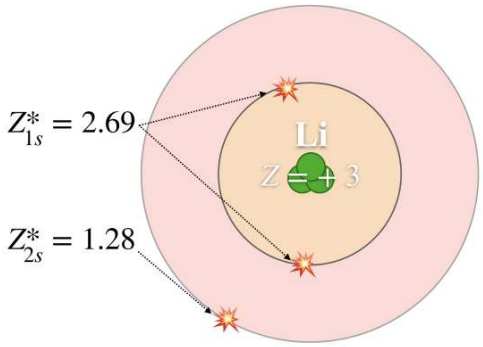


Figure 2.2.4.1. In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

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

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

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

In summary:

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

Shielding:

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

Explanation of shielding: Electrons in a multi-electron atom interact with the nucleus and all other electrons in the atom. To describe shielding, we can use a simplified model of the atom: we will choose an electron-of-interest in a multi-electron atom and

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

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

Shielding depends on electron penetration

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

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

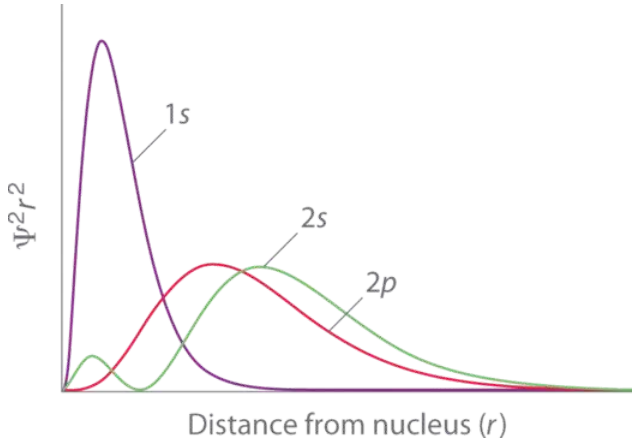


Figure 2.2.4.2. Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe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

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

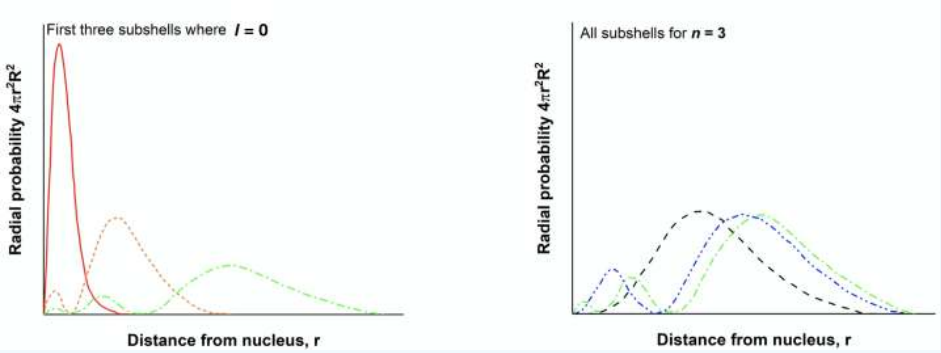
Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

s>p>d>f

Exercises

Exercises

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



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

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

Answer 1

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

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

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

Answer 2

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

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

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

Answer 3

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

Answer 4

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

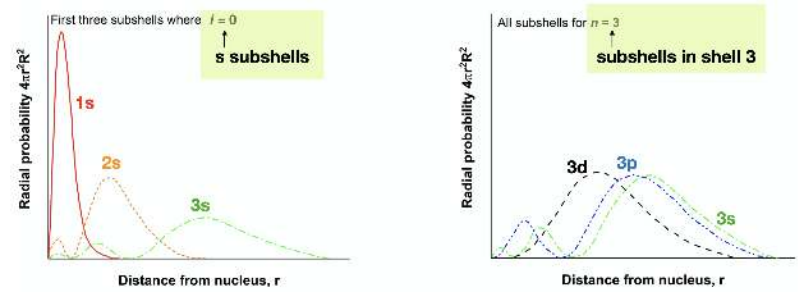
Answer 5

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

Answer 6

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

Answer 7



Answer 8

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

Answer 9

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

Slater's rules for estimating Z*

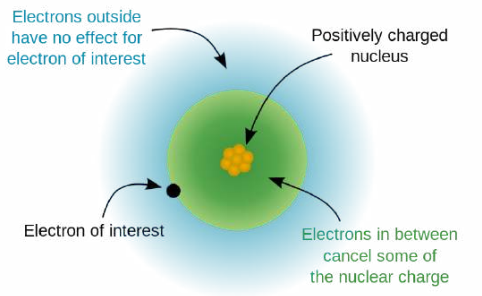


Figure 2.2.4.3. Diagram illustrating effective nuclear charge according to Slater's rules.

The Z* can be estimated using a number of different methods; probably the best known and most commonly used method is known as **Slater's Rules**. Slater developed a set of rules to estimate Z* based on how many other electrons exist in the atom and on the orbital location of the electron-of-interest. These two factors are important determinants in shielding, and they are used to calculate a **shielding constant (S)** used in Slater's formula:

$$Z* = Z - S$$

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

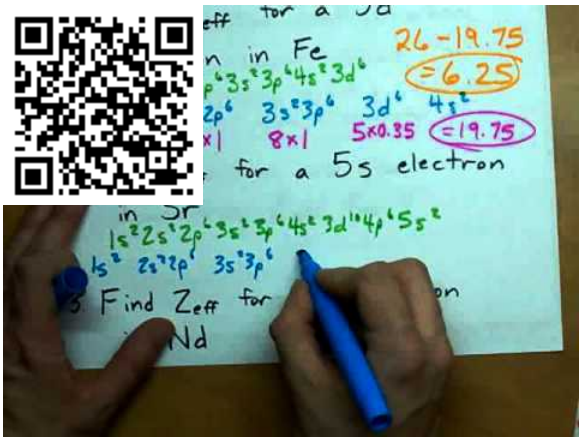
In the calculation of S, it is assumed that electrons closer to the nucleus than our electron-of-interest cancel some of the nuclear charge; those farther from the nucleus have no effect. To calculate S, all the relevant orbitals in an atom are written out in order of increasing energy, separating them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

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

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

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

A video explaining how to use Slater's Rules



Example 2.2.4.1: Fluorine, Neon, and Sodium

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

Solution

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

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

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

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

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

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

Exercise 2.2.4.1

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

Answer

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

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

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

$Z* = 30 - 21.15 = 8.85$

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

"Best" values for Z*

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

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

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

Z* modulates attraction

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

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

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

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

General Periodic Trends in Z*

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

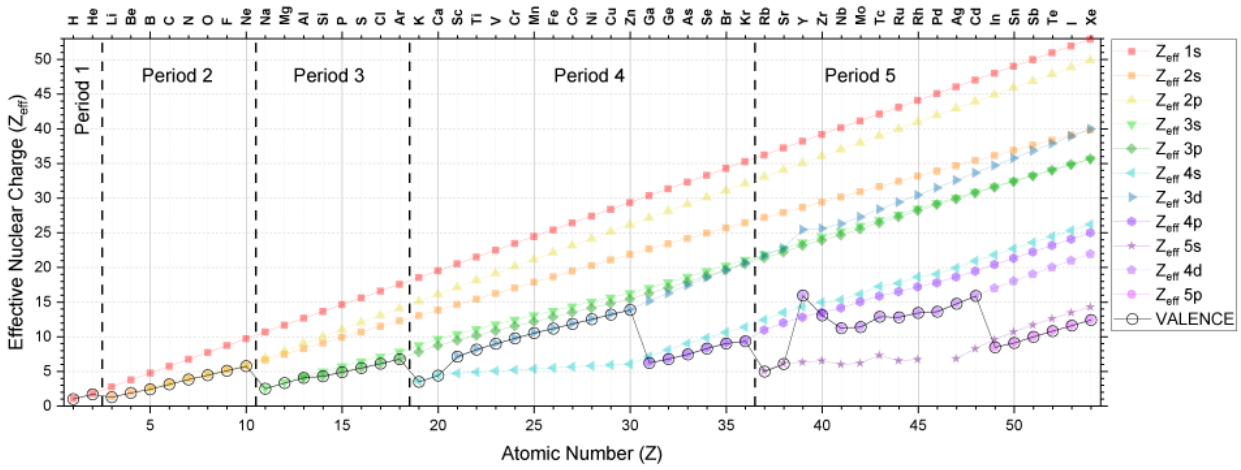


Figure 2.2.4.5: The Z* values for electrons in each subshell of the first 54 elements (H to Xe). Each subshell is plotted as a different series (see legend) and the valence shell is highlighted by a solid black line with open circles. (Kathryn Haas; CC-NC-BY-SA)

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

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

Do you notice any exceptions to this general trend?

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

For valence electrons:

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

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

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

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

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

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

Exercises

Exercise 2.2.4.2

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

Answer

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

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

References

1. Petrucci, Ralph H., William S. Harwood, F. Geoffrey Herring, and Jeffry D. Madura. General Chemistry: Principles and Modern Applications, Ninth Edition. Pearson Education Inc. Upper Saddle River, New Jersey: 2007.
2. Raymond Chang. Physical Chemistry for Biological Sciences. Sausalito, California: University Science Books, 2005
3. R. S. Mulliken, Electronic Structures of Molecules and Valence. II General Considerations, Physical Review, vol. 41, pp. 49-71 (1932)
4. Anastopoulos, Charis (2008). *Particle Or Wave: The Evolution of the Concept of Matter in Modern Physics*. Princeton University Press. pp. 236–237. ISBN 0691135126. http://books.google.com/?id=rDEvQZhpltEC&pg=PA236.

Contributors and Attributions

- Sidra Ayub (UCD), Alan Chu (UCD)
- Emily V Eames (City College of San Francisco)
- Curated or created by Kathryn Haas

2.2.4: Shielding is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **2.2.4: Shielding** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

2.3: Periodic Properties of Atoms

Introduction

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

2.3.1: Ionization energy

2.3.2: Electron Affinity

2.3.3: Covalent and Ionic Radii

References

1. Russo, Steve, and Mike Silver. Introductory Chemistry. San Francisco: Pearson, 2007.
2. Petrucci, Ralph H, et al. General Chemistry: Principles and Modern Applications. 9th Ed. New Jersey: Pearson, 2007.
3. Atkins, Peter et. al, *Physical Chemistry*, 7th Edition, 2002, W.H Freeman and Company, New York, pg. 390.
4. Alberty, Robert A. et. al, *Physical Chemistry*, 3rd Edition, 2001, John Wiley & Sons, Inc, pg. 380.
5. Kots, John C. et. al, *Chemistry & Chemical Reactivity*, 5th Edition, 2003, Thomson Learning Inc, pg. 305-309.

2.3: Periodic Properties of Atoms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.3.1: Ionization energy

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

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

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

1st, 2nd, and 3rd Ionization Energies

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

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

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

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

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

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

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

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

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

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

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

General periodic trends in electron affinity

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

- **Across a period:** As Z* increases across a period, the ionization energy of the elements generally increases from left to right. However there are breaks or variation in the trends in the following cases:
  - IE is especially low when removal of an electron creates a newly empty p subshell (examples include I_1 of B, Al, Sc)
  - IE energy is especially low where removal of an electron results in a half-filled p or d subshell (examples include I_1 of O, S)
  - IE increases more gradually across the d- and f-subshells compared to s- and p- subshells. This is because d- and f- electrons are weakly penetrating and experience especially low Z*.
- **From one period to the next:** There is an especially large decrease in IE with the start of every new period (from He to Li or from Ne to Na for example). This is consistent with the idea that IE is especially low when removal of an electron creates a newly empty s-subshell.
- **Noble gases:** The noble gases posses very high ionization energies. Note that helium has the highest ionization energy of all the elements.
- **Down a group:** Although Z* increases going down a group, there is no reliable trend in IE going down any group; in some cases IE increases going down a group, while in other cases IE decreases going down a group.

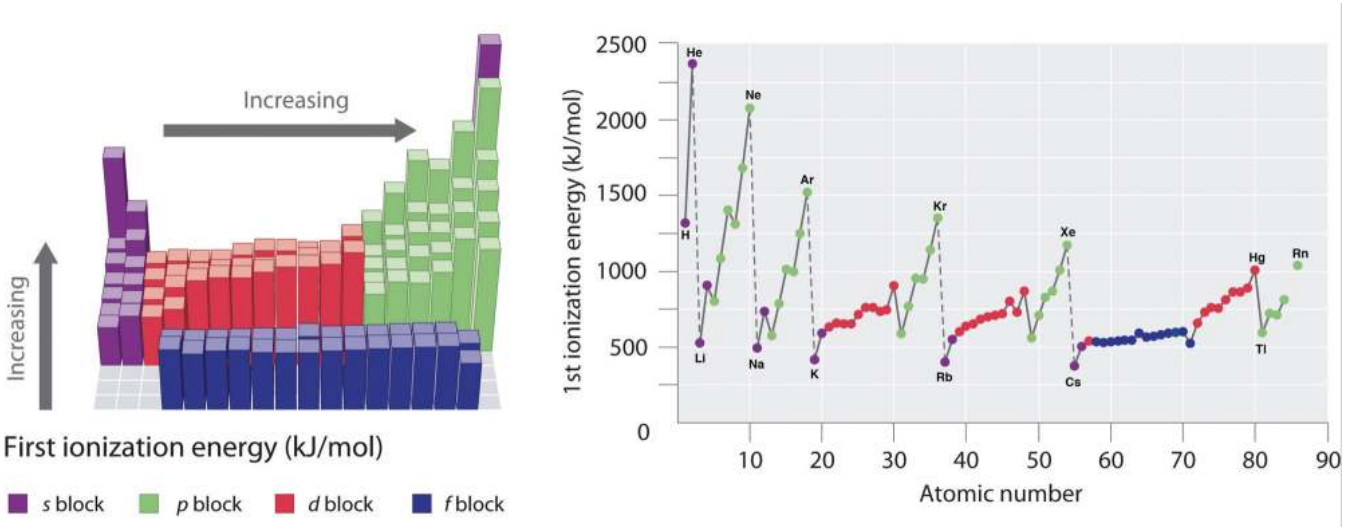


Figure 2.3.1.1: Graph showing the First Ionization Energy of the Elements. Left: ionization energies are mapped onto the periodic table, where the magnitude of ionization energy is depicted as a bar graph. Right: the first ionization energy is plotted against atomic number. In both panels the elements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

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

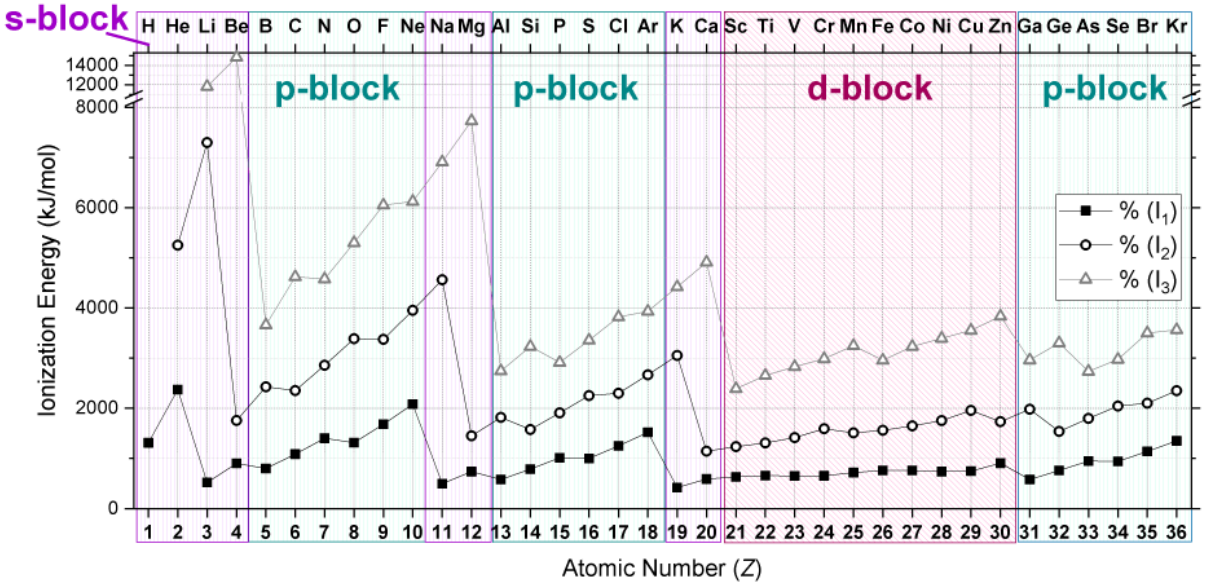


Figure 2.3.1.2. The first (I_1), second (I_2), and third (I_3) ionization energies plotted for elements with Z = 1 to 36 (H to Kr). The position of each element in its atomic form is indicated as s- p- or d-block. (CC-BY-NC-SA; Kathryn Haas)

2.3.1: Ionization energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **2.3.1: Ionization energy** by Bingyao Zheng, Emily Nguyen, Kathryn Haas, Swetha Ramireddy is licensed CC BY-NC-SA 3.0.

2.3.2: Electron Affinity

Definitions of Electron Affinity

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

Definition: Electron Affinity defined as removal of an electron

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

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

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

Definition: Electron Affinity defined as addition of an electron

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

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

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

Trends in Electron Affinity

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

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

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

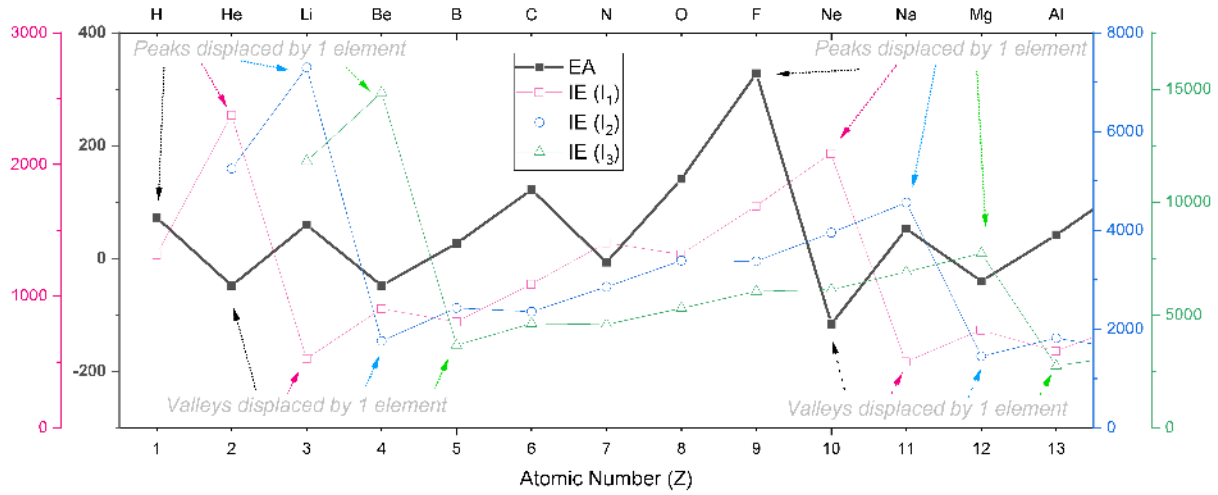


Figure 2.3.2.1. A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (I_1), second (I_2), and third (I_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys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

Sources

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

2.3.2: Electron Affinity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **2.3.2: Electron Affinity** by Kathryn Haas is licensed CC BY-NC 4.0.

2.3.3: Covalent and Ionic Radii

Measurement of Radius

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

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

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

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

Trends in Atomic Radius

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

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

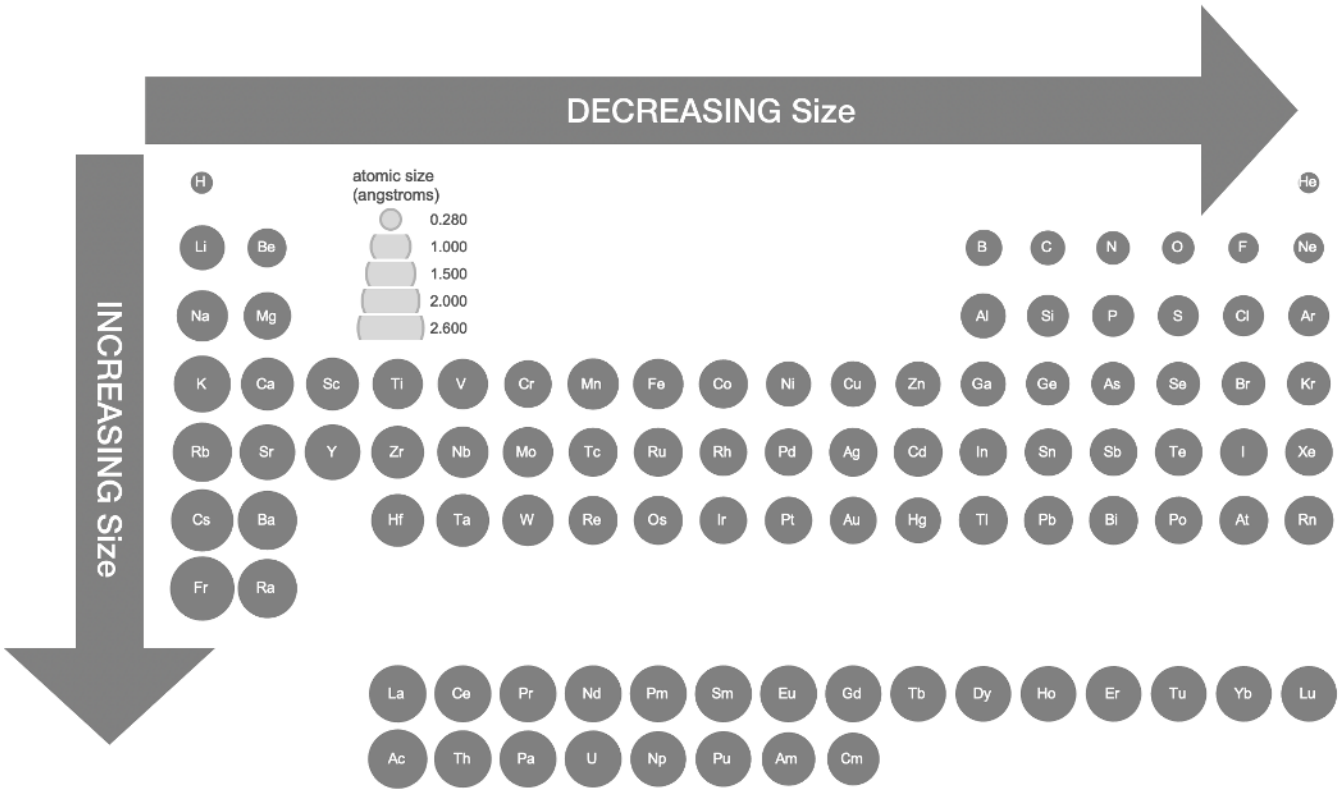


Figure 2.3.3.1. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.*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

Trends in Ionic Radius

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

Cations

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

Anions

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

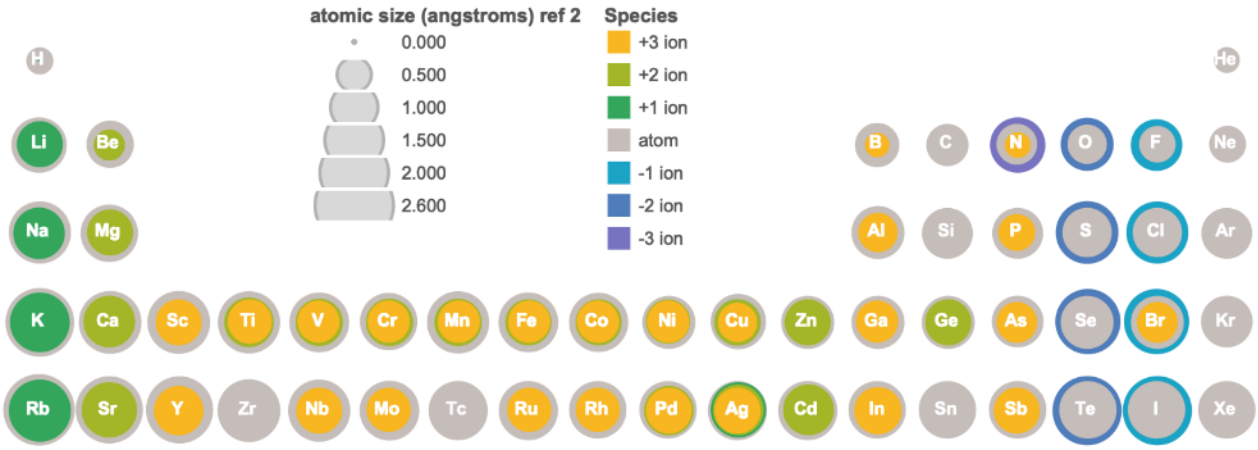


Figure 2.3.3.2. This figure illustrates relative size of atoms and ions of the first four periods of the periodic table. Atomic radius is indicated by grey circles. Radius of cations is shown in green (+1), lime (+2), and yellow (+3) circles. Radius of anions are shown as aqua (-1), blue (-2), and purple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

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

Figure 2.3.3.3.

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

References

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

2.3.3: Covalent and Ionic Radii is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **2.3.3: Covalent and Ionic Radii** by Bingyao Zheng, Emily Nguyen, Kathryn Haas, Swetha Ramireddy is licensed CC BY-NC 4.0.

2.4: Problems (do we want this here?)

Example Exercises

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

Exercises

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

Answer 1

Helium (He).

Answer 2

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

Answer 3

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

Answer 4

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

Answer 5

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

Answer 6

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

2.4: Problems (do we want this here?) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3: Simple Bonding Theory

3.1: Lewis Electron-Dot Diagrams

3.1.1: Resonance

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

3.1.3: Formal Charge

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

3.2: Valence Shell Electron-Pair Repulsion

3.2.1: Lone Pair Repulsion

3.2.2: Multiple Bonds

3.2.3: Electronegativity and Atomic Size Effects

3.2.4: Ligand Close Packing

3.3: Molecular Polarity

3.4: Hydrogen Bonding

3: Simple Bonding Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.1: Lewis Electron-Dot Diagrams

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

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

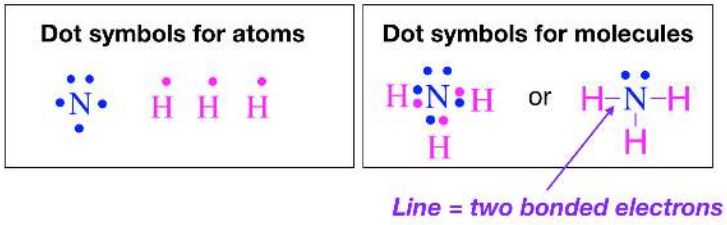


Figure 3.1.1: Lewis dot structure of atoms comprising ammonia and the dot structure of the molecule. (Kathryn Haas; CC-NC-BY-SA)

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

Common violations of the octet rule

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

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

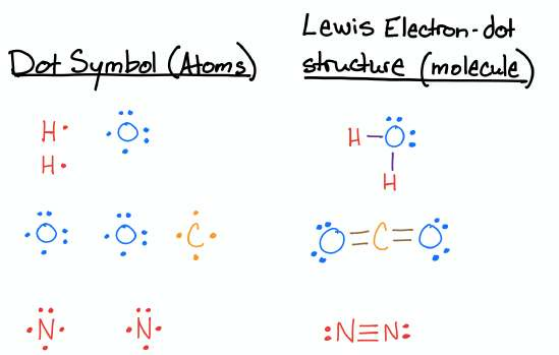
Electrons in valence (octet) = total unbonded electrons on the atom + total bonded electrons (2 electrons per bond)

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

Exercise 3.1.1

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

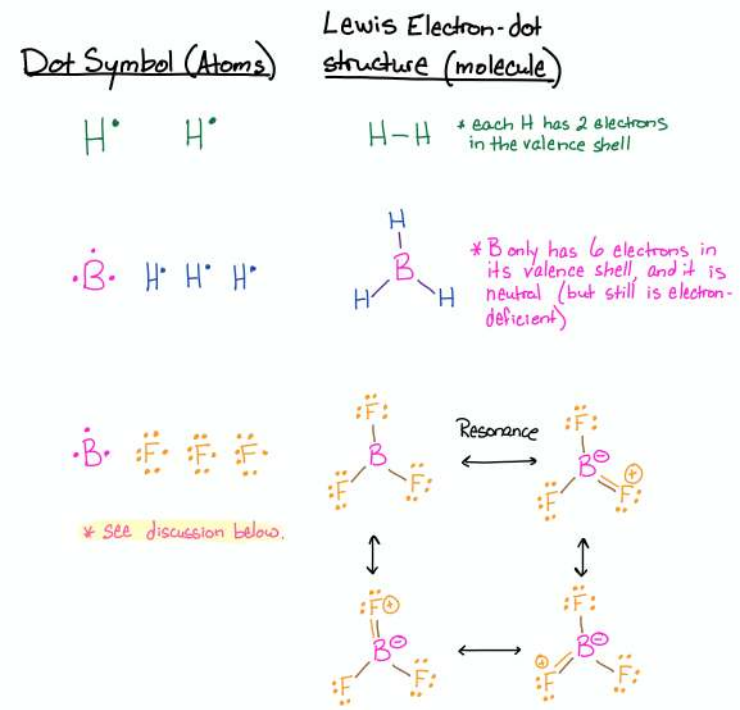
Answer



Exercise 3.1.2

Draw the Lewis structures for H_2, BH_3 and BF_3.

Answer



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

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

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

Outside Links

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

This page titled 3.1: Lewis Electron-Dot Diagrams is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.1: Lewis Electron-Dot Diagrams** by Kathryn Haas is licensed CC BY-NC 4.0.
- **2.1B: Lewis Structures** by Andrew Iskandar is licensed CC BY 4.0.

3.1.1: Resonance

Learning Objectives

- To understand the concept of resonance.

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

Sometimes one Lewis Structure is not Enough

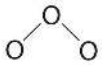
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula.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

Ozone (O_3)

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

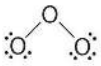
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

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



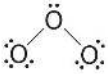
with 14 electrons left over.

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

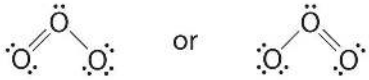


and have 2 electrons left over.

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



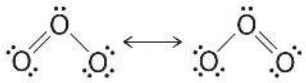
6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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

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

different resonance structures of a compound:



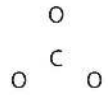
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

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

The Carbonate (CO_3^{2-}) Ion

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

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

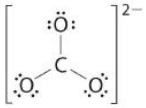


The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

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

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

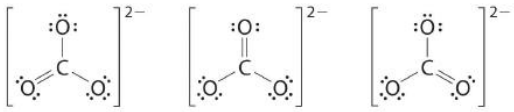
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



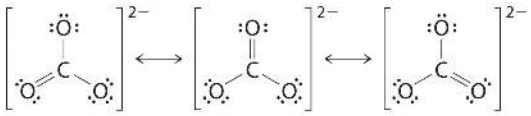
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

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



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



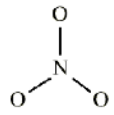
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

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

The Nitrate (NO_3^-) ion

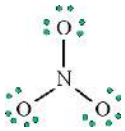
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

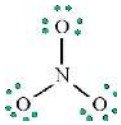


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

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

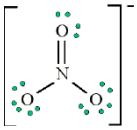


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

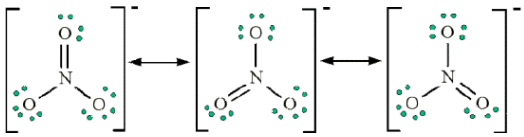
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



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

Example 3.1.1.1: Benzene

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

Given: molecular formula and molecular geometry

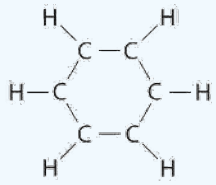
Asked for: resonance structures

Strategy:

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

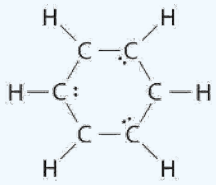
Solution:

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



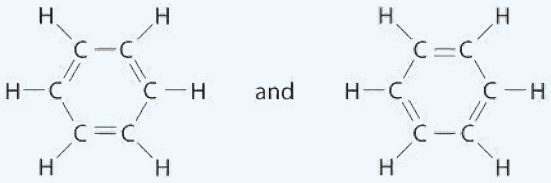
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

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

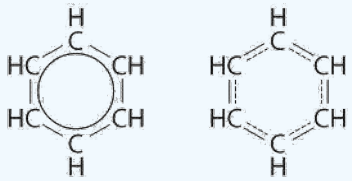


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double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

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



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



Benzene

? Exercise 3.1.1.1: Nitrite Ion

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

Answer

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

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

Warning

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

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

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance

structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

3.1.1: Resonance is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **8.6: Resonance Structures** is licensed CC BY-NC-SA 3.0.

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

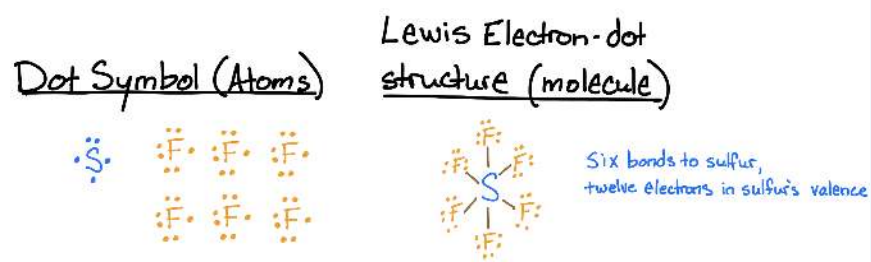
The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6. Even elements in the third and fourth row are known to follow this rule *sometimes*, but not always. In larger atoms, where $n \geq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

? Exercise 3.1.2.1

Draw the Lewis structures for sulfur hexafluoride (SF_6).

Answer

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

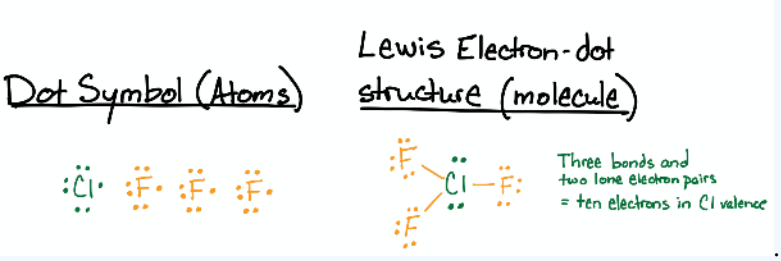


? Exercise 3.1.2.1

Draw the Lewis structure for chlorine trifluoride (ClF_3.

Answer

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



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

For main group molecules, chemists (like Pauling) thought a long time ago that hypervalence is due to expanded s^2p^6 octets. The consensus is now clear that d orbitals are NOT involved in bonding in molecules like SF_6 any more than they are in SF_4 and SF_2. In all three cases, there is a small and roughly identical participation of d-orbitals in the wavefunctions. This has been established in

both MO and VB theory. However, using hybrid orbitals with d-orbital contributions equips us with a language which can pragmatically describe the geometries of highly coordinated substances.

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

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

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

This page titled 3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms) is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)** by Kathryn Haas is licensed CC BY-NC 4.0.

3.1.3: Formal Charge

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

Calculating Formal Charges

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

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

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

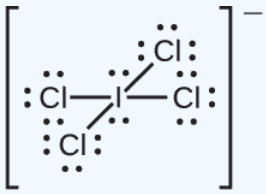
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

✔ Calculating Formal Charge from Lewis Structures

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

Solution

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



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

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

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

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

? Exercise 3.1.3.1

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

Answer

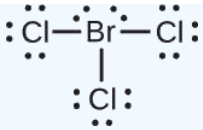
C −1, O +1

✔ Example: Calculating Formal Charge from Lewis Structures

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

Solution

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



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

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

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

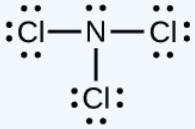
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 3.1.3.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



3.1.3: Formal Charge is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

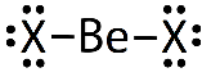
- **7.5: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

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

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

Beryllium

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



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

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

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

BeF_2

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

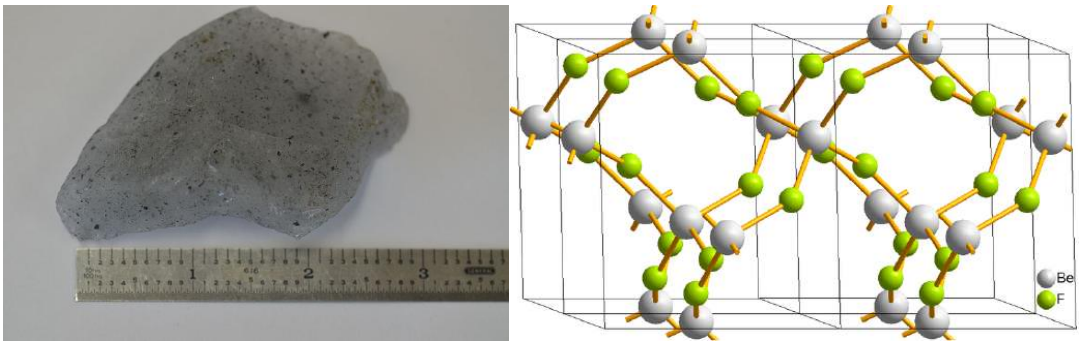


Figure 3.1.4.1: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

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

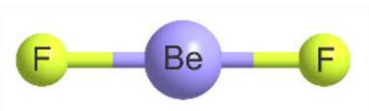


Figure 3.1.4.2: Geometries of BeF_2. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$BeCl_2$

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

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

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

Prediction based on Lewis structures:

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

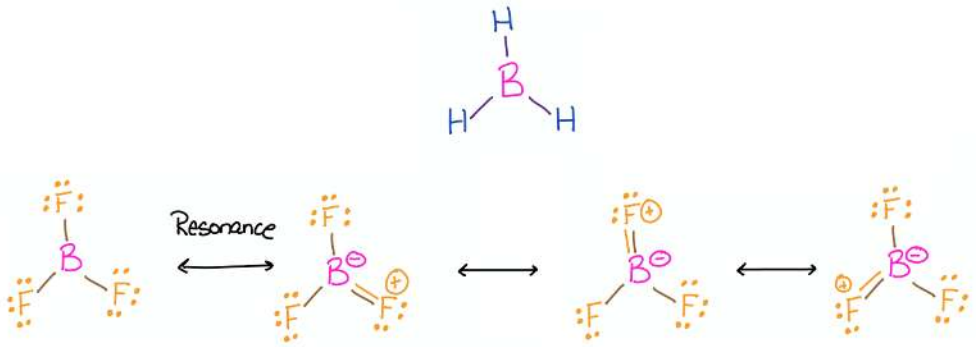


Figure 3.1.4.2: Lewis structures of BH_3 and BF_3. (Kathryn Haas; CC-NC-BY-SA)

Boron trihalides

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

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

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

Boron trihydride (BH_3 is really B_2H_6)

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

This page titled 3.1.4: Lewis fails to predict unusual cases- Boron and Beryllium is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium** by Kathryn Haas is licensed CC BY-NC 4.0.

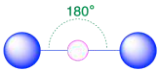
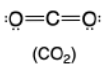
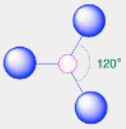
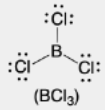
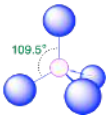
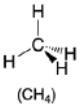
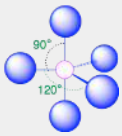
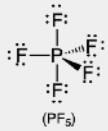
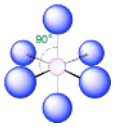
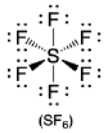
3.2: Valence Shell Electron-Pair Repulsion

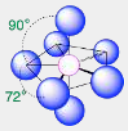
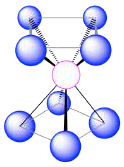
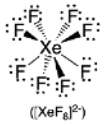
Introduction to VSEPR

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

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

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

Groups around central atom ($m + n$)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
2	linear		180°	 (CO_2)
3	trigonal plane		120°	 (BCl_3)
4	tetrahedron		109.5°	 (CH_4)
5	trigonal bipyramid		90° and 120°	 (PF_5)
6	octahedron		90°	 (SF_6)

Groups around central atom (m + n)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
7	pentagonal bipyramid		90° and 72°	
8	square antiprism		70.5°, 99.6° and 109.5°	

Practice

VSEPR to predict Molecular Geometry

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

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

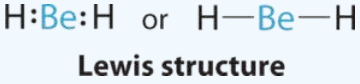
Use the procedure above to complete the exercises below

Exercise 3.2.1

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

Answer BeH_2

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



Lewis structure

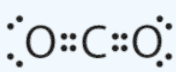
2. There are two groups around the central atom, and both groups are single bonds. Thus BeH_2 is designated as AX_2.

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

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

Answer CO_2

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



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

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

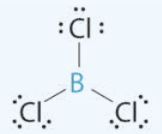
4. VSEPR only recognizes groups around the *central* atom (the carbon). Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonded groups on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Table 3.2.1). The structure of CO_2 is shown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

? Exercise 3.2.2

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

Answer BCl_3

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



Lewis structure

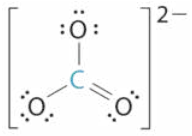
2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

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

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

Answer CO_3^{2-}

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

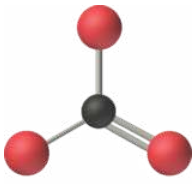


Lewis structure

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

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

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


Molecular geometry
(trigonal planar)

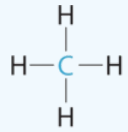
In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

? Exercise 3.2.3

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

Answer CH_4

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

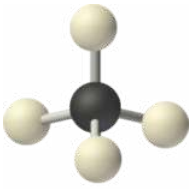


Lewis structure

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

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

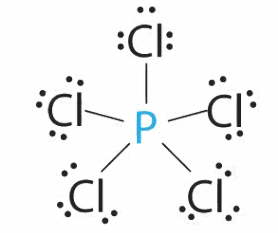
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table 3.2.1).



Molecular geometry (tetrahedral)

Answer PCl_5

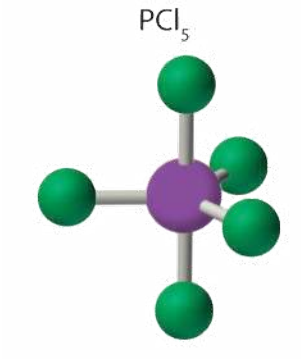
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



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

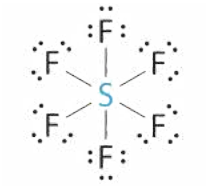
3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table 3.2.1).

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



Answer SF_6

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



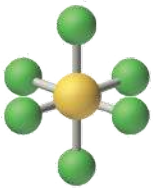
Lewis structure

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

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

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

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



Molecular geometry
(octahedral)

This page titled 3.2: Valence Shell Electron-Pair Repulsion is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.2: Valence Shell Electron-Pair Repulsion** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

3.2.1: Lone Pair Repulsion

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

Lone pairs have stronger repulsive forces than bonded groups.

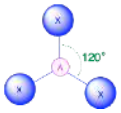
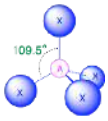
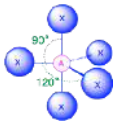
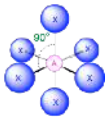
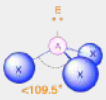
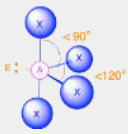
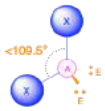
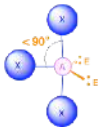
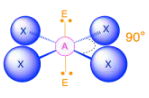
When one or more of the groups is a lone pair of electrons (non-bonded electrons), the experimentally-observed geometry around an atom is slightly different than in the case where all groups are bonds. The actual bond angles are similar, but not exactly the same, as those predicted based on the *total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

Trend in bond angles:

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

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

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

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

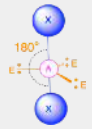
	Electron Groups (*m* + *n*)				
	2 (steric number = 2)	**3** (steric number = 3)	**4** (steric number = 4)	**5** (steric number = 5)	**6** (steric number = 6)
3 lone pairs AX_mE_3				 AX_2E_3, linear 180°	

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

Two Electron Groups (m + n = 2)

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

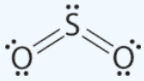
Three Electron Groups (m + n = 3)

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

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

✔ AX_2E Molecules: Example SO_2

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



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

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

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

Four Electron Groups (m + n = 4)

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

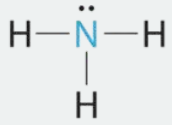
- When all electron groups are bonds (m=4 or AX_4), the molecular geometry is a ***tetrahedron*** with bond angles of **109.5°**.

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

AX_3E Molecules: Example NH_3

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

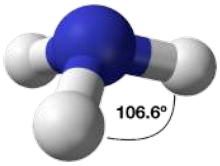
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

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

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



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

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

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

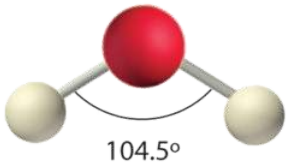
AX_2E_2 Molecules: Example H_2O

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

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

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

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



Five Electron Groups (m + n = 5)

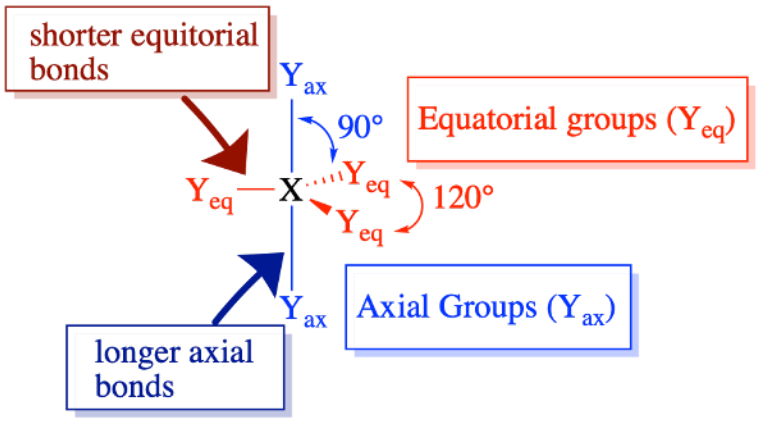


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

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

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

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

AX_4E Molecules: SF_4

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

Lewis structure

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

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

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

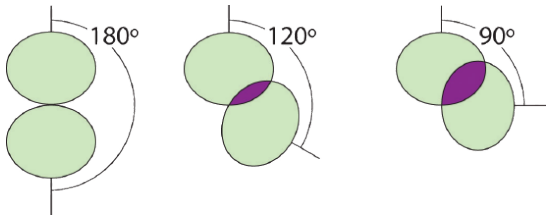
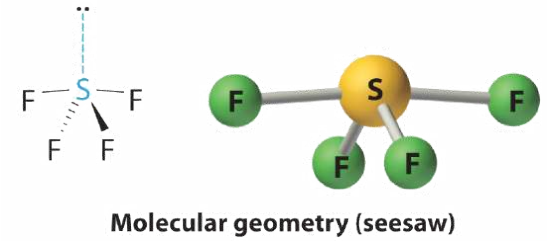


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

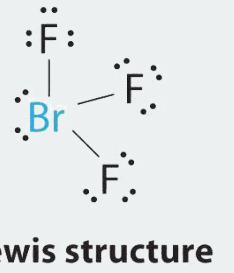
At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

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



AX_3E_2 Molecules: BrF_3

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



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

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

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

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

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

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

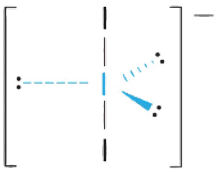
Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

AX_2E_3 Molecules: I_3^-

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

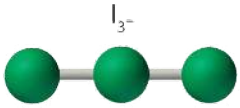
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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



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

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



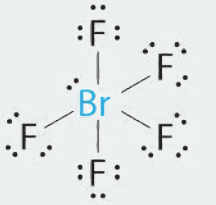
Six Electron Groups (m + n = 6)

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

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

AX_5E Molecules: BrF_5

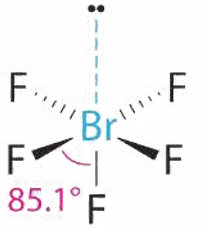
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

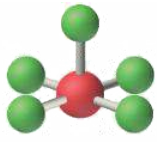
With its expanded valence, this species is an exception to the octet rule.

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



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

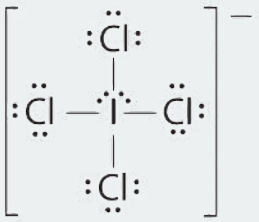
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



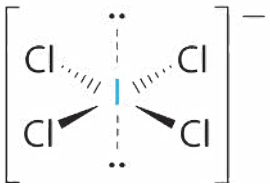
Molecular geometry
(square pyramidal)

AX_4E_2 Molecules: ICl_4^-

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

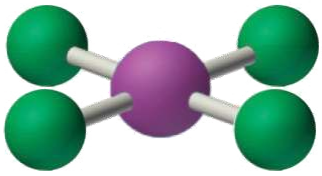


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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

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



Summary

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

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

Example Excercises

✔ Example 3.2.1.1

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

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

Given: two chemical species

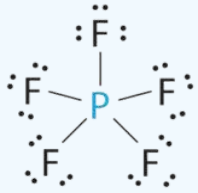
Asked for: molecular geometry

Strategy:

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

Solution:

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

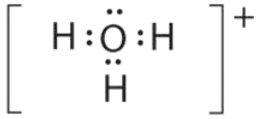


B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

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

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

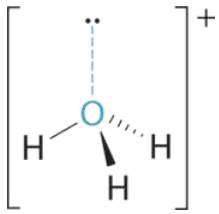
- **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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

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

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



Exercise 3.2.1.1

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

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

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 3.2.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example3.2.1.1.

Solution:

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

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

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

(a) (b) (c)

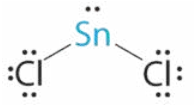
Interactions			
90 LP–LP	0	2	2

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the

central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

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

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



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

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

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

? Exercise 3.2.1.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

This page titled 3.2.1: Lone Pair Repulsion is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.2.1: Lone Pair Repulsion** by Kathryn Haas has no license indicated.
- **3.2.2: Multiple Bonds** by Kathryn Haas has no license indicated.

3.2.2: Multiple Bonds

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

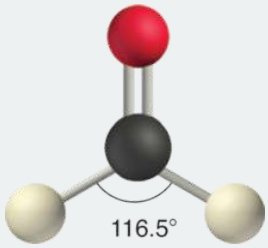
Double and triple bonds are more repulsive than single bonds

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

Examples 3.2.2.1

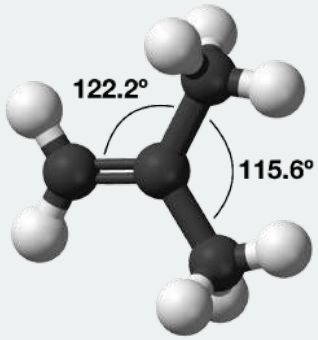
CH_2O

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



2-methybutene

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



Atoms with both lone pairs and multiple bonds

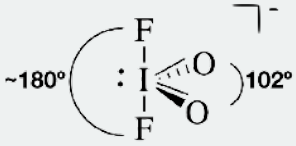
In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

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

Examples3.2.2.1

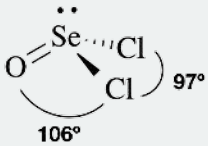
$IO_2F_2^-$

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



$SeOCl_2$

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



Practice

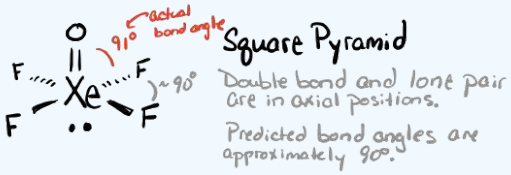
? Exercise 3.2.2.1

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

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

Answer a

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

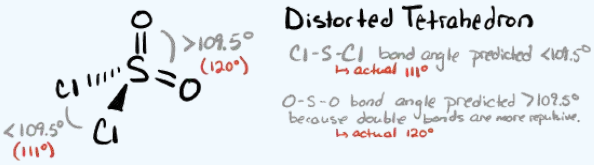


Answer b

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

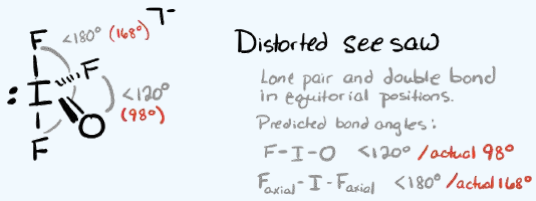
Answer c

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



Answer d

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



References

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

This page titled 3.2.2: Multiple Bonds is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.2.2: Multiple Bonds** by Kathryn Haas has no license indicated.

3.2.3: Electronegativity and Atomic Size Effects

Introduction

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

Definitions of Electronegativity

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

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

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

Periodic table of electronegativity using the Pauling scale

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

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

* Lanthanoids	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
** Actinoids	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

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

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

Scale Developer	Year first described	Characteristics
Linus Pauling[1]	1932	Based on bond energies
Robert S. Mulliken[5,6]	1934	Based on valence electron properties of atoms (electron affinity and ionization energy)
Louis Allred & Eugene G. Rochow[7]	1958	Based on electrostatic force (effective nuclear charge)

Scale Developer	Year first described	Characteristics
Robert T. Sanderson[8]	1983	Based on atomic electron density
Ralph G. Pearson[9]	1985	Related to Hard-Soft Acid-Based theory
Leland C. Allen, Joseph Mann, Terry L. Meek[10,11,12]	1989, 2000	Average ionization energies of valence shell electrons, configuration energies (CE) $$\mathrm{CE} = \frac{n\varepsilon_s + m\varepsilon_p}{n+m}$$ $n =$ number of s electrons $m =$ number of p electrons $\varepsilon_s, \varepsilon_p =$ experimental 1-electron s and p ener

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

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

Electronegativity and Size Influence Bond Angles

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

What trends can you identify?

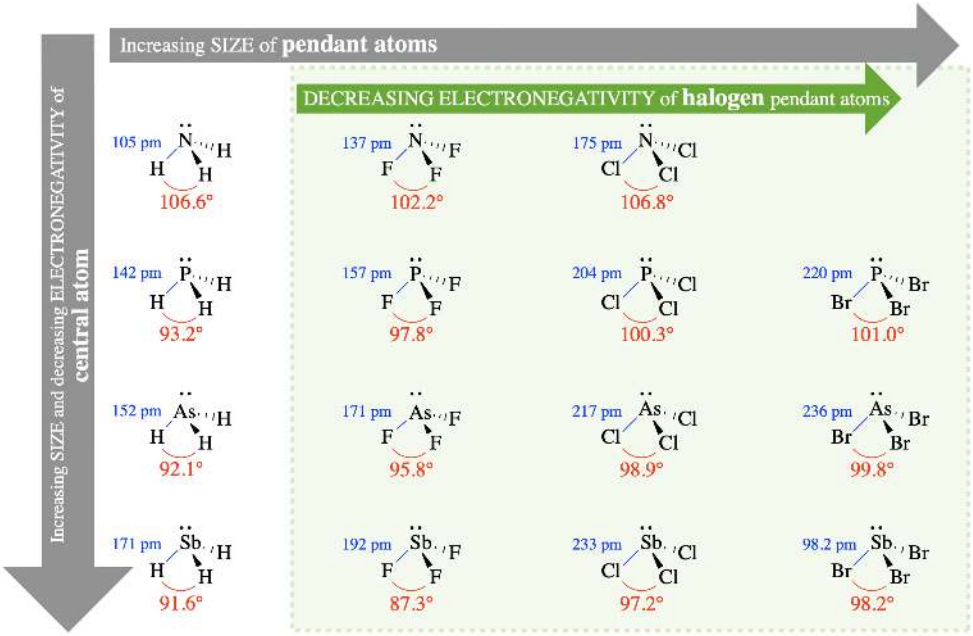


Figure 3.2.3.2: Several molecules with trigonal pyramidal electronic geometry are shown arranged according to size of the central atom (increasing size of central atom from top to bottom) and pendant atom (increasing size of pendant atoms from left to right). Bond angles and bond lengths are indicated.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

Trends in Size

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

Size of the central atom

Examine the relationship between the size of the central atom and the bond angles in Figure 3.2.3.2 (go down any column in the figure). For example, compare NH_3, PH_3, AsH_3, and SbH_3, with bond angles 106.6°, 93.2°, 92.1°, and 91.6°, respectively. In this series, the size of the central atom increases from N to Sb while the size of the pendant atom (hydrogen) remains constant. *As the size of the central atom increases, the bond angles decrease; thus, we observe a negative relationship between size of the central atom and the bond angle in these molecules*. This relationship is explained by sterics. As the central atom increases in size, the bond lengths also increase and the pendant atoms are farther from each other in space. In VSEPR theory, this will reduce steric interactions between the pendant groups. Since the lone pair on these molecules is more repulsive than bonded groups, the decrease in steric interactions between bonded groups results in a decrease in bond angles.

Size of the pendant atoms (or groups)

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

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

Trends in Electronegativity

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

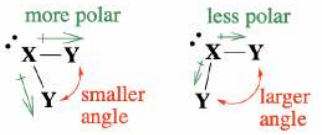


Figure 3.2.3.3. When electron pairs are distributed away from the central atom, repulsions are decreased, allowing smaller bond angles. (Kathryn Haas; CC-NC-BY-SA)

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

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

Exercise 3.2.3.1

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

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

Answer (a)

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

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

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

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

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

Answer (b)

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

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

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

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

Answer (c)

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

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

- *Size:* The size of pendant atoms increases in the order H < F < Cl where H is smallest and Cl is largest. Prediction of bond angles based on size alone would lead to the predicted order of increasing bond angle $H_2O < OF_2 < OCl_2$.

- *Electronegativity*: The electronegativity decreases in the order F > Cl > H where F has the greatest electronegativity and H has the least. Since we expect the most electronegative pendant atoms to have the smallest bond angles, prediction based on electronegativity alone would lead to the predicted order of increasing bond angle $OF_2 < OCl_2 < H_2O$.

The points above illustrate how the two different arguments would lead to different predictions about the trend in bond angle. This makes it difficult to predict the actual order of increasing bond angle. However, we saw above in the example of NH_3 vs NF_3 that electronegativity is more important than size; yet in the case of NH_3 vs NCl_3, the much larger size of the pendant atom is more important. If we apply this lesson to the current problem, we might predict the order $OF_2 < H_2O < OCl_2$, and in fact this more nuanced prediction, based on a similar case, matches the actual order for measured bond angles: OF_2 (103.3°) < H_2O (104.5°) < OCl_2 (110.9°).

Group Electronegativities

You probably heard the terms "electron donating group" and "electron withdrawing group" from your coursework in Organic Chemistry. For example, the acid trifluoroacetic acid (TFA) is more acidic than acetic acid due to the electron withdrawing effects of the CF_3 group compared to CH_3. CF_3 is an electron withdrawing group, while CH_3 is an electron donating group. In other words, CF_3 is more electronegative than CH_3.

The electron withdrawing ability (electronegativity) of groups can be estimated and compared, just as they are with atoms. Although there is no one scale that is used for group electronegativities, and published values even for the same groups vary widely, there are reliable trends within similar groups. The same size and electronegativity factors discussed above that affect bond angles for *pendant atoms*, also can be used to rationalize distorted bond angles for *pendant groups* around a central atom.

? Exercise 3.2.3.2

Consider the relative electronegativities and sizes of the pendant atoms/groups in the following examples. Is the trend in bond angles what you would expect from the relative group electronegativities and relative sizes? What, if any, is the more dominant factor in determining the trend?

a. $N(CH_3)_3$ has an C-N-C bond angle of 110.9°, while $N(CF_3)_3$ has a bond angle of 117.9°.
b. The X-S-X bond angles in molecules of the form $SO_2(X)_2$ are: $SO_2(OH)_2$ 101.3°; $SO_2(CF_3)_2$ 102.0°; $SO_2(CH_3)_2$ 102.6°.

Answer (a)

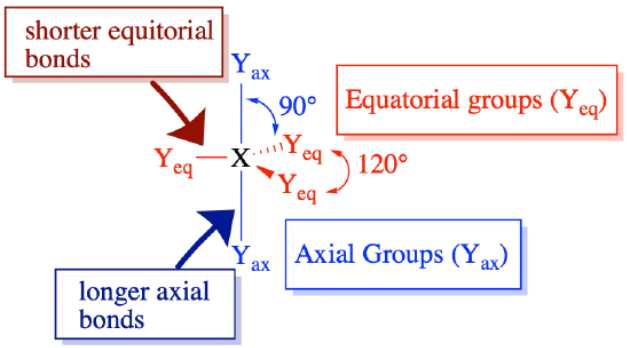
Add texts here. Do not delete this text first.

Answer (b)

Add texts here. Do not delete this text first.

Special case of electronegativity and size in steric number 5 (trigonal bypyramid)

Molecules with steric number 5 are interesting because they posses two different types of positions (equatorial and axial). These positions have unique bond angles and bond lengths. Pendant atoms/groups have different preferences for the axial and equatorial positions that depend somewhat on their electronegativity.



Molecules with steric number 5 possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas)

In a previous section, we discussed the preference of lone pairs and multiple bonds for the equatorial positions in trigonal bipyramidal molecules. VSEPR theory rationalizes this by assuming that lone pairs and multiple bonds are more repulsive than the electron pairs in single bonds. Equatorial positions are less crowded (with only two closest neighbors at 90°, and two farther neighbors at 120°) compared to axial positions (with three closest neighbors at 90°), thus the more repulsive groups prefer the less crowded equatorial positions.

Pendant groups that are more electronegative result in weaker electron pair repulsion around the central atom, while groups that are less electronegative result in stronger electron-pair repulsion around the central atom (as described above). The result for steric number 5: **bonding pairs to *less electronegative elements* are *more repulsive*, and *generally prefer equatorial* positions.** Still, lone pairs and multiple bonds are more repulsive than single bonds and would show a stronger preference for equatorial positions.

Examples and Nuances

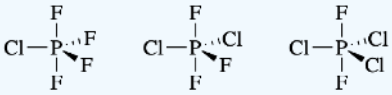
? Exercise 3.2.3.3

Some examples of molecule that demonstrate the equatorial preference of less electronegative groups are below. Predict (draw) their structures.

a. PF_4Cl, PF_3Cl_2, and PF_2Cl_3
b. $PF_4(CH_3)$ $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$

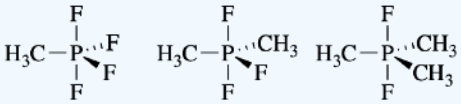
Answer (a)

Cl is less electronegative than F; thus we expect Cl to have stronger preference for the equatorial positions.

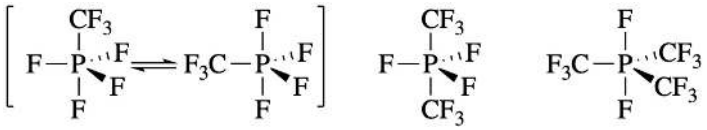


Answer (b)

CH_3, an electron donating group, is less electronegative than F. We expect CH_3 to have a stronger preference for the equatorial positions.



In the exercise above, the structures can be explained by the electronegativity of the pendant groups; less electronegative groups prefer the equatorial positions. There are other similar molecules for which explanations (or predictions) are difficult. For example, the series of molecules below seems to have completely random placement of F and CF_3 groups. **These structures could not be predicted based on VSEPR theory.** It seems that in this case, the more symmetrical arrangements of pendant groups is preferred.



References and resources

1. Pauling, L. (1932). "The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms". *J. Am. Chem. Soc.* **54**(9): 3570–3582. doi:10.1021/ja01348a011.
2. Housecroft, Catherine E. et. al. "Inorganic Chemistry" 3rd Edition. Pearson Education Limited 2008. Chapter 2.5 "Electronegativity Values" pgs. 42-44
3. International Union of Pure and Applied Chemistry. "Electronegativity". goldbook.iupac.org/E01990.html.
4. Pearson, R.G. *Acc. Chem. Res.* 1990, 23, 1, 1–2. https://doi.org/10.1021/ar00169a001
5. Mulliken, R. S. (1934). "A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities". *J. Chem. Phys.***2** (11): 782–793. doi:10.1063/1.1749394.
6. Mulliken, R. S. (1935). "Electronic Structures of Molecules XI. Electroaffinity, Molecular Orbitals and Dipole Moments". J. Chem. Phys. **3** (9): 573–585. doi:10.1063/1.1749731.
7. Allred, A. L.; Rochow, E. G. (1958). "A scale of electronegativity based on electrostatic force". *Journal of Inorganic and Nuclear Chemistry*. **5** (4): 264–268. doi:10.1016/0022-1902(58)80003-2

8. Sanderson, R. T. (1983). "Electronegativity and bond energy". *Journal of the American Chemical Society*. **105** (8): 2259–2261. doi:10.1021/ja00346a026
9. Pearson, R. G. (1985). "Absolute electronegativity and absolute hardness of Lewis acids and bases". J. Am. Chem. Soc. 107 (24): 6801. doi:10.1021/ja00310a009.
10. Allen, Leland C. (1989). "Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state free atoms". Journal of the American Chemical Society. 111 (25): 9003–9014. doi:10.1021/ja00207a003.
11. Mann, Joseph B.; Meek, Terry L.; Allen, Leland C. (2000). "Configuration Energies of the Main Group Elements". Journal of the American Chemical Society. 122 (12): 2780–2783. doi:10.1021/ja992866e.
12. Mann, Joseph B.; Meek, Terry L.; Knight, Eugene T.; Capitani, Joseph F.; Allen, Leland C. (2000). "Configuration energies of the d-block elements". Journal of the American Chemical Society. 122 (21): 5132–5137. doi:10.1021/ja9928677

Acknowledgment

- Matthew Salem (UC Davis) (Pauling Electronegativity)
- Introduction to Inorganic Chemistry Wikibook (https://chem.libretexts.org/Bookshel..._Bond_Strength)
- Curated or created by Kathryn Haas

This page titled 3.2.3: Electronegativity and Atomic Size Effects is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.2.3: Electronegativity and Atomic Size Effects** by Kathryn Haas has no license indicated.

3.2.4: Ligand Close Packing

Introduction

Ligand Close Packing (LCP) theory is complimentary to VSEPR, except that LCP focuses on repulsions between pendant *atoms* ("outer" atoms that are not directly bonded to one another), rather than focusing on the chemical environment around the central atom in a molecule. Both LCP and the VSEPR models were developed by Robert Gillespie.

The LCP model assumes that ligands (or pendant atoms) "pack" as closely as possible around a central atom. A given ligand will have a specific atomic radius when bound to a central atom. The distance between two ligands around the same central atom is simply the sum of the atomic radii of the pendant atoms. Therefore for a specific set of ligands around a specific central atom, the ligand-ligand distances are constant despite the coordination number or bond angles. In other words, for a series of similar molecules with the same central atom, while bond angles and bond distances of pendant atoms may change, the distances between two pendant atoms remain the same.

Ligand Close Packing Theory

According to LCP, distances between two pendant atoms are similar...

- even when steric number changes
- even when bond angles change
- Reason: pendant atoms "pack" around the central atom.

Ligand Close Packing and Bond Distances

If the distance between non-bonded atoms remains constant even while bond angles change, then the bond length between the pendant and central atom must change to accommodate. For example, PF_4^+ and PF_3O have almost identical $F-F$ distances of 238 and 237 pm, respectively. As expected from VSEPR, the $F-P-F$ bond angle in PF_4^+ is 109.5°. The $F-P-F$ bond angle in PF_3O (101.1°) is smaller due to the increased repulsion of the oxygen double bond. Therefore the P-F bond lengths must be different. In fact, the P-F bond distances are 145.7 pm in PF_4^+ and 154 pm in PF_3O.

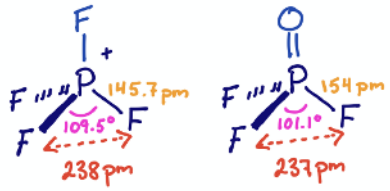


Figure 3.2.4.1: The molecular structures of PF_4^+ and PF_3O. The distances between neighboring F atoms are similar in the two molecules, while bond lengths and angles differ. The PF_4^+ ion has a $P-F$ bond length of 145.7 pm, an $F-P-F$ bond angle of 109.5°, and a distance of 238 pm between neighboring F atoms. The PF_3O molecule has a $P-F$ bond length of 154 pm, an $F-P-F$ bond angle of $F-P-F$ bond angle of 101.1°, and a distance of 237 pm between neighboring F atoms. (CC-BY-NC-SA; Kathryn Haas)

The relationship between bond angles, bond lengths, and close-packing distance is described by right angle trigonometry (recall SOA-CAH-TOA). In a right triangle, the hypotenuse is the longest side, opposite to the right angle. For either of the other two angles in the triangle, the angle (θ) and lengths of the sides (*opposite* and *adjacent* to θ) are related by the trigometric functions shown in Figure 3.2.4.2.

Figure 3.2.4.2: Visual depiction of SOA-CAH-TOA. (CC-BY-NC-SA; Kathryn Haas)

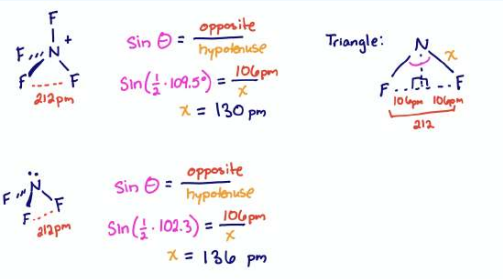
In the case of a molecule, we can apply right angle trigonometry by imagining that the bond angle is divided into two right angles, as illustrated in Figure 3.2.4.2 The hypotenuse of the triangles is the bond length, the opposite side is one half of the close-packing distance, and θ is one half the bond angle.

Figure 3.2.4.1: Illustration of how right angle trigonometry can be applied to determine bond angle, bond length, or distance between neighboring atoms: any bond angle can be divided into two right angles where the bond length is the hypotenuse, the distance between neighbors is twice the opposite side, and the bond angle is twice θ. (CC-BY-NC-SA; Kathryn Haas)

? Exercise 3.2.4.1

The distance between F atoms is 212 pm in both NF_4^+ and NF_3. The bond angles are 109.5° and 102.3°, respectively. What are the expected $N-F$ bond lengths?

Answer



The actual measured bond lengths are 130 pm for NF_4^+ and 136.5 pm for NF_3.

Sources and Resources

- https://en.Wikipedia.org/wiki/LCP_th...ieNyholm1957-3

3.2.4: Ligand Close Packing is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **3.2.4: Ligand Close Packing** by Kathryn Haas has no license indicated.

3.3: Molecular Polarity

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30}\ C\,m$). The dipole moment of a molecule can be calculated by Equation 3.3.1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{3.3.1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the ith charge, and
- $\vec{r}_i$ is the vector representing the position of ith charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is $\mathrm{H_2O}$. Because of the lone pair on oxygen, the structure of $\mathrm{H_2O}$ is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

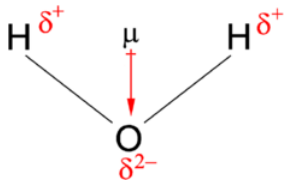


Figure 3.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 3.3.2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar $\mathrm{CCl_4}$ is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 3.3.2).

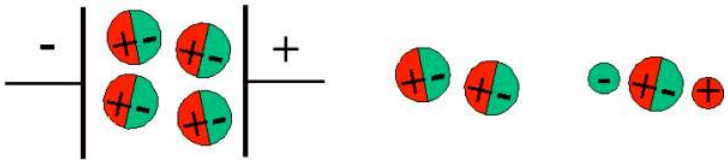


Figure 3.3.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 3.3.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{3.3.2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 3.3.2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\ C)(1.00 \times 10^{-10}\ m) \\ &= 1.60 \times 10^{-29}\ C \cdot m \end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is $4.80\ D$:

$$\begin{aligned} \mu &= (1.60 \times 10^{-29}\ C \cdot m)\left(\frac{1\ D}{3.336 \times 10^{-30}\ C \cdot m}\right) \\ &= 4.80\ D \end{aligned}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D \tag{3.3.3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D \tag{3.3.4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D \tag{3.3.5}$$

Example 3.3.1: Water

The water molecule in Figure 3.3.1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of the O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.

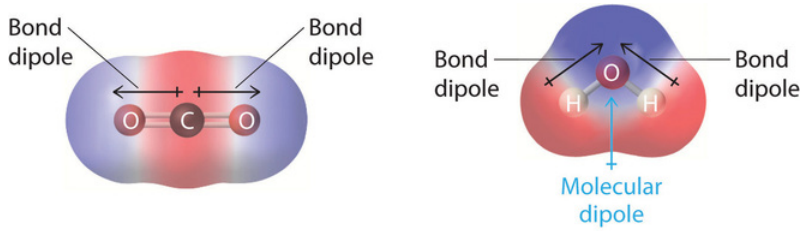


Figure 3.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 3.3.3*a*). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

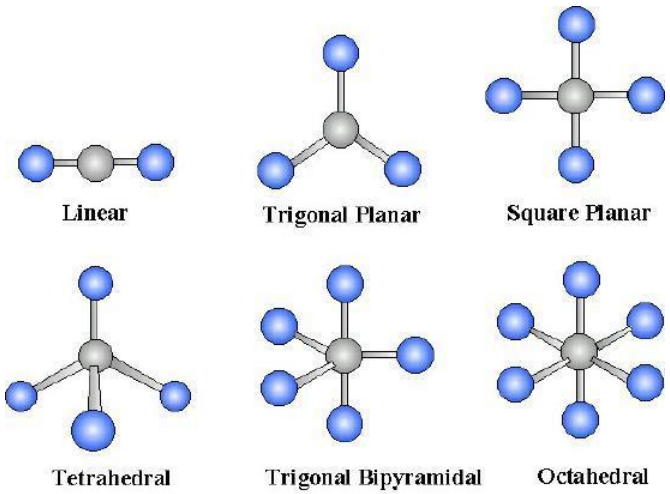
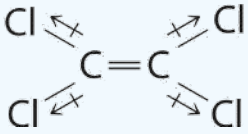


Figure 3.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 3.3.3: C_2Cl_4

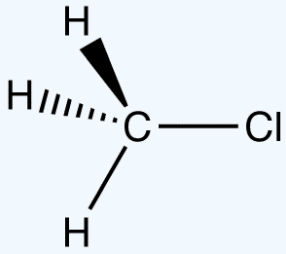
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 3.3.3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\mu = \frac{178}{100}(4.80\ D)$$
$$= 8.54\ D$$



Although the bond length is ***increasing***, the dipole is ***decreasing*** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the ***charge*** at the ends of the dipole).

Table 3.3.1: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

References

1. *Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pages 44-46)*
2. *Tro, Nivaldo J. Chemistry: A Molecular Approach. Upper Saddle River: Pearson Education, 2008. Print. (Pages 379-386)*

3.3: Molecular Polarity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Dipole Moments** by Delmar Larsen, Mike Blaber is licensed CC BY 4.0.

3.4: Hydrogen Bonding

A hydrogen bond is an intermolecular force (IMF) that forms a special type of dipole-dipole attraction when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. Intermolecular forces (IMFs) occur between molecules. Other examples include ordinary dipole-dipole interactions and dispersion forces. Hydrogen bonds are are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the group 14 elements with hydrogen, you find that the boiling points increase as you go down the group.

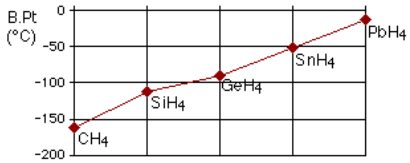


Figure 1: Boiling points of group 14 elemental halides.

The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater. If you repeat this exercise with the compounds of the elements in groups 15, 16, and 17 with hydrogen, something odd happens.

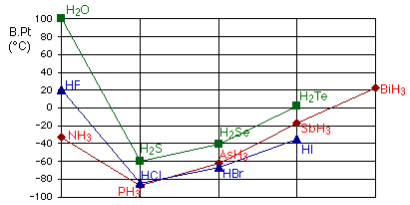


Figure 2: Boiling points of group 15-17 elemental halides.

Although the same reasoning applies for group 4 of the periodic table, the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break the IMFs. These relatively powerful intermolecular forces are described as hydrogen bonds.

Origin of Hydrogen Bonding

The molecules capable of hydrogen bonding include the following:

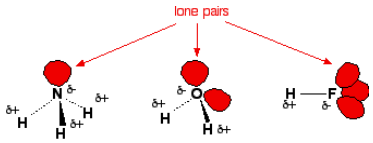


Figure 3: The lone pairs responsible for hydrogen bonding in NH_3, H_2O, and HF. The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you.

Notice that in each of these molecules:

- The hydrogen is attached directly to a highly electronegative atoms, causing the hydrogen to acquire a highly positive charge.
- Each of the highly electronegative atoms attains a high negative charge and has at least one "active" lone pair. Lone pairs at the 2-level have electrons contained in a relatively small volume of space, resulting in a high negative charge density. Lone pairs at higher levels are more diffuse and, resulting in a lower charge density and lower affinity for positive charge.

> *If you are not familiar with electronegativity, you should follow this link before you go on.*

Consider two water molecules coming close together.

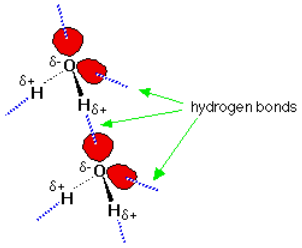


Figure 4: Hydrogen bonding in water

The δ^+ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water is an ideal example of hydrogen bonding. Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules: two with the hydrogen atoms and two with the with the oxygen atoms. There are exactly the right numbers of δ^+ hydrogens and lone pairs for every one of them to be involved in hydrogen bonding.

This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there are not enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, two hydrogen bonds and two lone pairs allow formation of hydrogen bond interactions in a lattice of water molecules. Water is thus considered an ideal hydrogen bonded system.

More complex examples of hydrogen bonding

The hydration of negative ions

When an ionic substance dissolves in water, water molecules cluster around the separated ions. This process is called hydration. Water frequently attaches to positive ions by co-ordinate (dative covalent) bonds. It bonds to negative ions using hydrogen bonds.

> *If you are interested in the bonding in hydrated positive ions, you could follow this link to co-ordinate (dative covalent) bonding.*

The diagram shows the potential hydrogen bonds formed with a chloride ion, Cl-. Although the lone pairs in the chloride ion are at the 3-level and would not normally be active enough to form hydrogen bonds, they are made more attractive by the full negative charge on the chlorine in this case.

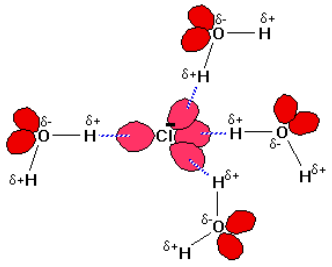


Figure 5: Hydrogen bonding between chloride ions and water.

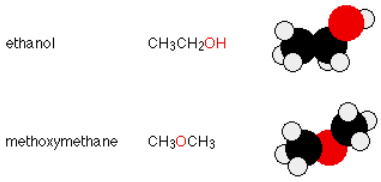
However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An alcohol is an organic molecule containing an -OH group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Hydrogen bonds also occur when hydrogen is bonded to fluorine, but the HF group does not appear in other molecules. Molecules with hydrogen bonds will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier," such that more

heat (energy) is required to separate them. This phenomenon can be used to analyze boiling point of different molecules, defined as the temperature at which a phase change from liquid to gas occurs.

Ethanol, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, C_2H_6O.

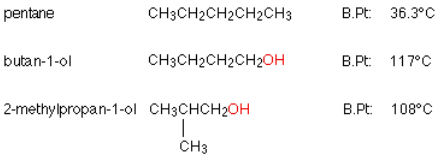


They have the same number of electrons, and a similar length. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be similar. However, ethanol has a hydrogen atom attached directly to an oxygen; here the oxygen still has two lone pairs like a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient $\delta+$ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens are not sufficiently $\delta+$ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)	78.5°C
methoxymethane (without hydrogen bonding)	-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C. It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two have similar chain lengths. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.



Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding; however, the values are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

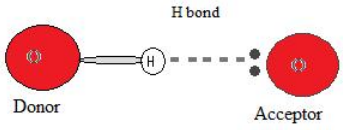
Hydrogen bonding in organic molecules containing nitrogen

Hydrogen bonding also occurs in organic molecules containing N-H groups; recall the hydrogen bonds that occur with ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Donors and Acceptors

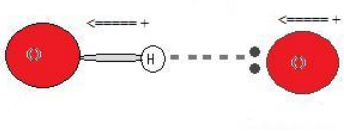
In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is usually a strongly electronegative atom such as N, O, or F that is covalently bonded to a hydrogen bond.

The hydrogen acceptor is an electronegative atom of a neighboring molecule or ion that contains a lone pair that participates in the hydrogen bond.



Why does a hydrogen bond occur?

Since the hydrogen donor (N, O, or F) is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus, and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor and the lone electron pair of the acceptor. This results in a hydrogen bond.(see Interactions Between Molecules With Permanent Dipoles)

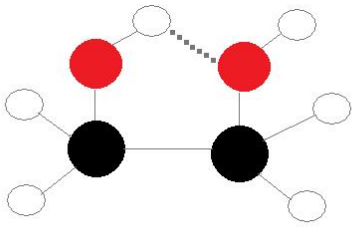


Types of hydrogen bonds

Although hydrogen bonds are well-known as a type of IMF, these bonds can also occur within a single molecule, between two identical molecules, or between two dissimilar molecules.

Intramolecular hydrogen bonds

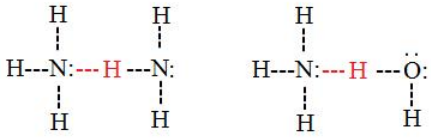
Intramolecular hydrogen bonds are those which occur *within* one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor a hydrogen acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups due to the molecular geometry.



Intramolecular h-bonding in Ethylene Glycol molecule

Intermolecular hydrogen bonds

Intermolecular hydrogen bonds occur *between* separate molecules in a substance. They can occur between any number of like or unlike molecules as long as hydrogen donors and acceptors are present in positions where they can interact with one another. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules.



Properties and effects of hydrogen bonds

On Boiling Point

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces (see Interactions Between Nonpolar Molecules). Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment. However, when we consider the table below, we see that this is not always the case.

Compound	Molar Mass	Normal Boiling Point
H_2O	18 g/mol	373 K
HF	20 g/mol	292.5 K
NH_3	17 g/mol	239.8 K
H_2S	34 g/mol	212.9 K
HCl	36.4 g/mol	197.9 K
PH_3	34 g/mol	185.2 K

We see that H_2O, HF, and NH_3 each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H_2O, HF, and NH_3 all exhibit hydrogen bonding, whereas the others do not. Furthermore, H_2O has a smaller molar mass than HF but partakes in more hydrogen bonds per molecule, so its boiling point is higher.

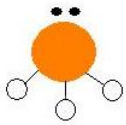
On Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be observed in the viscosity of certain substances. Substances capable of forming hydrogen bonds tend to have a higher viscosity than those that do not form hydrogen bonds. Generally, substances that have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

Factors preventing Hydrogen bonding

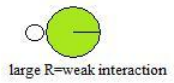
Electronegativity

Hydrogen bonding cannot occur without significant electronegativity differences between hydrogen and the atom it is bonded to. Thus, we see molecules such as PH_3, which do not participate in hydrogen bonding. PH_3 exhibits a trigonal pyramidal molecular geometry like that of ammonia, but unlike NH_3 it cannot hydrogen bond. This is due to the similarity in the electronegativities of phosphorous and hydrogen. Both atoms have an electronegativity of 2.1, and thus, there is no dipole moment. This prevents the hydrogen atom from acquiring the partial positive charge needed to hydrogen bond with the lone electron pair in another molecule. (see Polarizability)



Atom Size

The size of donors and acceptors can also affect the ability to hydrogen bond. This can account for the relatively low ability of Cl to form hydrogen bonds. When the radii of two atoms differ greatly or are large, their nuclei cannot achieve close proximity when they interact, resulting in a weak interaction.

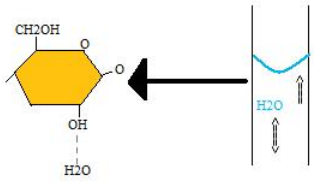


Hydrogen Bonding in Nature

Hydrogen bonding plays a crucial role in many biological processes and can account for many natural phenomena such as the Unusual properties of Water. In addition to being present in water, hydrogen bonding is also important in the water transport system of plants, secondary and tertiary protein structure, and DNA base pairing.

Plants

The cohesion-adhesion theory of transport in vascular plants uses hydrogen bonding to explain many key components of water movement through the plant's xylem and other vessels. Within a vessel, water molecules hydrogen bond not only to each other, but also to the cellulose chain that comprises the wall of plant cells. Since the vessel is relatively small, the attraction of the water to the cellulose wall creates a sort of capillary tube that allows for capillary action. This mechanism allows plants to pull water up into their roots. Furthermore, hydrogen bonding can create a long chain of water molecules, which can overcome the force of gravity and travel up to the high altitudes of leaves.



Proteins

Hydrogen bonding is present abundantly in the secondary structure of proteins, and also sparingly in tertiary conformation. The secondary structure of a protein involves interactions (mainly hydrogen bonds) between neighboring polypeptide backbones which contain nitrogen-hydrogen bonded pairs and oxygen atoms. Since both N and O are strongly electronegative, the hydrogen atoms bonded to nitrogen in one polypeptide backbone can hydrogen bond to the oxygen atoms in another chain and vice-versa. Though they are relatively weak, these bonds offer substantial stability to secondary protein structure because they repeat many times and work collectively.

In tertiary protein structure, interactions are primarily between functional R groups of a polypeptide chain; one such interaction is called a hydrophobic interaction. These interactions occur because of hydrogen bonding between water molecules around the hydrophobe that further reinforces protein conformation.

References

1. Brown, et al. Chemistry:The Central Science. 11th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2008.
2. Chang, Raymond. General Chemistry:The Essential Concepts. 3rd ed. New York: Mcgraw Hill, 2003
3. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

3.4: Hydrogen Bonding is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Hydrogen Bonding** by Jim Clark, Jose Pietri is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4: Symmetry and Group Theory

- 4.1: Symmetry Elements and Operations
  - 4.1.1: Symmetry Elements
- 4.2: Molecular Point Groups
  - 4.2.1: Point Groups
    - 4.2.1.1: Groups of Low and High Symmetry
    - 4.2.1.2: Other Groups
- 4.3: Properties and Representations of Groups
  - 4.3.1: Matrices
  - 4.3.2: Matrix
  - 4.3.3: Representations of Point Groups
  - 4.3.4: Representations
  - 4.3.5: Character Tables
- 4.4: Character Tables
- 4.5: Examples and Applications of Symmetry
  - 4.5.1: Chirality
  - 4.5.2: Molecular Vibrations
  - 4.5.3: Normal Modes of Vibration
  - 4.5.4: Selection Rules for IR and Raman Spectroscopy
  - 4.5.5: Stretching Frequencies and Structure Determination
- 4.6: Problems (do we want this here?)

4: Symmetry and Group Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.1: Symmetry Elements and Operations

Click here to see a lecture on this topic.

Introduction

The symmetry of a molecule consists of **symmetry operations** and **symmetry elements**. A symmetry operation is an operation that is performed to a molecule which leaves it indistinguishable and superimposable on the original position. Symmetry operations are performed with respect to symmetry elements (points, lines, or planes).

An example of a symmetry operation is a 180° rotation of a water molecule in which the resulting position of the molecule is indistinguishable from the original position (see Figure 4.1.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

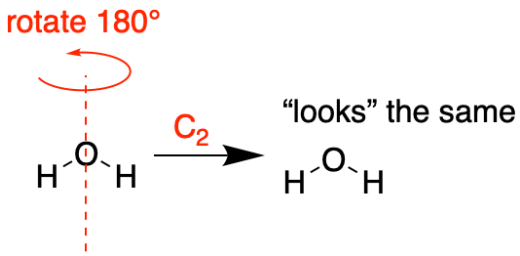


Figure 4.1.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

There are five types of symmetry operations including **identity**, **reflection**, **inversion**, **proper rotation**, and **improper rotation**. The improper rotation is the sum of a rotation followed by a reflection. The symmetry elements that correspond to the five types of symmetry operations are listed in Table 4.1.1.

Table 4.1.1: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by $(360/n)^o$	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by $(360/n)^o$, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

All molecules have the identity element. The identity operation is doing nothing to the molecule (it doesn't rotate, reflect, or invert...it just is).

Proper Rotation and Proper Axis (C_n)

A "proper" rotation is just a simple rotation operation about an axis. The symbol for any proper rotation or proper axis is $C_{(360/n)}$, where n is the degree of rotation. Thus, a 180° rotation is a C_2 rotation around a C_2 axis, and a 120° rotation is a C_3 rotation about a C_3 axis.

> **PRINCIPAL AXIS**: The principal axis of a molecule is the highest order proper rotation axis. For example, if a molecule had C_2 and C_4 axes, the C_4 is the principal axis.

Reflection and Symmetry Planes (σ)

Symmetry planes are mirror planes within the molecule. A reflection operation occurs with respect to a plane of symmetry. There are three classes of symmetry elements:

1. σ_h (horizontal): horizontal planes are perpendicular to principal axis
2. σ_v (vertical): vertical planes are parallel to the principal axis
3. σ_d (dihedral): dihedral planes are parallel to the principal axis and bisecting two C_2' axes

Inversion and Inversion Center (i)

The inversion operation requires a point of symmetry (a center of symmetry within a molecule). In other words, a point at the center of the molecule that can transform (x,y,z) into (-x,-y,-z) coordinate. Structures of tetrahedrons, triangles, and pentagons lack an inversion center.

Improper rotation (S_n)

Improper rotation is a combination of a rotation with respect to an axis of rotation (C_n), followed by a reflection through a plane perpendicular to that C_n axis. In short, an S_n operation is equivalent to C_n followed by σ_h.

References

1. Introduction to Molecular Symmetry by J. S Ogden
2. Inorganic Chemistry by Catherine Housecroft And Alan G. Sharpe.

4.1: Symmetry Elements and Operations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.1: Symmetry Elements and Operations** by Kathryn Haas has no license indicated.

4.1.1: Symmetry Elements

Symmetry elements of the molecule are geometric entities: an imaginary point, axis or plane in space, which symmetry operations: rotation, reflection or inversion, are performed. Their recognition leads to the application of symmetry to molecular properties and can also be used to predict or explain many of a molecule's chemical properties. Symmetry elements and symmetry operations are two fundamental concepts in group theory, which is the mathematical description of symmetry properties that describe the structure, bonding, and spectroscopy of molecules.

Point Symmetry Operations

Point symmetry of a molecule results when there exists at least one point in space that remains indistinguishable from the original molecule after any symmetry operation is applied. In other words, a rotation, reflection or inversion operations are called symmetry operations if, and only if, the newly arranged molecule is indistinguishable from the original arrangement. There are five kinds of point of symmetry elements that a molecule can possess, thus, there are also five kinds of point symmetry operations. All symmetry elements in a molecule must share at least one point in common and this point occurs at the center of the molecule.

Identity (E)

Identity operation comes from the German 'Einheit' meaning unity. This symmetry element means no change. All molecules have this element.

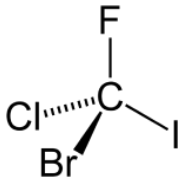


Figure 4.1.1.1: $\mathrm{CFClBrI}$. A chiral molecule possesses no symmetry other than the identity operation, E. (Public Domain; Benjah-bmm27 via Wikipedia)

Proper Rotation (C_n)

Proper rotation operates with respect to an axis called a **symmetry axis** (also known as n-fold rotational axis). An axis around which a rotation by 360°/n (or 2π/n) results in an identical molecule before and after the rotation. The axis with the highest n is called the **principal axis.**

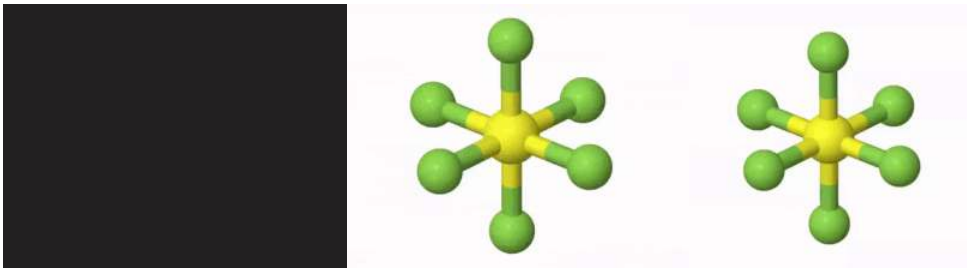


Figure 4.1.1.2: Octahedral structure of SF_6 with sulfur (yellow) and fluorine (green). Proper rotations of SF_6 with examples are $6C_2$, (left) $4C_3$ (middle) and $3C_4$ (right). We call C_4 the principal axis of SF_6. (Symmetry@Otterbein)

In general, a molecule contains n C_n operations such that $\{C_n^1, C_n^2, C_n^3,\ldots, C_n^{n-1}, C_n^n\}$ where $C_n^n = E$. For example, if there exists C_5 axis then there exists $5C_5$ ($2C_5^1$, $2C_5^2$, C_5^5) operations:

- $C_5^1 = C_5^4$ since the operation results indistinguishable molecule in clockwise and counter-clockwise, respectively.
- $C_5^2 = C_5^3$ since the operation results indistinguishable molecule in clockwise and counter-clockwise, respectively.
- $C_5^5 = E$

Reflection (σ)

Reflection operates with respect to a plane called a plane of symmetry (also known as a **mirror plane**). There exist three types of mirror planes:

- σ_h – a horizontal mirror plane of a molecule is **perpendicular** to the primary axis of a molecule.

- σ_v – a vertical mirror plane of a molecule includes the primary axis of a molecule and passes through the bonds (atoms).
- σ_d – a dihedral (also known as a **diagonal mirror plane**) of a molecule includes the primary axis of a molecule while bisecting the angle between two C_2 axes that are perpendicular to it. Therefore, σ_d does not pass through the bonds (atoms).

> **Note**
>
> σ_d is a special case of a σ_v.

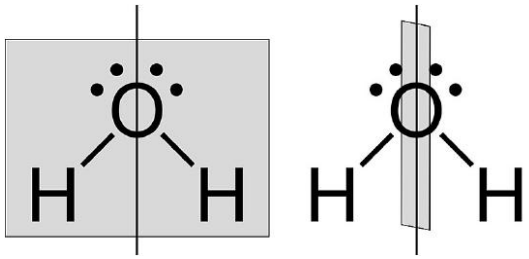


Figure 4.1.1.1: Bent structure of H_2O. The water molecule has two σ_v along C_2 axis and no σ_h. (CC BY-SA 4.0; Stars123kr via Wikipedia)

Inversion (i)

Inversion operates with respect to a point called a center of symmetry (also known as an **inversion center**). It gives the same result to rotating a molecule around C_2 axis then reflecting it with respect to a mirror plane that is perpendicular to C_2. For example, SF_6 in Figure 4.1.1.2has an inversion point at the center S.

Improper Rotation (S_n)

Improper rotation operates with respect to an axis called rotation-reflection axis. In other words, it is a combination operation of a rotation about an axis by 360°/n (or $2\pi/n$) followed by reflection in a plane perpendicular to the rotation axis.

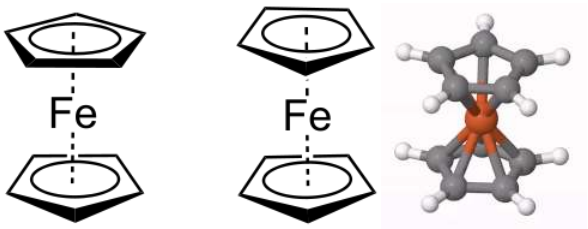


Figure 4.1.1.4: Staggered ferrocene *(left)* has an S_{10} operation while eclipsed ferrocene *(middle)* has an S_5 operation. (*right*) An example of a S_5 element in eclipsed ferrocene. (Public Domain; (left) Jü via Wikipedia and (right) Symmetry@Otterbein)

Point Groups

The complete collection of symmetry elements of a molecule forms the basis of a mathematical group, and the collection of symmetry operations that are interrelated to each other via certain kind of rules is known as a **point group**:

- **Closure** – if any two symmetry operations are in the same group then their product, resulting in another operation, will also be in the same group:

$$\text{If } A \in G \text{ and } B \in G, \text{ then } (A \cap B) \in G$$

- **Associativity** – the law of associativity applies to all symmetry operations:

$$(AB)C = A(BC)$$

- **Identity** – there exists an operation that commutes with other operations (identity, E) and leaves them unchanged:

$$\text{If } A \in G \text{ and } E \in G, \text{ then } AE = EA = A$$

- **Inverses** – for every symmetry operation in the group, there exists an inverse operation that their product results identity:

$$\text{If } A \in G, \text{ then there exists } A^{-1} \in G \text{ such that } AA^{-1} = A^{-1}A = E$$

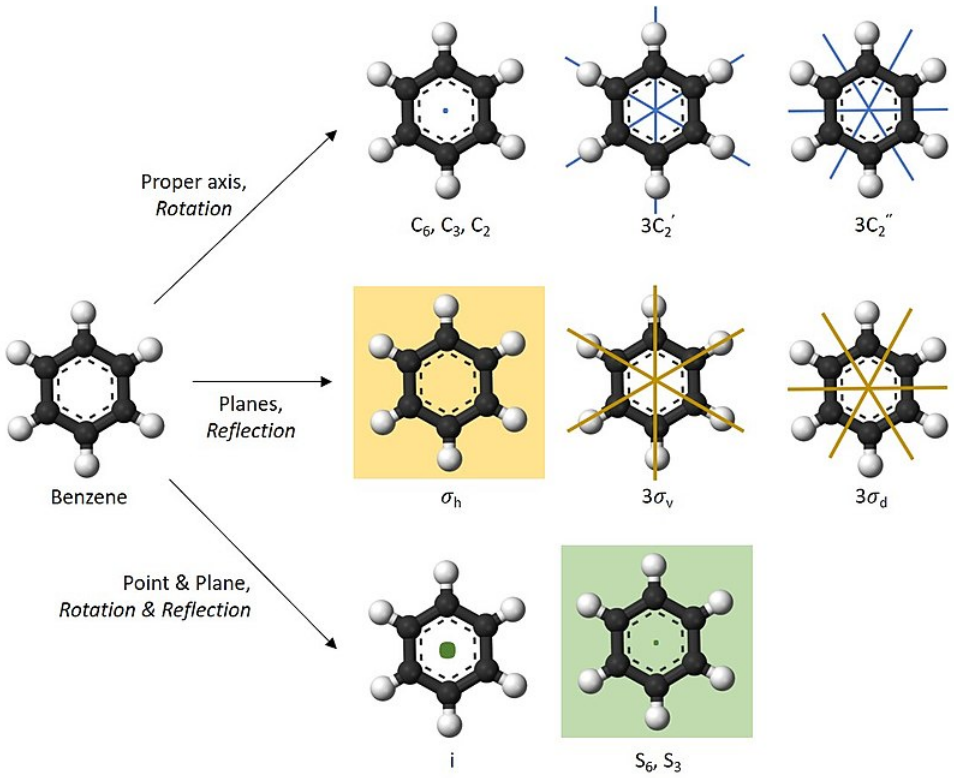


Figure 4.1.1.5: Benzene is one of the molecules that possess various symmetry elements and symmetry operations. (CC BY-SA 4.0; Stars123kr via Wikipedia)

References

1. Pfenning, Brian W. (2015). Principles of Inorganic Chemistry. Hoboken: John Wiley & Sons, Inc.. pp. 195.
2. https://www-e.openu.ac.il/symmetry/symmetry-tutorial.html

4.1.1: Symmetry Elements is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

- **1.1: Symmetry Elements** by Wikipedia is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Advanced_Inorganic_Chemistry.

4.2: Molecular 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.

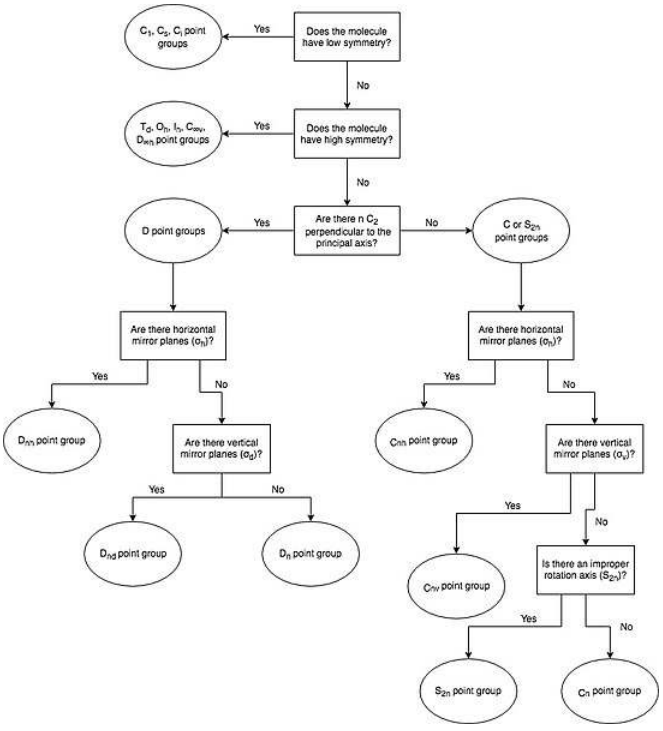


Figure 4.2.1 steps for determining a molecule's overall point group

Example 4.2.1

Find the point group of benzene (C_6H_6).

Answer

Solution

1. Benzene is neither high or low symmetry
2. Highest order rotation axis: C_6
3. There are 6 C_2 axes perpendicular to the principal axis
4. There is a horizontal mirror plane (σ_h)

Benzene is in the D_{6h} point group.

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 are 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 are classified as C_{nh}, C_{nv}, or C_n, where n refers to the principal axis of rotation. The C set of groups are 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 are classified as S_{2n}, where n refers to the principal axis of rotation. The S set of groups are 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

4.2: Molecular Point Groups is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

4.2.1: Point Groups

Click here to see a lecture on this topic.

Introduction

A **Point Group** describes all the symmetry operations that can be performed on a molecule that result in a conformation indistinguishable from the original. Point groups are used in Group Theory, the mathematical analysis of groups, to determine properties such as a molecule's molecular orbitals.

Assigning Point Groups

While a point group contains all of the symmetry operations that can be performed on a given molecule, it is not necessary to identify all of these operations to determine the molecule's overall point group. Instead, a molecule's point group can be determined by following a set of steps which analyze the presence (or absence) of particular symmetry elements.

Steps for assigning a molecule's point group:

1. Determine if the molecule is of high or low symmetry.
2. If not, find the highest order rotation axis, C_n.
3. Determine whether the molecule has any C_2 axes perpendicular to the principal C_n axis. If so, then there are n such C_2 axes, and the molecule is in the D set of point groups. If not, it is in either the C or S set of point groups.
4. Determine whether the molecule has a horizontal mirror plane (σ_h) perpendicular to the principal C_n axis. If so, the molecule is either in the C_{nh} or D_{nh} set of point groups.
5. Determine whether the molecule has a vertical mirror plane (σ_v) containing the principal C_n axis. If so, the molecule is either in the C_{nv} or D_{nd} set of point groups. If not, and if the molecule has n perpendicular C_2 axes, then it is part of the D_n set of point groups.
6. Determine whether there is an improper rotation axis, S_{2n}, collinear with the principal C_n axis. If so, the molecule is in the S_{2n} point group. If not, the molecule is in the C_n point group.

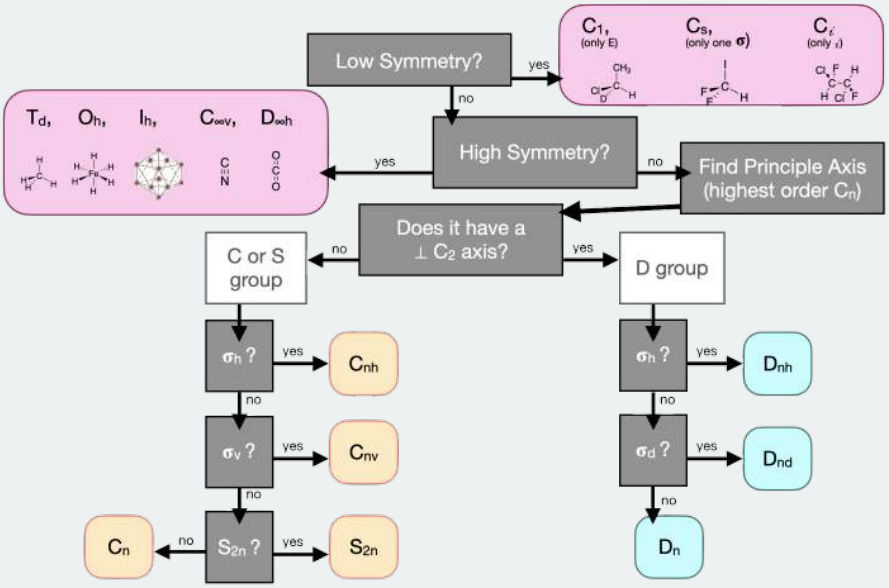


Figure 4.2.1.1: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

Example 4.2.1.1

Find the point group of benzene (C_6H_6).

Answer

Solution

1. Benzene is neither high nor low symmetry
2. Highest order rotation axis: C_6
3. There are 6 C_2 axes perpendicular to the principal axis
4. There is a horizontal mirror plane (σ_h)

Benzene is in the D_{6h} point group.

See Also

Symmetry Gallery

4.2.1: Point Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.2: Point Groups** by Kathryn Haas has no license indicated.

4.2.1.1: Groups of Low and High Symmetry

Click here to see a lecture on this topic.

Low Symmetry Point Groups

Low symmetry point groups include the C_1, C_s, and C_i groups

Group	Description	Example
C_1	only the identity operation (E)	CHFClBr
C_s	only the identity operation (E) and one mirror plane	C_2H_2ClBr
C_i	only the identity operation (E) and a center of inversion (i)	$C_2H_2Cl_2Br$

High Symmetry Point Groups

High symmetry point groups include the T_d, O_h, I_h, $C_{\infty v}$, and $D_{\infty h}$ groups. The table below describes their characteristic symmetry operations. The full set of symmetry operations included in the point group is described in the corresponding character table.

Group	Description	Example
$C_{\infty v}$	linear molecule with an infinite number of rotation axes and vertical mirror planes (σ_v)	HBr
$D_{\infty h}$	linear molecule with an infinite number of rotation axes, vertical mirror planes (σ_v), perpendicular C_2 axes, a horizontal mirror plane (σ_h), and an inversion center (i)	CO_2
T_d	typically have tetrahedral geometry, with 4 C_4 axes, 3 C_2 axes, 3 S_4 axes, and 6 dihedral mirror planes (σ_d)	CH_4
O_h	typically have octahedral geometry, with 3 C_4 axes, 4 C_3 axes, and an inversion center (i) as characteristic symmetry operations	SF_6
I_h	typically have an icosahedral structure, with 6 C_5 axes as characteristic symmetry operations	$B_{12}H_{12}^{2-}$

See Also

Symmetry Gallery

4.2.1.1: Groups of Low and High Symmetry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.2.1: Groups of Low and High Symmetry** by Kathryn Haas has no license indicated.
- **1.2: Molecular Point Groups** by Wikipedia is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Advanced_Inorganic_Chemistry.

4.2.1.2: Other Groups

Click here to see a lecture on this topic.

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

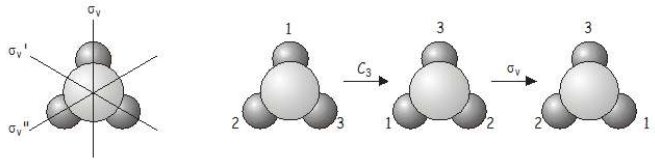
4.2.1.2: Other Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.2.2: Other Groups** by Kathryn Haas has no license indicated.
- **1.2: Molecular Point Groups** by Wikipedia is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Advanced_Inorganic_Chemistry.

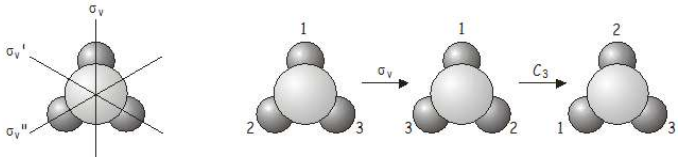
4.3: Properties and Representations of Groups

Group Multiplication

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3 rotation (120˚ counter-clockwise) followed by a σ_v reflection (reflection over the σ_v axis). We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.



The combined operation $\sigma_v C_3$ is equivalent to σ_v'' (note the double prime on σ_v''!), which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order, i.e., $C_3\sigma_v$ is (σ_v followed by C_3).



Again, the combined operation $C_3\sigma_v$ is equivalent to another operation of the point group, this time σ_v' (note the single prime on σ_v'!).

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general ***commute***. In some groups the symmetry elements do commute; such groups are said to be ***Abelian***.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same ***class***. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane).

Four Properties of Mathematical Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group. The definitions below will be put into the context of *molecular* symmetry.

A mathematical group is defined as a set of elements (A_1, A_2, A_3...) together with a rule for forming combinations A_i,A_j... For our purposes, A_1, A_2, A_3, etc. are symmetry elements and A_i, A_j, etc. are symmetry operations described in a previous section. The elements of the group and the rule for combining them must satisfy the following four criteria.

1. The group must include the **identity** $\boldsymbol{E}$, which commutes with other members of the group. In other terms, $\boldsymbol{EA_i = A_i}$ for all the elements of the group. Application of the identity operation before or after another operation, A_i, results in the same outcome as A_i alone.
2. The elements must satisfy the group property that the combination of any pair of elements is also an element of the group. For example, in the C_{3v} point group, a C_3 rotation followed by a σ_v gives another operation that is already part of the group: a σ_v ".
3. Each symmetry operation A_i must have an inverse A_i^{-1}, which is also an element of the group, such that

$$A_i A_i^{-1} = A_i^{-1} A_i = E$$

The inverse g_i^{-1} effectively 'undoes' the effect of the symmetry operation g_i. For example, in the C_{3v} point group, the inverse of C_3^+ is C_3^-.

4. The rule of combination must be associative

$$(A_i A_j)(A_k) = A_i(A_j A_k)$$

Or $A(BC) = (AB)C$. In other words, the order of operations should not matter.

Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

*This page was adapted from here (click).

Contributors and Attributions

- Claire Vallance (University of Oxford)
- Curated or created by Kathryn Haas

4.3: Properties and Representations of Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.3: Properties and Representations of Groups** by Kathryn Haas has no license indicated.

4.3.1: Matrices

The symmetry of molecules is essential for understanding the structures and properties of organic and inorganic compounds. The properties of chemical compounds are often easily explained by consideration of symmetry. For example, the symmetry of a molecule determines whether the molecule has a permanent dipole moment or not. The theories that describe optical activity, infrared and ultraviolet spectroscopy, and crystal structure involve the application of symmetry considerations. Matrix algebra is the most important mathematical tool in the description of symmetry.

The properties of symmetry groups are organized in character tables (discussed later in this chapter). Character tables are constructed based on matrices. This page is a brief description of matrices and matrix multiplication.

What is a matrix?

An $m \times n$ matrix $\mathbf{A}$ is a rectangular array of numbers with m rows and n columns. The numbers m and n are the dimensions of $\mathbf{A}$. The numbers in the matrix are called its entries. The entry in row i and column j is called a_{ij}.

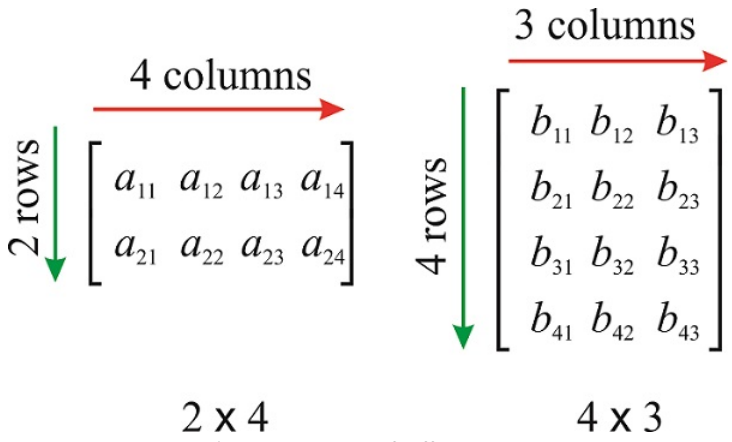


Figure 4.3.1.1: Matrices of different dimensions

Some types of matrices have special names:

- A square matrix:

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix}$$

  with $m = n$
- A rectangular matrix:

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \end{pmatrix}$$

  with $m \neq n$
- A column vector:

$$\begin{pmatrix} 3 \\ 5 \\ -i \end{pmatrix}$$

  with $n = 1$
- A row vector:

$$\begin{pmatrix} 3 & -2 & 4 \end{pmatrix}$$

  with $m = 1$
- The identity matrix:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

with $a_{ij} = \delta_{i,j}$, where $\delta_{i,j}$ is a function defined as $\delta_{i,j} = 1$ if $i = j$ and $\delta_{i,j} = 0$ if $i \neq j$.

- A diagonal matrix:

$$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

with $a_{ij} = c_i \delta_{i,j}$.

- An upper triangular matrix:

$$\begin{pmatrix} a & b & c \\ 0 & d & e \\ 0 & 0 & f \end{pmatrix}$$

All the entries below the main diagonal are zero.

- A lower triangular matrix:

$$\begin{pmatrix} a & 0 & 0 \\ b & c & 0 \\ d & e & f \end{pmatrix}$$

All the entries above the main diagonal are zero.

- A triangular matrix is one that is either lower triangular or upper triangular.

The Trace of a Matrix

The trace of an $n \times n$ square matrix $\mathbf{A}$ is the sum of the diagonal elements, and formally defined as $Tr(\mathbf{A}) = \sum_{i=1}^{n} a_{ii}$.

For example,

$$\mathbf{A} = \begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix} ; Tr(\mathbf{A}) = 12 + 3i$$

Singular and Nonsingular Matrices

A square matrix with nonzero determinant is called *nonsingular*. A matrix whose determinant is zero is called *singular*. (Note that you cannot calculate the determinant of a non-square matrix).

For a 2x2 matrix,

$$\mathbf{B} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} ; det(\mathbf{B}) = ad - cb$$

For a 3x3 matrix,

$$\mathbf{C} = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}$$

$$det(\mathbf{C}) = a \begin{pmatrix} e & f \\ h & i \end{pmatrix} - b \begin{pmatrix} d & f \\ g & i \end{pmatrix} + c \begin{pmatrix} d & e \\ g & h \end{pmatrix}$$

$$det(\mathbf{C}) = aei - ahf - bdi + bgf + cdh - cge$$

The Matrix Transpose

The matrix transpose, most commonly written $\mathbf{A}^T$, is the matrix obtained by exchanging $\mathbf{A}$'s rows and columns. It is obtained by replacing all elements a_{ij} with a_{ji}. For example:

$$\mathbf{A} = \begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \end{pmatrix} \rightarrow \mathbf{A}^T = \begin{pmatrix} 3 & 5 \\ -2 & 3i \\ 4 & 3 \end{pmatrix}$$

Matrix Multiplication

To multiply two matrices, the number of vertical columns in the first matrix must be the same as the number of rows in the second matrix. If $\mathbf{A}$ has dimensions $m \times n$ and $\mathbf{B}$ has dimensions $n \times p$, then the product $\mathbf{AB}$ is defined, and has dimensions $m \times p$.

$$c_{ij} = \sum a_{ij} \times b_{ij}$$

The entry $a_{ij} \times b_{ij}$ is obtained by multiplying row i of $\mathbf{A}$ by column j of $\mathbf{B}$, which is done by multiplying corresponding entries together and then adding the results:

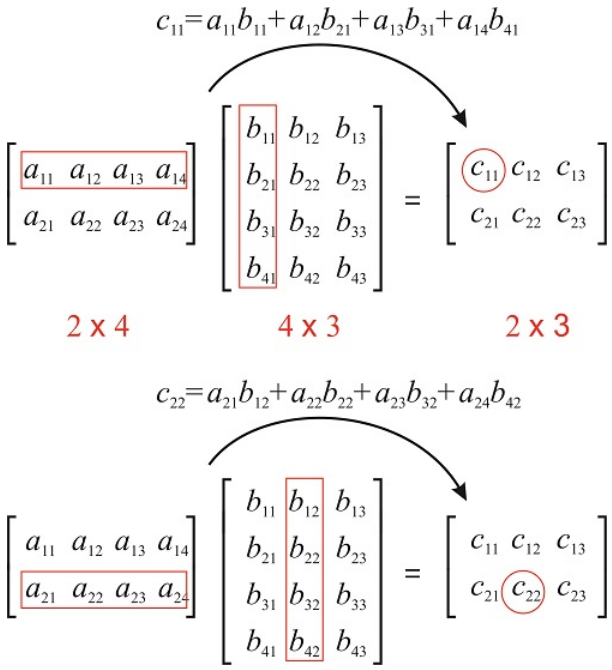


Figure 4.3.1.1: Matrix multiplication

Example 4.3.1.1

Calculate the product

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix}$$

Solution

We need to multiply a 3×3 matrix by a 3×2 matrix, so we expect a 3×2 matrix as a result.

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix}$$

To calculate a, which is entry (1,1), we use row 1 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow a = 1 \times 1 + (-2) \times 5 + 4 \times (-1) = -13$$

To calculate b, which is entry (1,2), we use row 1 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow b = 1\times 0 + (-2)\times 3 + 4\times 0 = -6$$

To calculate c, which is entry (2,1), we use row 2 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow c = 5\times 1 + 0\times 5 + 3\times (-1) = 2$$

To calculate d, which is entry (2,2), we use row 2 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow d = 5\times 0 + 0\times 3 + 3\times 0 = 0$$

To calculate e, which is entry (3,1), we use row 3 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow e = 0\times 1 + 1/2\times 5 + 9\times (-1) = -13/2$$

To calculate f, which is entry (3,2), we use row 3 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow f = 0\times 0 + 1/2\times 3 + 9\times 0 = 3/2$$

The result is:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} -13 & -6 \\ 2 & 0 \\ -13/2 & 3/2 \end{pmatrix}$$

Example 4.3.1.2

Calculate

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix}\begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix}$$

Solution

We are asked to multiply a 2×3 matrix by a 3×1 matrix (a column vector). The result will be a 2×1 matrix (a vector).

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix}\begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$a = 1\times 1 + (-2)\times 5 + 4\times (-1) = -13$$

$$b = 5\times 1 + 0\times 5 + 3\times (-1) = 2$$

The solution is:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix}\begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} -13 \\ 2 \end{pmatrix}$$

Need help? The link below contains solved examples: Multiplying matrices of different shapes (three examples): http://tinyurl.com/kn8ysqq

External links:

- Multiplying matrices, example 1: http://patrickjmt.com/matrices-multiplying-a-matrix-by-another-matrix/
- Multiplying matrices, example 2: http://patrickjmt.com/multiplying-matrices-example-2/
- Multiplying matrices, example 3: http://patrickjmt.com/multiplying-matrices-example-3/

The Commutator

Matrix multiplication is not, in general, commutative. For example, we can perform

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} -13 \\ 2 \end{pmatrix}$$

but cannot perform

$$\begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} \begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix}$$

Even with square matrices, that can be multiplied both ways, multiplication is not commutative. In this case, it is useful to define the **commutator**, defined as:

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$$

Example 4.3.1.3

Given $\mathbf{A} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix}$ and $\mathbf{B} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix}$

Calculate the commutator $[\mathbf{A}, \mathbf{B}]$

Solution

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$$

$$\mathbf{AB} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} = \begin{pmatrix} 3\times 1 + 1 \times (-1) & 3 \times 0 + 1 \times 2 \\ 2 \times 1 + 0 \times (-1) & 2 \times 0 + 0 \times 2 \end{pmatrix} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix}$$

$$\mathbf{BA} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} = \begin{pmatrix} 1\times 3 + 0 \times 2 & 1 \times 1 + 0 \times 0 \\ -1 \times 3 + 2 \times 2 & -1 \times 1 + 2 \times 0 \end{pmatrix} = \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix} - \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

Multiplication of a vector by a scalar

The multiplication of a vector $\overrightarrow{v_1}$ by a scalar n produces another vector of the same dimensions that lies in the same direction as $\overrightarrow{v_1}$;

$$n \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} nx \\ ny \end{pmatrix}$$

The scalar can stretch or compress the length of the vector, but cannot rotate it (figure [fig:vector_by_scalar]).

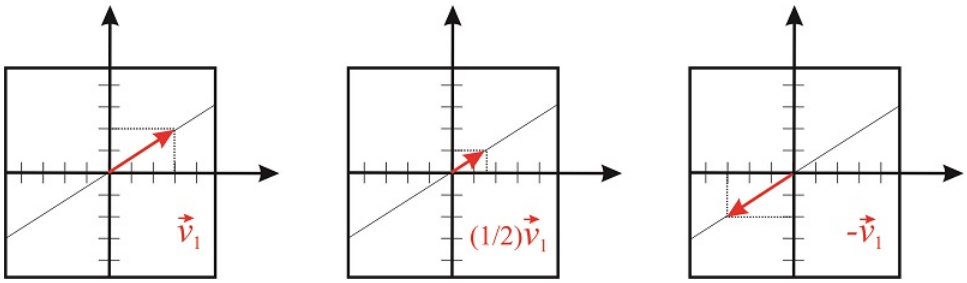


Figure 4.3.1.2: Multiplication of a vector by a scalar

Multiplication of a square matrix by a vector

The multiplication of a vector $\overrightarrow{v_1}$ by a square matrix produces another vector of the same dimensions of $\overrightarrow{v_1}$. For example, we can multiply a 2×2 matrix and a 2-dimensional vector:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} ax + by \\ cx + dy \end{pmatrix}$$

For example, consider the matrix

$$\mathbf{A} = \begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}$$

The product

$$\begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

is

$$\begin{pmatrix} -2x \\ y \end{pmatrix}$$

We see that 2×2 matrices act as operators that transform one 2-dimensional vector into another 2-dimensional vector. This particular matrix keeps the value of y constant and multiplies the value of x by -2 (Figure 4.3.1.3).

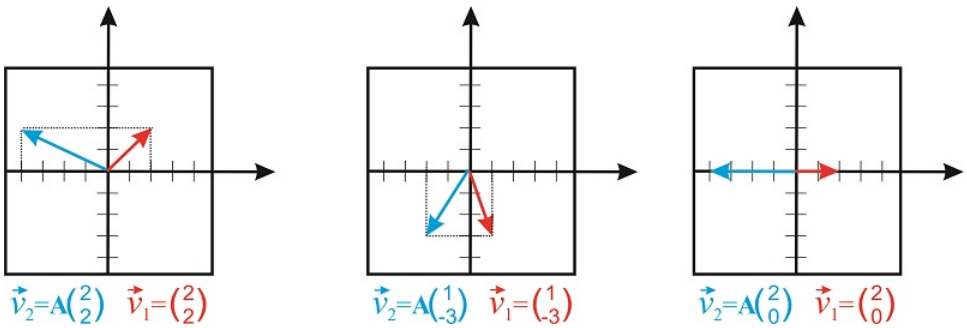


Figure 4.3.1.3: Multiplication of a vector by a square matrix

Notice that matrices are useful ways of representing operators that change the orientation and size of a vector. An important class of operators that are of particular interest to chemists are the so-called symmetry operators.

Attribution

This page was adapted from Matrices (click here), contributed by Marcia Levitus, Associate Professor (Biodesign Institute) at Arizona State University.

Curated or created by Kathryn Haas

4.3.1: Matrices is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.3.1: Matrices** by Kathryn Haas has no license indicated.

4.3.2: Matrix

A **matrix** is a rectangular array of quantities or expressions in rows (m) and columns (n) that is treated as a single entity and manipulated according to particular rules.[1] The dimension of a matrix is denoted by m × n. In inorganic chemistry, molecular symmetry can be modeled by mathematics by using group theory. The internal coordinate system of a molecule may be used to generate a set of matrices, known as a representation, that corresponds to particular symmetry operations.[2] Matrix modeling thus allows for symmetry operations performed on the molecule to be represented in an identical fashion mathematically.

Matrix Operations

Addition

The sum of two matrices, **A** and **B**, is carried out by adding or subtracting the element of one matrix with the corresponding element of another matrix. These operations may only be performed on matrices of identical dimension.

$$A+B=\sum_{i=1}^{m}\left(\sum_{i=1}^{n}A_{ij}+B_{ij}\right)$$ where *i* refers to a particular row and *j* to a particular column.

Example:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{pmatrix}+\begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \end{pmatrix}=\begin{pmatrix} a_{11}+b_{11} & a_{12}+b_{12} & a_{13}+b_{13} \\ a_{21}+b_{21} & a_{22}+b_{22} & a_{23}+b_{23} \end{pmatrix}$$

Scalar Multiplication

Multiplication of a matrix by a scalar, *c*, multiplies every element within the matrix by the scalar.

$$cA=C\cdot A_{ij}$$

Example:

$$c\cdot\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}=\begin{pmatrix} c\cdot a_{11} & c\cdot a_{12} \\ c\cdot a_{21} & c\cdot a_{22} \end{pmatrix}$$

Matrix Multiplication

Matrix multiplication entails computing the dot product of the row of one matrix, **A**, with the column of another matrix, **B**. Matrix multiplication is only defined if the number if columns of **A**, denoted by n, is equal to the number of rows of **B**, denoted by m. Their product is then the m × n matrix, **C**. Matrix multiplication entails some mathematical properties. First, it is associative; in other words, (**A** × **B**) × **C** = **A** × (**B** × **C**). Furthermore, matrix multiplication is not commutative; in other words, **A** × **B** =/= **B** × **A**

$$\mathrm{C_{m\times n}}=\mathrm{A_{m\times c}}\cdot\mathrm{B_{c\times n}}=\sum_{k=1}^{c}A_{i,k}B_{k,j}$$

Example:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{pmatrix}\times\begin{pmatrix} b_{11} \\ b_{21} \\ b_{31} \end{pmatrix}=\begin{pmatrix} a_{11}b_{11}+a_{12}b_{21}+a_{13}b_{31} \\ a_{21}b_{11}+a_{22}b_{21}+a_{23}b_{31} \end{pmatrix}$$

Row Operations

There are three kinds of elementary row operations that are used to transform a matrix:

Type	Definition	Operation
Row Switching	The swapping of one row with that of another row	$\mathrm{R}_i\leftrightarrow\mathrm{R}_j$
Row Addition	The addition of a multiple of one row to another row	$\mathrm{R}_i+k\mathrm{R}_j\rightarrow\mathrm{R}_i$

Row Multiplication	Multiplication of a row by a scalar, c, with $c \neq 0$	$c\mathrm{R}_i \rightarrow \mathrm{R}_i$

Square Matrices

Square matrices are matrices where the number of rows and number of columns are equal, resulting in an n × n matrix.

Identity Matrix

The identity matrix, $\mathbf{I}_n$, is a diagonal matrix which has all elements along the main diagonal equal to 1 and all other elements equal to 0. Multiplication of another matrix by the identity matrix leaves the first unchanged. Moreover, multiplication with the identity matrix is commutative; in other words, **A** × **I** = **I** × **A**.

Example:

$$A \cdot I_3 = \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$$

Trace

Only applicable to square matrices, the trace or *character*, χ, of a matrix is the sum of its diagonal entries along the main diagonal.

Determinant

The determinant of a matrix, denoted det(**A**), is a real number computed from a square matrix. A non-zero determinant implies matrix invertibility, which further implies that the set of linear equations comprising the matrix has exactly one solution.

For a 2 × 2 matrix, the determinant is computed as follows:

$$\det(\mathbf{A}) = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

For a 3 × 3 matrix, the determinant is computed as follows:

$$\det(\mathbf{A}) = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$

Higher order determinants may be calculated by using Cramer's Rule.

References

1. "Matrix [Def. 3. In Oxford Dictionaries (American English) (US)"].
2. ↑ Pfenning, Brian W. (2015). *Principles of Inorganic Chemistry*. Hoboken: John Wiley & Sons, Inc.. pp. 195. ISBN 9781118859100.

4.3.2: Matrix is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

4.3.3: Representations of Point Groups

Symmetry Operations: Matrix Representations

A **symmetry operation**, such as a rotation around a symmetry axis or a reflection through a plane, is an operation that, when performed on an object, results in a new orientation of the object that is indistinguishable from the original. For example, if we rotate a square in the plane by $\pi/2$ or π, the new orientation of the square is superimposable on the original one (Figure $4.3.3.1$).

If rotation by an angle θ of a molecule (or object) about some axis results in an orientation of the molecule (or object) that is superimposable on the original, the axis is called a rotation axis. The molecule (or object) is said to have an n-fold rotational axis, where n is $2\pi/\theta$. The axis is denoted as C_n. The square of Figure $4.3.3.1$ has a C_4 axis perpendicular to the plane because a 90° rotation leaves the figure indistinguishable from the initial orientation. This axis is also a C_2 axis because a 180° degree rotation leaves the square indistinguishable from the original square. In addition, the figure has several other C_2 axis that lie on the same plane as the square:

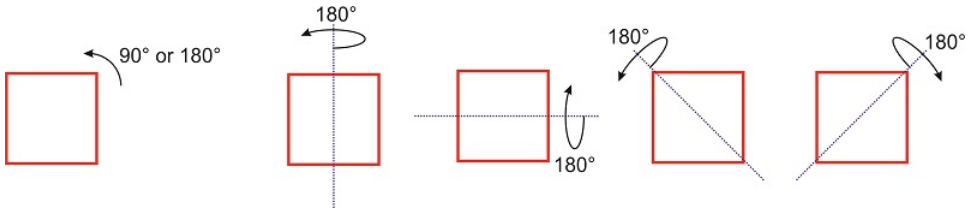


Figure 4.3.3.1: Symmetry operations performed on a square

A symmetry operation moves all the points of the object from one initial position to a final position, and that means that symmetry operators are 3×3 square matrices (or 2×2 in two dimensions). Each symmetry operation can be expressed as a **transformation matrix** where the vector (x', y', z') represents the new coordinates of the point (x, y, z) after the symmetry operation.

$$[\text{New Coordinates}(x', y', z')] = [\text{Transformation Matrix}] \times [\text{Old Coordinates}(x, y, z)]$$

We will use the example of water, which is in the C_{2v} point group, to illustrate how transformation matrices can be used to represent the symmetry of a group.

Figure $4.3.3.2$ shows the three symmetry elements of the molecule of water (H_2O). This molecule has only one rotation axis, which is 2-fold, and therefore we call it a "$\boldsymbol{C_2}$ axis." It also has two mirror planes, one that contains the two hydrogen atoms ($\boldsymbol{\sigma_{yz}}$), and another one perpendicular to it ($\boldsymbol{\sigma_{xz}}$). Both planes contain the C_2 axis.

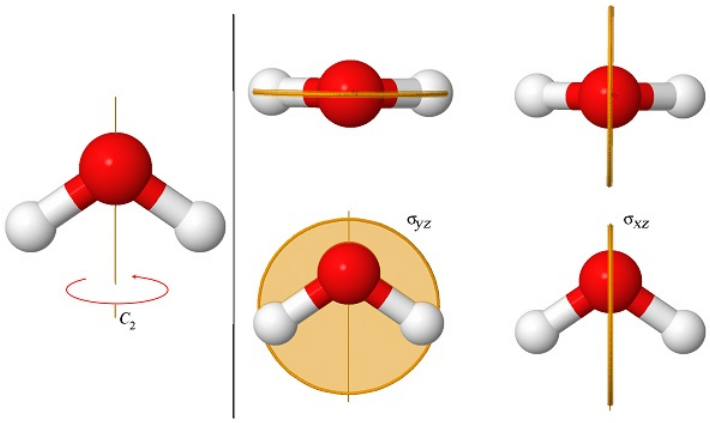


Figure 4.3.3.2: The symmetry elements of the molecule of water

Transformation Matrix of C_2 rotation

A 2-fold rotation around the $z-$axis changes the location of a point (x, y, z) to $(-x, -y, z)$ (see Figure $4.3.3.3$). By convention, rotations are always taken in the counterclockwise direction.

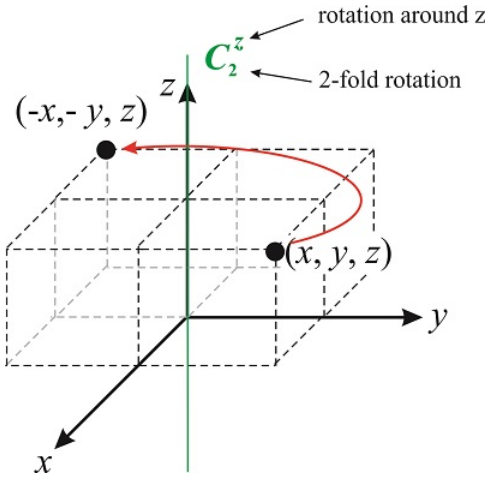


Figure 4.3.3.3: A 2-fold rotation around the z-axis

What is the matrix that represents the C_2 rotation? The matrix transforms the vector (x, y, z) into $(-x, -y, z)$, so

$$C_2(x, y, z) = (-x, -y, z)$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

We know the matrix is a 3×3 square matrix because it needs to multiply a 3-dimensional vector. In addition, we write the vector as a vertical column to satisfy the requirements of matrix multiplication.

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$a_{11}x + a_{12}y + a_{13}z = -x$$

$$a_{21}x + a_{22}y + a_{23}z = -y$$

$$a_{31}x + a_{32}y + a_{33}z = z$$

and we conclude that $a_{11} = -1$, $a_{12} = a_{13} = 0$, $a_{22} = -1$, $a_{21} = a_{23} = 0$ and $a_{33} = 1$, $a_{31} = a_{32} = 0$. The transformation matrix of the C_2 operation of the C_{2v} point group is:

$$\boldsymbol{C_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.3.3.1}$$

Transformation Matrix of σ_{xz} reflection

Rotations are not the only symmetry operations we can perform on a molecule. Figure 4.3.3.4 illustrates the reflection of a point through the xz plane. This operation transforms the vector (x, y, z) into the vector $(x, -y, z)$. Symmetry operators involving reflections through a plane are usually denoted with the letter σ, so the operator that reflects a point through the xz plane is $\hat{\sigma}_{xz}$:

$$\sigma_{xz}(x, y, z) = (x, -y, z)$$

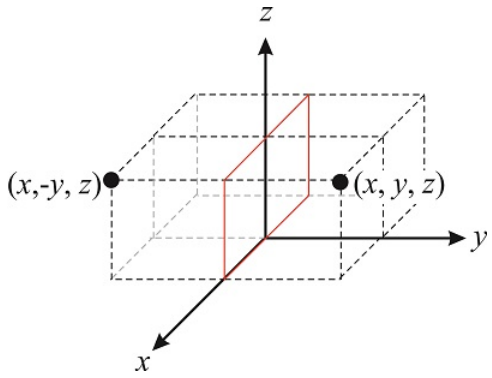


Figure 4.3.3.3: A reflection through the xz plane

Following the same logic we used for the rotation matrix, we can write the σ_{xz} transformation matrix as:

$$\boldsymbol{\sigma_{x,z}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.3.3.2}$$

This is true because

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

? Exercise 4.3.3.1

Find the transformation matrix of the identity (E) and the $\sigma_{y,z}$ operations under the C_{2v} point group.

Answer

The transformation matrix for E is $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

The transformation matrix for $\sigma_{v(yz)}$" is $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Characters

For a square matrix, the ***character*** is the trace of the matrix. For the C_2 operation, with the transformation matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

the trace is $(-1)+(-1)+1=-1$.

The set of characters for a point group is called a **reducible representation (Γ)**. The reducible representation for the C_{2v} point group is:

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Exercise 4.3.3.1

Prove that the characters in the reducible representation for C_{2v} are correct:

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Answer

For the E operation, with the transformation matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $1+1+1=$ 3.

For the C_2^z operation, with the transformation matrix $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $(-1)+(-1)+1=$ −1.

For the $\sigma_{v(xz)'}$ operation, with the transformation matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $1+(-1)+1=$ 1.

For the $\sigma_{v(yz)"}$ operation, with the transformation matrix $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $-1+1+1=$ 1.

This gives the reducible representation

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Reducible and Irreducible Representations

Let us now go back and look in more detail at the transformation matrices of the C_{2v} point group that we derived above. If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$E = \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, C_2 = \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \sigma'_{v(xz)} = \begin{pmatrix} [1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \sigma_{v(yz)"} = \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}$$

All the non-zero elements become 1x1 matrices that each represent individual x, y, z coordinates. In other words, the element a_{11} represents x, a_{22} represents y, and a_{33} represents z. The matrix elements for x from each transformation matrix combine to form an irreducible representation of the C_{2v} point group. Likewise, the matrix elements for y combine to form a second irreducible representation, and the same is true for z elements. These irreducible representations are shown below:

C_{2v}	E	C_2	σ_v	σ_v'	Coordinate Used
	1	−1	1	−1	x
	1	−1	−1	1	y
	1	1	1	1	z
Γ	3	−1	1	1	

The irreducible representations add to form the reducible representation, Γ. This Γ, which is the set of 3x3 matrices, can be reduced to the set of 1x1 matrices of the irreducible representations. The irreducible representations cannot be reduced further, hence their name.

Sources & Attribution

- Parts of this page was adapted from Matrices (click here) (Symmetry Operators), contributed by Marcia Levitus, Associate Professor (Biodesign Institute) at Arizona State University.
- Parts of this page were adapted from Reductions of Representations, contributed by

Claire Vallance (University of Oxford)

- Curated or created by Kathryn Haas

4.3.3: Representations of Point Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.3.2: Representations of Point Groups** by Kathryn Haas has no license indicated.

4.3.4: Representations

A **representation** is a set of matrices, each of which corresponds to a symmetry operation and combine in the same way that the symmetry operators in the group combine.[1] Symmetry operators can be presented in matrices, this allows us to understand the relationship between symmetry operators through calculation from matrices. In order to understand representations, knowing matrix notions for symmetry operations is essential.

Here is some examples of symmetry operations in matrix form:

$$\text{a point in space} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathrm{C_n} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$S_n = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Both C_n and S_n have z set as the principal axis.

For C_n operation, θ depends on n with the relationship of $\theta = \frac{360}{n}$. If the symmetry is C_2, then θ would be 180° because the molecule is rotated 180°. For C_3, θ would be 120°, C_4 θ would be 90°, etc.

To apply a symmetry operation on an atom of a molecule, matrices can be combined to produce another operation in the group. For a C_{2v} symmetry compound such as water shown in Figure 4.3.4.1, the operations (E, C_2, σ_{v1}, σ_{v2}) can be applied on the vector (x, y, z) to find the representation. To simplify the math, a 1x1 matrix can be done by block diagonalizing for individual vector.

Example 4.3.4.1

E(y) = [1] [y] = y

C_2(y) = [-1] [y] = -y

$\sigma_{v1}(y) = \sigma_{xz}$ = [-1] [y] = -y

$\sigma_{v2}(y) = \sigma_{yz}$ = [1] [y] = y

In this example, if you apply identity (E) on vector y shown in Figure 4.3.4.2 you would obtain y. If you apply C_2 rotation along the principal axis on y, then you would obtain -y, etc. These obtained results show the position of the vector after the symmetry operation. The coefficient of each vector after symmetry operation can be represented as Γ_y in character table 4.3.4.1. This set of matrices each of which corresponds to the character of a matrix a **representation**[1]. The same symmetry operation can be applied on x and z to obtain a representation for Γ_x and Γ_z.

Table 4.3.4.1: xyz representations in C_{2v}.

C_{2v}	E	C_2	σ_{v1}	σ_{v2}

C_{2v}	E	C_2	σ_{v1}	σ_{v2}
Γ_z	[1]	[1]	[1]	[1]
Γ_y	[1]	[-1]	[-1]	[1]
Γ_x	[1]	[-1]	[1]	[-1]

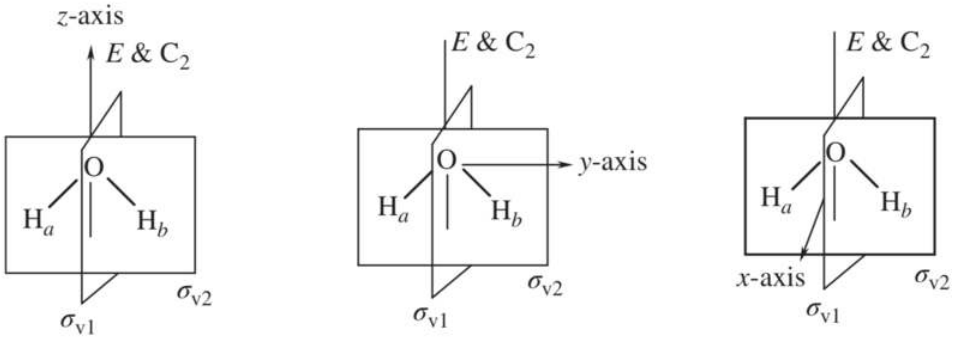


Figure 4.3.4.1. Water molecule a) z-axis b) y-axis c) x-axis.

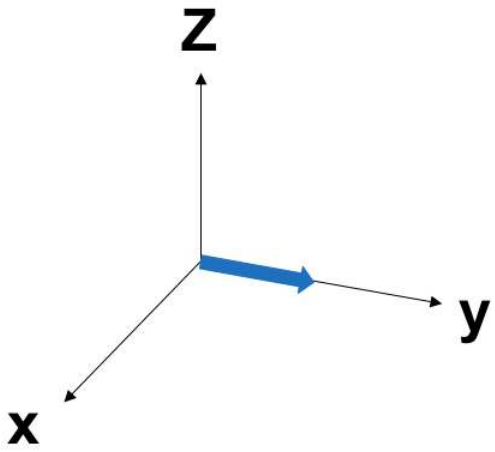


Figure 4.3.4.2: y vector on a Cartesian coordinate.

A **representation** can combine in the same way that the symmetry operators in the group combine, thus, the multiplication table for the matrices that represent each symmetry operation must also multiply together in the same way that the symmetry operators themselves multiply.[1] Refer to the following tables.

Table 4.3.4.1: Multiplication tables for the C_{2v} point group, showing how the 1 × 1 matrix representations multiply together in the same way that the symmetry operations do.

C_{2v}	E	C_2	σ_{v1}	σ_{v2}
E	E	C_2	σ_{v1}	σ_{v2}
C_2	C_2	E	σ_{v2}	σ_{v1}
σ_{v1}	σ_{v1}	σ_{v2}	E	C_2
σ_{v2}	σ_{v2}	σ_{v1}	C_2	E

Γ_z	**[1]**	**[1]**	**[1]**	**[1]**
[1]	[1]	[1]	[1]	[1]
[1]	[1]	[1]	[1]	[1]

Γ_z	[1]	[1]	[1]	[1]
[1]	[1]	[1]	[1]	[1]
[1]	[1]	[1]	[1]	[1]

Γ_y	[1]	[-1]	[-1]	[1]
[1]	[1]	[-1]	[-1]	[1]
[-1]	[-1]	[1]	[1]	[-1]
[-1]	[-1]	[1]	[1]	[-1]
[1]	[1]	[-1]	[-1]	[1]

Γ_x	[1]	[-1]	[1]	[-1]
[1]	[1]	[-1]	[1]	[-1]
[-1]	[-1]	[1]	[-1]	[1]
[1]	[1]	[-1]	[1]	[-1]
[-1]	[-1]	[1]	[-1]	[1]

Irreducible Representation and Reducible Representations

A **representation** can be categorized as **irreducible representation** and **reducible representations**. A character table is given with **irreducible representations**, which are the blue shaded part in Figure 5. There are 5 rules to irreducible representations, shown in the following box.

5 Rules to Irreducible Representations

1. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group.

$$h = \sum_i l_i^2$$

2. The sum of the squares of the characters in any irreducible representation equals h.

$$h = \sum_i [\chi_i(R)^2]$$

3. The vectors whose components are the characters of two different irreducible representations are orthogonal.

$$\sum_R [\chi_i R \times \chi_j R] = 0$$

if $i \neq j$.

4. In a given representation (reducible or irreducible), the characters of all matrices belonging to symmetry operations in the same class are identical.
5. The number of irreducible representations of a group is equal to the number of classes in the group.

The classes correspond directly to the sets of equivalent operations. Two operations belong to the same class when one may be replaced by the other in a new coordinate system that is accessible by a symmetry operation. For example, a C_7 point group would have C_7^1, C_7^2, C_7^3, C_7^4, C_7^5, C_7^6, C_7^7. Since cos(θ) = cos(θ), the characters associated with these matrices are the same. In this case, C_7^1=C_7^6, C_7^2 = C_7^5, C_7^3 = C_7^4, and C_7^7 = E because they belong to the same class. We can simplify the C_7 point group's symmetry into 2 C_7^1, 2C_7^2, 2C_7^3, and E because there are two operations belonging to the same class.

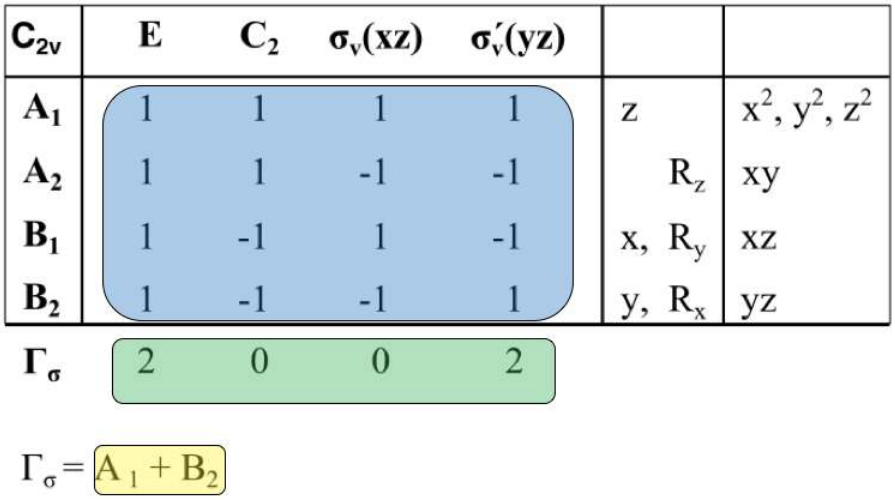


Figure 4.3.4.3: a) Blue shaded part: irreducible representation b) Green shaded part: reducible representation c) Yellow shaded part: Reducing reducible representations into irreducible representation

The green shaded part in Figure 4.3.4.3 is a the **reducible representation** that is found based on number of unmoved molecule after a symmetry operation. For example, if we are looking at Γ_σ of C_{2v} symmetry molecule such as water from Figure 4.3.4.3 we would focus on the number of unmoved σ bonds after the symmetry operation. In a water molecule, there are two s bonds which are the two O-H bonds. If we apply E, both of the bonds don't move, so the reducible representation would be 2 because each unmoved σ bonds contribute to 1 reducible representation. If we apply C_2 operation on it, both bonds would move, where the O-H bonds would switch places. This means that there are zero unmoved σ bonds, so the reducible representation would be zero as shown in Figure 4.3.4.3b

The yellow shaded part in Figure 4.3.4.3 is the **reduction of reducible representations** into irreducible representations. This can be done by using the formula,

$$n_i = \frac{1}{h}\sum_N \chi_R \chi_L$$

where

- n_i is the number of times the irreducible representation occurs in the reducible representation,
- N is the coefficient in front of each symmetry element symbol (shown on the top row of the character table),
- h is the order of the group (sum of the coefficients N),
- χ_R and χ_I are the characters of the reducible and irreducible representations.

Reference

1. Pfennig, Brian (2015). *Principles of Inorganic Chemistry*. Hoboken, New Jersey: John Wiley & Sons, Inc.. pp. 195–202. ISBN 978-1-118-85910-0.

4.3.4: Representations is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

- **1.4: Representations** by Wikipedia is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Advanced_Inorganic_Chemistry.

4.3.5: Character Tables

Introduction to Character Tables, using C_{2v} as example

A character table is the complete set of irreducible representations of a symmetry group. In the previous section, we derived three of the four irreducible representations for the C_{2v} point group. These three irreducible representations are labeled A_1, B_1, and B_2. The fourth irreducible representation, A_2, can be derived using the properties (or "rules") for irreducible representations listed below.

Properties of Characters of Irreducible Representations in Point Groups

1. There is always a totally symmetric representation in which all the characters are 1.
   e.g. In C_{2v}, A_1 is totally symmetric.
2. The order of the group (h) is the total number of symmetry operations in the group.
   e.g. In C_{2v}, $h = 4$
3. Similar operations are listed as classes (R) and appear as columns in the table.
   e.g. In C_{2v}, there are four classes of operations, E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$
4. The number of irreducible representations (rows) must equal the number of classes (columns). This results in all character tables being square.
   e.g. In C_{2v}, there are four classes and four irreducible representations.
5. The sum of squares of all characters under E is equal to the order of the group: $h = \sum[\chi_i]^2$
   e.g. In C_{2v}, $h = 1^2 + 1^2 + 1^2 + 1^2 = 4$
6. For any irreducible representation (i), the sum of squares of its characters multiplied by the number of operations in the class is the order of the group: $h = \sum[\chi_i(R)]^2$
   e.g. For A_2 in C_{2v}, $h = (1\times1)^2 + (1\times1)^2 + (-1\times1)^2 + (-1\times1)^2 = 4$
7. Irreducible representations are orthogonal. For any two representations (i and j): $\sum[\chi_i * (R)\chi_j(R)] = 0$
   e.g. For B_1 and B_2 of C_{2v}, $[1\times1] + [-1\times-1] + [1\times-1] + [-1\times1] = 0$

The complete character table for C_{2v} is given below.

C_{2v}	E	C_2	σ_v	σ'_v	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in Schoenflies (C_{2v}) notation.
ii. Along the first row are the symmetry operations of the group, E, C_2, σ_v and σ_v ", followed by the order of the group, h.
iii. In the first column are the irreducible representations of the group, represented by Mulliken Labels. In C_{2v} the irreducible representations are A_1, A_2, B_1 and B_2. The Mulliken labels indicate the symmetry of each representation (explained further below).
iv. The characters (χ) of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column(s) of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products $(z^2, x^2+y^2, xy, xz, yz)$, and the rotations (R_x, R_y, R_z) (explained further below).

Another example: C_{3v}

Th C_{3v} point group has three classes of operations: E, C_3, and $\sigma_{v(xz)}$. The derivation of transformation matrices for E and $\sigma_{v(xz)}$ is similar to the case for C_{2v}. However, the C_{3v} operation does not give simple 1 or -1 characters. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. The new axes can each be written as a linear combination of our original x and y axes. The derivation of the rotation matrices will not be covered in this text, but is described elsewhere:

$$\begin{aligned} x' &= x\cos\theta + y\sin\theta \\ y' &= -x\sin\theta + y\cos\theta \end{aligned}$$

For a C_3 rotation counterclockwise through 120° (or $\frac{2\pi}{3}$):

$$\begin{aligned} x' &= x\cos(2\pi/3) + y\sin(2\pi/3) &&= -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y \\ y' &= -x\sin(2\pi/3) + y\cos(2\pi/3) &&= \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y \end{aligned}$$

The transformation matrices for symmetry operations of C_{3v} are as follows:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma'_{v(xz)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix (Figure 4.3.5.1):

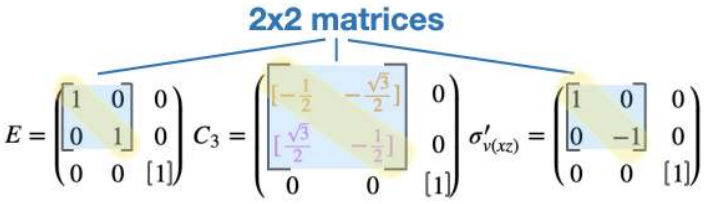


Figure 4.3.5.1: The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

The character from a 2x2 matrix is the sum of the trace of that matrix. So, for the C_3 operation, the 2x2 matrix gives the character -1 (from $-\frac{1}{2} + -\frac{1}{2}$).

The character table for C_{3v} is shown below.

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	z, z^2, x^2+y^2
A_2	1	1	−1	R_z
E	2	−1	0	$(x, y), (xy, x^2-y^2), (xz, yz), (R_x, R_y)$

Additional features of character tables

Additional Features of Character Tables

1. Symmetry operations of the same class are grouped into the same column (class) in the character table and not listed separately.
   e.g. In the C_{3v} point group, there are four operations: E, C_3, C_3^2, and σ_v. The C_3 and C_3^2 operations are listed together in the character table as $2C_3$.
2. IF there are multiple C_2 axes (in a D group), the C_2 axes that are perpendicular to the principle axis are labeled with primes (e.g. C_2' and C_2''); when there are multiple types of perpendicular C_2 axes, one prime (C_2') means that it passes through more atoms, while a double prime (C_2'') means it goes between atoms.
3. Mirror planes that are perpendicular to the principle axis are "horizontal" mirror planes and are designated with an h subscript (σ_h). Mirror planes that are in-plane with the principle axis are "vertical" mirror planes, σ_v. When there are two types of vertical mirror planes, those that run through more atoms are σ_v while those that run between atoms are "dihedral", σ_d.
4. Matching the symmetry operations listed in the character table to the symmetry operations of a molecule can confirm its point group.

5. Irreducible representations are each assigned a Mulliken label, listed in the left-hand column, that indicates the symmetry of that representation as follows:

Mulliken Labels	**meaning**
A	singly degenerate (1x1), symmetric to principle axis
B	singly degenerate (1x1), antisymmetric to principle axis
E	doubly degenerate (2x2)
T	triply degenerate (3x3)
Subscripts and superscripts	**meaning**
1	symmetric to $\sigma_v$or perpendicular to C_2
2	anti-symmetric to $\sigma_v$or perpendicular to C_2
g	symmetric to inversion center
u	anti-symmetric to inversion center
$'$	symmetric to σ_h
$''$	anti-symmetric to σ_h

6. The right-hand columns of the character table list a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products (z^2, x^2+y^2, xy, xz, yz), and the rotations (R_x, R_y, R_z). These expressions indicate the properties of orbitals within the symmetry group. The s-orbital, which is totally symmetric, corresponds to the irreducible representation that possesses symmetry of x^2, y^2 and z^2 combined. The p-orbitals each possess the symmetry of the corresponding axis (e.g. p_x corresponds to the x axis). Each of the d-orbitals possess the symmetry of the corresponding binary product (e.g. d_{xy} corresponds to the binary product, xy, in the character table).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. The transformation properties of x, y, and z can be used to determine whether or not a molecule is IR-active or whether or not it can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A visual summary of the sections and their significance is given in Figure 4.3.5.2 Character tables for common point groups are given in the References section of LibreTexts Bookshelves.

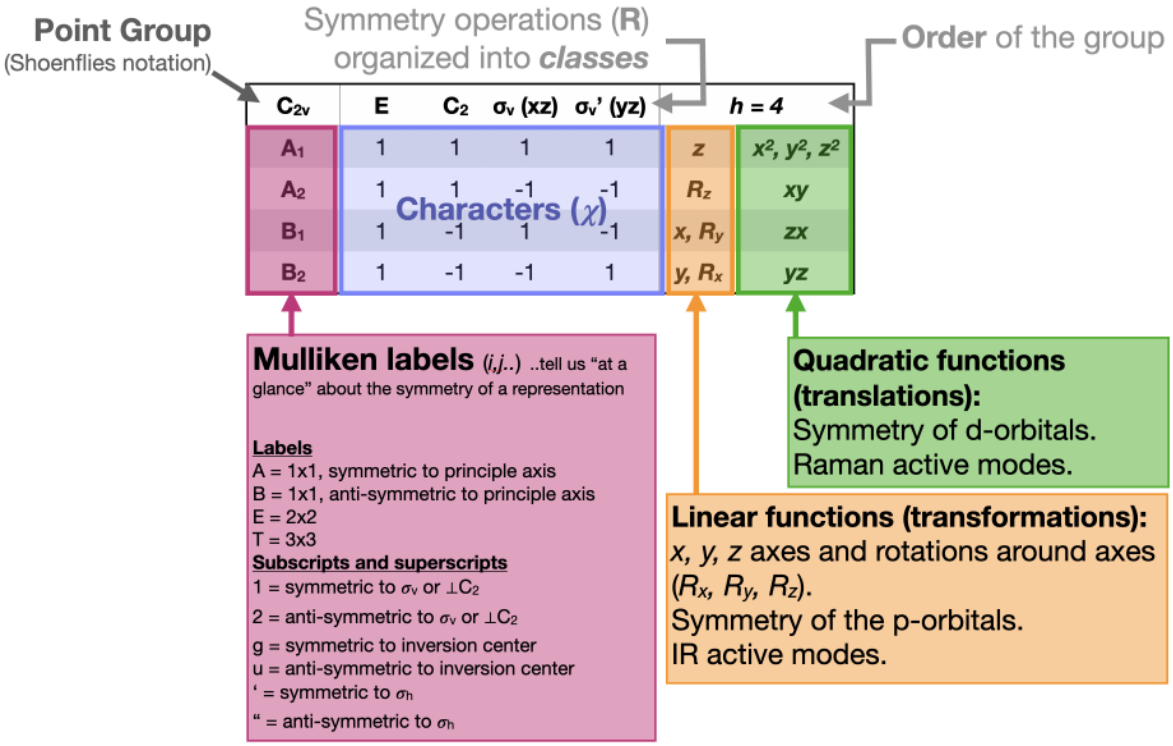


Figure 4.3.5.2: Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

Contributors and Attributions

- Curated or created by Kathryn Haas
- Claire Vallance (University of Oxford)

  adapted from Character Tables (click here)

This page titled 4.3.5: Character Tables is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **4.3.3: Character Tables** by Kathryn Haas has no license indicated.

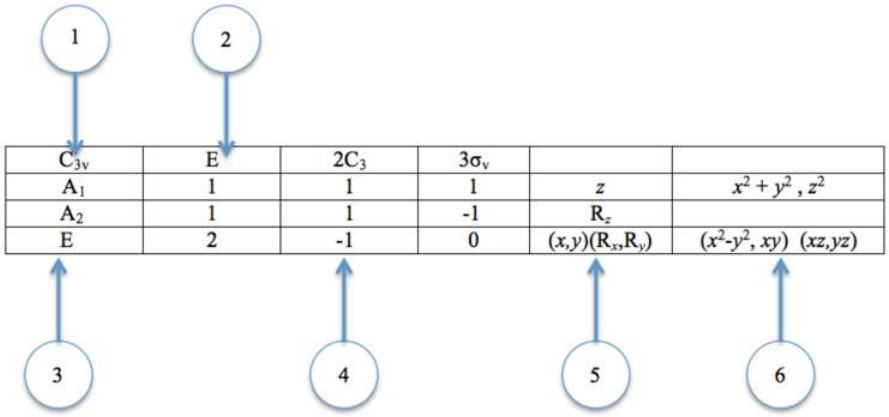
4.4: Character Tables

Definition of a Character Table

A character table is a 2 dimensional chart associated with a point group that contains the irreducible representations of each point group along with their corresponding matrix characters. It also contains the Mulliken symbols used to describe the dimensions of the irreducible representations, and the functions for symmetry symbols for the Cartesian coordinates as well as rotations about the Cartesian coordinates.

Components of a Character Table

A character table can be separated into 6 different parts, namely:



1. The Point Group
2. The Symmetry Operation
3. The Mulliken Symbols
4. The Characters for the Irreducible Representations
5. The Functions for Symmetry Symbols for Cartesian Coordinates and Rotations
6. The Function for Symmetry Symbols for Square and Binary Products

1. The Point Group

The symbol for the point group is found on the uppermost left corner of the character table. It denotes a collection of symmetry operations that are present in a molecule. It is called a point group because all the symmetry elements will intersect at one point[1].

2. The Symmetry Operations/Elements

A symmetry operation is “a geometrical operation that moves an object about some symmetry element in a way that brings the object into an arrangement that is indistinguishable from the original”(Pfennig, 199)[2]. The symmetry operations are at the first row at the top of the table. They are organized into classes, with each class having an order number in front of it. For example, $2S_4$ represents the operation S_4 with order number 2. Operations can belong to the same class when one operation may be replaced by another in a new coordinate system that is accessible by a similar symmetry operation.

Common symmetry operations that are present in character tables are:

E	C_n	C'_n
σ_d	σ_v	σ_d
I	S_n	C''_n

3. The Mulliken Symbols

These are symbols that occur under the first column of the character table. They are named after Robert S. Mulliken , who suggested using the symbols to describe the irreducible representations. The meanings of the symbols are as follows:

•The dimensions/degeneracy of characters are denoted by the letters A,B,E,T,G and H with each letter representing degeneracy 1,1,2,3,4 and 5 respectively i.e.

Mulliken Symbol	Number of Dimensions
A,B	1
E	2
T	3
G	4
H	5

For example, the Mulliken symbol A is singly degenerate and symmetric with respect to the rotation about the principal axis whereas the symbol B is anti-symmetric with respect to rotation about the principal axis even though it is also singly degenerate[3].

•The subscripts featured with each Mulliken symbol also represent different aspects of symmetry i.e.

4. The Characters for Irreducible Representations[4]

These are the rows of numbers at the center of the character table. They represent the irreducible representations of each Mulliken symbol under the point group. A representation is “a set of matrices, each corresponding to a single operation in the group, which can be combined amongst themselves similarly to how the group elements (symmetry operations) combine” .

These characters correspond to the characters of individual symmetry operations that can be described matrices, themselves. Each character can adopt a +1 or -1 or multiple of this numerical value depending on the symmetric or anti-symmetric behavior of the object undergoing a specific symmetry operation. If the object is symmetric with respect to itself after undergoing the operation, then the character is +1. If the object is anti-symmetric, then the character is -1[5].

5. The Functions for Symmetry Symbols for Cartesian Coordinates and Rotations

These are the symbols that correspond to the symmetry of the Cartesian coordinates (x, y, z) and the symmetry of the rotations about the Cartesian coordinates (R_x, R_y, R_z). They form basis representations for the group and are related to the transformation properties of the group.

For example, for the C_{3v} point group, it can be said that z forms a basis for the A_1 representation, x forms a basis for the E representation, and R_z forms a basis for the A_2 representation.

6. The Functions for Symmetry Symbols for Square and Binary Products

These are the symbols for the functions that correspond to the square (x^2+y^2, z^2, x^2-y^2) and binary products (xy, xy, yz) of the Cartesian Coordinates with respect to their transformation properties.

For example, for the C_{3v} point group, it can be said that z^2 forms a basis for the A_1 representation, (xz,yz) forms a basis for the E representation, and there is no function for the A_2 representation.

Mathematics of Character Tables

Each character table follows some main set of mathematical operations that allow for the calculation of important characteristics of the table. These operations are as follows:

a. The order of the group (h) can be calculated by taking the sum of the order of individual symmetry operations in a character table. For example, the order of the C_{3v} point group is 6.

b. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group.

c. The sum of the squares of the characters in any irreducible representation equals h.

d. The vectors whose components are the characters of two different irreducible representations are orthogonal.

e. In a given representation (reducible or irreducible) the characters of all matrices belonging to symmetry operations in the same class are identical.

f. The number of irreducible representations of a group is equal to the number of classes in the group.

Examples of Character Tables

The Character Table for the C2 Point Group

C_2	E	C_2	Linear Functions, Rotations	Quadratic Functions	Cubic Functions
A	+1	+1	z, R_z	x^2, y^2, z^2, xy	z^3, xyz, y^2z, x^2z
B	+1	-1	x, y, R_x, R_y	yz, xz	xz^2, yz^2, x^2y, xy^2, x^3, y^3

The Character Table for the Td Point Group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Linear Functions, Rotations	Quadratic Functions	Cubic Functions
A_1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	xyz
A_2	+1	+1	+1	-1	-1	-	-	-
E	+2	-1	+2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$
T_2	+3	0	-1	-1	+1	x, y, z	xy, xz, yz	(x^3, y^3, z^3), $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$

The Character Table for the D2d Point Group

D_{2d}	E	$2S_4$	$C_2(z)$	$2C'_2$	$2\sigma_d$	Linear Functions, Rotations	Quadratic Functions	Cubic Functions
A_1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	xyz
A_2	+1	+1	+1	-1	-1	R_z	-	$z(x^2-y^2)$
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_2	+1	-1	+1	-1	+1	z	xy	z^3, $z(x^2+y^2)$
E	+2	0	-2	0	0	(x, y),(R_x, R_y)	(xz, yz)	(xz^2, yz^2), (xy^2, x^2y), (x^3, y^3)

References

1. Johnston, Dean H. "Symmetry @ Otterbein". http://symmetry.otterbein.edu/index.html

2. Pfennig, Brian W. Principles of Inorganic Chemistry. , 2015. Internet resource.

3.“Understanding Character Tables of Symmetry Groups". https://chem.libretexts.org/Core/Phy...ymmetry_Groups

4. Rowland, Todd; Weisstein, Eric W. "Character Table". http://mathworld.wolfram.com/CharacterTable.html

5. Jones, Richard. “Character Tables”. University of Texas, Austin. 2015. https://sites.cns.utexas.edu/jones_c...aracter-tables

4.4: Character Tables is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

4.5: Examples and Applications of Symmetry

The purpose of learning group theory is that molecular symmetry can be applied to understand the properties of molecules. This chapter introduces two applications of symmetry: chirality and molecular vibrations (in the context of analyzing IR and Raman spectra). An additional application of symmetry, to understand molecular bonding, deserves its own chapter and will be explored in Chapter 5.

4.5.1: Chirality

4.5.2: Molecular Vibrations

4.5.3: Normal Modes of Vibration

4.5.4: Selection Rules for IR and Raman Spectroscopy

4.5.5: Stretching Frequencies and Structure Determination

4.5: Examples and Applications of Symmetry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.5.1: Chirality

Introduction

Around the year 1847, the French scientist Louis Pasteur provided an explanation for the optical activity of tartaric acid salts. When he carried out a particular reaction, Pasteur observed that two types of crystals precipitated. Patiently and carefully using tweezers, Pasteur was able to separate the two types of crystals. Pasteur noticed that the types rotated plane-polarized light by the same amount but in different directions. These two compounds are called enantiomers.

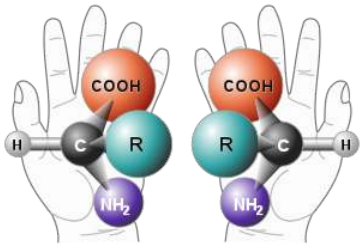


Figure 4.5.1.1: Two enantiomers of an amino acid (with side chain R).

What is chirality?

A molecule is **chiral** (or **dissymetric**) if it is non-superimposable on its mirror image. The two mirror images of a chiral molecule are called enantiomers. Enantiomers have the same physical properties (e.g., melting point, etc.). They differ in their ability to rotate plane polarized light and in their reactivity with other chiral molecules. Due to their ability to rotate plane polarized light, they are referred to as being *optically active*.

Using Symmetry to Determine Chirality

There are some general rules of thumb that help determine whether a molecule is chiral or achiral. The point group of the molecule, and the symmetry operations within that point group, can give clues as to whether the molecule is chiral.

Symmetry operations of chiral molecules

A chiral molecule cannot possess a plane of symmetry (σ), a center of inversion (i), or an improper rotation (S_n). Due to the fact that all groups that lack both σ and i also lack S_n, **a molecule that belongs to any group that lacks S_n is chiral**.

An example of an inorganic coordination complex is tris(ethylenediamine)cobalt(III) (Figure 4.5.1.1). Figure 4.5.1.1 shows the two enantiomers of tris(ethylenediamine)cobalt(III): the Δ and Λ isomers.

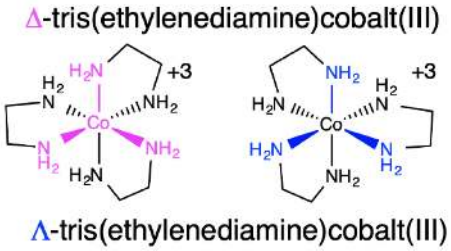


Figure 4.5.1.2: Two chiral enantiomers of tris(ethylenediamine)coalt(III).

You can visualize the Λ and Δ isomers by imagining that the ligands around the metal centers are blades of a fan. To push the air toward you, you would need to rotate the Δ isomer clockwise, and the Λ isomer counter-clockwise.

Exercise 4.5.1.1

Which point groups are possible for chiral molecules?

Answer

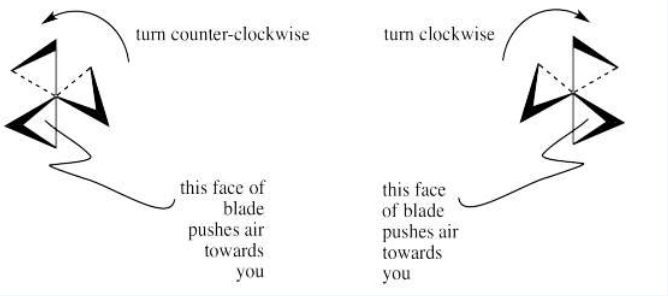


Figure 4.5.1.3: Another way of thinking about the chirality of the two chiral enantiomers of tris(ethylenediamine)coalt(III) shown in Figure 4.5.1.2. This figure was taken from Structure and Reactivity in Organic, Biological, and Inorganic Chemistry.

As a result of the previous discussion, there are a few classes of point groups that lack an improper axis. Those classes are C_1, C_n, and D_n.

4.5.1: Chirality is shared under a CC BY-NC license and was authored, remixed, and/or curated by LibreTexts.

- **4.4.1: Chirality** by Kathryn Haas is licensed CC BY-NC 4.0.

4.5.2: Molecular Vibrations

Symmetry and group theory can be applied to understand molecular vibrations. This is particularly useful in the context of predicting the number of peaks expected in the infrared (IR) and Raman spectra of a given compound.

We will use water as a case study to illustrate how group theory is used to predict the number of peaks in IR and Raman spectra.

How many IR and Raman peaks would we expect for H_2O?

To answer this question with group theory, a pre-requisite is that you **assign the molecule's point group and assign an axis system** to the entire molecule. By convention, the z axis is collinear with the principle axis, the x axis is in-plane with the molecule or the most number of atoms. It is a good idea to stick with this convention (see Figure 4.5.2.1).

What is the point group for H_2O? (click to see answer)

H_2O has the following operations: E, C_2, σ_v, σ_v'. The point group is C_{2v}.

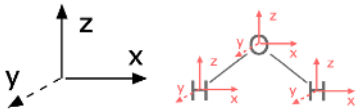


Figure 4.5.2.1: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom. (CC-BY-SA; Kathryn Haas)

Now that we know the molecule's point group, we can use group theory to determine the symmetry of all motions in the molecule, or the symmetry of each of its degrees of freedom. Then we will subtract rotational and translational degrees of freedom to find the vibrational degrees of freedom. The number of degrees of freedom depends on the number of atoms (N) in a molecule. Each atom in the molecule can move in three dimensions (x, y, z), and so the number of degrees of freedom is three dimensions times N number of atoms, or $3N$. The total degrees of freedom include a number of vibrations, three translations (in x, y, and z), and either two or three rotations. Linear molecules have two rotational degrees of freedom, while non-linear molecules have three. The vibrational modes are represented by the following expressions:

$$\begin{aligned} \text{Linear Molecule Degrees of Freedom} &= 3N-5 \\ \text{Non-Linear Molecule Degrees of Freedom} &= 3N-6 \end{aligned}$$

Our goal is to find the symmetry of all degrees of freedom, and then determine which are vibrations that are IR- and Raman-active.

STEP 1: Find the reducible representation for all normal modes Γ_{modes}.

The first major step is to **find a reducible representation (Γ)** for the movement of all atoms in the molecule (including rotational, translational, and vibrational degrees of freedom). We'll refer to this as Γ_{modes}. To find normal modes using group theory, **assign an axis system** to each individual atom to represent the three dimensions in which each atom can move. Each axis on each atom should be consistent with the conventional axis system you previously assigned to the entire molecule (see Figure 4.5.2.1).

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 $\boldsymbol{\Gamma_{modes}}$ for $\boldsymbol{H_2O}$ to illustrate how this works:

For the operation $\boldsymbol{E}$, performed on H_2O, all three atoms remain in place. The three axes x, y, z on each atom remain unchanged. Thus, each of the three axes on each of three atom (nine axes) is assigned the value $\cos(0^\circ) = 1$, resulting in a sum of $\boldsymbol{\chi = 9}$ for the Γ_{modes}.

For the operation $\boldsymbol{C_2}$, the two hydrogen atoms are moved away from their original position, and so the hydrogens are assigned a value of zero. The oxygen remains in place; the z-axis on oxygen is unchanged ($\cos(0^\circ) = 1$), while the x and y axes are inverted ($\cos(180^\circ)$). The sum of these characters gives $\boldsymbol{\chi = -1}$ in the Γ_{modes}.

Now you try! Find the characters of $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$ under the C_{2v} point group. Compare what you find to the Γ_{modes} for all normal modes given below.

C_{2v}	E	C_2	σ_v	σ'_v
Γ_{modes}	9	-1	3	1

(4.5.2.1)

STEP 2: Break $\boldsymbol{\Gamma_{modes}}$ into its component irreducible representations.

Now that we've found the Γ_{modes} (4.5.2.1), we need to break it down into the individual irreducible representations ($i, j, k \ldots$) for the point group. We can do this systematically using the following formula:

$$\#\text{ of } i = \frac{1}{h}\sum(\#\text{ of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \qquad (4.5.2.2)$$

In other words, the number of irreducible representations of type i is equal to the sum of the number of operations in the class $\times$ the character of the Γ_{modes} $\times$ the character of i, and that sum is divided by the order of the group (h).

Using equation 4.5.2.2, we find that for all normal modes of H_2O:

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2 \tag{4.5.2.3}$$

.

Notice there are 9 irreducible representations in Equation 4.5.2.3. These irreducible representations represent the symmetries of all 9 motions of the molecule: vibrations, rotations, and translations.

? Exercise 4.5.2.1: Derive the irreducible representation in equation 4.5.2.3.

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 4.5.2.3

Hint

To find the number of each kind of irreducible representation that combine to form the Γ_{modes}, we need the characters of Γ_{modes} that we found above (4.5.2.1), the C_{2v} character table (below), and equation 4.5.2.2

C_{2v}	$1E$	$1C_2$	$1\sigma_v$	$1\sigma_v'$	$h=4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

In the C_{2v} point group, each class has only one operation, so the number of operations in each class (from equation 4.5.2.2) is 1 for each class. This has been explicitly added to the character table above for emphasis.

Answer

The number of A_1 = $\frac{1}{4}[(1\times 9\times 1)+(1\times(-1)\times 1)+(1\times 3\times 1)+(1\times 1\times 1)] = 3A_1$

The number of A_2 = $\frac{1}{4}[(1\times 9\times 1)+(1\times(-1)\times 1)+((-1)\times 3\times 1)+((-1)\times 1\times 1)] = 1A_2$

The number of B_1 = $\frac{1}{4}[(1\times 9\times 1)+((-1)\times(-1)\times 1)+(1\times 3\times 1)+((-1)\times 1\times 1)] = 3B_1$

The number of B_2 = $\frac{1}{4}[(1\times 9\times 1)+((-1)\times(-1)\times 1)+((-1)\times 3\times 1)+(1\times 1\times 1)] = 2B_2$

STEP 3: Subtract rotations and translations to find vibrational modes.

Because we are interested in molecular vibrations, we need to subtract the rotations and translations from the total degrees of freedom.

$$\text{Vibrations} = \Gamma_{modes} - \text{Rotations} - \text{Translations}$$

In the example of H_2O, the total degrees of freedom are given above in equation 4.5.2.3, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{4.5.2.4}$$

But which of the irreducible representations are ones that represent rotations and translations? The symmetry of rotational and translational degree modes can be found by inspecting the right-hand columns of any character table. Rotational modes correspond to irreducible representations that include R_x, R_y, and R_z in the table, while each of the three translational modes has the same symmetry as the x, y and z axes. For a non-linear molecule, subtract three rotational irreducible representations and three translational irreducible representations from the total Γ_{modes}.

In the specific case of water, we refer to the C_{2v} character table:

C_{2v}	E	C_2	σ_v	σ_v'	$h=4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

In C_{2v}, translations correspond to B_1, B_2, and A_1 (respectively for x, yz), and rotations correspond to B_2, B_1, and A_1 (respectively for R_x, R_y, R_z). Subtracting these six irreducible representations from Γ_{modes} will leave us with the irreducible representations for vibrations.

$$\begin{aligned} H_2O \text{ vibrations} &= \Gamma_{modes} - \text{Rotations} - \text{Translations} \\ &= (3A_1 + 1A_2 + 3B_1 + 2B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) \\ &= 2A_1 + 1B_1 \end{aligned}$$

The three vibrational modes for H_2O are $2A_1 + 1B_1$. Note that we have the correct number of vibrational modes based on the expectation of $3N - 6$ vibrations for a non-linear molecule.

STEP 4: Determine which of the vibrational modes are IR-active and Raman-active.

The next step is to determine which of the vibrational modes is IR-active and Raman-active. To do this, we apply the IR and Raman Selection Rules below:

IR and Raman Selection Rules

Infrared selection rules:

If a vibration results in the change in the molecular dipole moment, it is IR-active. In the character table, we can recognize the vibrational modes that are IR-active by those with symmetry of the x, y, and z axes.

In C_{2v}, any vibrations with A_1, B_1 or B_2 symmetry would be IR-active.

Raman selection rules:

If a vibration results in a change in the molecular polarizability, it will be Raman-active. In the character table, we can recognize the vibrational modes that are Raman-active by those with symmetry of any of the binary products (xy, xz, yz, x^2, y^2, and z^2) or a linear combination of binary products (e.g. $x^2 - y^2$).

In C_{2v}, any vibrations with A_1, A_2, B_1 or B_2 symmetry would be Raman-active.

In our H_2O example, we found that of the three vibrational modes, two have A_1 and one has B_1 symmetry. Both A_1 and B_1 are IR-active, and both are also Raman-active. ***There are two possible IR peaks and three possible Raman peaks expected for water***.*

*It is important to note that this prediction tells only what is possible, but not what we might actually see in the IR and Raman spectra. For example, if the two IR peaks overlap, we might actually notice only one peak in the spectrum. Or, if one or more peaks is off-scale, we wouldn't see it in actual data. Group theory tells us what is *possible and allows us to make predictions or interpretations of spectra.*

Summary of Analysis for Water

Each molecular motion for water, or any molecule, can be assigned a symmetry under the molecule's point group. For water, we found that there are a total of 9 molecular motions; $3A_1 + A_2 + 3B_1 + 2B_2$. Six of these motions are not the translations and rotations. The remaining motions are vibrations; two with A_1 symmetry and one with B_1 symmetry.

We can tell what these vibrations would look like based on their symmetries. The two A_1 vibrations must be completely symmetric, while the B_1 vibration is antisymmetric with respect to the principal C_2 axis.

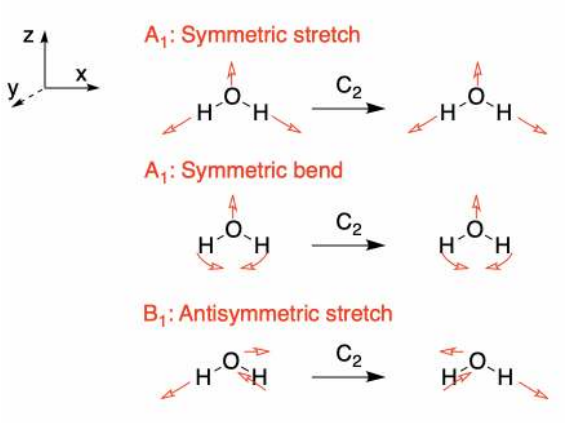


Figure 4.5.2.2: Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

Table 4.5.2.1: Summary of the Symmetry of Molecular Motions for Water

All Motions (step 2 above)	Translations (x,y,z)	Rotations (R_x, R_y, R_z)	**Remaining Vibrations**	Description of Vibration
$3A_1$	$1A_1$		$\mathbf{2A_1}$	One is a symmetric stretch. The other is a symmetric bend. Both are *IR-active* and *Raman-active*
A_2		$1A_2$		
$3B_1$	$1B_1$	$1B_1$	$\mathbf{1B_1}$	Antisymmetric stretch that is *IR-active* and *Raman-active*.
$2B_2$	$1B_2$	$1B_2$		

Exercise 4.5.2.2

Find the symmetries of all motions of the square planar complex, tetrachloroplatinate (II). Determine which are rotations, translations, and vibrations. Determine which vibrations are IR and Raman active.

Answer

The point group of $[PtCl_4]^{2-}$ is D_{4h} (refer to its character table). There are five atoms and 15 vectors (x, y, z for each atom $\times$ 5 atoms).

STEP 1: The first major step is to **find a reducible representation (Γ)** for the movement of all atoms in the molecule.

C_{2v}	E	$2C_4$	C_2	$2C_2'$	$2C_2$ ”	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{modes}	15	1	−1	−3	−1	−3	−1	5	3	1

(4.5.2.5)

.

STEP 2: Break Γ_{modes} into its component irreducible representations.

Following the process described earlier, we come to $A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$. This accounts for all modes of movement, including rotations and translations.

STEP 3: Subtract rotations and translations to find vibrational modes.

The translations are $A_{2u} + E_u$ and the rotations are $A_{2g} + E_g$.
The remaining normal modes are: $A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$

STEP 4: Determine which of the vibrational modes are IR-active and Raman-active:

$A_{2u} + E_u$ are IR-active. Since A_{2u} is singly degenerate and E_u is doubly degenerate, we expect three possible IR bands.
$A_{1g} + B_{1g} + B_{2g}$ are Raman-Active. Each of these is singly degenerate, so we expect three possible Raman bands.

Selected Vibrational Modes

The interpretation of CO stretching vibrations in an IR spectrum is particularly useful. Symmetry and group theory can be applied to predict the number of CO stretching bands that appear in a vibrational spectrum for a given metal coordination complex. A classic example of this application is in distinguishing isomers of metal-carbonyl complexes. For example, the *cis*- and *trans*-isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) have a different number of IR stretches that can be predicted and interpreted using symmetry and group theory. Another example is the case of *mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$). Structures of the two types of metal carbonyl configurations and their isomers are shown in Figure 4.5.2.1. The isomers in each case can be distinguished using vibrational spectroscopy.

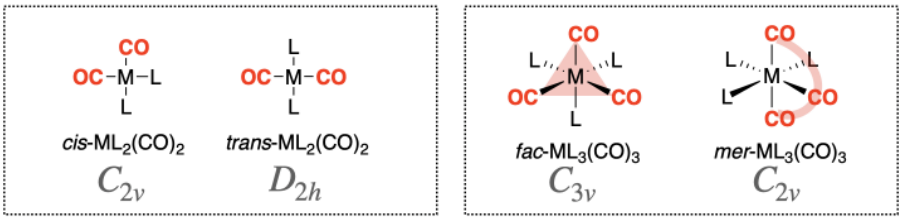


Figure 4.5.2.3: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box. *Mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$) are shown in the right box. The point group for each of the general structures is also shown. (CC-BY-NC-SA; Kathryn Haas)

EXAMPLE 1: Distinguishing *cis*- and *trans*- isomers of square planar metal dicarbonyl complexes

General structures of the *cis*- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box in Figure 4.5.2.1. We can use symmetry and group theory to predict how many carbonyl stretches we should expect for each isomer following the steps below.

Step 1: Assign the point group and Cartesian coordinates for each isomer.

The *cis*-isomer has C_{2v} symmetry and the *trans*-isomer has D_{2h} symmetry. We assign the Cartesian coordinates so that z is colinear with the principle axis in each case. For the D_2h isomer, there are several orientations of the z axis possible. The axes shown in Figure 4.5.2.2will be used here.

Figure 4.5.2.4: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown and oriented with respect to the Cartesian coordinates shown at the left so that the highest-order rotation axis is colinear with z and the molecule is co-planar with the xz plane. The vector along each C—O bond is shown using a red arrow (→). These vectors represent the direction of C—O stretching motions. (CC-BY-NC-SA; Kathryn Haas)

Step 2: Produce a reducible representation (Γ) for CO stretches in each isomer

First, assign a vector along each C—O bond in the molecule to represent the direction of C—O stretching motions, as shown in Figure 4.5.2.2(red arrows →). These vectors are used to produce a reducible representation (Γ) for the C—O stretching motions in each molecule. Using the symmetry operations under the appropriate character table, assign a value of 1 to each vector that remains in place during the operation, and a value of 0 if the vector moves out of place. There will be no occasion where a vector remains in place but is inverted, so a value of -1 will not occur.

cis- $ML_2(CO)_2$:

For *cis*- $ML_2(CO)_2$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{cis-CO}.

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0

trans- $ML_2(CO)_2$:

For trans- $ML_2(CO)_2$, the point group is D_{2h} and so we use the operations under the D_{2h} character table to create the $\Gamma_{trans-CO}$.

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0

Step 3: Break each Γ into its component irreducible representations

Each Γ can be reduced using inspection or by the systematic method described previously.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

(4.5.2.6)

In the case of *trans*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_{3u} irreducible representations:

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0	
A_g	1	1	1	1	1	1	1	1	$x^2,\ y^2,\ z^2$
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

These irreducible representations correspond to the symmetries of only the selected C—O vibrations. Since these motions are isolated to the C—O group, they do not include any rotations or translations of the entire molecule, and so we do not need to find and subtract rotationals or translations (unlike the previous cases where all motions were considered).

Step 4: Determine which vibrational modes are IR-active and/or Raman-active

Apply the infrared selection rules described previously to determine which of the CO vibrational motions are IR-active and Raman-active. The two isomers of $ML_2(CO)_2$ are described below.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations. The characters of both representations and their functions are shown above, in 4.5.2.6 (and can be found in the C_{2v} character table). Under C_{2v}, both the A_1 and B_1 CO vibrational modes are IR-active and Raman-active. Therefore, two bands in the IR spectrum and two bands in the Raman spectrum are possible.

In the case of the trans- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_g and B_{3u} irreducible representations. The characters of both representations and their functions are shown above, in 4.5.2.6 (and can be found in the D_{2h} character table). Under D_{2h}, the A_g vibrational mode is is Raman-active only, while the B_{3u} vibrational mode is IR-active only. Therefore, only one IR band and one Raman band are possible for this isomer.

Summary

It is possible to distinguish between the two isomers of square planar $ML_2(CO)_2$ using either IR or Raman vibrational spectroscopy. The *cis*- $ML_2(CO)_2$ can produce two CO stretches in an IR or Raman spectrum, while the *trans*- $ML_2(CO)_2$ isomer can produce only one band in either type of vibrational spectrum. If a sample of $ML_2(CO)_2$ produced two CO stretching bands, we could rule out the possibility of a pure sample of *trans*-$ML_2(CO)_2$.

Exercise 4.5.2.3

Repeat the steps outlined above to determine how many CO vibrations are possible for *mer*-$ML_3(CO)_3$ and *fac*-$ML_3(CO)_3$ isomers (see Figure 4.5.2.1) in both IR and Raman spectra. Could either of these vibrational spectroscopies be used to distinguish the two isomers?

Answer

Step 1: Assign the point group and Cartesian coordinates for each isomer.
The *fac*-isomer is C_{3v}. The *mer*-isomer is C_{2v}.

Step 2: Produce a reducible representation for CO stretches in each isomer.

Step 3: Break each into its component irreducible representations.

Step 4: Determine which vibrational modes are IR-active and/or Raman-active.

***For fac*-$ML_3(CO)_3$**, the point group is C_{3v} and so we use the operations under the C_{3v} character table to create the Γ_{fac-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

$\mathbf{C_{3v}}$	E	$2C_2$	$3\sigma_v$
$\mathbf{\Gamma_{fac-CO}}$	3	0	1

This reduces to $A_1 + E$. Both of these are IR active, and since one is singly degenerate while the other is doubly degenerate, we expect three possible IR bands from this isomer. Both vibrational modes are also Raman active, and again we would expect three possible bands in the Raman spectrum.

For mer-$ML_3(CO)_3$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{mer-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\mathbf{\Gamma_{mer-CO}}$	3	1	3	1

This reduces to $2A_1 + B_1$; both A_1 and B_1 are IR and Raman active. So this isomer would have three possible IR bands and three possible Raman Bands.

These two isomers have the same number of possible bands in both IR and Raman spectroscopy. It would not be straightforward to distinguish them from each other based on the number of possible bands in the vibrational spectrum.

This page titled 4.5.2: Molecular Vibrations is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **4.4.2: Molecular Vibrations** by Kathryn Haas is licensed CC BY-NC 4.0.

4.5.3: Normal Modes of Vibration

Molecular vibrations

Molecular vibrations are one of three kinds of motion, occurs when atoms in a molecule are in periodic motion. Molecular vibrations include constant translational and rotational motion. Translational motion occurs when the whole molecule goes in the same direction while the rotational motion occurs when the molecule spins like a top. Molecule vibrations fall into two main categories of stretching and bending. **Stretching** changes in interatomic distance along bong axis, while **bending** changes in angle between two bonds in a molecule.

There are two types of stretching, symmetric stretching and asymmetric stretching as the following figure shows:

There are four types of bend, rocking, scissoring, wagging, and twisting.

Normal modes of vibration

Each atom in a molecule has three degree of freedom. A molecule with n atoms has 3n degree of freedom. 3n degree of freedom composes of translation, rotations and vibrations. All 3n degrees of freedom have symmetry relationships consistent with the irreducible representations of the molecule's point groups. **Non-vibration modes** (NVM) include translations and rotations. The vibrational motions of the atoms in a molecule can always be resolved into fundamental vibrational modes for the entire molecule.

Atomic displacement coordinates

The number of normal modes of vibration:

- 3n-6 for non-linear molecules
- 3n-5 for linear molecules

To indicate the the number of normal modes of vibration:

- Locate a set of three vectors along the Cartesian coordinates at each atom, representing the 3n degrees of freedom
- Find the reducible representation
- Reduce it to irreducible representations, subtract rotations and translations
- The rest of irreducible representations will give the symmetry of the NMVs

Samples

vibrations for SO_2

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$		
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
Γ_{3n}	9	-1	1	3		
N_i	3	1	1	3		
X_i	3	-1	1	1		

Reduce

$\Gamma_{3n}=3A_1+A_2+2B_1+3B_2$

$\Gamma_{trans}=A_1+B_1+B_2$

$\Gamma_{rotations}=A_2+B_1+B_2$

$\Gamma_{NMV}=\Gamma_{3n-6}=2A_1+B_2$

NMVs are also identified by frequency numbers: v_1, v_2, v_3,... The numbering is often assigned systematically in descending order of the symmetry species and among modes of the same symmetry in descending order of the vibrational frequency. Stretching modes have **higher** frequency than bending modes.

4.5.3: Normal Modes of Vibration is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

4.5.4: Selection Rules for IR and Raman Spectroscopy

Infrared Spectroscopy

Infrared spectroscopy measures the frequency of absorption when a sample is irradiated with infrared electromagnetic radiation. It is a technique used to study the vibrations between atoms because atomic vibrational excitations occur in the infrared region of the electromagnetic spectrum. The bonds between atoms can be thought of as a spring connecting two masses. In the spring-mass analogy the moving system can be approximated by a simple harmonic oscillator. The frequency oscillation is proportional to $\sqrt{\frac{k}{m}}$,where k is the spring constant and m is the mass of the object. In a similar approximation, the frequency of vibration between two atoms is unique and varies depending on the strength of the bond (k) and the size of the atoms (m). When the frequency of electromagnetic radiation matches the natural frequency of vibration between atoms, the atoms are able to absorb this energy and exhibit vibrations. These vibrations can be detected as signals if they produce a change in the dipole moment between two atoms which can interact with the electric field. Representations for normal modes of vibration will be active in the infrared if they transform similar to any one of the cartesian coordinates (x,y,z). This would mean the vibrational motion has shifted the charge distribution in any of the x, y, or z directions resulting in a change in the dipole moment. Selection rules such as these are used to tell us whether such transitions are allowed, and therefore observed, or whether they are forbidden.

Raman Spectroscopy

Unlike IR spectroscopy which measures the energy absorbed, Raman spectroscopy consists of exposing a sample to high energy monochromatic light that interacts with the molecule and causes electronic, vibrational, or translational excitations. Upon interaction, the energy of the light is shifted either up or down and these changes can give information about the molecule's various vibrational states. A photon of light excites the molecule to an excited state and upon relaxation to a different rotational or vibrational state the molecule emits a photon of a different energy. A vibration will give rise to a Raman shift, due to a shift from the incident light, if it has the same symmetry as the molecular polarizability. Polarizability measures the ability for a molecule's electron cloud to become distorted. A dense electron cloud is more difficult to change than a more spread out electron density. The representation for one of the normal modes of vibration will be Raman active if it transforms similarly to the direct products of any one of the x, y, or z coordinates. That includes any of the functions: xy, xz, yz, x^2, y^2, z^2, or any combination.

Rule of Mutual Exclusion

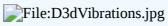
A molecule is centrosymmetric if it has a center of inversion and their corresponding point group contains the class for inversion. In such cases, the unit vectors transform as ungerade, or unsymmetric about the center of inversion, and direct products transform as gerade, or symmetric about the center of inversion. As a result, the normal modes of vibrational will show frequencies in either the IR or Raman, but the same frequency will not be observed in both.

Example 4.5.4.1

Boron Trifluoride or D_{3d} point group

D_{3d}	E	$2C_3(z)$	$3C'_2$	σ_h (xy)	$2S_3$	$3\sigma_v$	Linear Functions/ Rotations	Quadratic Functions	Cubic Functions
A'_1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	$x(x^2-3y^2)$
A'_2	+1	+1	-1	+1	+1	-1	R_z	-	$y(3x^2-y^2)$
E'	+2	-1	0	+2	-1	0	(x,y)	$(x^2-y^2$, xy)	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
A''_1	+1	+1	+1	-1	-1	-1	-	-	-
A''_2	+1	+1	-1	-1	-1	+1	z	-	z^3, $z(x^2+y^2)$
E''	+2	-1	0	-2	+1	0	(R_x, R_y)	(xz, yz)	$[xyz, z(x^2-y^2)$

Normal Modes of Vibration for D_{3d}:



4.5.4: Selection Rules for IR and Raman Spectroscopy is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

4.5.5: Stretching Frequencies and Structure Determination

Stretching Modes of Vibration

Often, we are only concerned with the stretching modes of vibrations for certain groups in a molecule. In this case, we can use the bonds to describe the stretching vibration for that group, though we have to consider all the bonds of the same type together. The general strategy is to come up with a reducible representation for only the bond vectors of the groups we are concerned with, then reduce them into their irreducible representations.

Figure *[Math Processing Error]*. Mo(CO)3(NCCH3)3 in its facial (left) and meridional (right) form.

Consider the compound *fac*-$Mo(CO)_3(NCCH_3)_3$ shown in Figure \(\PageIndex{1}\). We first determine the point group of the molecule, which is C_{3v} for this molecule (character table shown in Table *[Math Processing Error]*). We then use the Mo-CO bonds as a basis and generate a reducible representation using the character table. We therefore apply each operation to this basis and if a bond does not move we add a character of 1, if a bond is inverted it gets a character of -1, and if it moves we don't add anything to that character. Under the operation *E*, all three bonds are left unchanged so we give it a character of 3. Under the C_3 operation, all of the bond vectors move, so we have a character of 0. Lastly, for the σ_v two bond vectors move and one stays in place, so we give it a character of 1. So our reducible representation is:

	E	**C_2**	**σ_v (xz)**	**σ'_v (yz)**
Γ	3	1	0	3

This reduces into $\Gamma = A_1 + E$. We can then determine from the character table that both of these will be IR and Raman active stretches.

Structure Determination

In chemistry, we are often concerned with the exact molecular structure of the compounds we are working with. We can use spectroscopy to further identify the structure of the molecule by considering the number of IR or Raman modes of vibration present. For example, $Mo(CO)_3(NCCH_3)_3$ is can come in either its facial or meridional form (Figure 1) and therefore have different symmetries present - facial is C_{3v} and meridional is C_{2v} (C_{2v} character table shown in Table *[Math Processing Error]*). If we generate a reducible representation for the CO stretching vibrations in the meridional form, we get that:

	E	C_2	σ_v (xz)	σ'_v (yz)
Γ	3	1	0	3

This can then be reduced to $\Gamma_{mer} = 2A_1 + E$. All three of these stretching vibrations are IR active. If we compare that to the facial version: $\Gamma_{fac} = A_1 + E$ as determined above, we can see that the *fac*-$Mo(CO)_3(NCCH_3)_3$ will have 2 IR active CO vibrational modes and *mer*-$Mo(CO)_3(NCCH_3)_3$ has 3 IR active CO vibrational modes. This information can be used to distinguish between the two structures experimentally using IR spectroscopy. The same technique can be applied to Raman active modes.

Centrosymmetric Point Groups

We can further use Raman and IR spectroscopy to determine if our molecule has an inversion center present. This is because for molecules with an inversion center, all IR active modes are not Raman active and all Raman active modes are not IR active. This is known as the rule of mutual exclusion.

Table *[Math Processing Error]*. C_{3v} Character Table

	E	**$2C_3$**	**$3\sigma_v$**	

A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y), (R_x, R_y)$	$(x^2-y^2, xy), (xz, yz)$

Table *[Math Processing Error]*. C_{2v} Character Table

	E	**C_2**	**σ_v (xz)**	**σ'_v (yz)**		
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

4.5.5: Stretching Frequencies and Structure Determination is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

4.6: Problems (do we want this here?)

Problems

1. Chlorophyll *a* is a green pigment that is found in plants. Its molecular formula is $C_{55}H_{77}O_5N_4Mg$. How many degrees of freedom does this molecule possess? How many vibrational degrees of freedom does it have?
2. CCl_4 was commonly used as an organic solvent until its severe carcinogenic properties were discovered. How many vibrational modes does CCl_4 have? Are they IR and/or Raman active?
3. The same vibrational modes in H_2O are IR and Raman active. WF_6^- has IR active modes that are not Raman active and vice versa. Explain why this is the case.
4. How many IR peaks do you expect from SO_3? Estimate where these peaks are positioned in an IR spectrum.
5. Calculate the symmetries of the normal coordinates of planar BF_3.

Answers to Problems

1. Chlorophyll *a* has 426 degrees of freedom and 420 vibrational modes.
2. The point group is T_d, $T_{vib} = a_1 + e + 2t_2$; a_1 and e are Raman active, t_2 is both IR and Raman active.
3. For molecules that possess a center of inversion i, modes cannot be simultaneously IR and Raman active.
4. Point group is D_{3h}; one would expect three IR active peaks. Asymmetric stretch highest (1391 cm^{-1}), two bending modes (both around 500 cm^{-1}). The symmetric stretch is IR inactive.
5. $T_{3N} = A_1' + A_2' + 3E' + 2\ A_2'' + E''$ and $T_{vib} = A_1' + 2E' + A_2''$

Contributors and Attributions

- Kristin Kowolik, University of California, Davis

Problems

1. The water molecule H_2O was used as an example; it was mentioned that when water was rotated 180 degrees around an axis bisecting the oxygen, the molecule was superimposable on the original water molecule. How about CO_2? Will it be like the water molecule since CO_2 also has 2 atoms of oxygen?

Of course not, because every molecule has a different molecular shape. To recognize the symmetry of any molecule, the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degrees around the axis bisecting the C atom, then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to? Why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry, since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates whether we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bonding for that molecule.

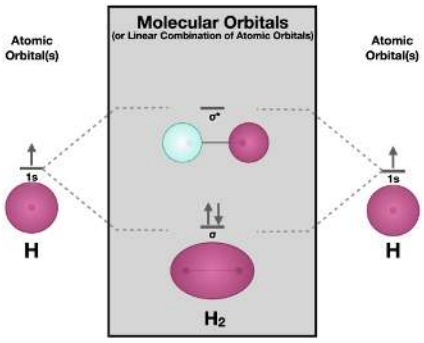
4.6: Problems (do we want this here?) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **4.P: Problems (under construction)** by Kathryn Haas has no license indicated.

CHAPTER OVERVIEW

5: Molecular Orbitals

Molecular Orbital Theory



Molecular Orbital (MO) Theory is a sophisticated bonding model. It is generally considered to be more powerful than *Lewis* and *Valence Bond Theories* for predicting molecular properties, however this power comes at the price of complexity. In its full development, MO Theory requires complex mathematics, though the ideas behind it are simple. Atomic orbitals (AOs) that are localized on individual atoms combine to make molecular orbitals (MOs) that are distributed over the molecule. The simplest example is the molecule, dihydrogen (H_2), in which two independent hydrogen 1s orbitals combine to form the sigma bonding and antibonding orbitals of the dihydrogen molecule (see figure). The MO's are also called Linear Combinations of Atomic Orbitals (LCAO).

5.1: Formation of Molecular Orbitals from Atomic Orbitals
- 5.1.1: Molecular Orbitals from s Orbitals
- 5.1.2: Molecular Orbitals from p Orbitals
- 5.1.3: Molecular orbitals from d orbitals
- 5.1.4: Nonbonding Orbitals and Other Factors

5.2: Homonuclear Diatomic Molecules
- 5.2.1: Molecular Orbitals
- 5.2.2: Orbital Mixing
- 5.2.3: Diatomic Molecules of the First and Second Periods
- 5.2.4: Photoelectron Spectroscopy

5.3: Heteronuclear Diatomic Molecules
- 5.3.1: Polar bonds
- 5.3.2: Ionic Compounds and Molecular Orbitals

5.4: Diatomic Molecular Orbitals
- 5.4.1: Molecular Orbital Theory

5.P: Problems

This page titled 5: Molecular Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

5.1: Formation of Molecular Orbitals from Atomic Orbitals

Molecular orbital theory extends from quantum theory and the atomic orbital wavefunctions (ψ) described by the Schrödinger equation. While the Schrödinger equation defines a Ψ for electrons in individual atoms, we can approximate the molecular wavefunction (what Ψ would look like if we combined the ψ of individual atoms). The addition or subtraction of wavefunctions is termed **linear combination of atomic orbitals** (LCAO). Molecular orbital theory is applied to LCAO to describe bonding.

The LCAO for the wavefunction of two atoms (ψ_a and ψ_b) is represented by the general expression below. The coefficients c_a and c_b quantify the contribution of each atomic ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

For two atomic ψs to form a bond, three conditions must be satisfied:

- First, the **distance between the atoms** must be small enough to provide good overlap. This is because the two orbitals must be able to overlap using regions of ψ^2 where the probability of finding electrons is significant. If atoms are not close enough, ψ_a and ψ_b cannot interact productively. At the same time, the atoms must be far enough apart that their nuclei do not repel each other.
- The **symmetry of the orbitals** must be compatible such that regions of ψ_a and ψ_b with the same sign constructively interfere more than regions with opposite sign destructively interfere. In other words, for a productive interaction, there must be a relatively high probability of finding an electron between the two nuclei, and this depends on the symmetry (and sign of the ψ) of the atomic orbitals.
- Third, the **energies of the atomic orbitals** must be similar. Orbitals with similar energy combine to make the most stable bonding molecular orbitals. Atomic orbitals with very different energies form less stable bonding interactions, and the larger the difference in the atomic orbitals, the weaker the bonding interaction will be.

Atomic orbitals combine to form molecular orbitals when these three conditions are met. The result is a set of bonding molecular orbitals that are lower in energy than the original atomic orbital energies.

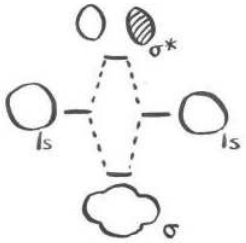
This page titled 5.1: Formation of Molecular Orbitals from Atomic Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.1: Formation of Molecular Orbitals from Atomic Orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

5.1.1: Molecular Orbitals from s Orbitals

In the case of the hydrogen molecule, we took two atomic orbitals and combined them to form two molecular orbitals. These new molecular orbitals had different wavelengths than the two atomic orbitals: one had a longer wavelength and was a little lower in energy, while the other had a shorter wavelength and was a little higher in energy. If we take into account the energy of the two original atomic wavefunctions, and compare them to the total energy of the two new molecular wavefunctions, there is no change overall.

We started with two atomic orbitals, and by combining them we produced two molecular orbitals. Both of these ideas are useful in considering the formation of more complex molecules from individual atoms.

- - The average energy of the orbitals has remained almost constant.
  - Also, the number of wavefunctions has remained constant.
  - 

Of course, from the point of view of the two real electrons, some remarkable changes have occurred. Both of these electrons have adopted a longer wavelength and a lower energy and that has made all the difference. There is an occupied molecular orbital and an unoccupied molecular orbital; only the occupied orbital makes a real energetic contribution to the overall stability of the molecule. The unoccupied orbital is completely imaginary.

A bonding picture of He_2 would look exactly the same, because it would also involve the overlap of 1s electrons on one atom with 1s electrons on the other atom. There would be a different electronic energy, however. That difference would affect the prospects of helium-helium bond formation.

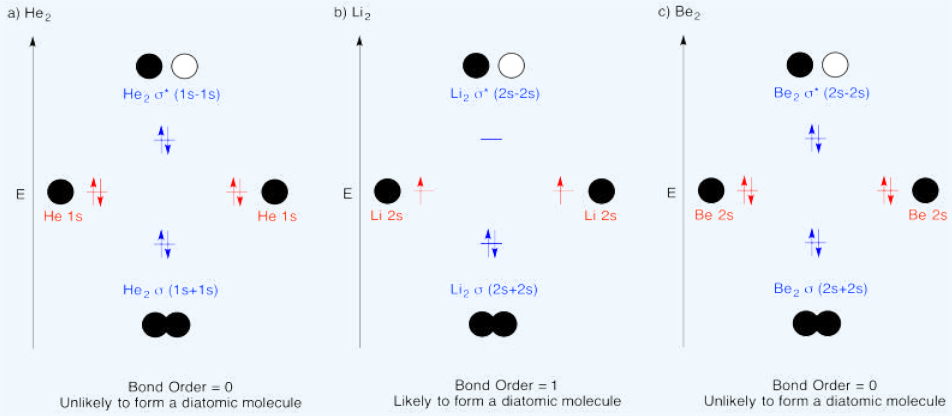
- The electrons have lower kinetic energy in the bond than they had before bonding.
- Electronic energy has decreased. A stable bond has formed.

? Exercise 5.1.1.1

Construct molecular orbital diagrams for the following diatomic species and discuss the likelihood of bond formation in each case.

a. He_2.
b. Li_2.
c. Be_2.

Answer



This page titled 5.1.1: Molecular Orbitals from s Orbitals is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

5.1.2: Molecular Orbitals from p Orbitals

Bonding with P-orbitals

Sigma bonding with p-orbitals

Other diatomic molecules in the upper right corner of the periodic table can be constructed in a similar way. Look at dinitrogen, N_2.

We can think about how dinitrogen would form if two nitrogen atoms were placed close enough together to share electrons. Nitrogen has more electrons than hydrogen, so this interaction is more complicated.

In our qualitative examination of bonding in main group diatomics, we will take the approach used in Lewis structures and just look at the valence electrons. A quantitative molecular orbital calculation with a computer would not take this shortcut, but would include all of the electrons in the atoms that are bonding together.

Nitrogen has five valence electrons, and these electrons are found in the 2s and 2p levels. There are three possible atomic orbitals in the 2p level where some of these electrons could be found: p_x, p_y and p_z. We need to look at the interaction between the s and p_x, p_y and p_z orbitals on one nitrogen atom with the s and p_x, p_y and p_z orbitals on the other nitrogen. That process could be extremely complicated, but:

- Orbital interactions are governed by symmetry.

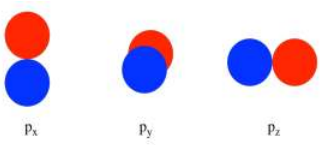
Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

- s orbitals interact with s orbitals. We can already see how that will work out in dinitrogen, because that is what happened in dihydrogen.
- p_x orbitals interact with p_x orbitals.
- p_y orbitals interact with p_y orbitals.
- p_z orbitals interact with p_z orbitals.

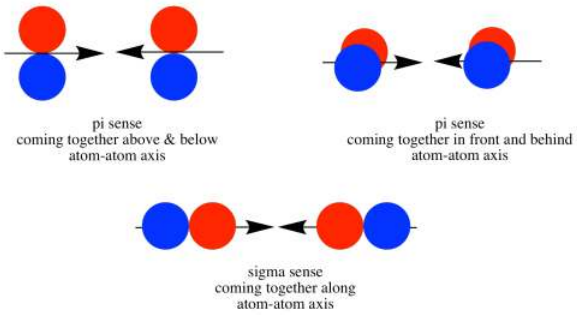
Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go lower in energy than the combinations from s orbitals? We will **simplify** and **assume** that the s and p levels remain completely separate from each other. This is not always true, but the situation varies depending on what atoms we are dealing with.

- The combination of one s orbital with another is just like in hydrogen. Two original orbitals will combine and rearrange to produce two new orbitals.
- There is a bonding combination in which the orbitals are in phase. The new orbital produced has a longer wavelength than the original orbital. It is lower in energy.
- There is an antibonding combination in which the orbitals are out of phase. The new orbital produced has a shorter wavelength than the original orbital. It is higher in energy.

In considering the interaction of two p orbitals, we have to keep in mind that p orbitals are directional. A p orbital lies along a particular axis: x, y or z. The three p orbitals on nitrogen are all mutually perpendicular (or orthogonal) to each other. That situation is in contrast to s orbitals, which are spherical and thus look the same from any direction.

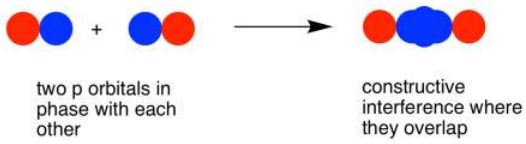


We first need to define one axis as lying along the N-N bond. It does not really matter which one. We arbitrarily say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas the p_y and p_x are orthogonal to it.

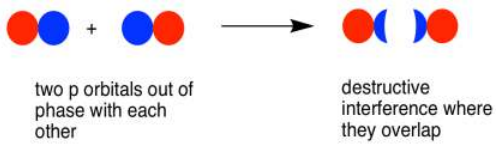


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

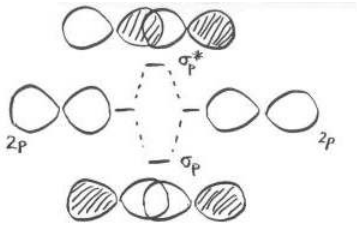
As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, so that one orbital is the mirror image of the other.) This combination is at a longer wavelength than the original orbital. It is a lower energy combination.



The out-of-phase combination (meaning in this case that the overlapping lobes are out-of-phase) results in destructive interference. This combination is at shorter wavelength than the original orbital. It is a higher energy combination.



As a result, we have two different combinations stemming from two different p orbitals coming together in two different ways. We get a low-energy, in-phase, bonding combination and a high-energy, out-of-phase, antibonding combination.

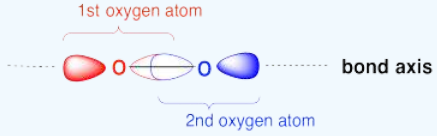


What about those other p orbitals, the ones that do not lie along the bond axis? We'll take a look at that problem on the next page.

? Exercise 5.1.2.2

Draw an MO cartoon of a sigma bonding orbital formed by the overlap of two p orbitals between two oxygen atoms. Label the positions of the oxygen nuclei with the symbol "O". Label the O-O bond axis.

Answer



Exercise 5.1.2.3

Chemical reactions can be described by MO diagrams too! Consider the following reaction in which a new sigma bond is formed.

Draw an MO diagram for the reaction above. In other words, start from the one frontier MO on each reactant to build the MO's of the new sigma bond in the product.

o Draw the orbital from the base (hydroxide) that is likely to donate its electrons.

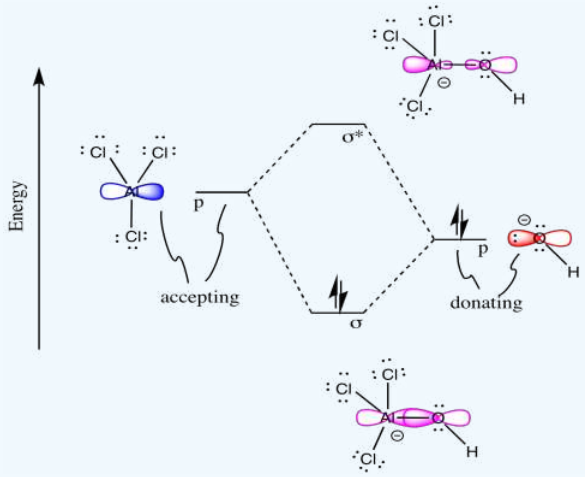
o Draw the orbital from the acid (aluminum chloride) that is likely to accept electrons.

o Complete the MO mixing diagram of these two orbitals:

- Label the electron donating orbital
- Label the electron accepting orbital
- Populate the MO mixing diagram with electrons

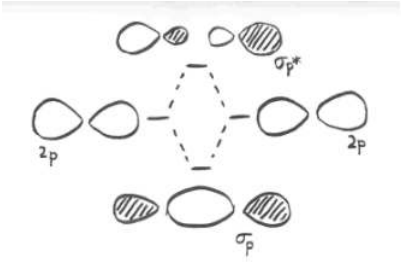
o Draw a cartoon showing each reactant and product MO that contributes to the bonding interaction.

Answer



Pi-bonding with p-orbitals

Earlier, we saw that p orbitals that lie along the same axis can interact to form bonds.

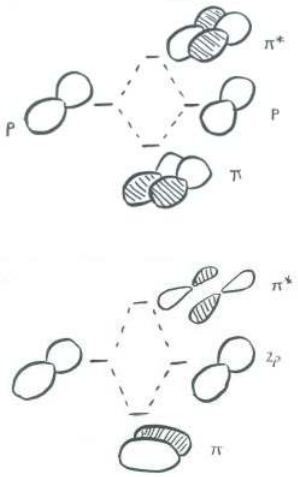


Parallel, but not collinear, p orbitals can also interact with each other. They would approach each other side by side, above and below the bond axis between the two atoms. They can be close enough to each other to overlap, although they do not overlap as strongly as orbitals lying along the bond axis. They can make an in-phase combination, as shown below.

They could also make an out-of-phase combination, as shown below.

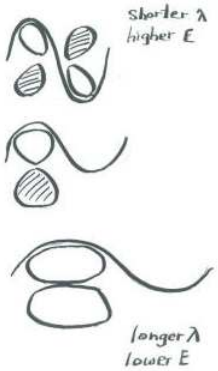
- parallel p orbitals can overlap to produce bonding and antibonding combinations.
- the resulting orbitals contain nodes along the bond axis.
- the electron density is found above and below the bond axis.
- this is called a p (pi) bond.

The illustration above is for one set of p orbitals that are orthogonal to the bond axis. The second picture shows the result of the constructive (or destructive) interference. A similar picture could be shown for the other set of p orbitals.

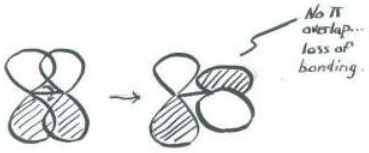


In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

Just as the sigma-bonding orbitals display progressively shorter wavelengths along the bonding axis as they go to higher energy, so do the pi bonding orbitals. In other words, there are more nodes in the higher-energy orbitals than in the lower-energy ones.



An important consequence of the spatial distribution or "shape" of a p orbital is that it is not symmetric with respect to the bond axis. An s orbital is not affected when the atom at one end of the bond is rotated with respect to the other. A p orbital is affected by such a rotation. If one atom turns with respect to the other, the p orbital would have to stretch to maintain the connection. The orbitals would not be able to overlap, so the connection between the atoms would be lost.



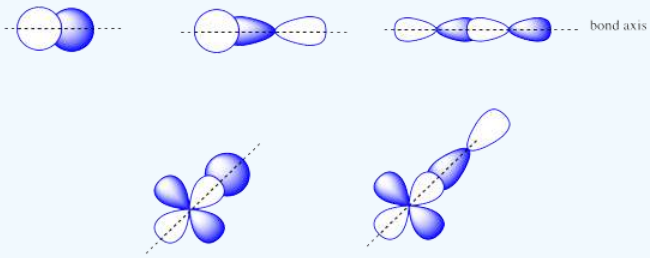
? Exercise 5.1.2.4

The combinations of _____ atomic orbitals leads to σ orbitals.

Draw pictures.

Answer

The combinations of ***s*** + ***s*** OR ***s*** + ***p*** OR ***p*** + ***p*** OR ***s*** + ***d*** OR ***p*** + ***d*** atomic orbitals can lead to σ orbitals.



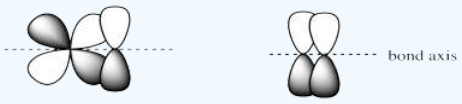
? Exercise 5.1.2.5

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer

The combinations of side by side p + p or p + d atomic orbitals leads to π orbitals.



Exercise 5.1.2.6

Which molecular orbital is typically the highest in energy?

a. p
b. σ
c. π*
d. π
e. σ*

Answer

e) σ*

Exercise 5.1.2.7

Why would a *core* 1s orbital not interact with a *valence* 2s orbital?

Hint: Why is a Li_2O bond stronger than a K_2O bond?

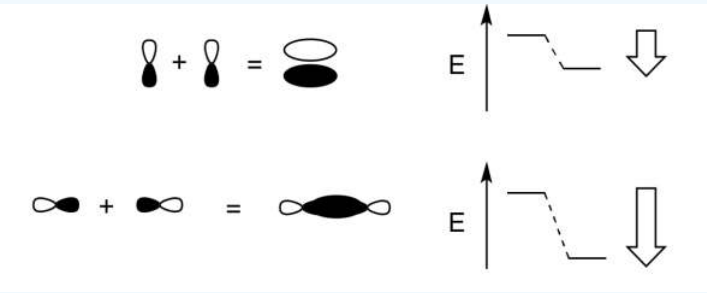
Answer

Li^+ and O^{2-} are more similar in size than K^+ and O^{2-}, so the bond between Li^+ and O^{2-} is stronger.

The energy difference between any core orbitals and valence orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

Exercise 5.1.2.8

Add a few words to explain the ideas conveyed in these drawings.



Answer

When two parallel p orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

Attribution

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

Curated or created by Kathryn Haas

This page titled 5.1.2: Molecular Orbitals from p Orbitals is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **5.1.2: Molecular Orbitals from p Orbitals** by Chris Schaller is licensed CC BY-NC 3.0.

5.1.3: Molecular orbitals from d orbitals

In transition metals and other heavier elements, the d orbitals may combine with other orbitals of compatible symmetry (and energy) to form molecular orbitals. Generally, there are three types of bonding and antibonding interactions that may occur with d orbitals: sigma (σ), pi (π), and delta (δ) bonds.

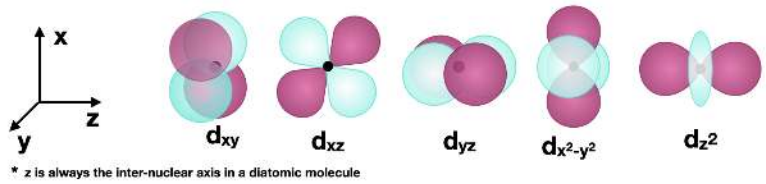


Figure 5.1.3.1: The five $3d$ orbitals are shown. The orientation of the axes is consistent and the z axis is horizontal for convenience in drawing bonding along the z axis (see examples below). (CC-BY-SA; Kathryn Haas)

Sigma (σ) bonding with d orbitals

σ bonds are symmetric with respect to the inter-nuclear axis (in a diatomic molecule, this is the z axis). An example of a σ bond formed by d orbitals is that of two d_{z^2} orbitals (see Figure 5.1.3.2). If a bonded atom is in a position other than on the z axis (in an octahedral geometry, for example), σ bonds can also form. For example, two $d_{x^2-y^2}$ orbitals on atoms bonded along the x or y axes could also form a σ bond.

d orbitals can also form σ bonds with other types of orbitals with the appropriate symmetry. Examples of orbitals with appropriate symmetry are the s orbital and certain p orbitals on another atom, as shown below in Figure 5.1.3.2

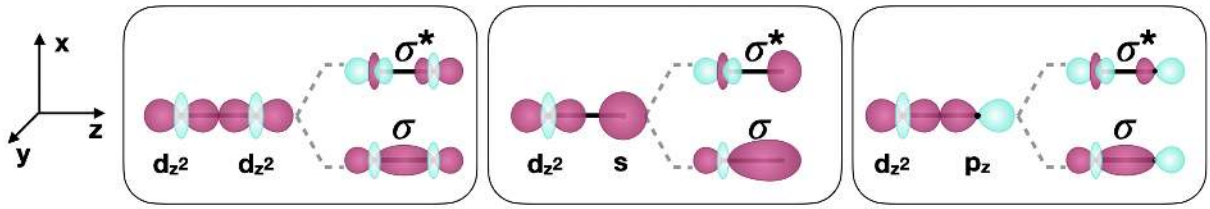


Figure 5.1.3.2: Selected examples of σ bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Pi (π) bonding with d orbitals

π bonds are those with one node that is in-plane with the internuclear axis. A π bond can form between two d orbitals or between d orbitals and other types of orbitals with comparable symmetry. An example of a π bond between two d orbitals is that formed by two d_{xz} orbitals along the z axis (shown in Figure 5.1.3.3). d orbitals can also form π bonds using p orbitals with compatible symmetry, as shown in Figure 5.1.3.3

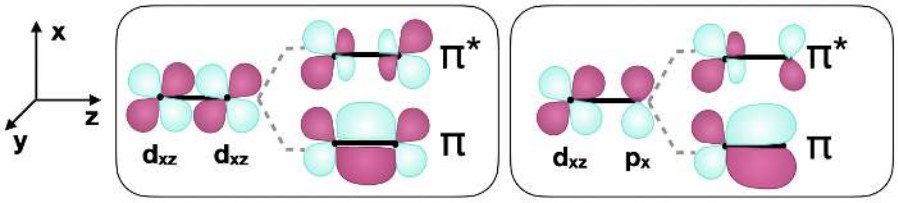


Figure 5.1.3.3: Selected examples of π bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Delta (δ) bonding with d orbitals

δ bonds are those with two nodes that are in-plane with the internuclear axis. δ bonds can form between two d orbitals with appropriate symmetry. For example, when two atoms bond along the z axis, the d_{xy} orbitals and the two $d_{x^2-y^2}$ orbitals can form δ bonds (Figure 5.1.3.4).

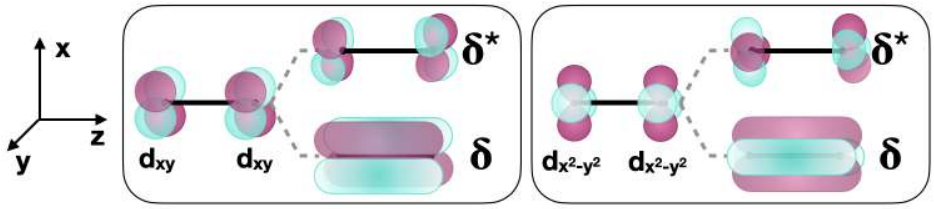


Figure 5.1.3.4: Selected examples of δ bonds involving d orbitals along the z internuclear axis (shown in bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Incompatible orbitals

In the descriptions above, we focused on how bonds (and antibonds) can be formed with d orbitals. All bonding and non-bonding interactions require that orbitals have compatible symmetry to form productive interactions. It is worth mentioning that orbitals with symmetry that is incompatible with the d orbitals will not have bonding or antibonding interactions with d orbitals. The figure below shows several sets of orbitals that are incompatible for bonding.

Curated or created by Kathryn Haas

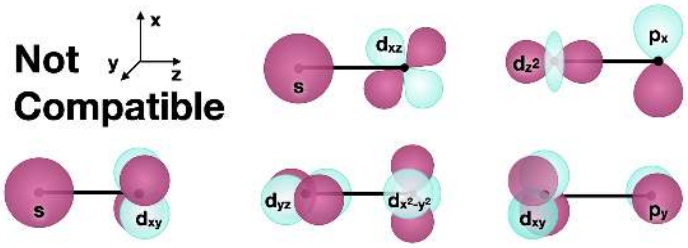


Figure 5.1.3.5: Several incompatible pairs of orbitals. (CC-BY-SA; Kathryn Haas)

This page titled 5.1.3: Molecular orbitals from d orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.1.3: Molecular orbitals from d orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

5.1.4: Nonbonding Orbitals and Other Factors

The simplest case is when there is an even number of atomic orbitals that all combine to form strong bonding and antibonding orbitals. But what if there is an uneven number of atomic orbitals? Or what if there are some orbitals that don't meet the criteria for bonding? Or what if the bonding interactions are weak? In these cases, there will be molecular orbitals on the molecule that have non-bonding character.

It is important to note that the bonding, non-bonding, and antibonding nature of orbitals exist on a spectrum. Some bonding and anti-bonding orbitals may have some non-bonding character depending on where their energies lie with respect to the original atomic orbital energies. When molecular orbitals have energies similar to their original atomic orbitals, they will have some non-bonding character. The closer the energies of atomic and molecular orbitals, the more non-bonding the molecular orbitals.

Two major factors to consider

Uneven number of atomic orbitals: In the case that there is an uneven number of atomic orbitals with compatible symmetry, orbitals with non-bonding character will form. For example, in the case where three atomic orbitals combine, the most common result is formation of a low-energy bonding orbital, a high energy antibonding orbital, and a non-bonding orbital of intermediate energy (Figure 5.1.4.1).

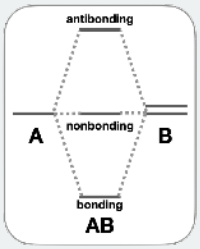


Figure 5.1.4.1. This figure illustrates the most common case for three atomic orbitals that combine to form three molecular orbitals; formation of one low-energy bonding, one high-energy antibonding, and one intermediate energy non-bonding molecular orbital. (CC-BY-NC-SA, Kathryn Haas)

Differences in energy: Combination of orbitals with different energies may lead to orbitals with non-bonding character. Atomic orbitals that have similar energies will have the strongest interactions, and result in bonding molecular orbitals with much lower energies than the component atomic orbitals. On the other hand, atomic orbitals with very unequal energies have a weaker interaction because the molecular orbitals are closer in energy to the atomic orbital energies, thus there is less energy benefit to putting electrons in the bonding molecular orbitals (Figure 5.1.4.2). When bonding or antibonding orbitals are close to the energies of the contributing atomic orbitals, those molecular orbitals may have some non-bonding character.

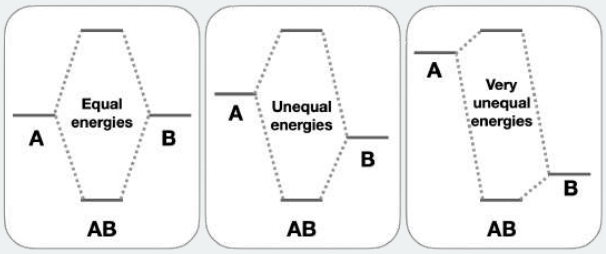


Figure 5.1.4.2. This figure illustrates how relative energies of atomic orbitals result in molecular orbitals that are more or less favorable. The greater the energy difference between atomic orbitals and the bonding molecular orbital, the more eneretically favorable it is for bonding to occur. (CC-BY-NC-SA, Kathryn Haas)

This page titled 5.1.4: Nonbonding Orbitals and Other Factors is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.1.4: Nonbonding Orbitals and Other Factors** by Kathryn Haas is licensed CC BY-SA 4.0.

SECTION OVERVIEW

5.2: Homonuclear Diatomic Molecules

In this section you will be introduced to the molecular orbital diagrams of several homonuclear diatomic molecules. Homonuclear diatomic molecules are molecules made of exactly two identical atoms, and they are relatively simple.

5.2.1: Molecular Orbitals

5.2.2: Orbital Mixing

5.2.3: Diatomic Molecules of the First and Second Periods

5.2.4: Photoelectron Spectroscopy

This page titled 5.2: Homonuclear Diatomic Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

5.2.1: Molecular Orbitals

There are several cases where our more elementary models of bonding (like Lewis Theory and Valence Bond Theory) fail to predict the actual molecular properties and reactivity. A classic example is the case of O_2 and its magnetic properties. At very cold temperatures, O_2 is attracted to a magnetic field, and thus it must be paramagnetic (unpaired electrons give rise to magnetism). Watch the video below!

The magnetic properties of O_2 are easily rationalized by its **molecular orbital diagram**. A molecular orbital diagram is a diagram that shows the relative energies and identities of each molecular orbital in a molecule. Figure $5.2.1.1$ shows a simplified and generic molecular orbital diagram for a second-row homonuclear diatomic molecule. The diagram is simplified in that it assumes that interactions are limited to degenerate orbitals from two atoms (see next section).

There are some things you should note as you inspect Figure $5.2.1.1$ (and keep these in mind as you draw your own diagrams!). First, notice that there are the **same number of molecular orbitals as there are atomic orbitals**. Second, notice that **each orbital in the diagram is rigorously labeled** using labels (σ and π) that include the subscripts u and g. These labels and subscripts indicate the symmetry of the orbitals. The σ symbol indicates that the orbital is symmetric with respect to the internuclear axis, while the π label indicates that there is one node along that axis. The g and u stand for *gerade* and *ungerade*, the German words for *even* and *uneven*, respectively. The subscript g is given to orbitals that are *even*, or *symmetric*, with respect to an inversion center. The subscript u is given to orbitals that are *uneven*, or *antisymetric*, with respect to an inversion center. The pictures of calculated molecular orbitals are shown in Figure $5.2.1.1$ to illustrate the symmetry of each orbital.

Another important thing to notice is that the diagram in Figure $5.2.1.1$ lacks electrons (because it is generic for any second-row diatomic molecule). If this were a *complete* molecular orbital diagram it would **include the electrons for each atom and for the molecule**. Electrons in molecular orbitals are filled in the same way an atomic orbital diagram would be filled, where electrons occupy lower energy orbitals before higher energy orbitals, and electrons occupy empty degenerate orbitals before pairing. A complete molecular orbital diagram would show whether the molecule is diamagnetic or paramagnetic. It can also be used to calculate the bond order of the molecule (the number of bonds between atoms) using the formula below:

$$\text{Bond order } = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons}\\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding orbitals}\end{pmatrix}\right]$$

In general, non-valence (core) electrons can be ignored because they contribute nothing to the bond order. In fact, many molecular orbital diagrams will ignore the core orbitals, as they are insignificant for bonding interactions and reactivity.

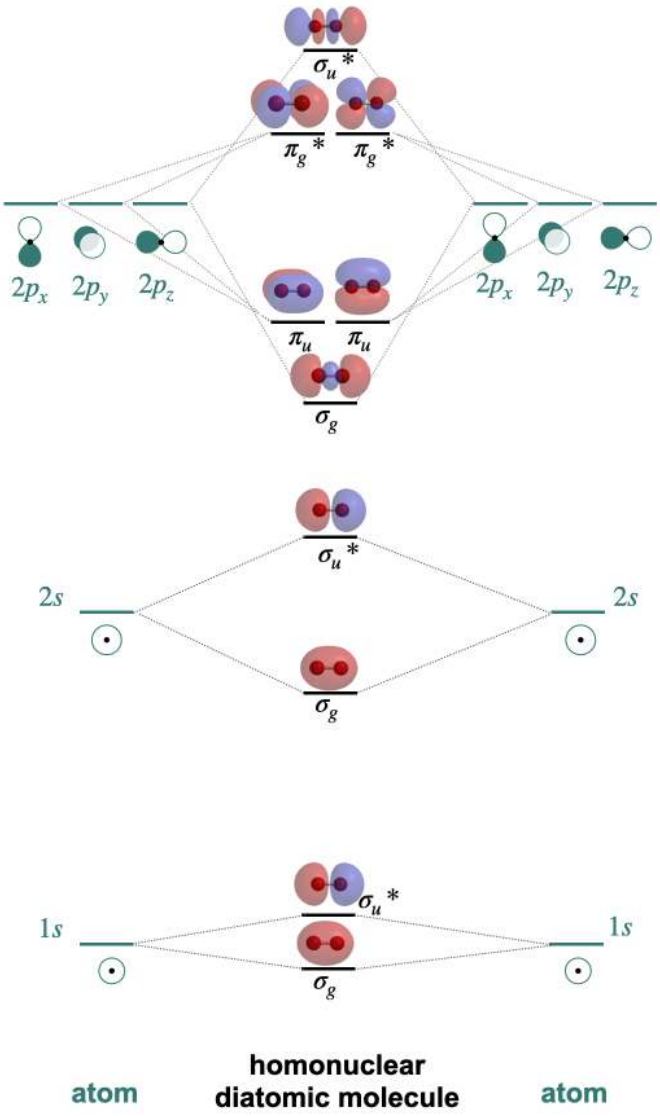


Figure 5.2.1.1: A generic molecular orbital diagram for a homonuclear diatomic molecule of second-row elements assuming no orbital mixing (interactions are formed by orbitals of the same energy from each atom). (CC-BY-NC-SA, Kathryn Haas)

Now, to see how this molecular orbital diagram can explain the magnetic behaviour of O_2, complete the example below.

Example 5.2.1.1

Let's change Figure 5.2.1.1 to make it specific for O_2. Re-draw the MO diagram (no need to draw the shapes of orbitals). Fill in the correct number of electrons for each oxygen atom on either side of the diagram. Then, fill in the total molecular electrons in the center. Calculate the bond order and determine whether it is diamagnetic or paramagnetic.

Solution

The diagram in Figure 5.2.1.1 includes core orbitals (the 1s) and valence electrons (2s, 2p). Therefore, we will consider all the electrons in an oxygen atom and a dioxygen molecule. An oxygen atom has eight total electrons. So we fill eight electrons into the atomic orbitals for the oxygen atom on the right, and eight electrons into the atomic orbitals for oxygen on the left. The total number of electrons for the molecule is sixteen, so fill in 16 electrons into the molecular orbitals, being sure to apply Hund's rule and the Aufbau principle. The result is a diagram that looks like the one drawn below in Figure 5.2.1.2

The bond order is calculated using the molecular orbitals (we can ignore atomic orbitals). There are 10 electrons in binding orbitals and 6 electrons in antibonding orbitals). This gives a bond order of $\frac{1}{2}(10-6)=2$. This bond order is consistent with valence bond theory!

This diagram indicates that dioxygen is paramagnetic; it has two unpaired electrons in the π^* orbitals. This paramagnetic electron configuration explains why dioxygen is attacted to magnetic fields!

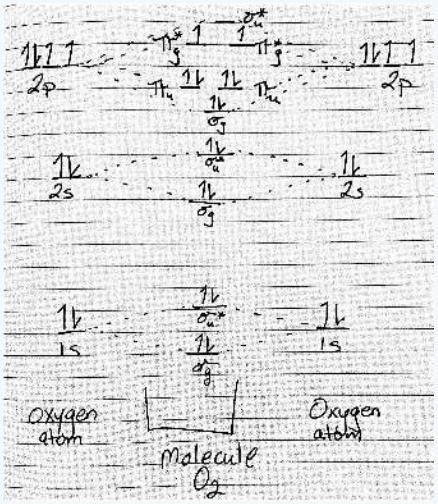


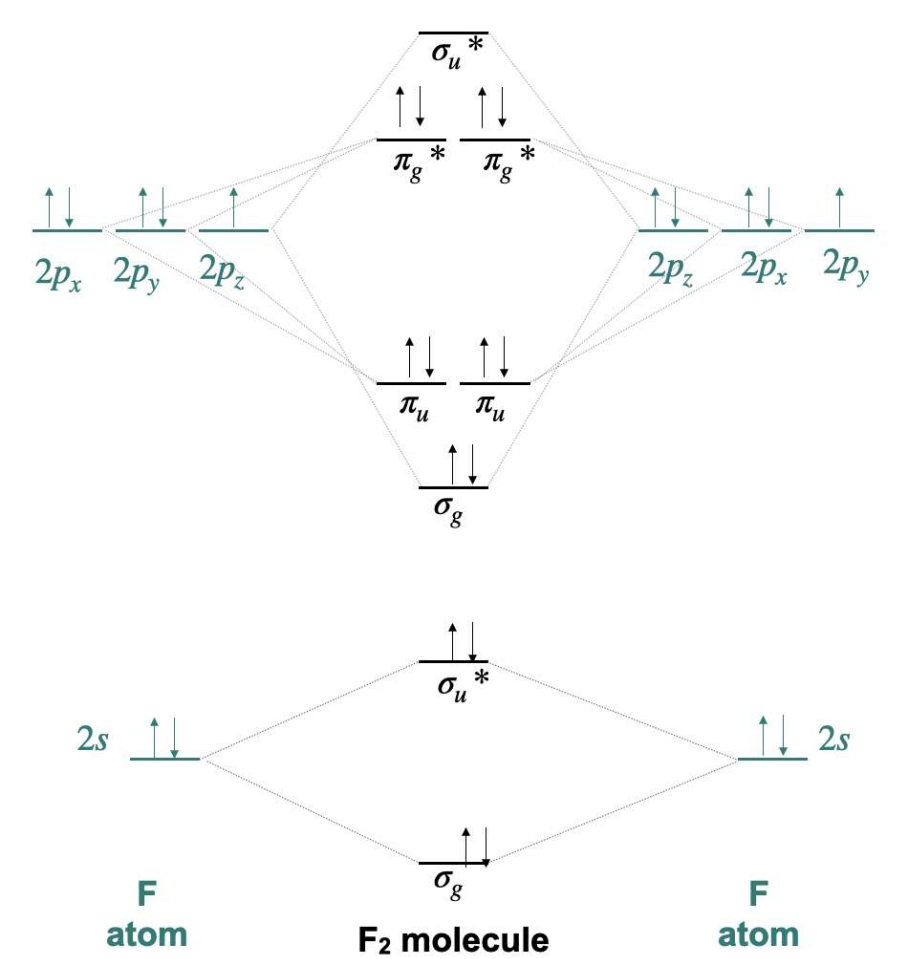
Figure 5.2.1.2: Hand-drawn molecular orbital diagram for dioxygen. (CC-BY-SA; Kathryn Haas)

Exercise 5.2.1.1

Draw the molecular orbital diagram for 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 5.2.1: Molecular Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.2.1: Molecular Orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

5.2.2: Orbital Mixing

In the previous section, we introduced a simplified molecular orbital (MO) diagram, assuming that interactions were limited to degenerate orbitals of compatible symmetry. A version of that *simplified* diagram for second-row homonuclear diatomics is shown on the left side of Figure $5.2.2.1$(only valence orbitals shown).

In reality, orbitals of compatible symmetry can combine, or mix, even when they have different energies. When sets of orbitals mix, it has the effect of decreasing the energy of the lower-energy set and increasing the energy of the higher-energy set. There are two ways to explain mixing, described in the points below. The diagram on the right of side of Figure $5.2.2.1$shows how energy levels are affected by orbital mixing.

- **Starting from the simplified MO diagram and mixing molecular orbitals of like symmetry**: If we start with the "no mixing" simplified diagram shown on the left, we can pick out the orbitals with like symmetry and consider what will happen if these molecular orbitals mix. For example, starting from the MO diagram on the left side of Figure $5.2.2.1$, we see that there are two σ_g orbitals that have identical symmetry (hence they have identical symmetry labels). Upon mixing, the lower-energy $\sigma_g(2s)$ will decrease in energy while the higher-energy $\sigma_g(2p)$ will increase in energy. Likewise, there are two σ_u^* orbitals that will mix, decreasing the energy of $\sigma_u^*(2s)$ while increasing the energy of $\sigma_u^*(2p)$.
- **Starting from and mixing atomic orbitals of compatible symmetry**: Starting from the atomic orbitals, we can select the orbitals that have compatible symmetry to make productive interactions, and combine them as a set to make molecular orbitals. From the two sets of atomic orbitals on the right panel in Figure $5.2.2.1$, there are two sets of four orbitals with compatable symmetry; one is the set of two $2s$ and two $2p_z$ orbitals. These four orbitals can combine to form molecular orbitals with σ symmetry. They combine to form one lowest-energy bonding σ_g, a highest-energy σ_u^*, and two orbitals with intermediate energy (σ_g, and σ_u^*). This treatment can be expressed as the linear combination of four atomic orbitals:

$$\Psi = c_1\psi\left(2s_a\right) \pm c_2\psi\left(2s_b\right) \pm c_3\psi\left(2p_a\right) \pm c_4\psi\left(2p_b\right)$$

  where the coefficients $c_1 = c_2$ and $c_3 = c_4$ for homonuclear diatomic molecules.

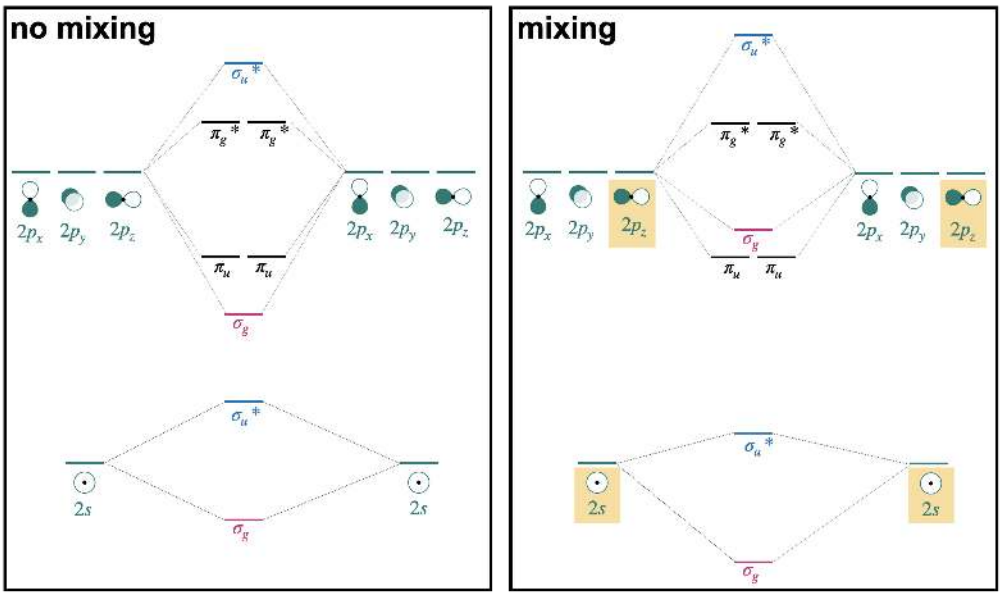


Figure 5.2.2.1: Mixing of orbitals with like symmetry affects the energies of molecular orbitals. The simplified case where no mixing occurs is shown on the left. The effects of mixing are shown on the right. The σ_g orbitals of like symmetry are highlighted in fuschia and the σ_u^* orbitals of like symmetry are highlighted in blue. A group of atomic orbitals of similar symmetry are highlighted in yellow boxes; these atomic orbitals combine to give all σ molecular orbitals. (CC-BY-SA, Kathryn Haas)

In the case of homonuclear diatomic molecules of the second row, orbital mixing has important consequences for the energetic order of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. This will be discussed in the next section.

This page titled 5.2.2: Orbital Mixing is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.2.2: Orbital Mixing** by Kathryn Haas is licensed CC BY-SA 4.0.

5.2.3: Diatomic Molecules of the First and Second Periods

First Period Homonuclear Diatomic Molecules

In the first row of the periodic table, the valence atomic orbitals are $1s$. There are two possible homonuclear diatomic molecules of the first period:

Dihydrogen, H_2 $[\sigma_g^2(1s)]$: This is the simplest diatomic molecule. It has only two molecular orbitals (σ_g and σ_u^*), two electrons, a bond order of 1, and is diamagnetic. Its bond length is 74 pm. MO theory would lead us to expect bond order to decrease and bond length to increase if we either add or subtract one electron. The calculated bond length for the H_2^+ ion is approximately 105 pm.[1]

Dihelium, He_2 $[\sigma_g^2\sigma_u^{*2}(1s)]$: This molecule has a bond order of zero due to equal number of electrons in bonding and antibonding orbitals. Like other nobel gases, He exists in the atomic form and does not form bonds at ordinary temperatures and pressures.

? Exercise 5.2.3.1

Draw the complete molecular orbital diagrams for H_2 and for He_2. Include sketches of the atomic and molecular orbitals.

Answer

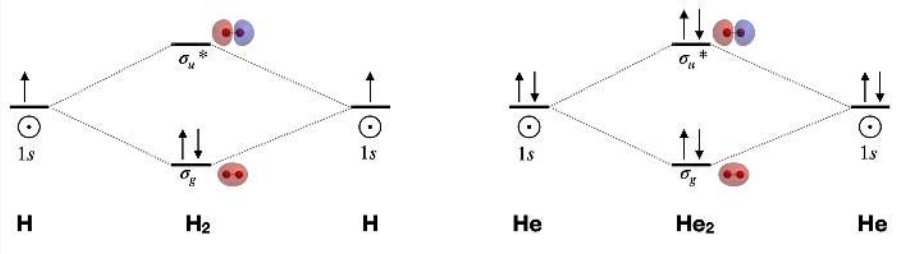


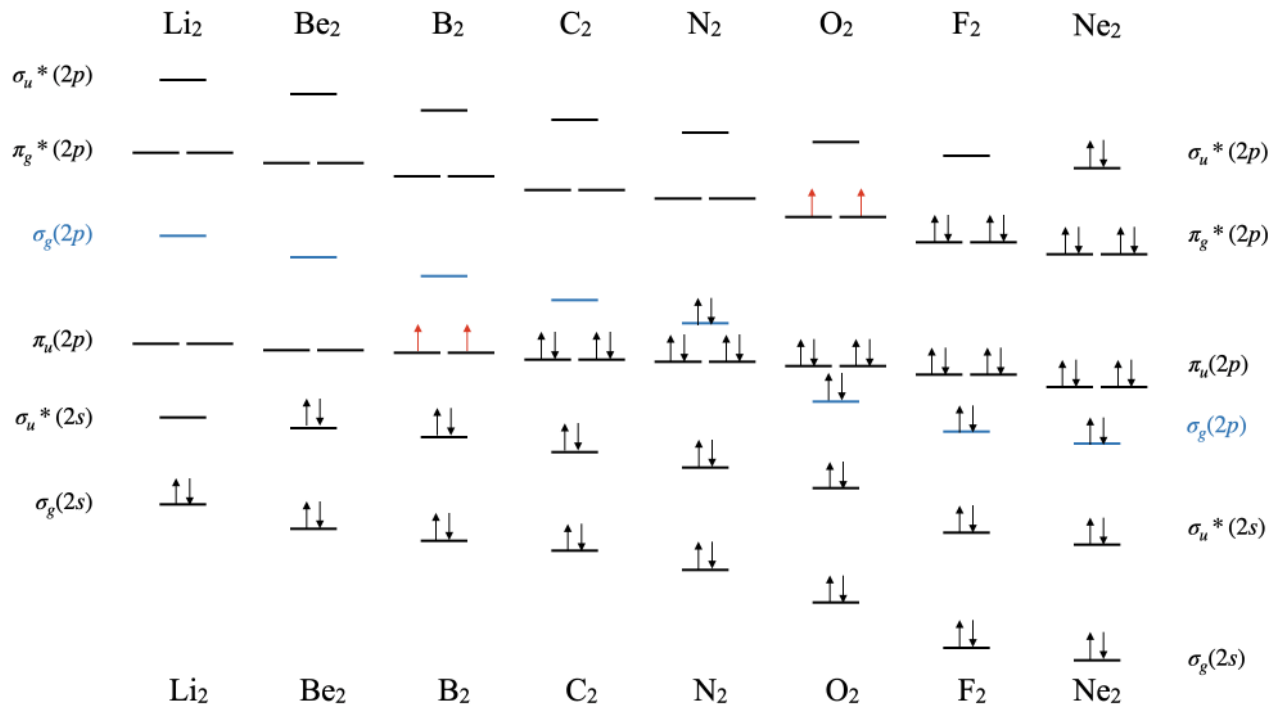
Figure for Exercise 5.2.3.1: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

A complete molecular orbital diagram includes all atomic orbitals and molecular orbitals, their symmetry labels, and electron filling.

Second Period Homonuclear Diatomic Molecules

The second period elements span from Li to Ne. The valence orbitals are 2s and 2p. In their molecular orbital diagrams, non-valence orbitals (1s in this case) are often disregarded in molecular orbital diagrams.

Orbital mixing has significant consequences for the magnetic and spectroscopic properties of second period homonuclear diatomic molecules because it affects the order of filling of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. Early in period 2 (up to and including nitrogen), the $\pi_u(2p)$ orbitals are lower in energy than the $\sigma_g(2p)$ (see Figure $5.2.3.1$). However, later in period 2, the $\sigma_g(2p)$ orbitals are pulled to a lower energy. This lowering in energy of $\sigma_g(2p)$ is not unique; all of the σ orbitals in the molecule are pulled to lower energy due to the increasing positive charge of the nucleus. The π orbitals in the molecule are also affected, but to a much lesser extent than σ orbitals. The reason has to do with the high penetration of s atomic orbitals compared to p atomic orbitals (recall our previous discussion on penetration and shielding, and its effect on periodic trends). The σ molecular orbitals have more s character and thus their energy is more influenced by increasing nuclear charge. As nuclear charge increases, the energy of the $\sigma_g(2p)$ orbital is lowered significantly more than the energy of the $\pi_u(2p)$ orbitals (Figure $5.2.3.1$).



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Unpaired e⁻	0	0	2	0	0	2	0	0
Bond Order	1	0	1	2	3	2	1	0
Experimental* Bond Length (pm)	267.3	246.0	159.0	124.3	109.8	120.8	141.2	310.0

*Experimental bond lengths from "List of Experimental Diatomic Bond Lengths", NIST, https://cccbdb.nist.gov/diatomicexpbondx.asp

Figure 5.2.3.1: Molecular orbital energy-level diagrams for the diatomic molecules of the period 2 elements. Unlike earlier diagrams, *only the valence molecular orbital energy levels for the **molecules** are shown here (atomic orbitals not shown for simplicity).* For Li_2 through N_2, the $\sigma_g(2p)$ orbital is higher in energy than the $\pi_u(2p)$ orbitals. In contrast, from O_2 onward, the $\sigma_g(2p)$ orbital is *lower* in energy than the $\pi_u(2p)$ orbitals because the nuclear charge increases across the row. The experimental bond lengths correlate with the calculated bond order. (CC-BY-NC-SA, Kathryn Haas)

Dilithium, Li_2 $[\sigma_g^2(2s)]$: This molecule has a bond order of one and is observed experimentally in the gas phase to have one Li-Li bond.

Diberylium, Be_2 $[\sigma_g^2\sigma_u^{*2}(2s)]$: This molecule has a bond order of zero due to the equal number of electrons in bonding and antibonding orbitals. Although Be_2 does not exist under ordinary conditions, it can be produced in a laboratory and its bond length measured (Figure 5.2.3.2). Although the bond is very weak, its bond length is surprisingly ordinary for a covalent bond of the second period elements.[2]

Diboron, B_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^1\pi_u^1(2p)]$: The case of diboron is one that is much better described by molecular orbital theory than by Lewis structures or valence bond theory. This molecule has a bond order of one. The molecular orbital description of diboron also predicts, accurately, that diboron is paramagnetic. The paramagnetism is a consequence of orbital mixing, resulting in the σ_g orbital's being at a higher energy than the two degenerate π_u^* orbitals.

Dicarbon, C_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2(2p)]$: This molecule has a bond order of two. Molecular orbital theory predicts two bonds with π symmetry, and no σ bonding. C_2 is rare in nature because its allotrope, diamond, is much more stable.

Dinitrogen, N_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2\sigma_g^2(2p)]$: This molecule is predicted to have a triple bond. This prediction is consistent with its short bond length and bond dissociation energy. The energies of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals are very close, and their relative energy levels have been a subject of some debate (see next section for discussion).

Dioxygen, O_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*1}\pi_g^{*1}(2p)]$: This is another case where valence bond theory fails to predict actual properties. Molecular orbital theory correctly predicts that dioxygen is paramagnetic, with a bond order of two. Here, the molecular orbital diagram returns to its "normal" order of orbitals where orbital mixing could be somewhat ignored, and where $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Difluorine, F_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}(2p)]$: This molecule has a bond order of one and like oxygen, the $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Dineon, Ne_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}\sigma_u^{*2}(2p)]$: Like other noble gases, Ne exists in the atomic form and does not form bonds at ordinary temperatures and pressures. Like Be_2, Ne_2 is an unstable species that has been created in extreme laboratory conditions and its bond length has been measured (Figure 5.2.3.2)

Exercise 5.2.3.2

Draw the complete molecular orbital diagram for O_2. Show calculation of its bond order and tell whether it is diamagnetic or paramagnetic.

Answer

O_2 is paramagnetic with a bond order of 2. Its $\sigma_g(2p)$ molecular orbital is lower in energy that the set of $\pi_u(2p)$ orbitals.

$$\text{Bond order} = \frac{1}{2}\left[\begin{pmatrix}\text{8 electrons in}\\ \text{valence bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{4 electrons in}\\ \text{valence antibonding orbitals}\end{pmatrix}\right]$$

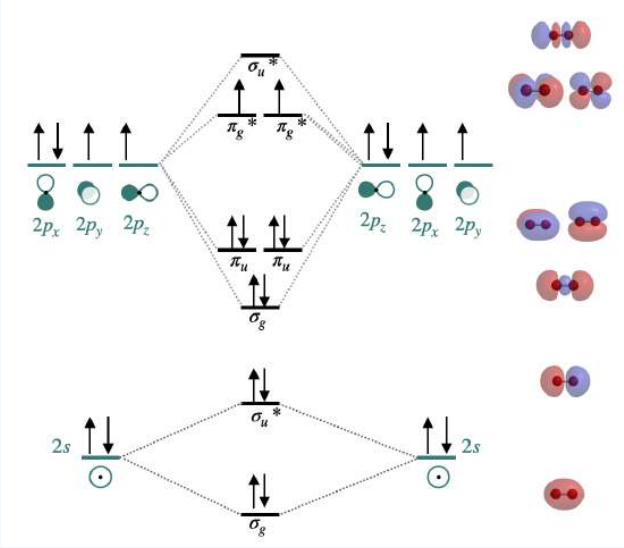


Figure for Exercise 5.2.3.2. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

Exercise 5.2.3.3: The Peroxide Ion

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

This diagram looks similar to that of O_2, except that there are two additional electrons.
$(\sigma_g(2s))^2(\sigma_u^*(2s))^2(\sigma_g(2p))^2(\pi_u(2p))^4(\pi_g(2p))^4$; bond order of 1; no unpaired electrons.

Bond Lengths in Homonuclear Diatomic Molecules

The trends in experimental bond lengths are predicted by molecular orbital theory, specifically by the calculated bond order. The values of bond order and experimental bond lengths for the second period diatomic molecules are given in Figure 5.2.3.1, and shown in graphical format on the plot in Figure 5.2.3.2 From the plot, we can see that bond length correlates well with bond order,

with a minimum bond length occurring where the bond order is greatest (N_2). The shortest bond distance is at N_2 due to its high bond order of 3. From N_2 to F_2 the bond distance increases despite the fact that atomic radius decreases.

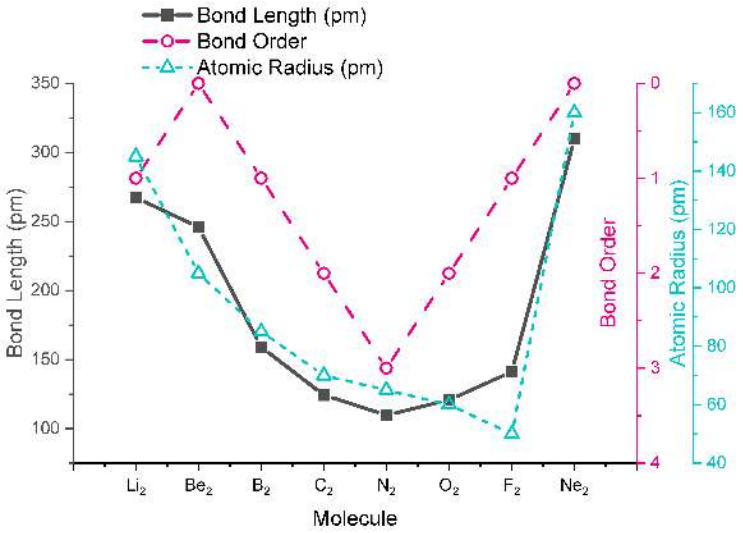


Figure 5.2.3.2: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

References

1. NIST, Calculated Geometries available for H_2^+ (Hydrogen cation) 2Σg+ D∞h, available at https://cccbdb.nist.gov/diatomicexpbondx.asp
2. Merritt, J. M.; Bondybey, V. E.; Heaven, M. C., Beryllium Dimer-Caught in the Act of Bonding. *Science* **2009,** *324* (5934), 1548-1551.

This page titled 5.2.3: Diatomic Molecules of the First and Second Periods is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **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.

5.2.4: Photoelectron Spectroscopy

A photoelectron spectrum can show the relative energies of occupied molecular orbitals by ionization. The *ionization energy* is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

$$A + \text{photon} \rightarrow A^+ + e^-$$

The information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals (by Koopmans' theorem).

Example: Photoelectron spectrum of dihydrogen

The molecular orbital description of dihydrogen involves two $1s$ atomic orbitals generating two molecular orbitals: a bonding σ_g and an antibonding σ_u^*. The two electrons occupy the σ_g bonding orbital, leaving the molecule with a bond order of one (Figure 5.2.4.1). The PES spectrum of dihydrogen (Figure 5.2.4.1) has a single band that corresponds to the ionization of one electron from the σ_g. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length due to decrease in bond order).

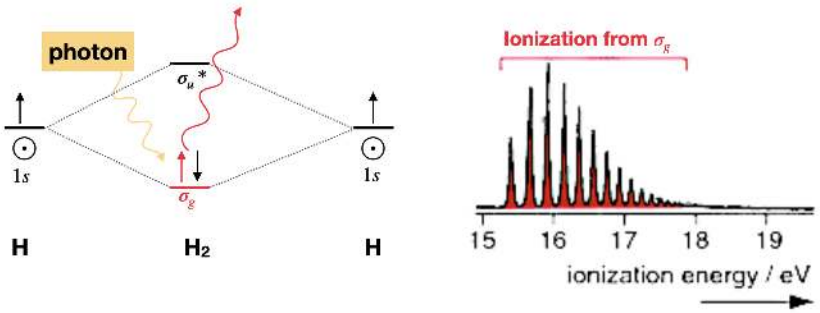


Figure 5.2.4.1: The molecular orbital diagram and photoelectron spectrum of dihydrogen. (CC-BY-NC-SA; Libretexts)

Example: Photoelectron spectrum of dinitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Five molecular orbitals are occupied; two of them are degenerate. Three bands in the photoelectron spectrum correspond to ionization of an electron in $\sigma_g(2p)$, $\pi_u(2p)$ and $\sigma_u^*(2s)$ molecular orbitals. Ionization of the fourth type of orbital, $\sigma_g(2s)$, does not appear in Figure 5.2.4.2because it is either off scale or because the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital. Note that extensive vibrational structure for the $\pi_u(2p)$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

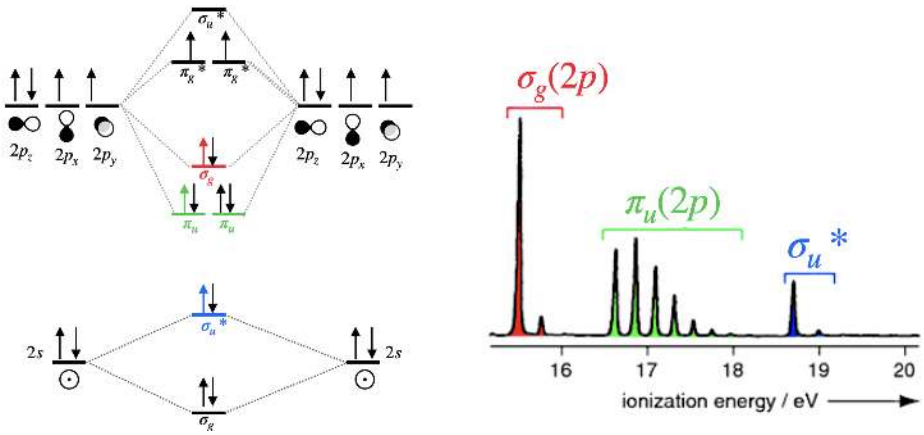


Figure 5.2.4.2: The molecular orbital diagram and photoelectron spectrum of dinitrogen. (CC-BY-NC-SA; Libretexts)

From the photoelectron spectrum of dinitrogen, we can see that the electrons in the $\sigma_g(2p)$ orbital can be ionized using less energy than required to ionize electrons in the $\pi_u(2p)$ orbital. This is evidence for $\sigma_g(2p)$ existing at a higher energy than the $\pi_u(2p)$ orbitals.

This page titled 5.2.4: Photoelectron Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **10.4: Photoelectron Spectroscopy** by Roger Nix is licensed CC BY 4.0.

SECTION OVERVIEW

5.3: Heteronuclear Diatomic Molecules

Diatomic molecules with two non-identical atoms are called **heteronuclear** diatomic molecules. When atoms are not identical, the molecule forms by combining atomic orbitals of unequal energies. *The result is a polar bond in which atomic orbitals contribute unevenly to each molecular orbital*.

The application of molecular orbital theory to heteronuclear diatomic molecules is similar to the case of homonuclear diatomics, except that the atomic orbitals from each atom have different energies and contribute unequally to molecular orbitals. Recall that atomic orbitals must have compatible symmetry and similar energy to combine into molecular orbitals. In the case where atomic orbitals of like symmetry have different energies, they combine less favorably than orbitals that are closer to one another in energy. As a general rule, orbitals that have energy differences of greater than 10-14 eV do not combine favorably. In the molecular orbital diagram, the closer a molecular orbital is to an atomic orbital, the more that atomic orbital contributes to the molecular orbital. This last point is helpful for back-of-the napkin estimations of what the molecular orbitals "look" like.

In this section, you should learn how to generate molecular orbital diagrams of heteronuclear diatomic molecules. To approach such a problem, we must start with a knowledge of the relative energies of electrons in different atomic orbitals. In other words, we need knowledge of the orbital potential energies (or orbital ionization energies).

5.3.1: Polar bonds

5.3.2: Ionic Compounds and Molecular Orbitals

Sources:

- Gray, Harry. *Electrons and Chemical Bonding*, Benjamin, 1964.
- Miessler, Gary L, and Donald A. Tarr. *Inorganic Chemistry*. Upper Saddle River, N.J: Pearson Education, 2014. Print.

5.3: Heteronuclear Diatomic Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

5.3.1: Polar bonds

Molecular orbital diagrams for heteronuclear diatomic molecules

The molecular orbital diagram of a heteronuclear diatomic molecule is approached in a way similar to that of a homonuclear diatomic molecule. The orbital diagrams may also look similar. A major difference is that the more electronegative atom will have orbitals at a lower energy level. Two examples of heteronuclear diatomic molecules will be explored below as illustrative examples.

Carbon monoxide MO diagram

Carbon monoxide is an example of a heteronuclear diatomic molecule where both atoms are second-row elements. The valence molecular orbitals in both atoms are the $2s$ and $2p$ orbitals. The molecular orbital diagram for carbon monoxide (Figure $5.3.1.1$) is constructed in a way similar to how you would construct dicarbon or dioxygen, except that the oxygen orbitals have a lower potential energy than analogous carbon orbitals. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial labels according to type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts.

A consequence of unequal atomic orbital energy levels is that orbital mixing is significant. Notice the order of the molecular orbitals labeled 1π and 3σ in Figure $5.3.1.1$. This is a similar order of π and σ orbitals to the one we saw in the case of the σ_g and π_u orbitals of N_2 and lighter diatomics of the second period. Because the oxygen $2p_z$ orbital is close in energy to both the carbon $2p_z$ and carbon $2s$, these three orbitals will have significant interaction (mixing). The result is an increase in the energy of the 3σ orbital and a decrease in energy of the $2\sigma^*$ orbital, resulting in the diagram shown in Figure $5.3.1.1$.

In the case of carbon monoxide (Figure $5.3.1.1$), atomic orbitals contribute unequally to each molecular orbital. For example, because the $2s$ orbital of oxygen is very close in energy to the 2σ moelcular orbital, it contributes to that molecular orbital more than the $2s$ orbital from carbon. Notice the shape of this 2σ orbital and how it is unevenly distributed over the two atoms; it is more heavily distributed on the oxygen because it is most like the oxygen $2s$. This is in line with the assumption that electron density is distributed more on oxygen because it is more electronegative than carbon. Likewise, the 1π orbitals are unevenly distributed, with more distribution close to the oxygen.

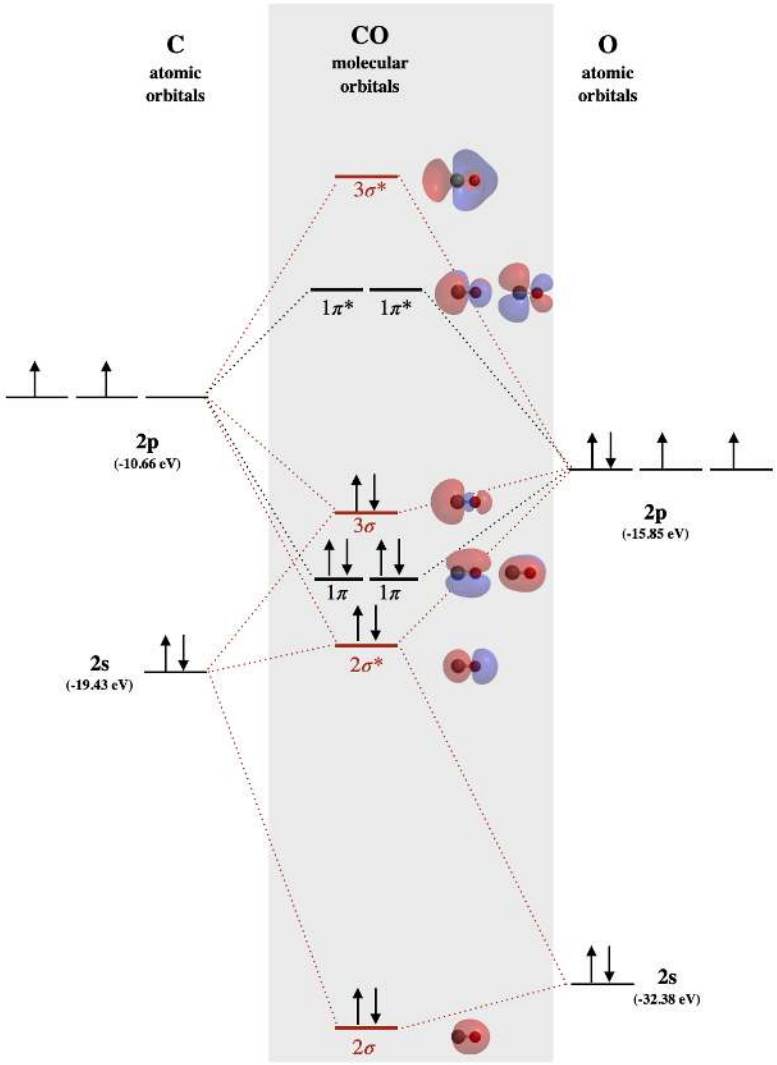


Figure 5.3.1.1: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts. Molecular orbital surfaces were calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

? Exercise 5.3.1.1

Examine the shape of the 3σ orbital of carbon monoxide in Figure 5.3.1.1. Describe what ways this shape is different from the shape of the σ_g orbitals from second period homonuclear diatomic molecules (see Fig. 5.2.1.1). Rationalize these differences. Both orbitals are re-created below for convenience.

σ_g of homonuclear diatomic

3σ of CO

Answer

The 3σ orbital is like the σ_g in that it has three lobes and two nodes distributed along the internuclear bond. They are different in their distribution. The two external lobes of σ_g are evenly distributed because they are an equal combination of

two p_z orbitals (one from each atom). The 3σ orbital is more heavily distributed toward the carbon atom, the less electronegative atom, than toward the oxygen. The unequal distribution of 3σ is apparent in the unequal sizes of its exterior lobes and the uneven shape of the interior lobe. The heavier distribution within the exterior lobe on carbon is caused by the mixing of the carbon $2s$ orbital with carbon and oxygen $2p_z$ orbitals. The uneven shape of the interior lobe, where it leans toward oxygen, is best explained by the fact that the 3σ orbital is closer in energy to the oxygen $2p_z$ than the carbon $2p_z$.

Hydrogen fluoride MO diagram

Hydrogen fluoride is an example of a heteronuclear diatomic molecule in which the two atoms are from different periods. In this case, the valence orbital of H is $1s$ while those of F are $2s$ and $2p$. The molecular orbital diagram for HF is shown in Figure $5.3.1.2$

Three of these orbitals have compatible symmetry for mixing; these are the hydrogen $1s$, fluorine $2s$, and fluorine $2p$. However, the extent to which they will interact depends on their relative energies. Fluorine is more electronegative than H, and the fluorine atom has a higher first ionization energy than does hydrogen. From these trends, we can expect that the fluorine valence orbitals are lower in energy than that of hydrogen. From Table 5.3.1, we find that the 1s orbital of H (-13.6 eV) is higher in energy than both fluorine orbitals (-18.7 and -40.2 eV, respectively for $2p$ and $2s$). The energies of hydrogen $1s$ and fluorine $2p$ are a good match for combination; however, the fluorine $2s$ orbital is much too different to create a productive interaction. Therefore, we expect that the fluorine $2s$ will create a non-bonding molecular orbital, while the $1s$ and $2p_z$ orbitals combine to make σ bonding and σ^* antibonding molecular orbitals. The remaining $2p_x$ and $2p_y$ orbitals do not have compatible symmetry for bonding with hydrogen, and they will form non-bonding π molecular orbitals. The non-bonding orbitals will have similar energy and character as their component atomic orbitals.

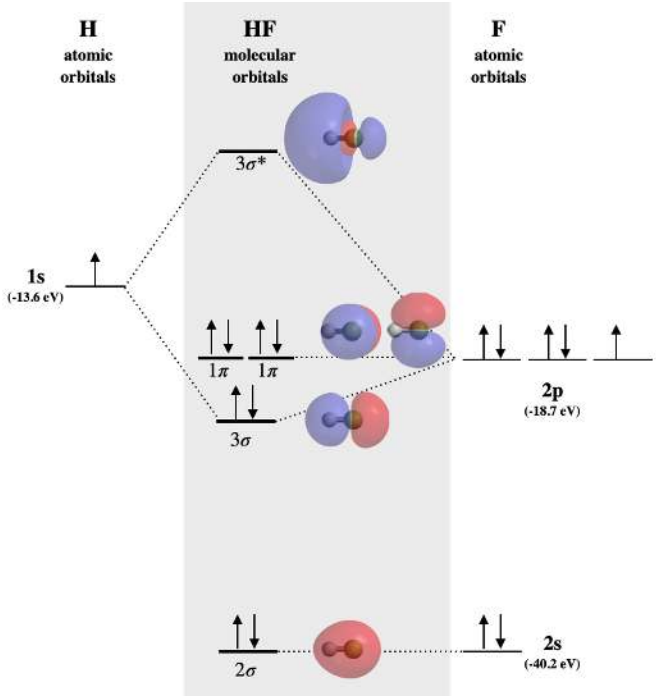


Figure 5.3.1.2: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

Chemical reactions take place at the HOMO and LUMO orbitals

Knowledge of molecular orbital diagrams, and the shapes of molecular orbitals, can be used to accurately explain and predict chemical reactivity. Chemical reactions take place using the highest occupied molecular orbitals (HOMO) of a nucleophile or Lewis base, and the lowest unoccupied molecular orbital (LUMO) of an electrophile or Lewis acid.

> *Lewis bases react using electrons in the HOMO, while Lewis acids react using the empty LUMO.*

Example: Reactivity of CO with metal ions

CO is an excellent ligand for many metal ions. In fact, the strong affinity between CO and the heme iron (Fe) ions in hemoglobin can explain the mechanism of carbon monoxide poisoning. When CO binds in place of O_2 to hemoglobin, that hemoglobin can no longer carry O_2 to tissue cells. CO binding to hemoglobin is strong and practically irreversible. When CO binds to metal ions, it does so through the carbon atom. This is contrary to expectations based on the Lewis structure and the known bond polarity, where electron density is polarized toward oxygen. The distribution of the electron density of the HOMO of CO can explain this observation!

? Exercise 5.3.1.2

Refer to the MO diagram for CO. Identify the HOMO and explain why CO bonds to metal ions through the carbon atom rather than through the oxygen atom.

Answer

In the interaction between CO and a metal ion, CO would act as a Lewis base; thus it will react using electrons in its HOMO. The MO diagram for CO is shown in Figure 5.3.1.1 the HOMO is the 3σ orbital (also discussed in ? Exercise 5.3.1.1). 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 5.3.1: Polar bonds is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.3.2: Polar bonds** by Kathryn Haas is licensed CC BY-SA 4.0.

5.3.2: Ionic Compounds and Molecular Orbitals

Ionic interactions lie at one extreme on a spectrum of bonding. On the opposite end of the spectrum are the non-polar covalent bonds (e.g., homonuclear diatomics). In these molecules, molecular orbitals are formed by equal-energy atomic orbitals, resulting in electron density evenly distributed over the molecule. In the middle of the spectrum are the cases of polar covalent bonds (e.g., heteronuclear diatomics), in which atomic orbitals of unequal energies contribute unequally to molecular orbitals, resulting in uneven distribution of electron density across the molecule. In the case of polar bonds, the electron density is shifted toward the more electronegative atom since that atom contributes more to the lowest energy bonding molecular orbitals. Molecular orbital diagrams can be drawn for ionic compounds as if they are extremely polar bonds in which electrons are not only shifted toward, but are transferred completely to the more electronegative atom.

Example: NaCl

In NaCl, the sodium $3s$ orbital (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals. The chlorine $3s$ and $3p_z$ orbitals have compatible symmetry, yet only the $3p_z$ orbital (-13.8 eV) is close enough in energy to interact with the Na $3s$; still, the energy difference is large enough to make bonding weak. The Na $3s$ orbital combines with Cl $3p_z$ to form the molecular orbitals labeled 4σ and $4\sigma^*$ in Figure 5.3.2.1. The 4σ orbital is weakly bonding, but is very close in energy to the Cl $3p_z$ orbital, and is mostly Cl-like in character. Notice that all σ orbitals look very much like either s or p orbitals centered on the Cl atom, while the $4\sigma^*$ orbital is centered almost entirely on Na. The lack of molecular orbitals that are distributed over both atoms at once is consistent with a lack of significant covalent bond character in NaCl. The bonding here is characterized by transfer of one electron from Na to Cl and is almost entirely electrostatic. Bonding that is mostly electrostatic in character is non-directional, unlike true covalent bonding.

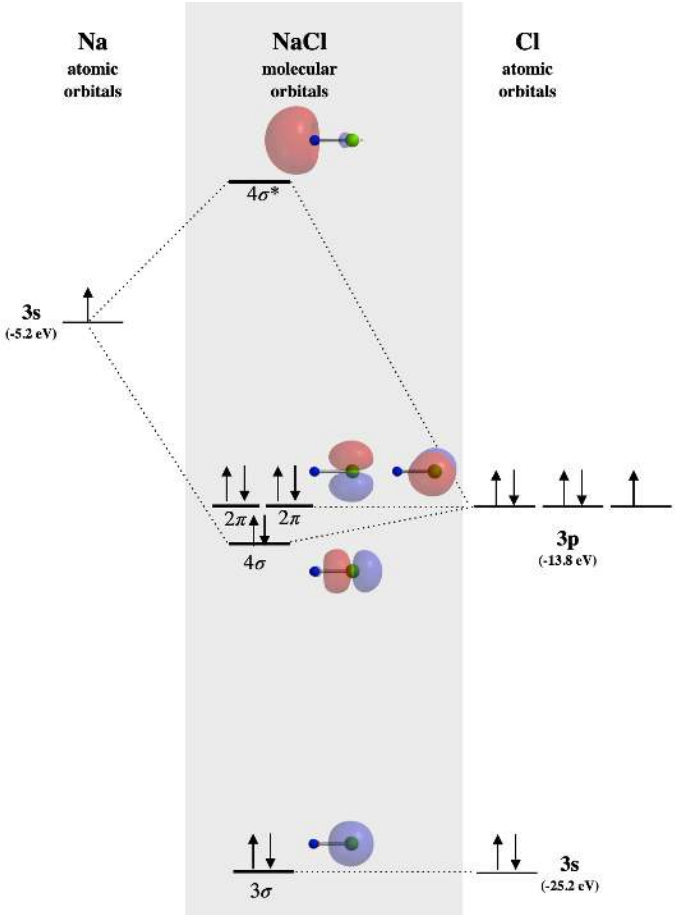


Figure 5.3.2.1: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding. (CC-BY-NC-SA, Kathryn Haas)

Exercise 5.3.2.1

Draw the molecular orbital diagram for LiF. Make sure to label all molecular orbitals appropriately, and specify whether they are mostly bonding, non-bonding, or antibonding. Identify the HOMO and LUMO. Sketch the approximate shapes of all orbitals.

Answer

We expect LiF to be an ionic compound because the energy difference in valence orbitals is at least 10-14 eV. (See Table 5.3.1) There are a variety of ways used to label molecular orbitals. In the figure below, we are using the convention of labeling each type of orbital with numbers starting from the lowest-energy orbitals. The 1σ orbital would be mostly F $1s$ in character and is not shown. The 2σ orbital is mostly non-bonding in nature, although it has a very small contribution from $2s$ of Li due to compatible symmetry. The 3σ orbital is slightly bonding but it is mostly F$2p$ in character. The two 1π orbitals are completely non-bonding. The $3\sigma^*$ orbital is antibonding.

- HOMO is 1π
- LUMO is $3\sigma^*$

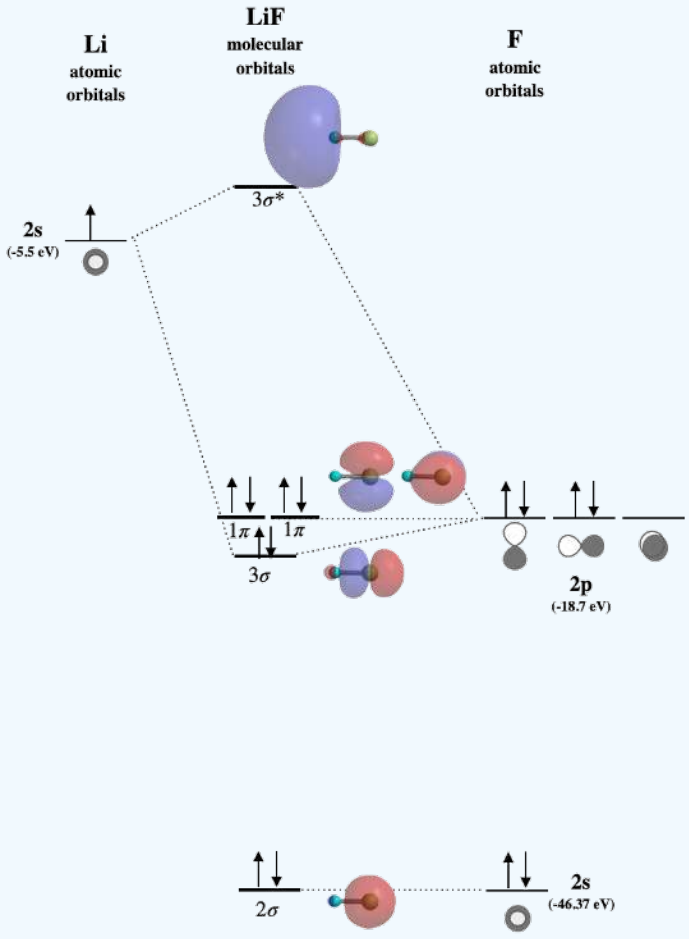


Figure for Exercise 5.3.2.1: Molecular orbital diagram for the ionic compund, LiF. (CC-BY-NC-SA, Kathryn Haas)

This page titled 5.3.2: Ionic Compounds and Molecular Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.3.3: Ionic Compounds and Molecular Orbitals** by Kathryn Haas is licensed CC BY-SA 4.0.

5.4: Diatomic Molecular Orbitals

The simplicity of diatomic molecular orbitals allows for their inspection using the theory of linear combinations of atomic orbitals (LCAO). As two atoms approach each other, their atomic orbitals overlap. In order to form bonding molecular orbitals, sufficient overlap should occur between atomic orbitals and they must have similar energies and matching symmetries. Anti-bonding molecular orbitals occur when two atomic orbitals cancel each other out. This gives rise to a node or area with zero electron density in between the two atoms.

Molecular Orbitals

Just like the atomic orbitals, **molecular orbitals(MO)** are used to describe the bonding in molecules by applying the group theory. The basic thought of what is molecular orbitals can be the organized combinations of the atomic orbitals according to the symmetry of the molecules and the characteristics of atoms. By applying the MO diagram, the properties such as magnetism and chirality of the molecules can be predicted.

Just like atomic orbitals can be solved as wavefunctions by applying Hermitian Operator to Schrödinger equations, molecule orbitals can be approximated by the **linear combinations of atomic orbitals(LCAO)**:

$$\Psi = \sum_{n=0}^{N} c_i \psi_i$$

Ψ is the molecular wave function, ψ is the atomic wave functions for atoms, c_i is the adjustable coefficients. This means that when the atoms get closer to each other, their atomic orbitals can overlap and the probability of the occurring of the electrons from the atoms becomes significantly in the overlap regions, which is the formation of the **molecular orbitals**.

Bonding, Anti-bonding and Non-bonding Molecular Orbitals

Before it goes further, some acknowledge about bonding and anti-bonding should be emphasized. When two atomic orbitals overlap, they can form new orbitals in two ways: one is the bonding orbital and another one is the anti-bonding orbital. In a molecular orbital diagram, if atomic orbitals form a bonding orbital, they must form an anti-bonding orbital. The bonding orbitals and anti-bonding orbitals always have the same number and relate with each other. For example, if there is a 1σ bonding orbital, then there must be a $1\sigma^*$, which is the relevant anti-bonding orbital of 1σ, where * is used to represent anti-bonding. This bonding and anti-bonding orbitals caused by the different ways of overlapping of the atomic orbitals.

Besides the bonding and anti-bonding molecular orbitals, there can also be some non-bonding orbitals. These orbitals only exist when some atomic orbitals of an atom cannot find any atomic orbital from another atom that has the same symmetry properties, then these atomic orbitals will remain at the same energy and form no bond. That's why they are called "non-bonding" molecular orbitals.

Diatomic Molecular Orbitals

Normally, in diatomic molecular orbitals, the atomic orbitals with the closest energy level can overlap with each other and form molecular orbitals. Therefore, the atomic orbitals generally tend to overlap one by one from the lowest potential energy to the highest potential energy. For example, in a homonuclear diatomic molecule, which means that both atoms are the same element, the same orbitals will overlap together and form molecular orbitals.

Eg. in the oxygen $\mathbf{O_2}$, the 1s orbital will overlap with 1s orbital to form a σ orbital and a σ^* orbital and the 2s orbital will overlap with 2s orbital to form a σ orbital and a σ^* orbital. The 1s orbital cannot overlap with 2s orbital in this case.

For another example, in a heteronuclear diatomic molecule, which means that the atoms in the molecule are different elements, the orbitals with the closest energy can overlap with each other and form molecular orbitals.

Eg. in the hydrogen fluoride **HF**, hydrogen's 1s orbital will overlap with one of the fluorine's 2p orbitals to form a σ orbital and a σ^* orbital since the orbital potential energy of H1s orbital is -13.61eV and of F2p is -18.65eV. Comparing with F2s orbital which has -40.17eV as its orbital potential energy, they are really close to each other. That's why H1s will form molecular orbitals with F2p instead of F2s.[1]

Also notice that only two atomic orbitals with similar symmetry properties can combine together. For example, s orbital can't overlap with p_x orbital if the overlap equally with both the same and opposite signs, this will cancel the bonding and anti-bonding

effect which will result in no molecular orbital forms.

Besides that, we normally only consider the valence atomic orbitals. That's why the F1s orbital does not be considered here since it's full-filled.

MO from s Orbitals

The overlap of two s orbitals will form a σ orbital and a σ^* orbital.

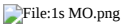


Figure 5.4.1. Molecular orbital diagram from 1s orbital overlapping

MO from p Orbitals

The overlap of two p orbitals will form either a σ and a σ^* orbitals or a π and a π^*orbitals. Generally, we choose to assign the z axis of two atoms point to each other which allows the p_z orbitals overlap “head” to “head” and form σ and σ^* orbitals. This also allows the p_x orbitals overlap “side” to “side” and form π and π^*orbitals. This also applies for the p_y orbitals.

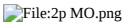


Figure 5.4.2. This is the MO diagram form by two 2p atomic orbitals.Note: In this figure, two p_x orbitals are used to form the sigma and sigma* molecular orbitals. This is just a label issue.

Sometimes, when p orbitals can’t find another orbital has a similar symmetry with it, these p orbitals will remain as non-bonding orbitals.

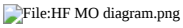


Figure 5.4.3. This is the valence MO diagram of HF. The H1s orbital overlap with one of the F2p orbitals. The other two F2p orbitals remain as non-bonding orbitals.

MO from d Orbitals

Start from the third row, all the elements after sodium (Na) have d orbitals. There are totally 5 d orbitals, which are named as d_{z^2},d_{xy},d_{xz},d_{yz} and $d_{x^2-y^2}$. Elements with d orbitals, especially the transition metals, can also form bonds by using d orbitals. As shown in figure 5.4.4, the different overlap of the d orbitals will result in different electron density, which results in different types of bonds. Just like what happens to the p-orbital-overlapping molecular orbitals, d atomic orbitals can also overlap with other orbitals in different orbital potential energy levels such as p orbitals and s orbitals. This is also the reason for the formation of a metal complex. However, d orbitals normally are not applied to form molecular orbitals in a diatomic molecule.

Nonbonding Orbitals

As mentioned before, if an atomic orbital cannot find any other orbital with similar symmetry, then it will remain as non-bonding molecular orbital. The non-bonding molecular orbitals normally have the same energies as the atomic orbitals that form them, although there are some special cases can happen (not in diatomic MO, but in some metal complex). For example, in the ion FHF^-, by solving the irreducible representation, it can be found that the base of FHF^- has a_g, b_{2u}, b_{3u}, b_{2g}, b_{3g} and b_{1u}. However, since the H atom has only a 1s orbital, it can only form molecular orbitals with a_g. Therefore, b_{2u}, b_{3u}, b_{2g}, b_{3g} and b_{1u} will remain as non-bonding molecular orbitals. Also, notice that b_{1u} has a higher level in energy state. This can be caused by the extreme unsymmetrical structure of this molecular orbital. Another guess of the increase in the b_{1u} energy level can be the slightly mixing with the 2s orbital from two fluorines.

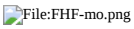


Figure 5.4.6. This is the MO diagram of O_2.

Orbital Mixing

This is the most tricky part for the diatomic molecular orbitals. In general, we only consider the interactions between atomic orbitals have the same energies unless there is no atomic orbital satisfy the request. However, the interaction between two atomic orbitals with relatively close energies that have the same symmetry can also happen. This will result in the raising of the energies of the molecular orbitals.

Considering **figure 5.4.2** above, this is an example without interaction between two atomic orbitals with close energies that have the same symmetry. The π_u molecular orbitals have higher energy than the σ_g molecular orbital. However, since the $\sigma_g(2s)$ and

$\sigma_g(2p)$ orbitals both have σ_g symmetry,these orbitals can interat to lower the energy of the $\sigma_g(2s)$ and to increase the energy of the $\sigma_g(2p)$. This will result the energy of $\sigma_g(2p)$ orbital has higher energy than $\pi_u(2p)$ orbitals, as shown in **figure 5.4.7**. This phenomenon is called ***mixing***.

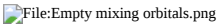


Figure 5.4.7. This is the mixing MO diagram.For example, this *s*-*p* mixing will happen for B_2 and C_2.

Heteronuclear Diatomic Molecule

Unlike the homonuclear diatomic molecule, many heteronuclear diatomic molecules are polar molecules. This means that the electron density does not evenly distribute over each atom. The electron density always favors the atom that is more electronegative. MO theory can also be applied in this situation.

As mentioned before, since here we deal with different two elements in molecules, the orbital potential energies will be considered. This will result in uneven contributions of molecular orbitals from the overlap of the atomic orbitals. Fortunately, farther the two atomic potential energies (APE) are, less the magnitude of the interaction between them. This means that only two atomic orbitals with similar energies can overlap enough to form molecular orbitals. Use the example of HF (**Figure 5.4.3**). According to **Table 5.4.1**, 1s orbital of the hydrogen atom has APE as -13.61eV, 2s orbital of fluorine has APE as -40.17eV and 2p orbitals of fluorine have APE as -18.65eV. It is obvious that $H1s$ orbital has a much closer potential energy to the $F2p$ instead of $F2s$. Therefore, $H1s$ orbital overlaps much more with $F2p$ and form molecular orbitals. $F2s$ will remain as a non-bonding orbital.

Table 5.4.1. Orbital Potential Energy. Notice that only the valence atomic orbitals are counted.

Atomic Number	Elemment	1s	2s	2p	3s	3p	4s
1	H	-13.61					
2	He	-24.59					
3	Li		-5.39				
4	Be		-9.32				
5	B		-14.05	-8.3			
6	C		-19.43	-10.66			
7	N		-25.56	-13.18			
8	O		-32.38	-15.85			
9	F		-40.17	-18.65			
10	Ne		-48.47	-21.59			
11	Na				-5.14		
12	Mg				-7.65		
13	Al				-11.32	-5.98	
14	Si				-15.89	-7.78	
15	P				-18.84	-9.65	
16	S				-22.71	-11.62	
17	Cl				-25.23	-13.67	
18	Ar				-29.24	-15.82	
19	K						-4.34
20	Ca						-6.11

Drawing Diatomic MO Diagram

Here are some common steps to help you draw the diatomic MO diagram.

1. Recognize the diatomic molecule is a homonuclear molecule or heteronuclear molecule;
2. Recognize the orbital potential energies of their valence atomic orbitals, find the closest pair;
3. Recognize the symmetry of these atomic orbitals to figure out if the interaction can actually happen. Then determine the {\displaystyle \sigma }σ and {\displaystyle \pi }π bonding and anti-bonding, and even non-bonding orbitals;
4. Recognize the ***mixing*** effect to see if there are any energy shift for the molecular orbitals;
5. Draw the electrons from the lowest molecular orbital. Follow the rules like the **Pauli exclusion principle** to draw the ground state MO diagram.

Reference

1. Miessler, Gary. “Chapter 5. Molecular Orbital Theory.” *Inorganic Chemistry*, by Gary L. Miessler et al., Pearson, 2014, pp. 117–138.
2. ↑ Greeves, Nick. “ChemTube3D.” *ChemTube3D*. [1]

5.4: Diatomic Molecular Orbitals is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

5.4.1: Molecular Orbital Theory

Learning Objectives

- To use molecular orbital theory to predict bond order
- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As discussed previously, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = \quad & AO(atom\ A) \quad + \quad AO(atom B) \\ MO(1) = \quad & AO(atom\ A) \quad - \quad AO(atom B) \end{aligned} \tag{5.4.1.1}$$

The molecular orbitals created from Equation 5.4.1.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 5.4.1.1). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

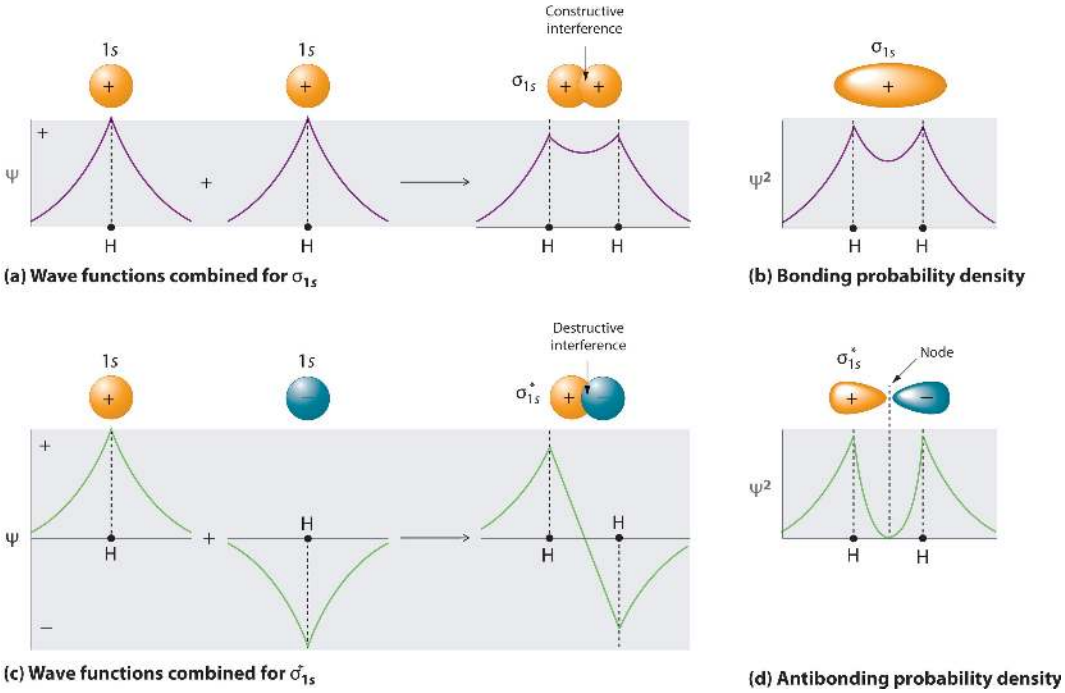


Figure 5.4.1.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{5.4.1.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 5.4.1.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{5.4.1.3}$$

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^\star_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from

the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 5.4.1.2

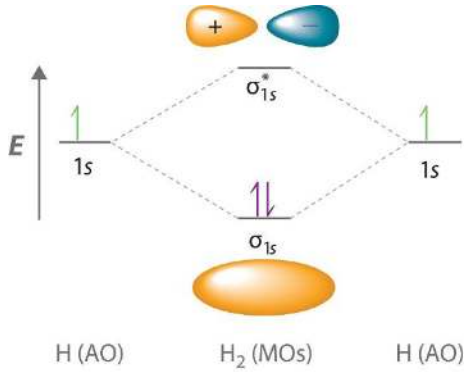


Figure 5.4.1.2: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 5.4.1.2). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{5.4.1.4}$$

To calculate the bond order of H_2, we see from Figure 5.4.1.2that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{5.4.1.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 5.4.1.2to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

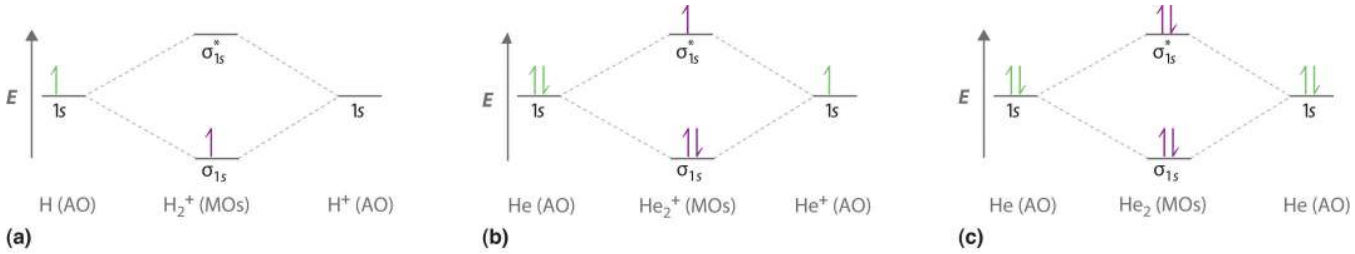


Figure 5.4.1.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure 5.4.1.3 shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 5.4.1.1, these predictions agree with the experimental data.

Part (b) in Figure 5.4.1.3 is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma_{1s}^\star$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 5.4.1.1).

Table 5.4.1.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^\star)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^\star)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 5.4.1.3 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^\star$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ electron configuration, with a predicted bond order of $(2-2)\div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Molecular Orbital Theory: https://youtu.be/XgtOG0ezw78

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 5.4.1.1

Use a molecular orbital energy-level diagram, such as those in Figure 5.4.1.3, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

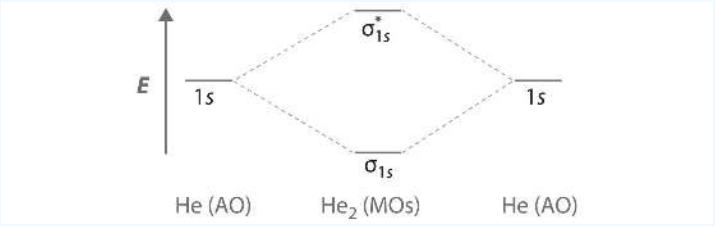
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

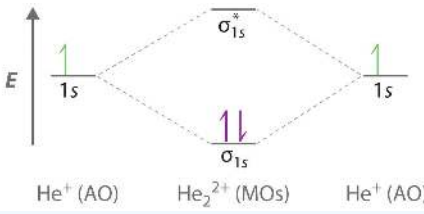
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma_{1s}^{\star}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^{+} ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

? Exercise 5.4.1.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^{\star})^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 5.4.1.4 where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure 5.4.1.2 Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

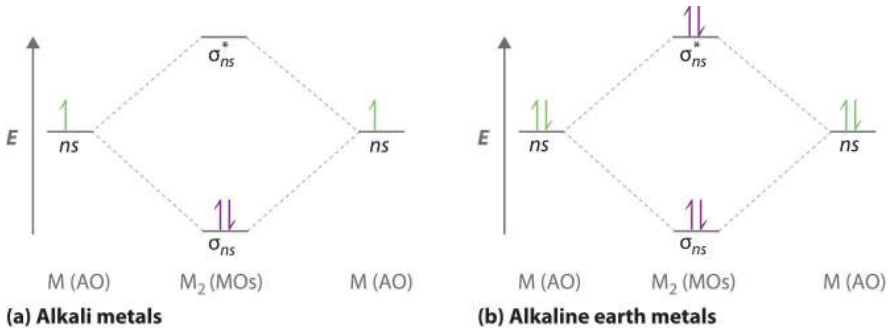


Figure 5.4.1.4: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.*

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 5.4.1.3

As shown in part (b) in Figure 5.4.1.4 this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

✔ Example 5.4.1.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

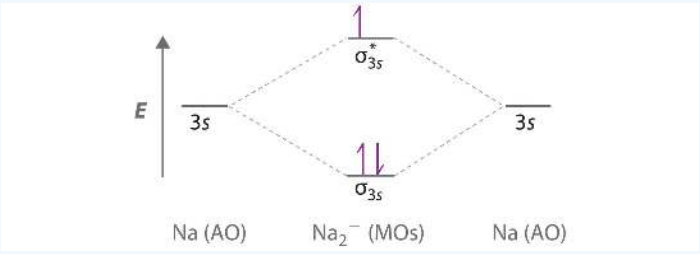
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 5.4.1.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{5.4.1.6}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 5.4.1.5, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{5.4.1.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{5.4.1.8}$$

In this combination, shown in part (b) in Figure 5.4.1.5, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

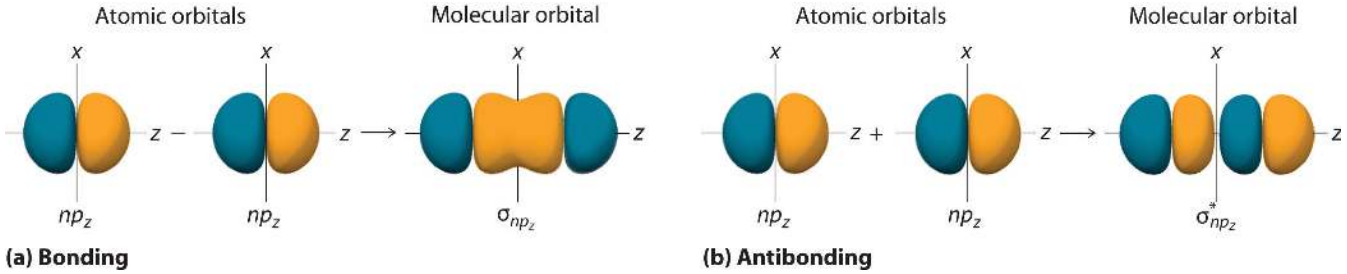


Figure 5.4.1.5: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 5.4.1.6, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{5.4.1.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{5.4.1.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the

same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

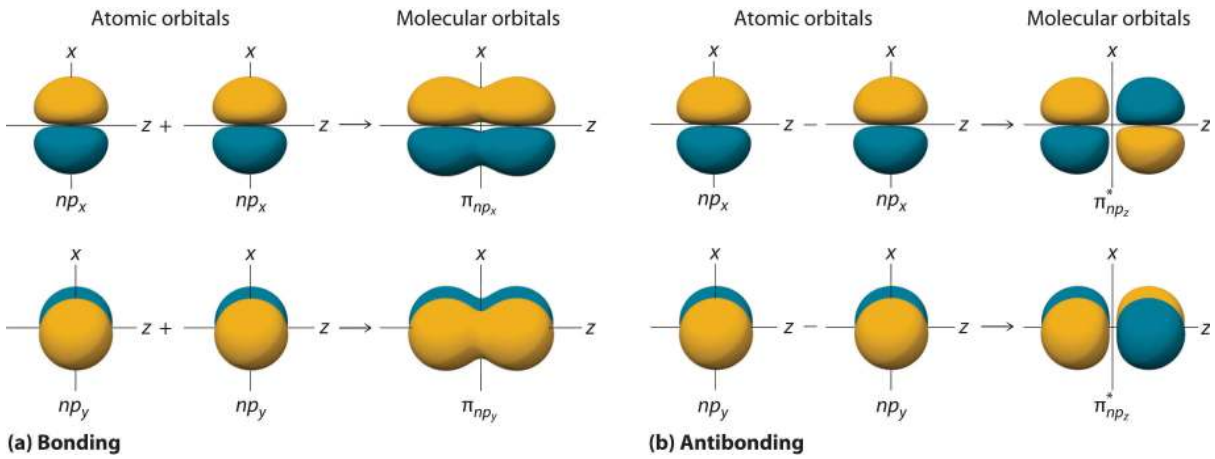


Figure 5.4.1.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 5.4.1.7is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

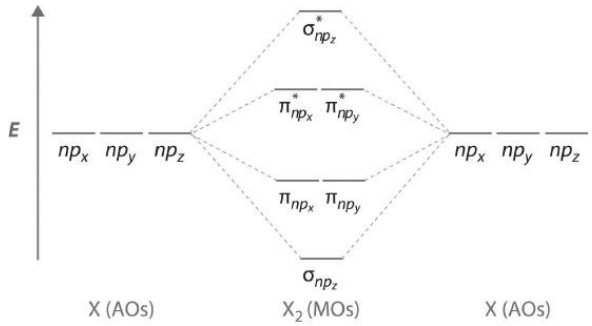


Figure 5.4.1.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 5.4.1.8, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

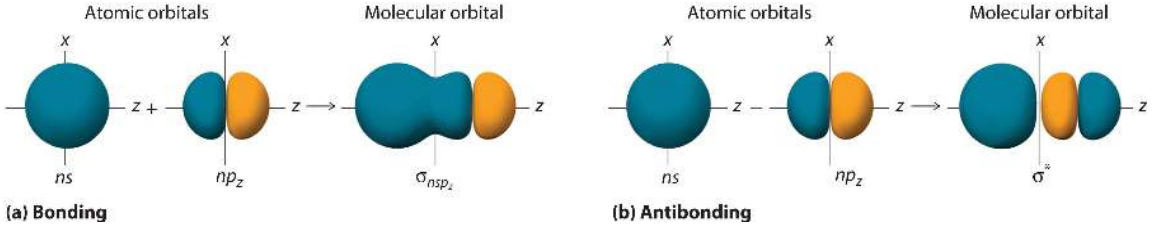


Figure 5.4.1.8: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 5.4.1.9; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2p atomic orbitals because of the large difference in energy between the 2s and 2p atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2p orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of (8 − 6) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

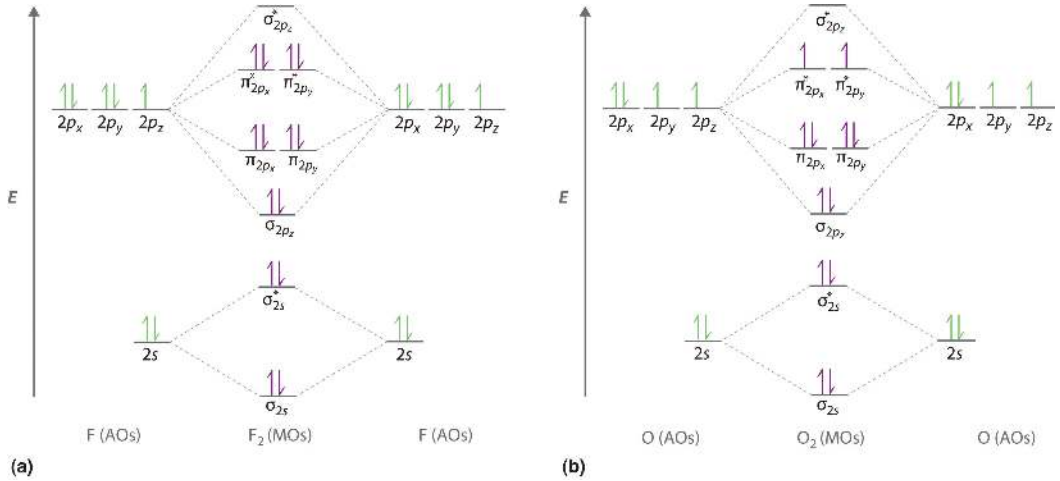


Figure 5.4.1.9: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^{\star}_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 5.4.1.9. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 5.4.1.10, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

Figure 5.4.1.10: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 5.4.1.11Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 5.4.1.11). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

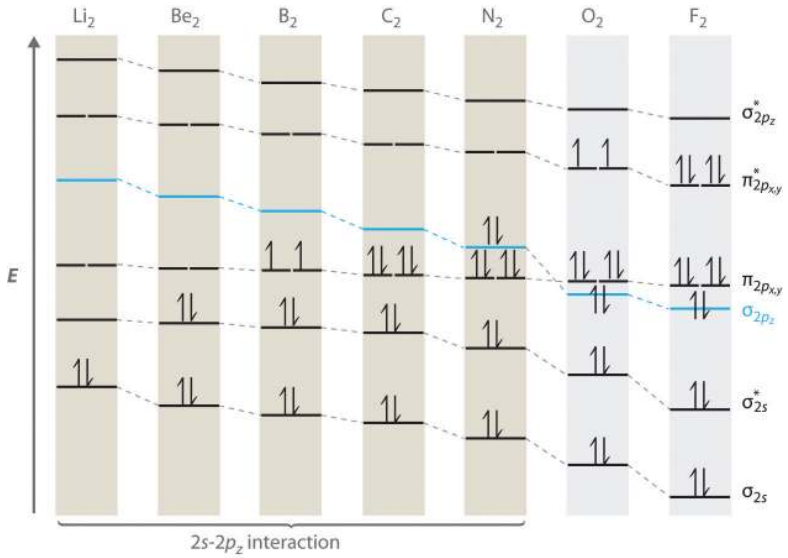


Figure 5.4.1.11: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 5.4.1.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

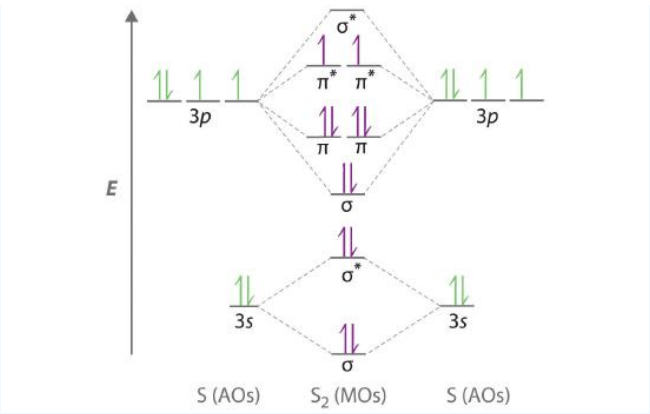
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 5.4.1.9 and Figure 5.4.1.11, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 5.4.1.11), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^{\star}_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 5.4.1.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^{\star}_{x,y}})^4$

bond order of 1;

no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 5.4.1.12 The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

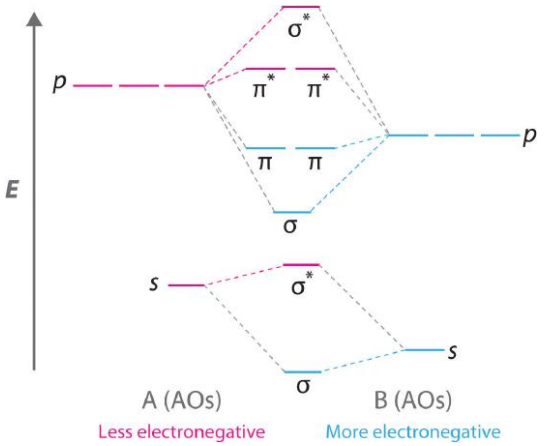


Figure 5.4.1.12: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 5.4.1.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 5.4.1.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

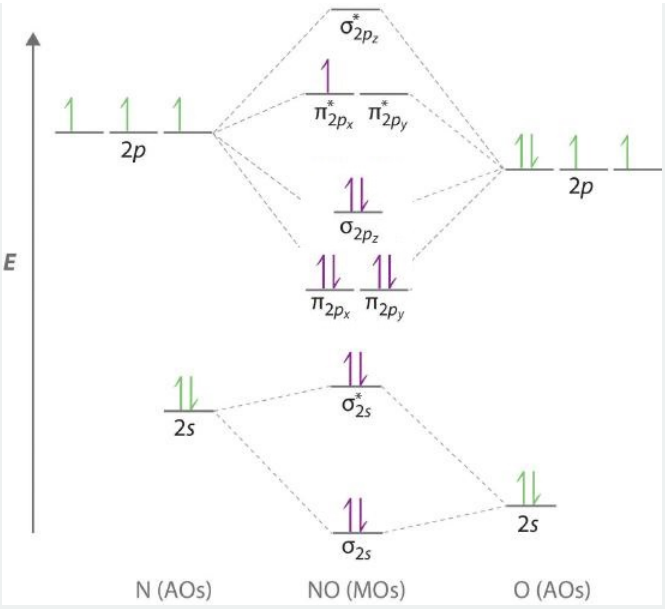


Figure 5.4.1.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\left(\sigma^{\star}_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi_{2p^{\star}_{x,y}}\right)^2$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 5.4.1.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 5.4.1.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^{+} cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Molecular Orbital Bonding for Second Row Elements: https://youtu.be/A_5Xa3sK_YE

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 5.4.1.14 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can

interact with the H 1*s* orbital. The 3p_x and 3p_y atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, 3p_x, and 3p_y orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl 3p_z than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

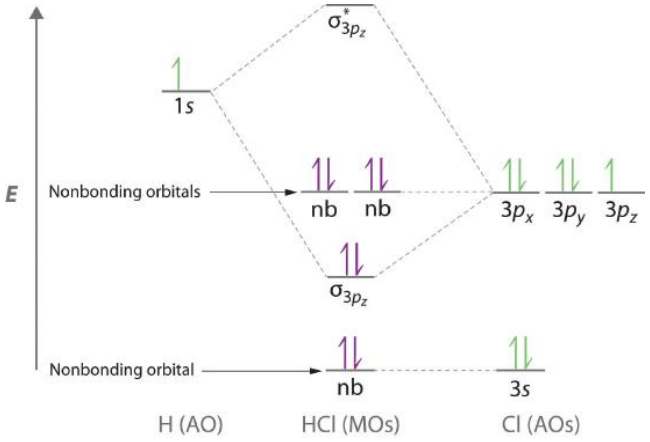


Figure 5.4.1.14: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have **no effect** on bond order.*

Example 5.4.1.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 5.4.1.12 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

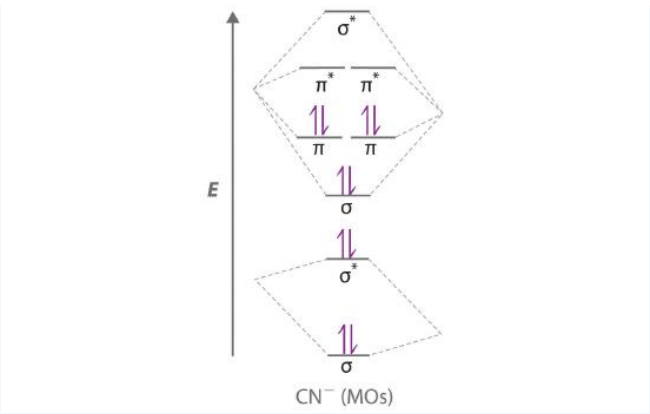
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 5.4.1.12 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 5.4.1.12 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 5.4.1.4

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer: All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

5.4.1: Molecular Orbital Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **11.5: Molecular Orbital Theory** is licensed CC BY-NC-SA 4.0.

5.P: Problems

Concept Review Questions

1. What are the assumptions (axioms) of molecular orbital (MO) theory?

2. Explain qualitatively why the vectorial addition of atomic orbitals creates molecular orbitals (which underlying physical phenomenon is described by the vectorial addition?).

3. Explain qualitatively why molecular orbital theory is suitable to describe covalent bonding.

4. What are the three criteria that determine the degree of covalent interaction in MO theory?

5. Which three rules determine the degree of orbital overlap in MO theory?

6. Explain why the combination of a large, diffuse orbital and a small orbital produces only weak covalent interaction.

7. Explain why sigma interactions between atomic orbitals typically produce larger orbital overlaps than pi interactions.

8. Explain why the combination of orbitals of the same energy leads to the largest degree of covalent interaction.

9. What can be said about energy and location of a bonding and an anti-bonding molecular orbital that are made from atomic orbitals of large energy difference?

10. MO theory – even though designed for covalent bonding – can also make statements about ionic bonding. Explain why.

11. Explain the principles of SALC.

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.

Homework Problems

Section 1

Exercise 1

What will most likely lead to the smallest covalent interaction?

a) Overlap of a small and a large orbital.

b) Overlap of two small orbitals.

c) Overlap of two large orbitals.

Answer

a) Overlap of a small and a large orbital.

Exercise 2

What will most likely lead to the largest covalent interaction?

a) orbital overlap in sigma-fashion

b) orbital overlap in pi-fashion

c) orbital overlap in delta-fashion

Answer

a) orbital overlap in sigma-fashion

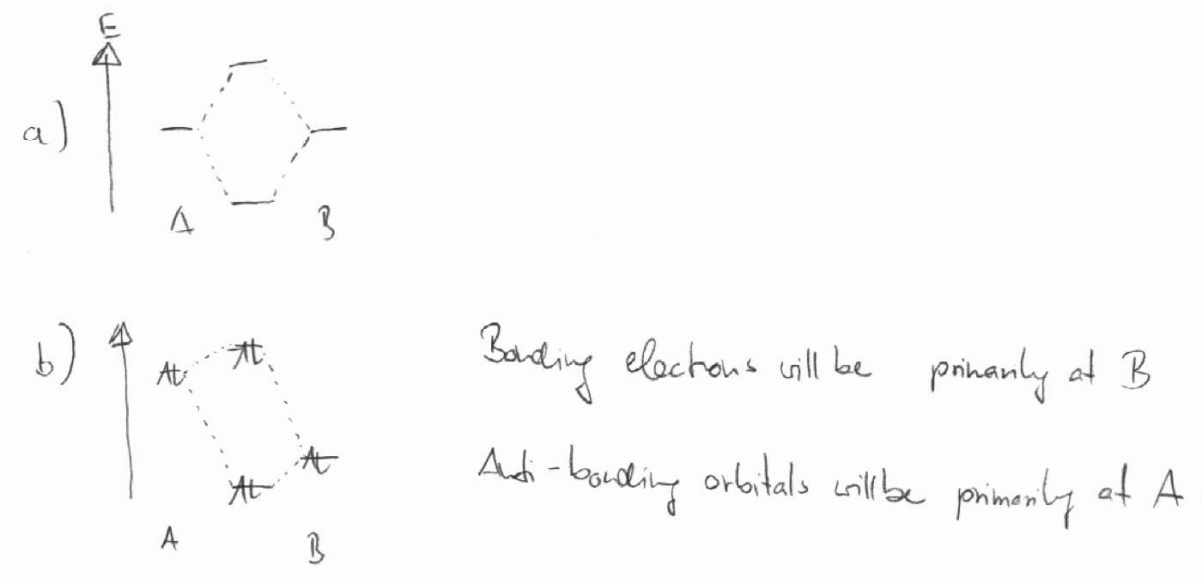
Exercise 3

Qualitatively construct the MO diagrams composed of

a) two 2s atom orbitals A and B of equal energy.

b) two 2s atom orbitals where the orbital energy of atom A is significantly higher than that of B. If both the bonding and the antibonding MO are filled with electrons, where will bonding and antibonding electrons primarily be located? Briefly explain your decision.

Answer



Exercise 4

Decide by "inspection" which of the following combinations of orbitals have the "right" symmetries to form molecular orbitals.

a) The $2p_x$ orbital of the first N atom and the $2p_y$ orbital of the second N atom in the molecule N_2. The z axis is defined as the bond axis in N_2.

b) The F $2p_x$ and the H 1s orbital in the HF molecule. The z axis is defined as the bond axis.

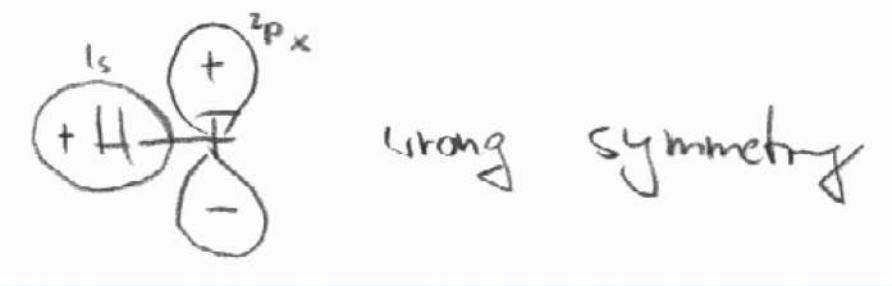
c) The $2p_z$ orbital of F and the 1s orbital in the HF molecule. The z axis is defined as the bond axis.

Answer

a)

https://chem.libretexts.org/@go/page/263140

b)



c)

Exercise 5

The CH_4 molecule belongs to the point group T_d. You can find the character table of the point group in the internet.

a) Calculate the reducible representation for the ligand group orbitals (LGOs).

b) Calculate the irreducible representations of the ligand group orbitals (LGOs).

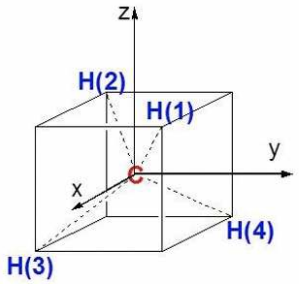
c) Draw a qualitative molecular orbital diagram for CH_4.

Answer

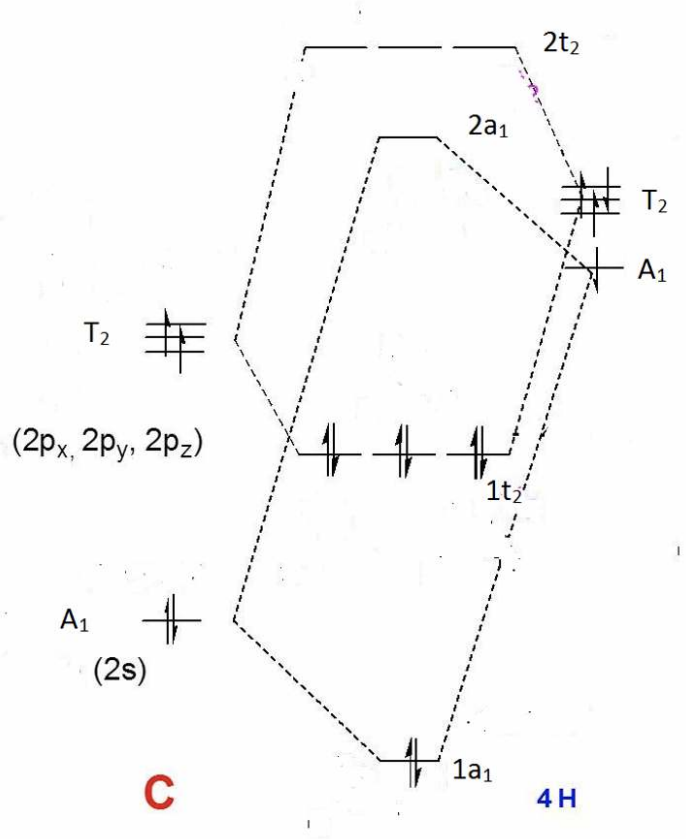
https://chem.libretexts.org/@go/page/263140

The symmetry of 4H group orbitals:

$\Gamma_r = 4E+1C_3+0C_2+0S_4+2\sigma_d = A_1 + T_2$



T_d		
A_1		$x^2+y^2+z^2$
A_2		
E		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	(R_x,R_y,R_z)	
T_2	(x,y,z)	(xz, yz, xy)



Exercise 6

Which are the symmetry types of the central atom orbitals in the PCl_5 molecule?

Answer

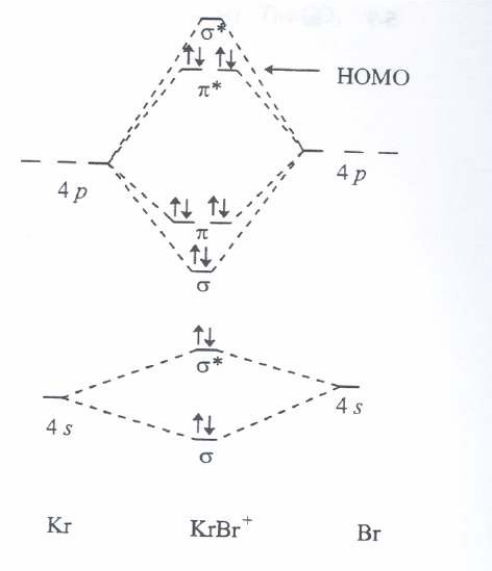
1. Determine point group of PCl_5. --> D_{3h}.
2. Decide what are the valence orbitals of the central atom: 3s, 3p
3. Look up the character table of D_{3h}, e.g., in the internet. You will find their symmetries to be: A_1' (3s), A_2'' ($3p_z$), E'($3p_x$, $3p_y$)

Exercise 7

For the hypothetical $BrKr^+$ molecule: Toward which atom is the HOMO polarized? Explain briefly why.

Answer

https://chem.libretexts.org/@go/page/263140



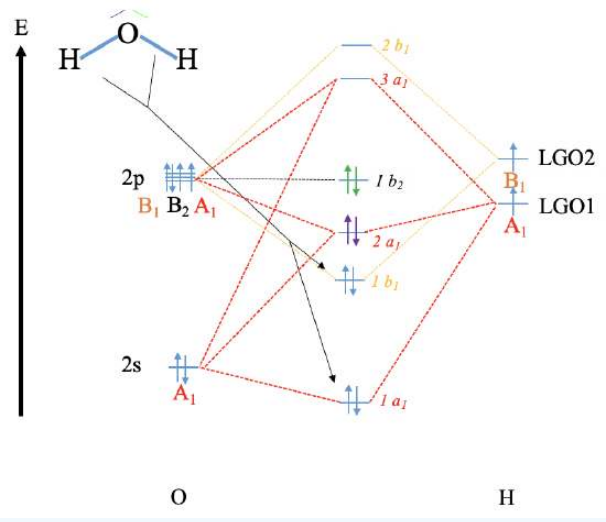
Orbital energies of Kr must be somewhat lower than the ones of Br because the electrons experience higher effective nuclear charge (Z_{eff} increases within a period). This means that the antibonding HOMO is polarized towards Br (HOMO energetically closer to 4p(Br) than 4p(Kr)).

Exercise 8

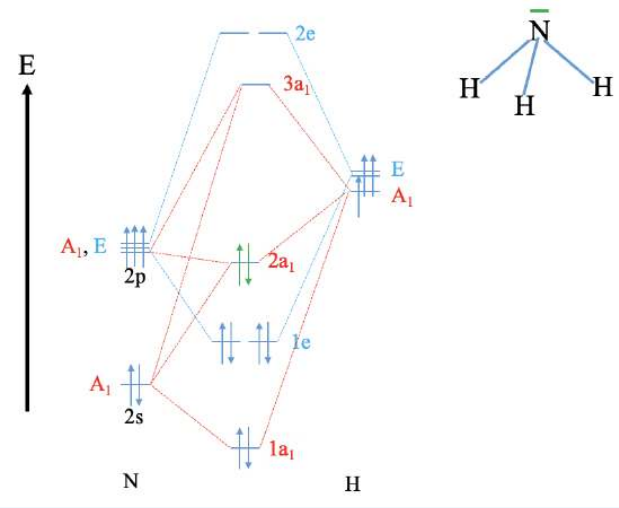
Reconstruct the MO diagram for water and NH_3 (repeat what we did in class without looking at your notes (only use the respective character tables).

Answer

Water



NH_3



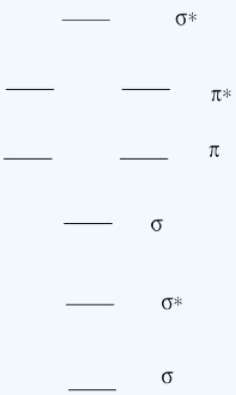
Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

Exercise 5.P.1

A Molecular Orbital Diagram for a diatomic molecule (two atoms) always has the same basic pattern.

- Draw a picture of the levels.
- Label each level with σ, σ*, π, π*

Answer



Exercise 5.P.2

A Molecular Orbital Diagram for a diatomic molecule (two atoms) varies in the number of electrons. How do you populate the electrons?

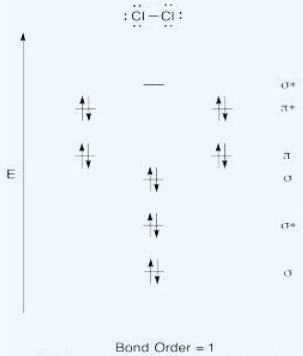
Answer

• Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg C_2^{2-} has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
• Fill electrons into the lowest energy orbitals first.
• Pair electrons after all orbitals at the same energy level have one electron.

Exercise 5.P.3

Construct a qualitative molecular orbital diagram for chlorine, Cl_2. Compare the bond order to that seen in the Lewis structure (remember that an electron in an antibonding orbital cancels the stabilization due to bonding of an electron in a bonding orbital).

Answer

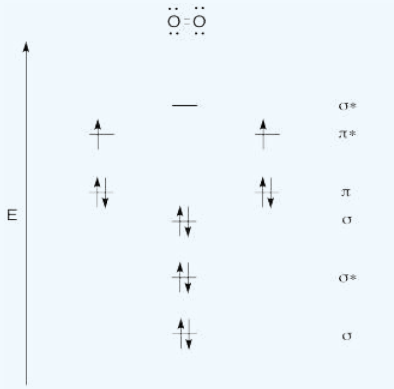


Bond Order = 1
MO diagram matches the Lewis structure

Exercise 5.P.4

a. Construct a qualitative molecular orbital diagram for oxygen, O_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Compounds that have all of their electrons paired are referred to as diamagnetic. Those with unpaired electrons are referred to as paramagnetic. Paramagnetic materials are attracted by a magnetic field, but diamagnetic things are not. How would you expect molecular oxygen to behave?

Answer



Bond Order = 2
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

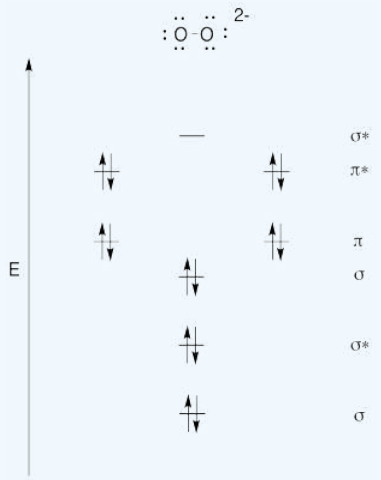
Exercise 5.P.5

a. Construct a qualitative molecular orbital diagram for peroxide anion, O_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?

https://chem.libretexts.org/@go/page/263140

d. Based on molecular orbital pictures, how easily do you think dioxygen could be reduced to peroxide (through the addition of two electrons)?

Answer

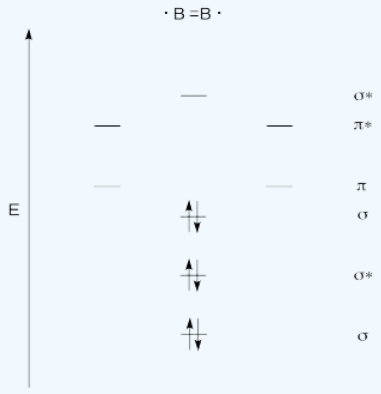


Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise 5.P.6

Construct a qualitative molecular orbital diagram for diboron, B_2. Do you think boron-boron bonds could form easily, based on this picture?

Answer



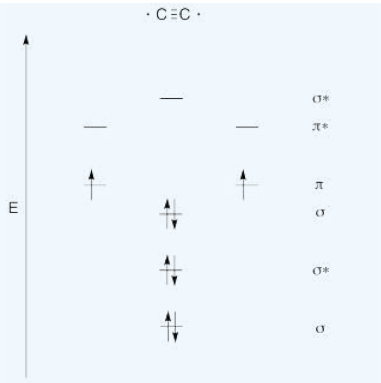
Bond Order = 1
Boron-Boron bonding should be possible

Exercise 5.P.7

a. Construct a qualitative molecular orbital diagram for dicarbon, C_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?

Answer

https://chem.libretexts.org/@go/page/263140

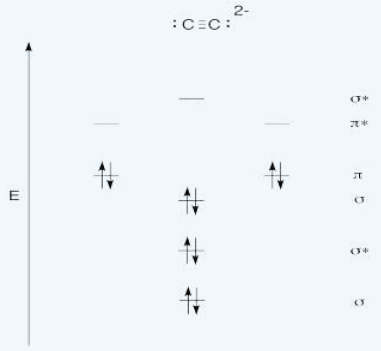


Bond Order = 2
MO diagram does not match the Lewis structure. However, the MO diagram does concur about the 2 unpaired electrons.

Exercise 5.P.8

a. Construct a qualitative molecular orbital diagram for acetylide anion, C_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Based on molecular orbital pictures, how easily do you think dicarbon could be reduced to acetylide (through the addition of two electrons)?

Answer

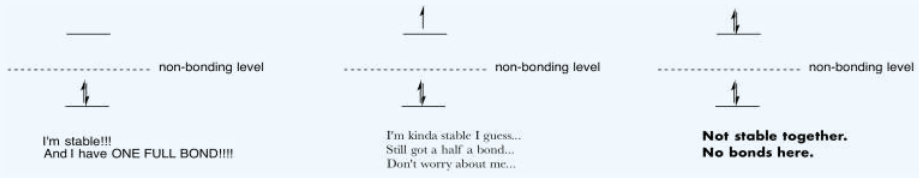


Bond Order = 3
MO diagram matches the Lewis structure. Both predict a Bond Order of 3 and 2 lone pairs of electrons. The addition of two electrons to C_2 to C_2^{2-} would be possible.

Exercise 5.P.9

Make drawings and notes to summarize the effect of populating antibonding orbitals.

Answer



Exercise 5.P.10

Researchers at Johns Hopkins recently reported the formation of Na_4Al_2 in a pulsed arc discharge (they put a lot of electric current through a sample of sodium and aluminum; Xinxing Zhang, Ivan A. Popov, Katie A. Lundell, Haopeng Wang, Chaonan Mu, Wei Wang, Hansgeorg Schnöckel, Alexander I. Boldyrev, Kit H. Bowen, *Angewandte Chemie International Edition*, **2018**, *57*(43), 14060-14064. Copyright 2018, John Wiley & Sons. Used with permission.).

a. The compound is ionic. Explain which atoms form the cations, based on periodic trends.
b. Therefore, what atoms form the anion?
c. The anion is one molecule. What is the charge on this molecule?
d. Show how to calculate the total valence electrons in this molecular anion.
e. Draw a Lewis structure for this molecular anion.
f. Construct a diatomic molecular orbital energy level diagram for this molecule. Label the energy levels (sigma, pi, etc.) and add in the correct number of electrons.
g. Show how to calculate the bond order in the molecule.

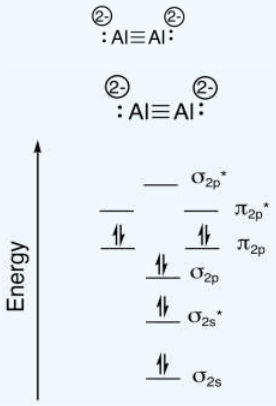
Answer

a) Na, because Na has a lower ionization potential (and a lower electronegativity) than Al.

b) Al

c) 4-, because there are four Na^+

d) total e^- = 2 x 3 e^- (per Al) + 4 e^- (for the negative charge) = 10 e-



g) bond order $= \frac{(\#bonding\ e^- - \#antibonding\ 3^-)}{2} = \frac{8-2}{2} = 3$

Exercise 5.P.1

Draw the molecular orbital diagram for (NO^-).

Answer

Add texts here. Do not delete this text first.

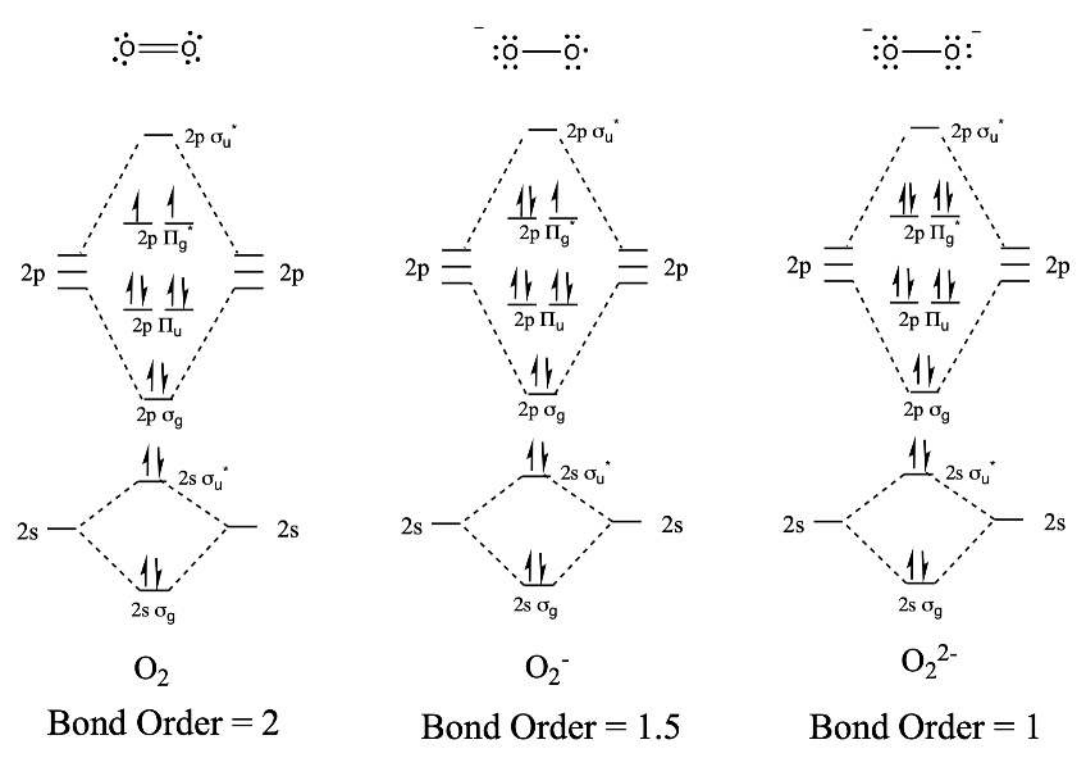
Exercise 5.P.1

Draw and compare the molecular orbital diagrams to the Lewis structure diagrams for O_2, O_2^-, and O_2^{2-}.

Answer

The Lewis structures and MO diagrams are shown below. In general, the bond order derived from the MO diagram agrees with the Lewis structure for each species. In the case of the two ions, the number of unpaired electrons from MO theory and the Lewis structure also agrees. In the case of dioxygen, however, there is an inconsistency between the Lewis

representation and the MO diagram. While the Lewis structure would lead us to believe that all electrons are paired, the MO diagram indicates paramagnetism, with two unpaired electrons. The MO diagram explains the magnetic behaviour of dioxygen.



? Exercise 5.P.1

Draw the molecular orbital diagram for hydroxide ion (OH^-).

Answer

Add texts here. Do not delete this text first.

? Exercise 5.P.1

Draw the molecular orbital diagram for hydroxide fluoride (HF).

Answer

Add texts here. Do not delete this text first.

? Exercise 5.P.1

Draw the molecular orbital diagram for borane (BN).

Answer

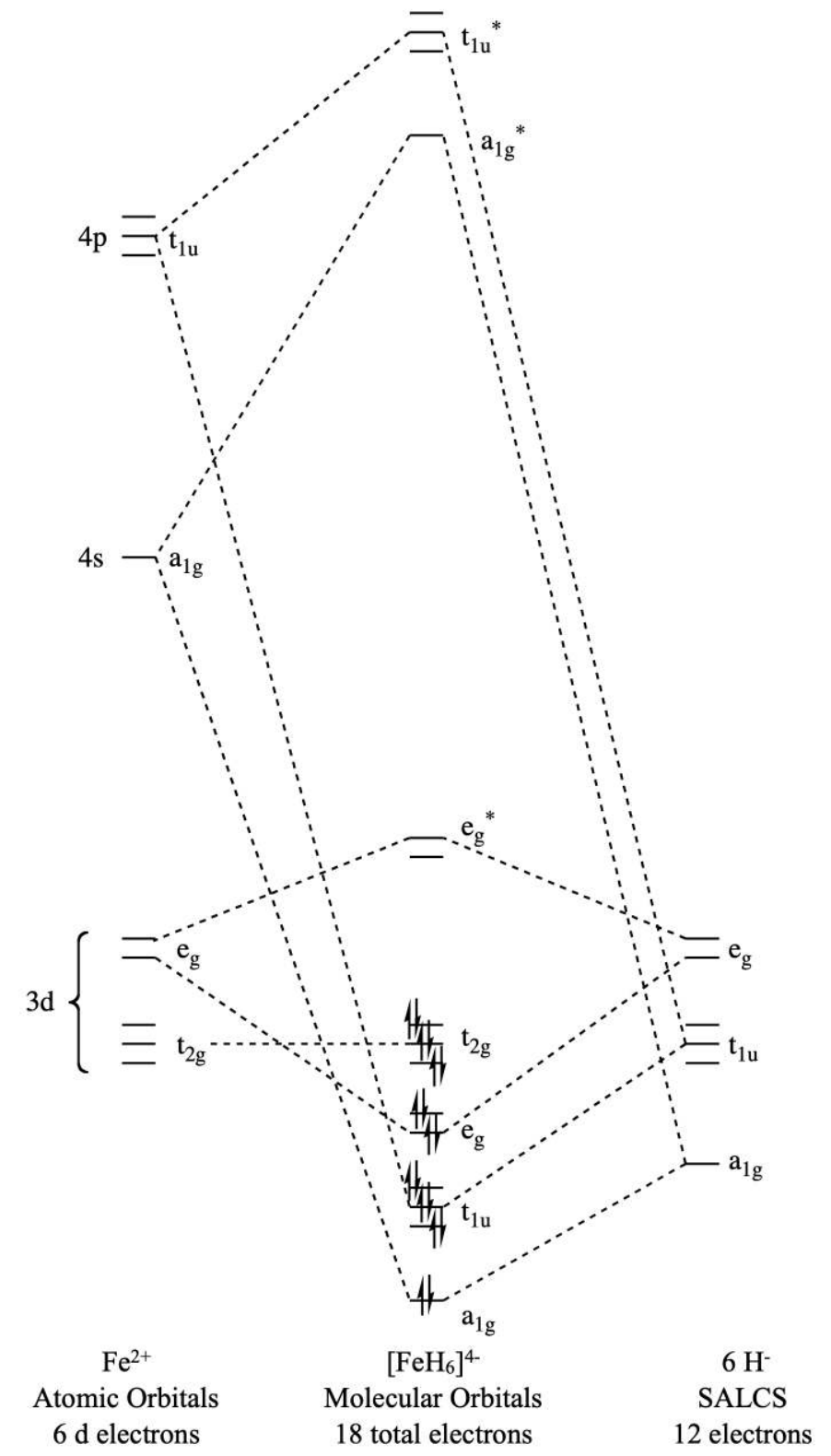
Add texts here. Do not delete this text first.

BH3

Exercise 5.P.1

Draw the molecular orbital diagram for (FeH_6).

Answer



https://chem.libretexts.org/@go/page/263140

Exercise 5.P.1

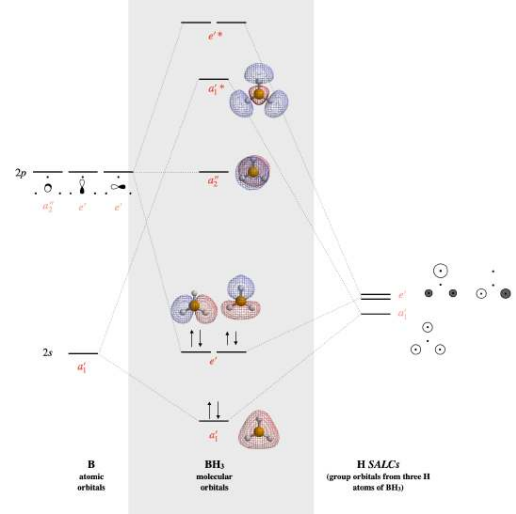
Draw the molecular orbital diagram for boron trifluoride (BF_3).

- What is the non-bonding orbital?
- What are the HOMO and LUMO orbitals?
- Why does e' have 2 lines of energy levels compared to a1', which has only a 1-line energy level?
- What is the bond order of BH_3 in this MO diagram?

Answer

The calculated MO diagram is shown below.

- a_2'' is the lone non-bonding orbital.
- The HOMO is the a_2'' nonbonding orbital, the LUMO is a bonding e' set of two degenerate orbitals/
- e' is doubly degenerate
- The bond order is 3



5.P: Problems is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Concept Review Questions Chapter 3** by Kai Landskron is licensed CC BY 4.0.
- **Homework Problems Chapter 3** by Kai Landskron is licensed CC BY 4.0.
- **13.6: Assembling the Complete Diagram and Electron Population** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/structure.htm.

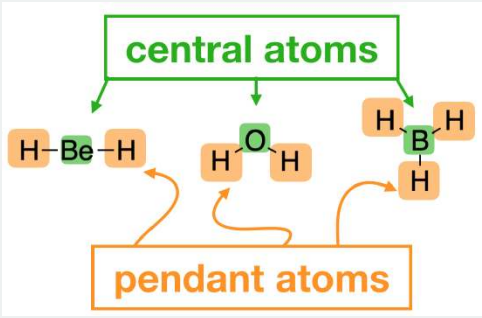
CHAPTER OVERVIEW

6: Larger (Polyatomic) Molecules

We can extend the method we used for diatomic molecules to draw the molecular orbitals of more complicated, polyatomic molecules (molecules with more than two atoms). To combine several different atoms in a molecular orbital diagram, we will group orbitals from different atoms into sets that match the symmetry of a central atom. These **group orbitals** are also referred to as **symmetry adapted linear combinations (SALCs)**. We'll use a stepwise approach to do this as summarized below.

Symmetry adapted linear combinations (SALCs)

We need SALCs (aka group orbitals) to draw molecular orbital (MO) diagrams of *polyatomic* molecules. SALCs are groups of orbitals on **pendant atoms**. These groups of orbitals much match the symmetry of valence orbitals on the **central atom** in order to create a productive interaction. When we combine SALCs with the atomic orbitals on the central atom, we can generate an MO diagram that gives us information about the molecule's bonding and electronic states.



Below is a set of steps you can follow to find SALCs and draw an MO Diagram. Each step will be illustrated in detail through the examples in the subsections that follow this page.

1. Find the **point group** of the molecule and assign Cartesian coordinates so that z is the principal axis.
   Sometimes we can simplify things by looking only at the point group of the relevant orbitals. Only simplify when instructed to do so.*
2. Identify and count the pendant atoms' valence orbitals.
   Is there more than 1 type for each atom (ex. just s, or s and p?) We expect 1 SALC for each ligand orbital.
3. Generate a **reducible representation (Γ)** for the group of pendant atom orbitals using the appropriate character table.
   You have to do this for each set of orbital types. If you only have s orbitals for each ligand, you only need to generate 1 reducible representation. If you have p orbitals, you would generate additional Γ's for p_x, p_y, and p_z.
4. Break the Γ into its component **irreducible representations** from the character table. Note the symmetry of each irreducible representation, its associated orbitals, and their degeneracy.
5. If you are asked to sketch the shapes of SALCs, determine what they "look like" using one of the following strategies.
   (a) Shortcut: if the reducible representations are listed with s, p, or d orbitals in the character table, just draw them (… and skip steps b-c)
   (b) Systematic (Projection Operator) method: Draw an expanded character table and draw your molecule with each ligand identified by letters or numbers (*a,b,c...* or *i,j,k...* or *1,2,3...*) Determine where each pendant atom/orbital ends up under each of the operations of your expanded table. Project the values for each irreducible representation onto the chart you created and then add up the values. Positive and negative values are opposite signed orbitals.
6. Draw the MO diagram by combining SALCs with AO's of like symmetry. When drawing SALC energy levels, remember that the more nodal planes in your SALC orbital drawing, the higher the energy for that SALC orbital.

** When we are focused on orbitals, as in the case for finding group orbitals and drawing molecular orbital diagrams, the symmetry of the orbitals is what we are interested in. In the case of high-symmetry point groups, like $D_{\infty h}$ and $C_{\infty v}$, even though the molecule may have a C_∞ axis, the orbitals do not necessarily retain this symmetry element. For example, the p_x orbital would not have a C_∞ axis, but rather a C_2 axis. It is sufficient and useful to substitute D_{2h} for $D_{\infty h}$ and C_{2v} for $C_{\infty v}$ to simplify the problem.*

6.1: Bifluoride anion
6.2: CO_2
6.3: H_2O
6.4: NH_3

6.5: CO_2 revisted with Projection Operators
6.6: BF_3
6.7: SALCs and the projection operator technique
6.7.1: NH3 Molecular Orbitals
6.7.2: Td Molecular Orbitals
6.7.3: D4h Molecular Orbitals
6.7.4: Pi Donor and Acceptor Ligands

6: Larger (Polyatomic) Molecules is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

6.1: 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 6.1.1). 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 6.1.1).

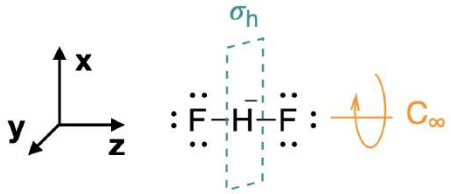


Figure 6.1.1: The [FHF]$^-$ anion belongs to the $D\infty_h$ point group. (CC-BY-NC-SA; Kathryn Haas)

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 6.1.2.

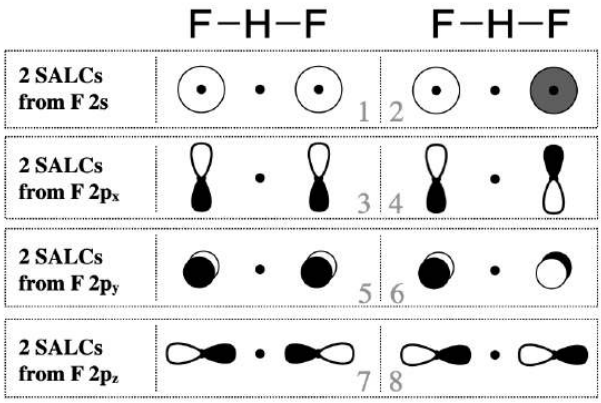


Figure 6.1.2: Eight SALCs from the valence orbitals of two fluorine atoms. (CC-BY-NC-SA; Kathryn Haas)

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 6.1.2 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* 6.1.2). 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 6.1.3.

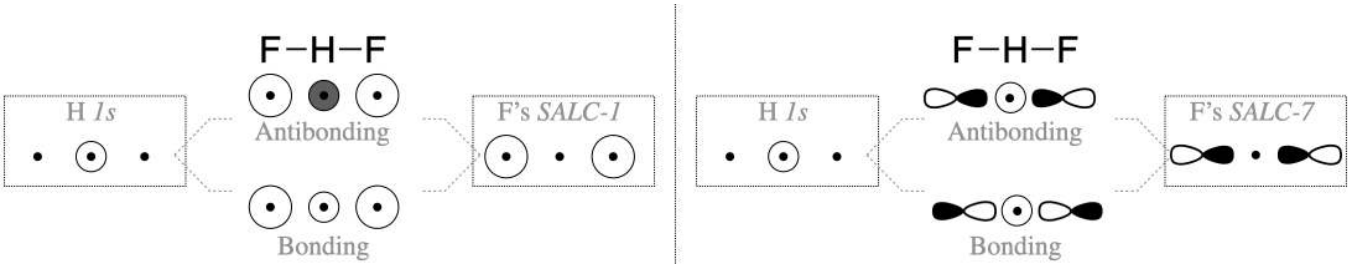


Figure 6.1.3: Combinations of a central H $1s$ orbital with the group orbitals, SALC-1 and SALC-7 from Figure 6.1.2, to create bonding and antibonding interactions. (CC-BY-NC-SA; Kathryn Haas)

Before we assume that both SALC-1 and SALC-7 will combine with the H $1s$ orbital, we must consider the energies of all atomic orbitals. The F $2p_z$ orbital has a potential energy of -18.7 eV (see Table 5.3.1). This is a good match for the H $1s$ orbital (-13.6 eV). However, the F $2s$ orbital has a much lower energy of -46.37 eV and would have weak interaction with the H $1s$.

The molecular orbital diagram for [F-H-F]$^-$ is shown in Figure 6.1.4. Notice that all atomic orbitals, group orbitals (SALCs), and molecular orbitals in Figure 6.1.4 are assigned a symmetry label that corresponds to each element's symmetry under the D_{2h} point group. The molecular orbital labels correspond to **lower-case Mulliken Labels** of individual reducible representations from the D_{2h} character table. Upper-case symbols are used to indicate symmetry and irreducible representations, while lower-case symbols are used to indicate the identity of an orbital with that symmetry. The labeling methods described for simple diatomic linear molecules (σ, π) are not sufficient to indicate the more complex symmetries of the molecular orbitals in polyatomic molecules. The use of lower-case Mulliken symbols is the most rigorous way to label the orbitals. Refer to your instructor for how you should label orbitals for any graded work.

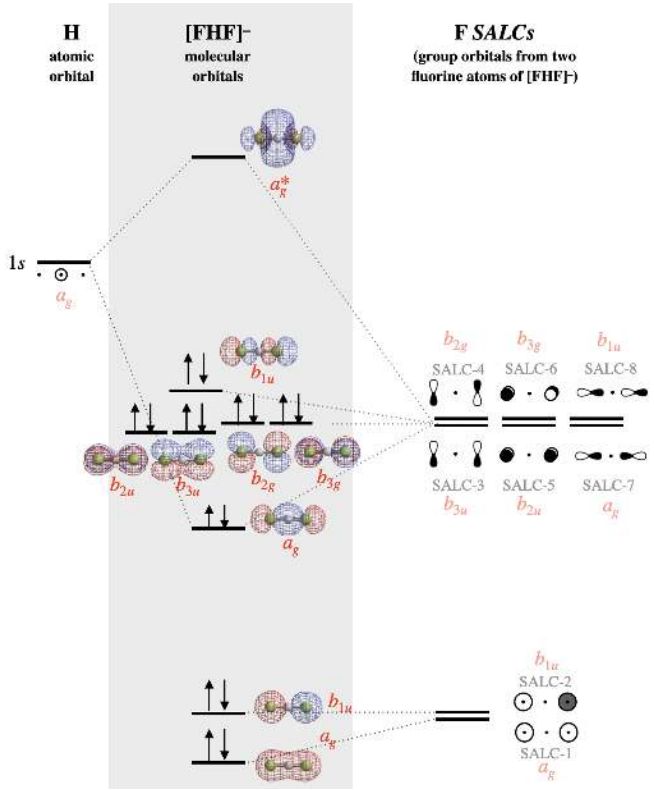
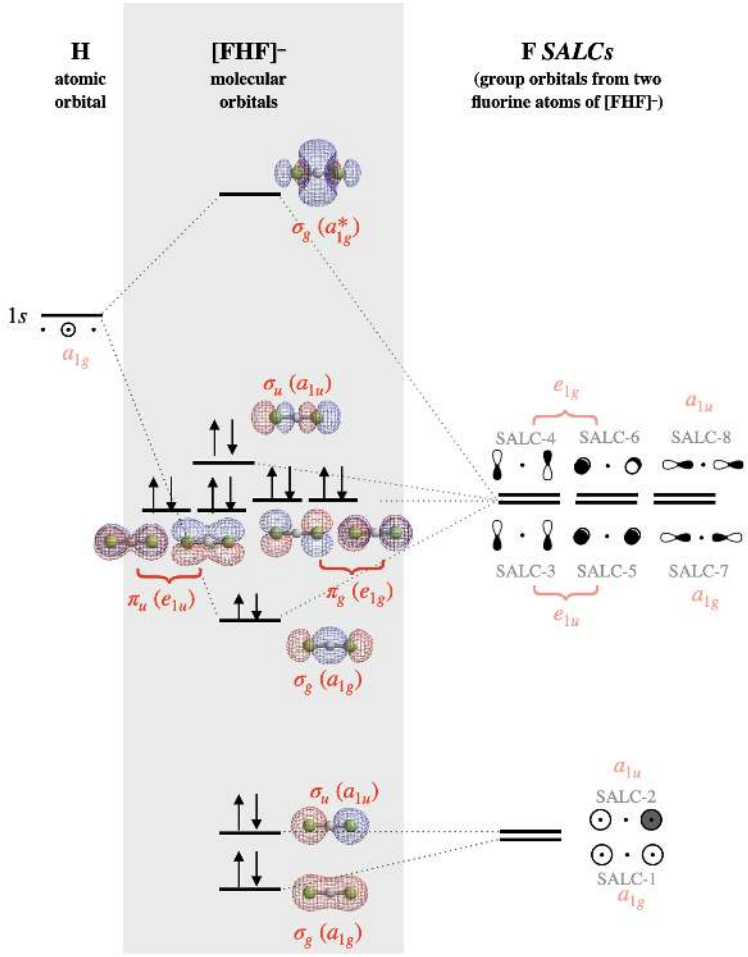


Figure 6.1.4:The molecular orbital diagram for $[F\text{-}H\text{-}F]^-$. The molecular orbital surfaces and relative energy levels were calculated using Spartan software. SALCs are labeled according to numbers assigned in Figure 6.1.2. The symmetry of each SALC and orbital under the D_{2h} **point group** is shown in red font. (CC-BY-NC-SA; Kathryn Haas)

Click here for a version of Figure 6.1.4 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 6.1.4: 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 6.1.2. 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 6.1.4).

6.1: Bifluoride anion is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.4.1: Bifluoride anion** is licensed CC BY-SA 4.0.

6.2: CO_2

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.

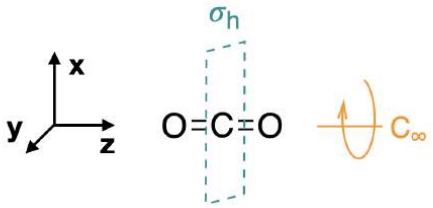


Figure 6.2.1: CO_2 belongs to the $D_{\infty h}$ point group. (CC_BY-NC-SA; Kathryn Haas)

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:

$$\#\text{ of } i = \frac{1}{h}\sum(\#\text{ of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \tag{6.2.1}$$

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 6.2.2.

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 6.2.2.

All other SALCs shown below are derived using a strategy similar to the one in the two cases described above.

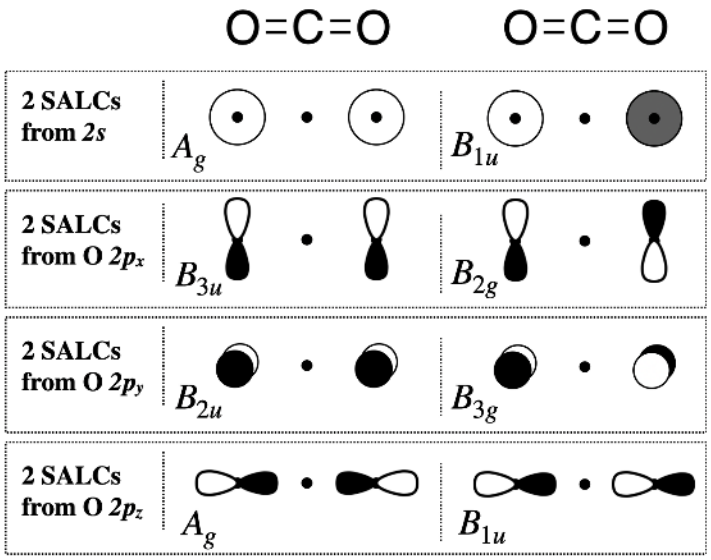


Figure 6.2.2: SALCs from the valence orbitals of oxygen atoms in CO_2. (CC-BY-NC-SA; Kathryn Haas)

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:

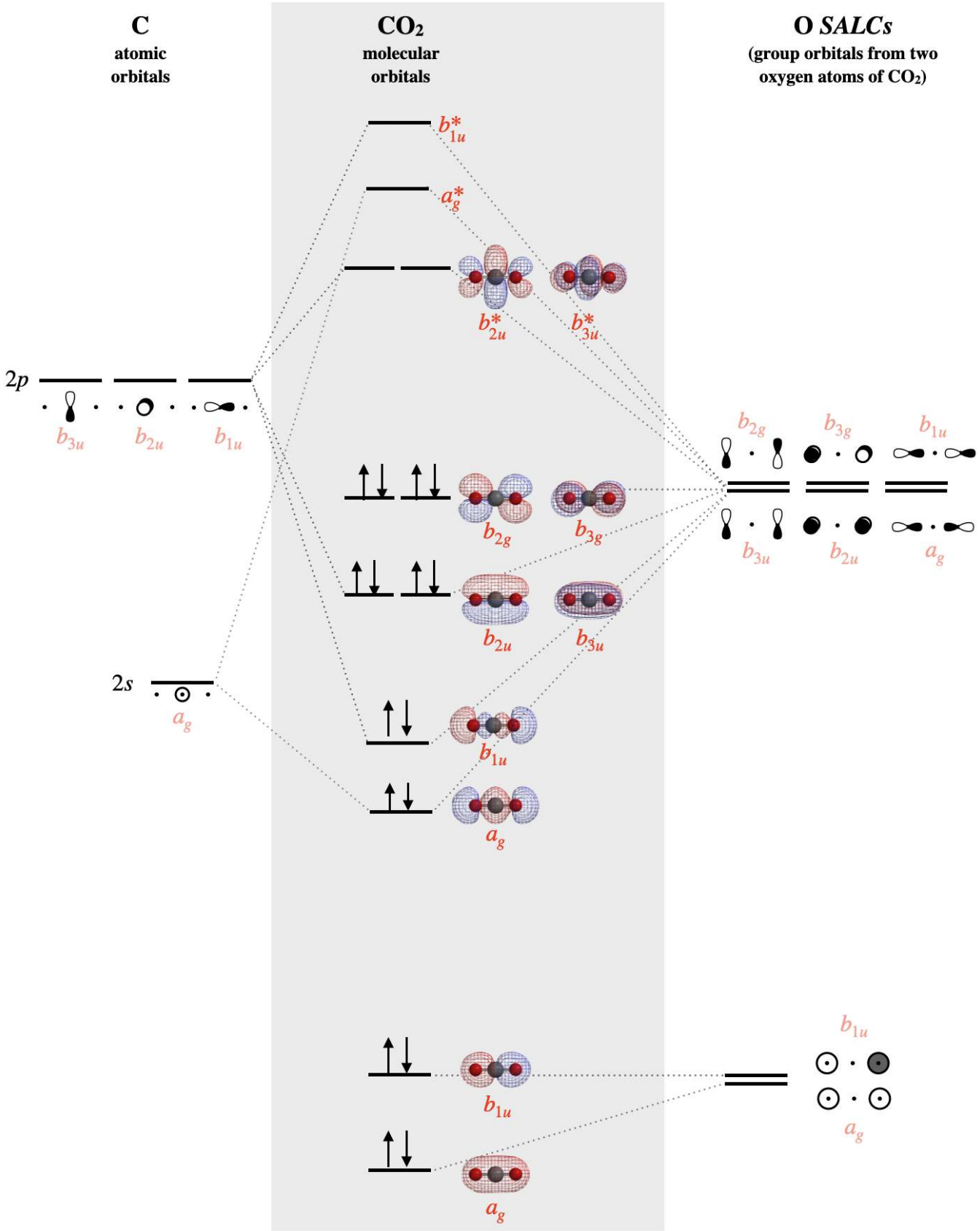


Figure 6.2.3: Molecular orbital diagram for carbon dioxide. (CC-BY-NC-SA; Kathryn Haas)

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 $6.2.3$. 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 6.2: CO_2 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.4.2: Carbon Dioxide** by Kathryn Haas is licensed CC BY-SA 4.0.

6.3: 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.

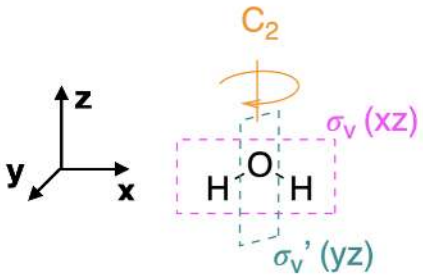


Figure 6.3.1: The water molecular is in the C_{2v} point group. (CC-BY-NC-SA; Kathryn Haas)

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 6.3.2. *If it is not obvious how the A_1 sketch in Fig. 6.3.2 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. 6.3.3.*

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 6.3.2. *If it is not obvious how the B_1 sketch in Fig. 6.3.2 is compatible with the p_x orbital of oxygen, inspect the drawing corresponding to molecular orbital $1b_1$ in Fig. 6.3.3.*

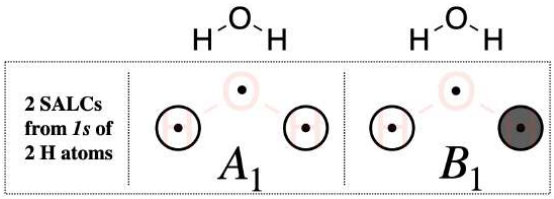


Figure 6.3.2: Sketch of the A_1 and B_1 hydrogen SALCs of water. (CC-BY-NC-SA; Kathryn Haas)

Not convinced about the sketches of these SALCs? You can convince yourself by putting them to the test. Try the exercise below.

? Exercise 6.3.1

Perform all operations of the C_{2v} point group on the two sketches of H SALCs shown in Figure 6.3.2, 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 6.3.3:

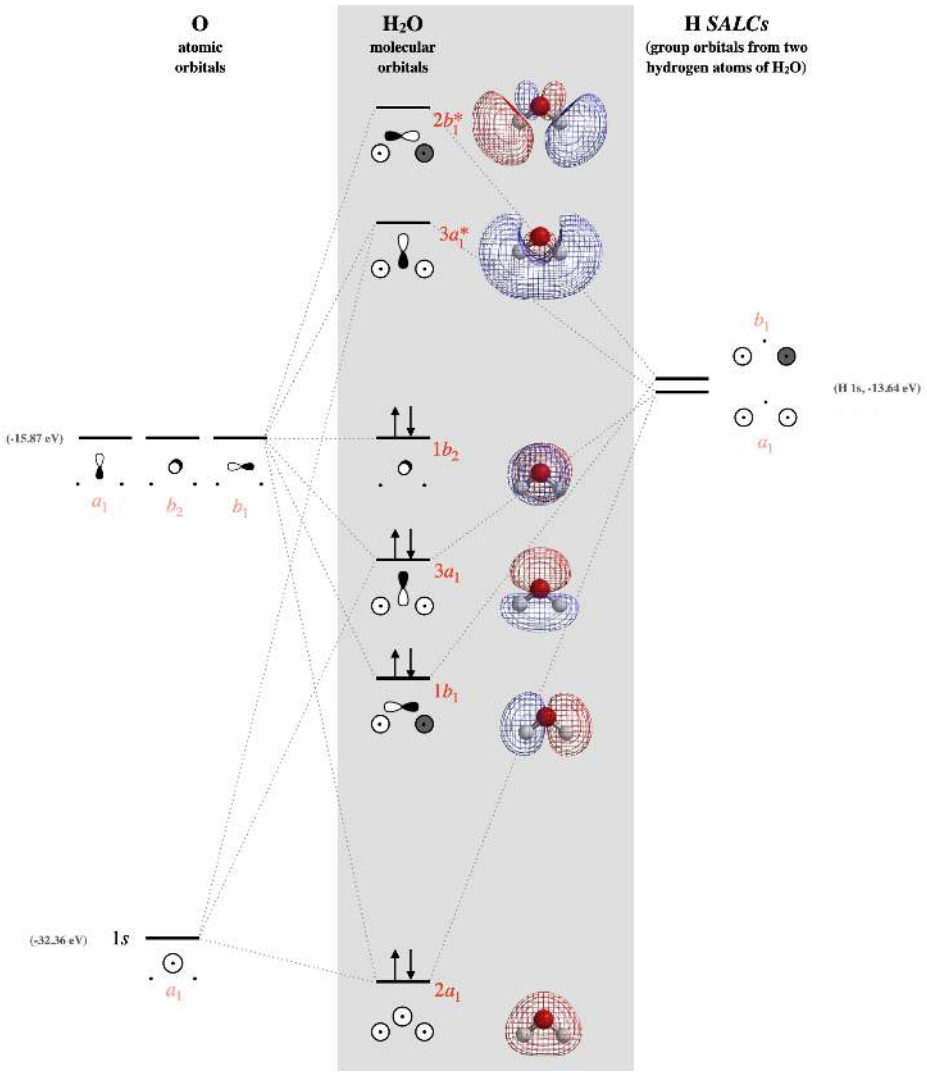


Figure 6.3.3: The molecular orbital diagram of water. Molecular orbital surfaces calculated using Spartan software. The surface of the $3a_1^*$ orbital has been trimmed. (CC-BY-NC-SA; Kathryn Haas)

Example 6.3.1

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 $6.3.3$), 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 $6.3.3$, 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 $6.3.3$ 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 $6.3.3$).

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

6.3: H_2O is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.4.3: H_2O** is licensed CC BY-SA 4.0.

6.4: 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.

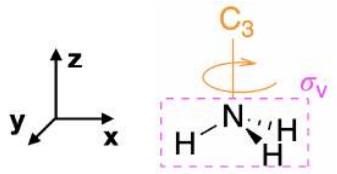


Figure 6.4.1: The ammonia molecule is in the C_{3v} point group. (CC-BY-NC-SA; Kathryn Haas)

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 6.4.2).

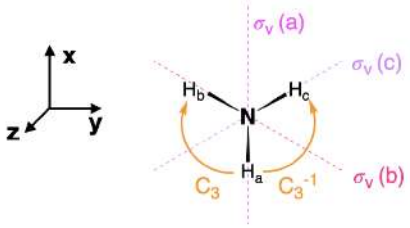


Figure 6.4.2: The three H's in NH_3 are chemically identical, but we can distinguish them using labels for the purpose of applying the projection operator method. In this figure, we have placed the z axis along the principal C_3 axis and placed the x axis colinear with one H. Each of the three H atoms 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 6.4.2). We take into account the result of each operation using an expanded character table (refer to the table below, 6.4.1). 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 6.4.1: 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

(6.4.1)

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 6.4.2: 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	$=\mathbf{2H_a-H_b-H_c}$

(6.4.2)

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 6.4.2 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 6.4.2 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:

$$A_1 \text{ group orbital } = \frac{1}{\sqrt{3}}[\psi_{H_a} + \psi_{H_b} + \psi_{H_c}]$$

This is shown visually in Figure 6.4.3.

- **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 6.4.2 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 6.4.3 (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 6.4.2 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:

    $$\text{First } E \text{ group orbital } = \frac{1}{\sqrt{6}}[2\psi_{H_a} - \psi_{H_b} - \psi_{H_c}]$$

    This is shown visually in Figure 6.4.3 (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 6.4.3 (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 6.4.3, 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:

    $$\text{Second } E \text{ group orbital } = \frac{1}{\sqrt{2}}[\psi_{H_b} - \psi_{H_c}]$$

    This is shown visually in Figure 6.4.3.

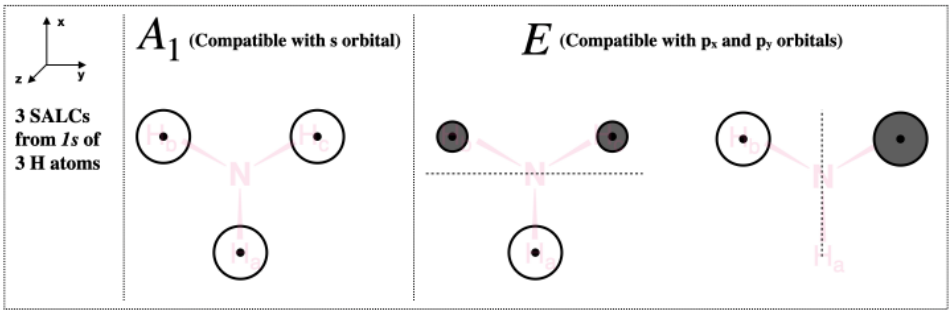


Figure 6.4.3: Sketches of H SALCs of ammonia from the perspective of the C_3 axiz (z axis). The A_1 SALC is shown at the left, while two degenerate SALCs with E symmetry are shown on the right. Nodes for E group orbitals are shown as dashed lines. (CC-BY-NC-SA; Kathryn Haas)

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 6.4.4).

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 6.4.4, with calculated electron density surfaces of each MO shown.

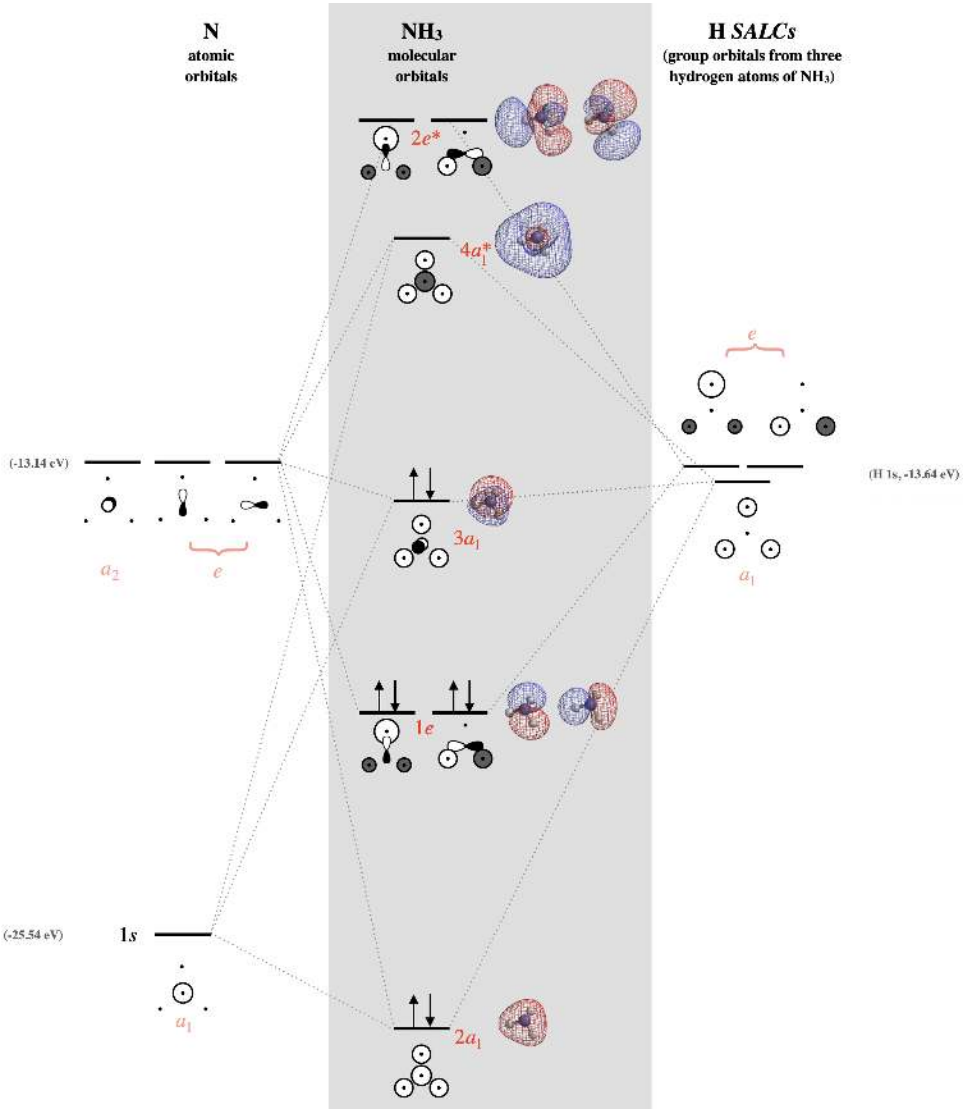


Figure 6.4.4: The molecular orbital diagram of ammonia. Molecular orbitals surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

6.4: NH3 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.4.4: NH3** by Kathryn Haas is licensed CC BY-SA 4.0.

6.5: 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 6.5.1.

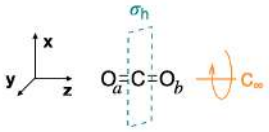


Figure 6.5.1: The structure of carbon dioxide with pendant oxygen atoms distinguished with labels a and b. Note that we will approximate the C_∞ axis as a C_2 axis to simplify the process of finding the SALCs. (CC-BY-SA; Kathryn Haas)

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 $\mathbf{O_a}$	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 6.5.1: 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 $\mathbf{O_a}$	$\mathbf{O_a}$	$\mathbf{O_a}$	$\mathbf{O_b}$	$\mathbf{O_b}$	$\mathbf{O_b}$	$\mathbf{O_b}$	$\mathbf{O_a}$	$\mathbf{O_a}$	
A_g	1	1	1	1	1	1	1	1	$= \mathbf{4O_a + 4O_b}$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= \mathbf{4O_a - 4O_b}$
B_{2g}	1	−1	1	−1	1	−1	1	−1	$= \mathbf{0}$
B_{3u}	1	−1	−1	1	−1	1	1	−1	$= \mathbf{0}$
B_{3g}	1	−1	−1	1	1	−1	−1	1	$= \mathbf{0}$
B_{2u}	1	−1	1	−1	−1	1	−1	1	$= \mathbf{0}$

(6.5.1)

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:

$$A_g \text{ group orbital } = \frac{1}{\sqrt{2}}[\psi_{O_a} + \psi_{O_b}]$$

The linear combination $4O_a + 4O_b$ indicates that wavefunctions from each oxygen atom contribute equally to each of the two SALCs, with the same sign of the wavefunction for each. Because we know that A_g is totally symmetric (all 1's in the characters), we can assume that the SALC's will look like a symmetric arrangement of oxygen orbitals. But which orbitals contribute? We could peek at the character table to get a hint. But we'll treat this problem systematically.

The SALCs with B_{1u} symmetry: The linear combination $4O_a - 4O_b$ indicates that each oxygen atom contributes equally, but that they have opposite wavefunctions. Application of the normalizing factor would give us:

$$B_{1u} \text{ group orbital } = \frac{1}{\sqrt{2}}[\psi_{O_a} + \psi_{O_b}]$$

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 6.5.1 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 $\mathbf{O_a}$	$\mathbf{O1s_a}$	$\mathbf{O1s_a}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_a}$	$\mathbf{O1s_a}$	
A_g	1	1	1	1	1	1	1	1	$= \mathbf{4O1s_a + 4O1s_b}$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= \mathbf{4O1s_a - 4O1s_b}$

(6.5.2)

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 6.5.2.

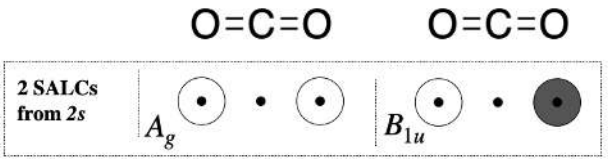


Figure 6.5.2: SALCs derived from two oxygen 2s orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

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	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Linear Combination
Projection of 2px orbital of O_a	$+\mathbf{O2pz_a}$	$+\mathbf{O2pz_a}$	$-\mathbf{O2pz_b}$	$+\mathbf{O2pz_b}$	$-\mathbf{O2pz_b}$	$-\mathbf{O2pz_b}$	$+\mathbf{O2pz_a}$	$+\mathbf{O2pz_a}$	
A_g	1	1	1	1	1	1	1	1	$=\mathbf{4O2pz_a - 4O2pz_b}$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$=\mathbf{4O2pz_a + 4O2pz_b}$

(6.5.3)

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 6.5.3, 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 6.5.3, right).

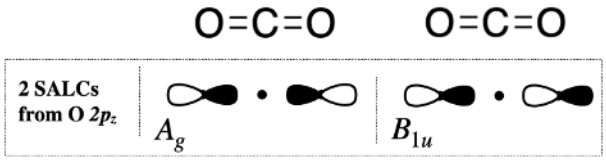


Figure 6.5.3: SALCs derived from two oxygen 2p_z orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

Now we have reached the same SALCs that we found previously in Section 5.4.2, but by an alternate method.

6.5: 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 LibreTexts.

- **5.4.4: NH_3** by Kathryn Haas is licensed CC BY-SA 4.0.

6.6: 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.

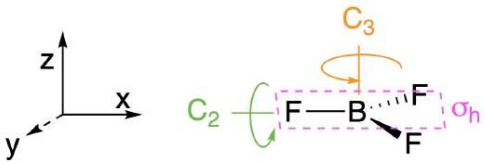


Figure 6.6.1: The molecule is in the D_{3h} point group. (CC-BY-NC-SA; Kathryn Haas)

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.

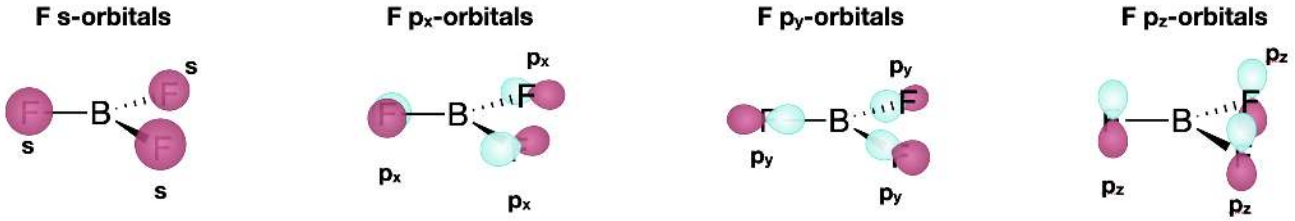


Figure 6.6.2: Individual sets of pendant fluorine atomic orbitals will create separate sets of SALCs. (CC-BY-SA; Kathryn Haas)

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 6.6.2; 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 $\mathbf{\Gamma}$'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.

6.6: BF_3 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.4.4: NH_3** by Kathryn Haas is licensed CC BY-SA 4.0.

6.7: SALCs and the projection operator technique

SALCs refers to Symmetry Adapted Linear Combinations, which are generated via use of the projection operator technique. This technique is a mathematical method which outputs a function called a SALC that models the orbitals of the atoms of interest.[1] These SALCs are mathematical representations and therefore bare no physical meaning. They are commonly used in the generation of molecular orbitals.

Projection Operator Technique

The Projection Operator Technique utilizes the extended character table which includes each symmetry operation separately. The technique involves multiple steps, listed below in the form of the BF_3 example.

1. We begin by determining the reducible representations of the orbitals in question. For BF_3, which has the D_{3h} point group, the D_{3h} character table is used. For our example, we will consider the sigma and pi bonds of the fluorine atoms and determine their reducible representations. Using the character table, we identify the reducible representations. They are listed below.

$\Gamma_{\sigma} = A_1' + E'$

$\Gamma_{\pi x} = A_2' + E'$

$\Gamma_{\pi y} = A_2'' + E''$

$\Gamma_{\pi z} = A_1' + E'$

It is noted here that the π_z orbitals transform as σ orbitals.

Table 6.7.1. This is the character table for the D3h point group which can be used to determine the irreducible representations of the orbitals.

D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
$A_{1'}$	1	1	1	1	1	1
$A_{2'}$	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
$A_{1''}$	1	1	1	-1	-1	-1
$A_{2''}$	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

2. We now use the extended character table for the D_{3h} Character table to generate the SALCs of the stated orbitals. To do this, we apply each symmetry operation to the given orbital and note which orbital it transforms into. We then add up each projector operator function in accordance to each irreducible representation.

Table 6.7.2. This is the extended character table for the D3h point group which is used to deduce the functions for the SALCs using the projector operator technique.

D_{3h}	E	C_3	C_3^2	C_2	C_2'	C_2''	σ_h	S_3
Γ_{σ}	σ_1	σ_2	σ_3	σ_1	σ_2	σ_3	σ_1	σ_2
$\Gamma_{\pi z}$	π_1	π_2	π_3	π_1	π_2	π_3	π_1	π_2
$\Gamma_{\pi x}$	π_1	π_2	π_3	$-\pi_1$	$-\pi_2$	$-\pi_3$	π_1	π_2
$\Gamma_{\pi y}$	π_1	π_2	π_3	$-\pi_1$	$-\pi_2$	$-\pi_3$	$-\pi_1$	$-\pi_2$

3. Common techniques for dealing with the double degeneracy of the E' and E'' representations[2]:

i. If the principal axis is a C_3 axis, we subtract the functions corresponding to the σ_2 and σ_3 orbitals.

ii. If the principal axis is a C_4 axis, we apply the projection operator technique to the σ_2 and use the function that is derived.

iii. We must ensure that the representations are orthogonal to one another in order for them to be correct.

4. We can now apply the coefficients within the matrix to determine the coefficients of the function found via the projection operator technique.

We determine the SALCs for the example orbitals to be the following:

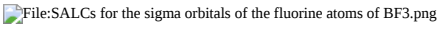


Figure 6.7.1. This is a rendering of the SALCs for the sigma orbitals of the fluorine atoms of BF3. From left to right, the A1', E', and E' SALCs are depicted.

$SALC_{\sigma}(A_1') = 3\sigma_1 + 3\sigma_2 + 3\sigma_3 = \sigma_1 + \sigma_2 + \sigma_3$

$SALC_{\sigma}(E') = 4\sigma_1 - 2\sigma_2 - 2\sigma_3 = 2\sigma_1 - \sigma_2 - \sigma_3$

$SALC_{\sigma}(E') = 2\sigma_2 - 2\sigma_3 = \sigma_2 - \sigma_3$

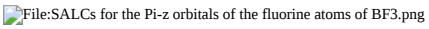


Figure 6.7.2. This is a rendering of the SALCs for the pi-z orbitals of the fluorine atoms of BF_3. From left to right, the A1', E', and E' SALCs are depicted.

$SALC_{\pi z}(A_1') = 3\pi_1 + 3\pi_2 + 3\pi_3 = \pi_1 + \pi_2 + \pi_3$

$SALC_{\pi z}(E') = 4\pi_1 - 2\pi_2 - 2\pi_3 = 2\pi_1 - \pi_2 - \pi_3$

$SALC_{\pi z}(E') = 2\pi_2 - 2\pi_3 = \pi_2 - \pi_3$

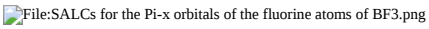


Figure 6.7.2. This is a rendering of the SALCs for the pi-x orbitals of the fluorine atoms of BF_3. From left to right, the A2', E', and E' SALCs are depicted.

$SALC_{\pi x}(A_2') = 3\pi_1 + 3\pi_2 + 3\pi_3 = \pi_1 + \pi_2 + \pi_3$

$SALC_{\pi x}(E') = 4\pi_1 - 2\pi_2 - 2\pi_3 = 2\pi_1 - \pi_2 - \pi_3$

$SALC_{\pi x}(E') = 2\pi_2 - 2\pi_3 = \pi_2 - \pi_3$

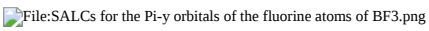


Figure 6.7.3. This is a rendering of the SALCs for the pi-y orbitals of the fluorine atoms of BF3. From left to right, the A2", E", and E" SALCs are depicted.

$SALC_{\pi y}(A_2'') = 3\pi_1 + 3\pi_2 + 3\pi_3 = \pi_1 + \pi_2 + \pi_3$

$SALC_{\pi y}(E'') = 4\pi_1 - 2\pi_2 - 2\pi_3 = 2\pi_1 - \pi_2 - \pi_3$

$SALC_{\pi y}(E'') = 2\pi_2 - 2\pi_3 = \pi_2 - \pi_3$

Uses of SALCs

SALCs help us to understand which orbitals will be bonding, antibonding, and nonbonding. For example, by comparing the symmetry of the SALCs to that of the orbitals of the central atom, it is possible to generate the corresponding molecular orbitals. Although SALCs are mathematical representations that have no physical meaning, they are useful in providing a tool for deriving molecular orbitals.

References

1. www4.ncsu.edu/~franzen/public...ojection_1.pdf

2. http://troglerlab.ucsd.edu/GroupTheory224/Chap2B.pdf

6.7: SALCs and the projection operator technique is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

6.7.1: NH3 Molecular Orbitals

Point Group of NH3

The symmetry elements of NH3 are E, 2C3, and 3 sigma-v. To elaborate, the molecule is of C3v symmetry with a C3 principal axis of rotation and 3 vertical planes of symmetry. The image of the ammonia molecule (NH3) is depicted in Figure 6.7.1.1 and the following character table is displayed below.[1]

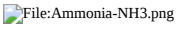


Figure 6.7.1.1. The structure of NH_3

C3v	E	2C3v	3 σ_v		
A1	1	1	1	z	x2+y2, z2
A2	1	1	-1	Rz	
E	2	-1	0	(x,y)(Rx,Ry)	(x2-y2,xy)(xz,yz)

The Construction of Molecular Orbitals of NH_3

The Molecular Orbital Theory (MO) is used to predict the electronic structure of a molecule. Molecular orbitals are formed from the interaction of 2 or more atomic orbitals, and the interactions between atomic orbitals can be bonding, anti-bonding, or non-bonding. A bonding orbital is the interaction of two atomic/group orbitals in phase while an anti-bonding orbital is formed by out-of-phase combinations.

In general, the energy level of molecular orbitals increases from bonding, to non-bonding, and anti-bonding molecular orbitals. Pi-bonding molecular orbitals generally have greater energies than sigma-bonding molecular orbitals because the pi interactions are less effective than sigma interactions. The energy of molecular orbitals increases when the number of nodes also increases, and vice versa.[6] Within bonding molecular orbitals of the same symmetry, the lowest energy are from completely symmetrical sigma bonding molecular orbitals.

Projection Operator Methode:

The Projection Operator Methode can be used to determine MO of NH_3, the next steps can be used:

1) Determine the point group of melecular;

2) Lable S orbital of H;

3) Generate a reducible representation (Γ) for H;

4) Reduce reducible representation to irreducible representation;

5) Generate the symmetry adapted linear combinations (SALCs) of orbitals that arise from these irreducible representations;

6) Drawing group orbital combinations and determine the atomic orbitals of the centeral atom;

7) MO

Example 6.7.1.1

Add text here.

Solution

Add text here.

6.7.1: NH3 Molecular Orbitals is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

6.7.2: Td Molecular Orbitals

T_d Point Group

The T_d symmetry group is a one of the point groups considered to have higher symmetry. Molecules in the T_d group, such as methane (CH_4) have four C_3 rotational axes.

The character table for the T_d point group is shown below:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

Constructing Molecular Orbitals

Determining Reducible Representations

The first step to constructing the molecular orbitals (MOs) is to determine the reducible representations for the σ and π bond vectors, denoted Γ_σ and Γ_π, respectively. The character corresponding to each symmetry operation can be determined by tracking how the bond vectors transform. Each vector that is left unmoved will contribute +1, each vector that is shifted to a new position will contribute 0, and each vector that undergoes a sign reversal will contribute −1. The reducible representations Γ_σ and Γ_π are listed below:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_σ	4	1	0	0	2
Γ_π	8	−1	0	0	0

Figure 6.7.2.1. Bond vectors in a tetrahedral (T_d) molecule.

Reducing the Reducible Representations

The reducible representations obtained from the previous section can be written as linear combinations of the irreducible representations shown in the character table. The contribution of each irreducible representation to the reducible representation is given by the formula:

$$n_i = \frac{1}{h}\sum N\chi_R\chi_I$$

where n_i is the coefficient of the ith reducible representation, h is the order of the point group, N is the number of symmetry operations in the class, χ_R is the character of the reducible representation corresponding to the class, χ_I is the character of the irreducible representation corresponding to the class, and the summation is taken over all classes of symmetry operations. Applying this method to the Γ_σ and Γ_π representations gives:

$$\Gamma_\sigma = A_1 + T_2$$

$$\Gamma_\pi = E + T_1 + T_2$$

Determining SALCs of Pendant Ligands

The Symmetry Adapted Linear Combinations (SALCs) can be found using the projection operator technique. For example, suppose we using the following labeling scheme for the ligand groups in Figure 1: (1) top-left-front, (2) top-right-back, (3) bottom-right-front, (4) bottom-left-back. Then the normalized SALCs for the *s* orbitals of the ligand groups are:

$$SALC\,(A_1) = \frac{1}{2}(s_1 + s_2 + s_3 + s_4)$$

$$SALC\,(T_2) = \frac{1}{2}(s_1 - s_2 - s_3 + s_4)$$

$$SALC\,(T_2) = \frac{1}{2}(s_1 - s_2 + s_3 - s_4)$$

$$SALC\,(T_2) = \frac{1}{2}(s_1 + s_2 - s_3 - s_4)$$

The purpose of using the projection operator method is to be able to draw the SALCs.

Drawing the Molecular Orbital Diagram

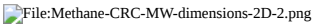


Figure 6.7.2.2 Structure of methane molecule.

Consider CH_4 as a specific example of a molecule within the T_d symmetry group. Before drawing the MO diagram, the valence atomic orbitals on the central atom and their symmetries must be noted. The symmetry of the orbitals can be determined by determining how they transform under the symmetry operations or by simply looking at the right most columns on the character table. The valence orbitals of the carbon atom include 2*s* (A_1 symmetry) and 2p_x, 2p_y, 2p_z (T_2 symmetry).

In CH_4, the only potentially bonding orbitals of the ligand groups are the 1*s* orbitals in the hydrogen atom. The irreducible representations contributing to the symmetry of the ligand group SALCs determines the AOs of the central atom with which they can interact. As found previously, the SALCs of the hydrogen atoms have A_1 + T_2 symmetry, so they can interact with all of the valence orbitals on the carbon atom to form bonding and antibonding MOs. Bonding MOs are positive linear combinations of the central atom AOs and ligand group SALCs, while antibonding MOs are negative linear combinations. The number of bonding and antibonding MOs created must be equal to the number of AOs and ligand group orbitals used to create them.

Although in CH_4, all AOs and SALCs formed of bonding and antibonding MOs, this is not always the case. For example, if a central atom AO has symmetry that is absent from the ligand group SALCs, it will be unable to participate in the formation of bonding and antibonding MOs. In such cases, non-bonding MOs are formed.

The relative energy of the MOs are influenced by a few trends. For MOs formed with similar AOs, the following tend to be true:

- Bonding MOs have lower energy than antibonding MOs. Non-bonding MOs tend to have energy intermediate between bonding and antibonding MOs.
- π bonding MOs have higher energy than σ bonding MOs.
- The energy of MOs increases with the number of nodes.
- The totally symmetric σ bonding MO has the lowest energy among σ bonding MOs.

Illustrations of CH_4 MOs can be found in Pfennig's text, *Principles of Inorganic Chemistry*, pp. 300.

6.7.2: Td Molecular Orbitals is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

6.7.3: D4h Molecular Orbitals

The D4h point group are one of the most common molecular symmetry found in nature. For example, the XeF4 molecule belongs to the D4h point group. the XeF4 contains one C4 rotation axis, one C2 rotation axis, and four C2 perpendicular rotation axis, 2σv planes, 2σd planes and 1σh plane, those composed the character table of the D4h Point group.

	E	$2C_4$	C2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Linear's Rotation	Quadractic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	x^2-y^2
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		(xz, yz)
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	
σ	4	0	0	2	0	0	0	4	2	0		
π	8	0	0	-4	0	0	0	0	0	0		

To compose a Molecular Diagram of a molecule with D4h symmetry group, we should first find the irreducible representation of the ligands and of the center molecule. and then find the SALCS for each of the irreducible representation and finally, compose the molecular diagram. To take an easy example, the Square Planar Complexes.. starting with the sigma orbital of the ligands, the reducible representation of the sigma orbital is the total number of atoms that do not move under each operation. For the Pi orbital, we have to degenerate the pi orbital has two degrees of freedom, thus, the reducible representation of the pi orbital can also be found by using the similar method. and then, by using the projection operation method, we can find the irreducible representations of the ligand's sigma and pi orbital. In this case, the sigma orbital has A1g, B1g, Eu three irreducible representations and the pi orbital has A2g, A2u, B2g, B2u, Eg and Eu.

	E	2C4	C2	2C'2	2C"2	i	2S4	σh	2σv	2σd
sigma	4	0	0	2	0	0	0	4	2	0
Pi	8	0	0	-4	0	0	0	0	0	0

Move on the central atom, we can find irreducible representation of the valence orbitals on the central atoms by using the character table. The results are as follow:

Representation	Orbital
A1g	s, dz2
B1g	dx2- y2
B2g	dxy

Representation	Orbital
Eg	dxz, dyz
A2u	Pz
Eu	Px, py

Figure 6.7.3.1 D4h Character Table

6.7.3: D4h Molecular Orbitals is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

6.7.4: Pi Donor and Acceptor Ligands

The nature of ligands coordinated to the center metal is an important feature of a complex compound along with other properties such as metal identify and its oxidation state. More specifically, it is the identity and consequently the ability of the ligand to donate or accept electrons to the center atom that will determine the molecular orbitals.

The spectrochemical series shows the trend of compounds as weak field to strong field ligands. Furthermore, ligands can be characterized by their π-bonding interactions. This interaction reveals the amount of split between e_g and t_{2g} energy levels of the molecular orbitals that ultimately dictates the strength of field of the ligands.

Examples of Weak Field Ligands X^-, OH^-, H_2O ; Examples of Strong Field Ligands H^-, NH_3, CO, PR_3

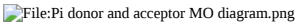


Figure 6.7.4.1. MO Diagrams of Pi Donor Ligands and Pi Acceptor Ligands.

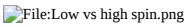


Figure 6.7.4.2. Electron configuration of high and low spin.

Electron configuration of high and low spin.

In a π-donor ligand, the SALCs of the ligands are occupied, hence it donates the electrons to the molecular σ σ* and π π* orbitals. The orbitals associated to eg are not involved in π interactions therefore it stays in the same energy level (figure 6.7.4.1). On the other hand, the occupied ligand SALC t_{2g} orbitals that would form molecular orbitals with the metal t_{2g} orbitals (ie. d_{xy}, d_{xz}, d_{yz}) are lower in energy than its metal counterparts. The resulting MO has π* orbitals that are energetically lower than the σ* orbitals that are formed from the non bonding orbitals (e_g). The difference between the t_{2g} π* and e_g σ orbitals is denoted as Δ, split. In the π-donor case, the Δ is small due to the low π* level.

Conversely, the t_{2g} SALCs of a pi accepting orbitals are higher in energy than the metal t_{2g} orbitals because they are unoccupied. The resulting t_{2g} π* orbitals are higher than the σ* orbitals. This creates a larger Δ between the e_g and t_{2g} π orbitals, making these π-accepting orbitals high split ligands.

Finally, the magnitude of Δ as influenced by the identify of the ligand will dictate how electrons are distributed in the metal d orbitals (figure 6.7.4.2). Weak field ligands produce a small Δ hence a high spin configuration. Strong field ligands produce a large Δ hence a low spin configuration on the d electrons.

6.7.4: Pi Donor and Acceptor Ligands is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

7: Solids

7.1: Crystal Lattices
7.1.1: Inorganic Solids
7.1.2: Lattice Basics
7.1.2.1: Covalent Network Solids
7.1.2.2: How to Decide What Type of Structure
7.1.2.3: Ionic Structures
7.1.2.4: Metallic Structures
7.1.2.5: Molecular Structures
7.1.3: Lattice Defects
7.1.3.1: Frenkel Defect
7.1.3.2: Metal Oxides
7.1.3.3: Schottky Defects
7.1.3.4: Solid Defects
7.1.4: Metal Lattices
7.1.4.1: Structure and Properties of Metals
7.1.4.2: Metal Packing- Layers
7.1.4.3: Metal Packing- Three Dimensions
7.1.4.4: Problems
7.1.4.5: Solutions to Selected Problems
7.1.5: Solids
7.1.5.1: Body Centered Packing
7.1.5.2: Metal Structures
7.1.5.3: Simple Cubic
7.1.5.4: Solids
7.1.5.5: Sphere Packing
7.1.5.6: Tetrahedral and Octahedral Sites
7.1.6: Thermodynamics of Lattices
7.1.6.1: Lattice Energy
7.1.6.2: Lattice Energy- The Born-Haber cycle
7.1.6.3: Lattice Enthalpies and Born Haber Cycles
7.1.6.4: The Born-Lande' equation
7.2: Solids
7.2.1: Crystalline and Amorphous Solids
7.2.2: Arrangement of Atoms in Crystals
7.2.3: Stucture of Simple Binary Compounds
7.2.4: Crystal Defects
7.2.5: Bonding and Properties of Solids
7.2.6: Metals and Semiconductors
7.2.7: Superconductors
7.2.8: Polymers
7.2.9: Modern Materials

7.2.10: End of Chapter Material

Thumbnail: The crystal structure of sodium chloride, $NaCl$, a typical ionic compound. The purple spheres represent sodium cations, Na^+, and the green spheres represent chloride anions, Cl^-. (Public Domain; Benjah-bmm27 via Wikipedia)

7: Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1: Crystal Lattices

A crystal structure is a unique arrangement of atoms, ions or molecules in a crystalline liquid or solid. It describes a highly ordered structure, occurring due to the intrinsic nature of its constituents to form symmetric patterns.

7.1: Crystal Lattices is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1.1: Inorganic Solids

Discussion Questions

- Discuss the crystal structures of NaCl, CaF_2, zinc-blende, and Li_3Bi in relation to the cubic close packing of spheres.
- Describe the features of NiAs structure.
- What are the features of wurtzite structure?

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.1: Inorganic Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Inorganic Solids** is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

7.1.2: Lattice Basics

Topic hierarchy

7.1.2.1: Covalent Network Solids

7.1.2.2: How to Decide What Type of Structure

7.1.2.3: Ionic Structures

7.1.2.4: Metallic Structures

7.1.2.5: Molecular Structures

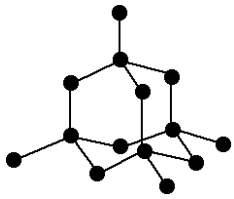
7.1.2: Lattice Basics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1.2.1: Covalent Network Solids

Covalent Network Solids are giant covalent substances like diamond, graphite and silicon dioxide (silicon(IV) oxide). This page relates the structures of covalent network solids to the physical properties of the substances.

Diamond

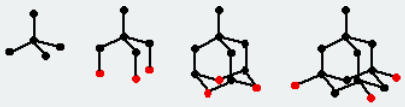
Carbon has an electronic arrangement of 2,4. In diamond, each carbon shares electrons with four other carbon atoms - forming four single bonds.



In the diagram some carbon atoms only seem to be forming two bonds (or even one bond), but that's not really the case. We are only showing a small bit of the whole structure. This is a giant covalent structure - it continues on and on in three dimensions. It is not a molecule, because the number of atoms joined up in a real diamond is completely variable - depending on the size of the crystal.

How to draw the structure of diamond

Don't try to be too clever by trying to draw too much of the structure! Learn to draw the diagram given above. Do it in the following stages:



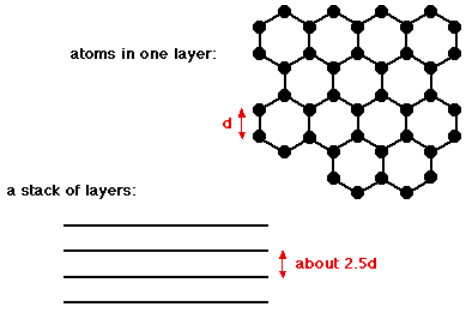
Practice until you can do a reasonable free-hand sketch in about 30 seconds.

Physical Properties of Diamond

- has a very high melting point (almost 4000°C). Very strong carbon-carbon covalent bonds have to be broken throughout the structure before melting occurs.
- is very hard. This is again due to the need to break very strong covalent bonds operating in 3-dimensions.
- doesn't conduct electricity. All the electrons are held tightly between the atoms, and aren't free to move.
- is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and carbon atoms which could outweigh the attractions between the covalently bound carbon atoms.

Graphite

Graphite has a layer structure which is quite difficult to draw convincingly in three dimensions. The diagram below shows the arrangement of the atoms in each layer, and the way the layers are spaced.



Notice that you cannot really draw the side view of the layers to the same scale as the atoms in the layer without one or other part of the diagram being either very spread out or very squashed. In that case, it is important to give some idea of the distances involved. The distance between the layers is about 2.5 times the distance between the atoms within each layer. The layers, of course, extend over huge numbers of atoms - not just the few shown above.

> *You might argue that carbon has to form 4 bonds because of its 4 unpaired electrons, whereas in this diagram it only seems to be forming 3 bonds to the neighboring carbons. This diagram is something of a simplification, and shows the arrangement of atoms rather than the bonding.*

The Bonding in Graphite

Each carbon atom uses three of its electrons to form simple bonds to its three close neighbors. That leaves a fourth electron in the bonding level. These "spare" electrons in each carbon atom become delocalized over the whole of the sheet of atoms in one layer. They are no longer associated directly with any particular atom or pair of atoms, but are free to wander throughout the whole sheet. The important thing is that the delocalized electrons are free to move anywhere within the sheet - each electron is no longer fixed to a particular carbon atom. There is, however, no direct contact between the delocalized electrons in one sheet and those in the neighboring sheets. The atoms within a sheet are held together by strong covalent bonds - stronger, in fact, than in diamond because of the additional bonding caused by the delocalized electrons.

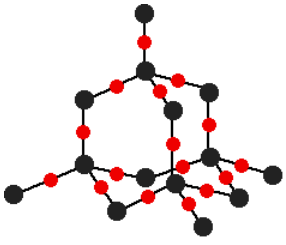
So what holds the sheets together? In graphite you have the ultimate example of van der Waals dispersion forces. As the delocalized electrons move around in the sheet, very large temporary dipoles can be set up which will induce opposite dipoles in the sheets above and below - and so on throughout the whole graphite crystal.

Graphite has a high melting point, similar to that of diamond. In order to melt graphite, it isn't enough to loosen one sheet from another. You have to break the covalent bonding throughout the whole structure. It has a soft, slippery feel, and is used in pencils and as a dry lubricant for things like locks. You can think of graphite rather like a pack of cards - each card is strong, but the cards will slide over each other, or even fall off the pack altogether. When you use a pencil, sheets are rubbed off and stick to the paper. Graphite has a lower density than diamond. This is because of the relatively large amount of space that is "wasted" between the sheets.

Graphite is insoluble in water and organic solvents - for the same reason that diamond is insoluble. Attractions between solvent molecules and carbon atoms will never be strong enough to overcome the strong covalent bonds in graphite. conducts electricity. The delocalized electrons are free to move throughout the sheets. If a piece of graphite is connected into a circuit, electrons can fall off one end of the sheet and be replaced with new ones at the other end.

Silicon dioxide: SiO_2

Silicon dioxide is also known as silica or silicon(IV) oxide has three different crystal forms. The easiest one to remember and draw is based on the diamond structure. Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, all you need to do is to modify the silicon structure by including some oxygen atoms.



Notice that each silicon atom is bridged to its neighbors by an oxygen atom. Don't forget that this is just a tiny part of a giant structure extending on all 3 dimensions.

Silicon Dioxide has a high melting point - varying depending on what the particular structure is (remember that the structure given is only one of three possible structures), but around 1700°C. Very strong silicon-oxygen covalent bonds have to be broken throughout the structure before melting occurs. Moreover, it hard due to the need to break the very strong covalent bonds.Silicon Dioxide does not conduct electricity since there aren't any delocalized electrons with all the electrons are held tightly between the

atoms, and are not free to move.Silicon Dioxide is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and the silicon or oxygen atoms which could overcome the covalent bonds in the giant structure.

This page titled 7.1.2.1: Covalent Network Solids is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Covalent Network Solids** by Jim Clark is licensed CC BY-NC 4.0.

7.1.2.2: How to Decide What Type of Structure

This page explains how you can decide what sort of structure a substance has by looking at its physical properties.

Melting and boiling points

The best place to start is usually the physical state. Melting point isn't always a good guide to the size of the attractions between particles, because the attractive forces have only been loosened on melting - not broken entirely. Boiling point is a much better guide, because enough heat has now been supplied to break the attractive forces completely. The stronger the attractions, the higher the boiling point.

That being said, melting points are often used to judge the size of attractive forces between particles in solids, but you will find the occasional oddity. Those oddities usually disappear if you consider boiling points instead.

Example 1

You would expect stronger metallic bonding in aluminum than in magnesium, because aluminum has 3 electrons to delocalize into the "sea of electrons" rather than magnesium's 2. The boiling points reflect this: Al 2470 °C vs. Mg 1110 °C. However, aluminum's melting point is only 10 °C higher than magnesium's: Al 660 °C vs. Mg 650 °C.

So, if it is a gas, liquid or low melting point solid, it will consist of covalently bound molecules (except the noble gases which have molecules consisting of single atoms). The size of the melting point or boiling point gives a guide to the strength of the intermolecular forces. That is then the end of the problem. If it is a gas, liquid or low melting point solid then you are talking about a simple molecular substance. Full stop!

If it is a high melting point solid, it will be a giant structure - either ionic, metallic or giant covalent. You now have to sort out which of these it is.

Effect of water

Solubility of a solid in water (without reaction) suggests it is ionic. There are exceptions to this, of course. Sugar (sucrose) is soluble in water despite being a covalent molecule. It is capable of extensive hydrogen bonding with water molecules. And there are a lot of ionic compounds which are insoluble in water, of course. Solubility of a low melting point solid or a liquid in water (without it reacting) suggests a small molecule capable of hydrogen bonding - or, at least, a small very polar molecule.

Conduction of electricity

Conduction of electricity in the solid state suggests delocalized electrons, and therefore either a metal or graphite. The clue as to which you had would usually come from other data - appearance, malleability, etc (see below).

Note

Semiconductors like silicon - a giant covalent structure with the same arrangement of atoms as diamond - also conduct electricity.

If a substance doesn't conduct electricity as a solid, but undergoes electrolysis when it is molten, that would confirm that it was ionic. Electrolysis is the splitting up of a compound using electricity. For example, molten sodium chloride conducts electricity and is split into sodium and chlorine in the process

Appearance

Don't forget about obvious things like the shiny appearance of most metals, and their ease of working. Metals are malleable (can be bent or beaten into shape easily) and ductile (can be pulled out into wires). By contrast, giant ionic or giant covalent structures tend to be brittle - shattering rather than bending.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 7.1.2.2: How to Decide What Type of Structure is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **How to Decide What Type of Structure** by Jim Clark is licensed CC BY-NC 4.0.

7.1.2.3: Ionic Structures

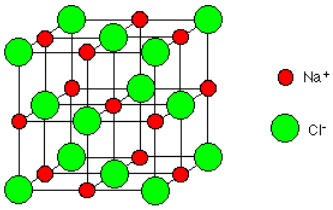
This page explains the relationship between the arrangement of the ions in a typical ionic solid like sodium chloride and its physical properties - melting point, boiling point, brittleness, solubility and electrical behavior. It also explains why cesium chloride has a different structure from sodium chloride even though sodium and cesium are both in Group 1 of the Periodic Table.

The structure of a typical ionic solid - sodium chloride

Sodium chloride is taken as a typical ionic compound. Compounds like this consist of a giant (endlessly repeating) lattice of ions. So sodium chloride (and any other ionic compound) is described as having a giant ionic structure.

You should be clear that giant in this context does not just mean very large. It means that you can't state exactly how many ions there are. There could be billions of sodium ions and chloride ions packed together, or trillions, or whatever - it simply depends how big the crystal is. That is different from, say, a water molecule which always contains exactly 2 hydrogen atoms and one oxygen atom - never more and never less. A small representative bit of a sodium chloride lattice looks like this:

If you look at the diagram carefully, you will see that the sodium ions and chloride ions alternate with each other in each of the three dimensions. This diagram is easy enough to draw with a computer, but extremely difficult to draw convincingly by hand. We normally draw an "exploded" version which looks like this:

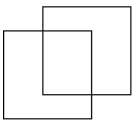


Only those ions joined by lines are actually touching each other. The sodium ion in the center is being touched by 6 chloride ions. By chance we might just as well have centered the diagram around a chloride ion - that, of course, would be touched by 6 sodium ions. Sodium chloride is described as being 6:6-coordinated. This diagram represents only a tiny part of the whole sodium chloride crystal; the pattern repeats in this way over countless ions.

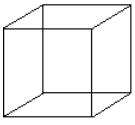
How to draw this structure

Draw a perfect square:

Now draw an identical square behind this one and offset a bit. You might have to practice a bit to get the placement of the two squares right. If you get it wrong, the ions get all tangled up with each other in your final diagram.

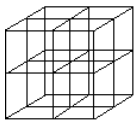


Turn this into a perfect cube by joining the squares together:

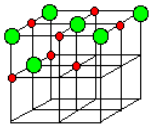


Now the tricky bit! Subdivide this big cube into 8 small cubes by joining the mid point of each edge to the mid point of the edge opposite it. To complete the process you will also have to join the mid point of each face (easily found once you've joined the

edges) to the mid point of the opposite face.



Now all you have to do is put the ions in. Use different colors or different sizes for the two different ions, and don't forget a key. It does not matter whether you end up with a sodium ion or a chloride ion in the center of the cube - all that matters is that they alternate in all three dimensions.



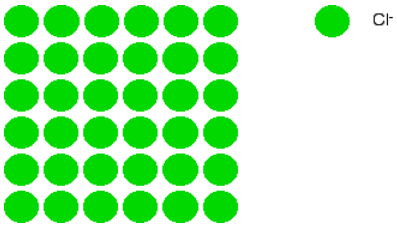
You should be able to draw a perfectly adequate free-hand sketch of this in under two minutes - less than one minute if you're not too fussy!

Why is sodium chloride 6:6-coordinated?

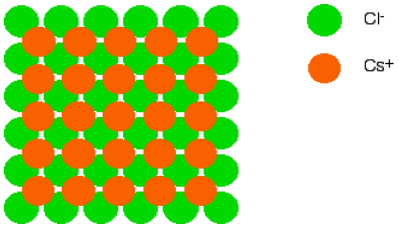
The more attraction there is between the positive and negative ions, the more energy is released. The more energy that is released, the more energetically stable the structure becomes. That means that to gain maximum stability, you need the maximum number of attractions. So why does each ion surround itself with 6 ions of the opposite charge? That represents the maximum number of chloride ions that you can fit around a central sodium ion before the chloride ions start touching each other. If they start touching, you introduce repulsions into the crystal which makes it less stable.

The different structure of cesium chloride

We'll look first at the arrangement of the ions and then talk about why the structures of sodium chloride and cesium chloride are different afterwards. Imagine a layer of chloride ions as shown below. The individual chloride ions aren't touching each other. That's really important - if they were touching, there would be repulsion.

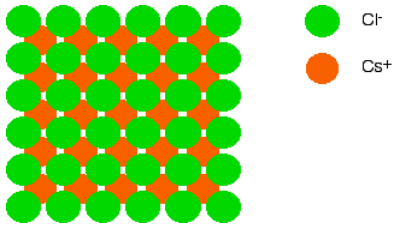


Now let's place a similarly arranged layer of cesium ions on top of these.



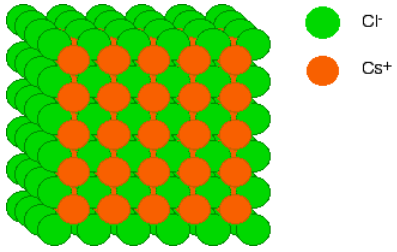
Notice that the cesium ions aren't touching each other either, but that each cesium ion is resting on four chloride ions from the layer below.

Now let's put another layer of chloride ions on, exactly the same as the first layer. Again, the chloride ions in this layer are NOT touching those in the bottom layer - otherwise you are introducing repulsion. Since we are looking directly down on the structure, you can't see the bottom layer of chloride ions any more, of course.

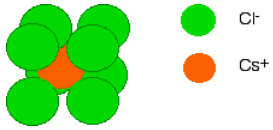


If you now think about a cesium ion sandwiched between the two layers of chloride ions, it is touching four chloride ions in the bottom layer, and another four in the top one. Each cesium ion is touched by eight chloride ions. We say that it is 8-coordinated. If we added another layer of cesium ions, you could similarly work out that each chloride ion was touching eight cesium ions. The chloride ions are also 8-coordinated. Overall, then, cesium chloride is 8:8-coordinated.

The final diagram in this sequence takes a slightly tilted view of the structure so that you can see how the layers build up. These diagrams are quite difficult to draw without it looking as if ions of the same charge are touching each other. They aren't!



Diagrams of ionic crystals are usually simplified to show the most basic unit of the repeating pattern. For cesium chloride, you could, for example, draw a simple diagram showing the arrangement of the chloride ions around each cesium ion:

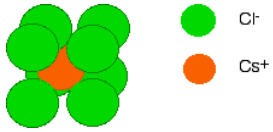


By reversing the colors (green chloride ion in the center, and orange cesium ions surrounding it), you would have an exactly equivalent diagram for the arrangement of cesium ions around each chloride ion.

Why are the cesium chloride and sodium chloride structures different?

When attractions are set up between two ions of opposite charges, energy is released. The more energy that can be released, the more stable the system becomes. That means that the more contact there is between negative and positive ions, the more stable the crystal should become.

If you can surround a positive ion like cesium with eight chloride ions rather than just six (and vice versa for the chloride ions), then you should have a more stable crystal. So why does not sodium chloride do the same thing? Look again at the last diagram:



Now imagine what would happen if you replaced the cesium ion with the smaller sodium ion. Sodium ions are, of course, smaller than cesium ions because they have fewer layers of electrons around them.

You still have to keep the chloride ions in contact with the sodium. The effect of this would be that the whole arrangement would shrink, bringing the chloride ions into contact with each other - and that introduces repulsion.

Any gain in attractions because you have eight chlorides around the sodium rather than six is more than countered by the new repulsions between the chloride ions themselves. When sodium chloride is 6:6-coordinated, there are no such repulsions - and so that is the best way for it to organize itself.

Which structure a simple 1:1 compound like NaCl or CsCl crystallizes in depends on the radius ratio of the positive and the negative ions. If the radius of the positive ion is bigger than 73% of that of the negative ion, then 8:8-coordination is possible. Less

than that (down to 41%) then you get 6:6-coordination.

In CsCl, the cesium ion is about 93% of the size of the chloride ion - so is easily within the range where 8:8-coordination is possible. But with NaCl, the sodium ion is only about 52% of the size of the chloride ion. That puts it in the range where you get 6:6-coordination.

The physical properties of sodium chloride

Sodium chloride is taken as typical of ionic compounds, and is chosen rather than, say, cesium chloride, because it is found on every syllabus at this level.

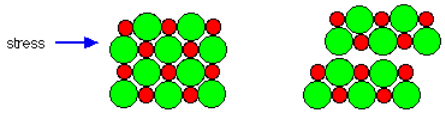
Sodium chloride has a high melting and boiling point

There are strong electrostatic attractions between the positive and negative ions, and it takes a lot of heat energy to overcome them. Ionic substances all have high melting and boiling points. Differences between ionic substances will depend on things like:

- *The number of charges on the ions*: Magnesium oxide has exactly the same structure as sodium chloride, but a much higher melting and boiling point. The 2+ and 2- ions attract each other more strongly than 1+ attracts 1-.
- *The sizes of the ions*: If the ions are smaller they get closer together and so the electrostatic attractions are greater. Rubidium iodide, for example, melts and boils at slightly lower temperatures than sodium chloride, because both rubidium and iodide ions are bigger than sodium and chloride ions. The attractions are less between the bigger ions and so less heat energy is needed to separate them.

Sodium chloride crystals are brittle

Brittleness is again typical of ionic substances. Imagine what happens to the crystal if a stress is applied which shifts the ion layers slightly.



Ions of the same charge are brought side-by-side and so the crystal repels itself to pieces!

Sodium chloride is soluble in water

Many ionic solids are soluble in water - although not all. It depends on whether there are big enough attractions between the water molecules and the ions to overcome the attractions between the ions themselves. Positive ions are attracted to the lone pairs on water molecules and co-ordinate (dative covalent) bonds may form. Water molecules form hydrogen bonds with negative ions.

Sodium chloride is insoluble in organic solvents

This is also typical of ionic solids. The attractions between the solvent molecules and the ions are not big enough to overcome the attractions holding the crystal together.

The electrical behavior of sodium chloride

Solid sodium chloride does not conduct electricity, because there are no electrons which are free to move. When it melts, sodium chloride undergoes electrolysis, which involves conduction of electricity because of the movement and discharge of the ions. In the process, sodium and chlorine are produced. This is a chemical change rather than a physical process.

The positive sodium ions move towards the negatively charged electrode (the cathode). When they get there, each sodium ion picks up an electron from the electrode to form a sodium atom. These float to the top of the melt as molten sodium metal. (And assuming you are doing this open to the air, this immediately catches fire and burns with an orange flame.)

$$Na^+ + e^- \rightarrow Na$$

The movement of electrons from the cathode onto the sodium ions leaves spaces on the cathode. The power source (the battery or whatever) moves electrons along the wire in the external circuit to fill those spaces. That flow of electrons would be seen as an

electric current (the external circuit is all the rest of the circuit apart from the molten sodium chloride.)

Meanwhile, chloride ions are attracted to the positive electrode (the anode). When they get there, each chloride ion loses an electron to the anode to form an atom. These then pair up to make chlorine molecules. Chlorine gas is produced. Overall, the change is . . .

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The new electrons deposited on the anode are pumped off around the external circuit by the power source, eventually ending up on the cathode where they will be transferred to sodium ions. Molten sodium chloride conducts electricity because of the movement of the ions in the melt, and the discharge of the ions at the electrodes. Both of these have to happen if you are to get electrons flowing in the external circuit. In solid sodium chloride, of course, that ion movement ca not happen and that stops any possibility of any current flow in the circuit.

Contributors

- Jim Clark (Chemguide.co.uk)

This page titled 7.1.2.3: Ionic Structures is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Ionic Structures** by Jim Clark is licensed CC BY-NC 4.0.

7.1.2.4: Metallic Structures

This page describes the structure of metals, and relates that structure to the physical properties of the metal.

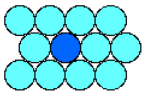
The structure of metals

Metals are giant structures of atoms held together by metallic bonds. "Giant" implies that large but variable numbers of atoms are involved - depending on the size of the bit of metal.

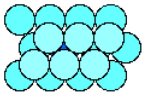
12-coordination

Most metals are close packed - that is, they fit as many atoms as possible into the available volume. Each atom in the structure has 12 touching neighbors. Such a metal is described as 12-coordinated.

Each atom has 6 other atoms touching it in each layer.



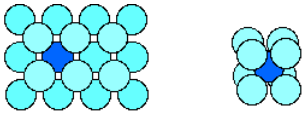
There are also 3 atoms touching any particular atom in the layer above and another 3 in the layer underneath.



This second diagram shows the layer immediately above the first layer. There will be a corresponding layer underneath (there are actually two different ways of placing the third layer in a close packed structure, but that goes beyond the topic here).

8-coordination

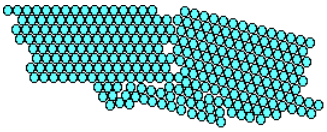
Some metals (notably those in Group 1 of the Periodic Table) are packed less efficiently, having only 8 touching neighbors. These are 8-coordinated.



The left hand diagram shows that no atoms are touching each other within a particular layer . They are only touched by the atoms in the layers above and below. The right hand diagram shows the 8 atoms (4 above and 4 below) touching the darker colored one.

Crystal grains

It would be misleading to suppose that all the atoms in a piece of metal are arranged in a regular way. Any piece of metal is made up of a large number of "crystal grains", which are regions of regularity. At the grain boundaries atoms have become misaligned.



The physical properties of metals

Melting points and boiling points

Metals tend to have high melting and boiling points because of the strength of the metallic bond. The strength of the bond varies from metal to metal and depends on the number of electrons which each atom delocalizes into the sea of electrons, and on the packing. Group 1 metals like sodium and potassium have relatively low melting and boiling points mainly because each atom only has one electron to contribute to the bond - but there are other problems as well:

- Group 1 elements are also inefficiently packed (8-coordinated), so that they aren't forming as many bonds as most metals.
- They have relatively large atoms (meaning that the nuclei are some distance from the delocalized electrons) which also weakens the bond.

Electrical conductivity

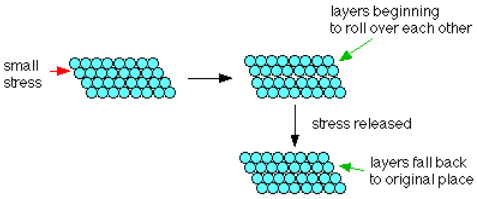
Metals conduct electricity. The delocalized electrons are free to move throughout the structure in 3-dimensions. They can cross grain boundaries. Even though the pattern may be disrupted at the boundary, as long as atoms are touching each other, the metallic bond is still present. Liquid metals also conduct electricity, showing that although the metal atoms may be free to move, the delocalization remains in force until the metal boils.

Thermal conductivity

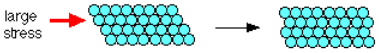
Metals are good conductors of heat. Heat energy is picked up by the electrons as additional kinetic energy (it makes them move faster). The energy is transferred throughout the rest of the metal by the moving electrons.

Malleability and ductility

Metals are described as malleable (can be beaten into sheets) and ductile (can be pulled out into wires). This is because of the ability of the atoms to roll over each other into new positions without breaking the metallic bond. If a small stress is put onto the metal, the layers of atoms will start to roll over each other. If the stress is released again, they will fall back to their original positions. Under these circumstances, the metal is said to be elastic.



If a larger stress is put on, the atoms roll over each other into a new position, and the metal is permanently changed.



The hardness of metals

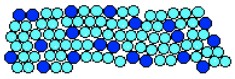
This rolling of layers of atoms over each other is hindered by grain boundaries because the rows of atoms don't line up properly. It follows that the more grain boundaries there are (the smaller the individual crystal grains), the harder the metal becomes.

Offsetting this, because the grain boundaries are areas where the atoms aren't in such good contact with each other, metals tend to fracture at grain boundaries. Increasing the number of grain boundaries not only makes the metal harder, but also makes it more brittle.

Controlling the size of the crystal grains

If you have a pure piece of metal, you can control the size of the grains by heat treatment or by working the metal. Heating a metal tends to shake the atoms into a more regular arrangement - decreasing the number of grain boundaries, and so making the metal softer. Banging the metal around when it is cold tends to produce lots of small grains. Cold working therefore makes a metal harder. To restore its workability, you would need to reheat it.

You can also break up the regular arrangement of the atoms by inserting atoms of a slightly different size into the structure. **Alloys** such as brass (a mixture of copper and zinc) are harder than the original metals because the irregularity in the structure helps to stop rows of atoms from slipping over each other.



Contributor

Jim Clark (Chemguide.co.uk)

This page titled 7.1.2.4: Metallic Structures is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Metallic Structures** by Jim Clark is licensed CC BY-NC 4.0.

7.1.2.5: Molecular Structures

The physical properties of substances having molecular structures varies with the type of intermolecular attractions: hydrogen bonding or van der Waals forces.

Molecules are made of fixed numbers of atoms joined together by covalent bonds, and can range from the very small (even down to single atoms, as in the noble gases) to the very large (as in polymers, proteins or even DNA). The covalent bonds holding the molecules together are very strong, but these are largely irrelevant to the physical properties of the substance. Physical properties are governed by the intermolecular forces - forces attracting one molecule to its neighbors - van der Waals attractions or hydrogen bonds.

Melting and boiling points

Molecular substances tend to be gases, liquids or low melting point solids, because the intermolecular forces of attraction are comparatively weak. You don't have to break any covalent bonds in order to melt or boil a molecular substance. The size of the melting or boiling point will depend on the strength of the intermolecular forces. The presence of hydrogen bonding will lift the melting and boiling points. The larger the molecule the more van der Waals attractions are possible - and those will also need more energy to break.

Solubility in water

Most molecular substances are insoluble (or only very sparingly soluble) in water. Those which do dissolve often react with the water, or else are capable of forming hydrogen bonds with the water.

Why doesn't methane dissolve in water?

The methane, CH_4, itself is not the problem. Methane is a gas, and so its molecules are already separate - the water doesn't need to pull them apart from one another. The problem is the hydrogen bonds between the water molecules. If methane were to dissolve, it would have to force its way between water molecules and so break hydrogen bonds. That costs a reasonable amount of energy.

The only attractions possible between methane and water molecules are the much weaker van der Waals forces - and not much energy is released when these are set up. It simply isn't energetically profitable for the methane and water to mix.

Why does ammonia dissolve in water?

Ammonia has the ability to form hydrogen bonds. When the hydrogen bonds between water molecules are broken, they can be replaced by equivalent bonds between water and ammonia molecules. Some of the ammonia also reacts with the water to produce ammonium ions and hydroxide ions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The reversible arrows show that the reaction doesn't go to completion. At any one time only about 1% of the ammonia has actually reacted to form ammonium ions. The solubility of ammonia is mainly due to the hydrogen bonding and not the reaction. Other common substances which are freely soluble in water because they can hydrogen bond with water molecules include ethanol (alcohol) and sucrose (sugar).

Solubility in organic solvents

Molecular substances are often soluble in organic solvents - which are themselves molecular. Both the solute (the substance which is dissolving) and the solvent are likely to have molecules attracted to each other by van der Waals forces. Although these attractions will be disrupted when they mix, they are replaced by similar ones between the two different sorts of molecules.

Electrical conductivity

Molecular substances will not conduct electricity. Even in cases where electrons may be delocalized within a particular molecule, there isn't sufficient contact between the molecules to allow the electrons to move through the whole solid or liquid.

Jim Clark (Chemguide.co.uk)

This page titled 7.1.2.5: Molecular Structures is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Molecular Structures** by Jim Clark is licensed CC BY-NC 4.0.

SECTION OVERVIEW

7.1.3: Lattice Defects

An ideal crystalline solid exhibit a periodic crystal structure with the positions of atoms or molecules occurring on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atoms or molecules in most crystalline materials is not perfect and the regular patterns are interrupted by crystallographic defects. Lattice structures (or crystals) are more prone to defects when their temperature is greater than 0 K.

Topic hierarchy

7.1.3.1: Frenkel Defect

7.1.3.2: Metal Oxides

7.1.3.3: Schottky Defects

7.1.3.4: Solid Defects

7.1.3: Lattice Defects is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1.3.1: Frenkel Defect

The **Frenkel defect** (also known as the Frenkel pair/disorder) is a defect in the lattice crystal where an atom or ion occupies a normally vacant site other than its own. As a result the atom or ion leaves its own lattice site vacant.

The Frenkel Defect in a Molecule

The Frenkel Defect explains a defect in the molecule where an atom or ion (normally the cation) leaves its own lattice site vacant and instead occupies a normally vacant site (Figure 7.1.3.1.1). The cation leaves its own lattice site open and places itself between the area of all the other cations and anions. This defect is only possible if the cations are smaller in size when compared to the anions.

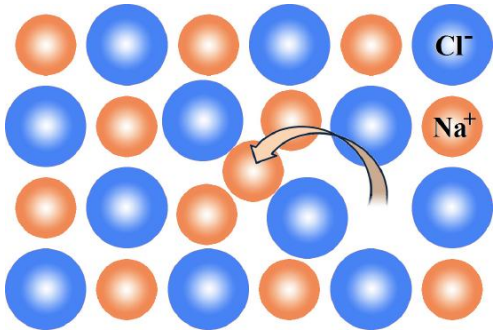


Figure 7.1.3.1.1 : The Frenkel defect within the NaCl structure. (CC BY-SA 3.0; VladVD via Wikipedia)

The number of Frenkel Defects can be calculated using the equation:

$$\sqrt{NN^*}\, e^{\frac{\Delta H}{2RT}}$$

where N is the number of normally occupied positions, N^* is the number of available positions for the moving ion, the ΔH of formation is the enthalpy formation of one Frenkel defect, and R is the gas constant. Frenkel defects are intrinsic defects because the existence causes the Gibbs energy of a crystal to decrease, which means it is favorable to occur.

Solids Found with a Frenkel Defect

The crystal lattices are relatively open and the coordination number is low.

References

1. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print.
2. Tilley, Richard. *Understanding Solids.* John Wiley & Sons, LTD. 2004.

Problems

1. What requirements are needed in order for the Frenkel defect to occur in an atom?
2. What are the differences between the Schottky defect and the Frenkel defect?

Answers

1. A low coordination number as well as having the crystal lattices open for the molecule.
2. The Frenkel defect causes an cation to leave its own lattice and go to another, while Sckhotty defect depicts that an equal number of cations and anions must be absent to maintain charge neutraility.

Contributors and Attributions

- Stanley Hsia, UC Davis

7.1.3.1: Frenkel Defect is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Frenkel Defect** is licensed CC BY-NC-SA 4.0.

7.1.3.2: Metal Oxides

Discussion Questions

- How does metal oxides protect a metal from further oxidation?
- How does oxidation rate progress on metal surfaces?
- How is iron erroded?
- What are the major iron oxides and their structures?

Defects in Metal Oxides

Metal oxides are very common commodities, widely applied, and have many different varieties. For example, zinc oxide sintered together with other metal oxide additives have been made into nonlinear resistors, which are called Varistors for surge suppressing function. The suppressing function has been applied for switching and for protection of random voltage protections. Iron oxide and other metal oxides are used in thermite reactions, and this has been applied in many ways, including welding in spaceship repairs. Iron oxides are also the raw material for all magnets and magnetic materials used for computer disks and recording tapes.

How does metal oxides protect a metal from further oxidation?

Metals are protected from further oxidation by forming a hard scale of oxides when it is being oxidized. Not all metal oxides form a scale. In general, when the oxide formed is not very dense, it is not under stress, and the oxide layer forms a scale. Usually, a mole of metal oxide should occupy more volume than a mole of the metal itself. If this is true, the oxide is not under stress, and a protective scale is formed. In general, **if the volume of the metal oxide per mole of metal is greater than the molar volume of the metal, the oxide will form a protective scale**.

On the other hand, if the oxide formed occupies a smaller volume than the volume occupied by the metal itself, the oxide layer will be under tension and at some point it will crack. Thus, the oxide offers no protection for further oxidation. The molar volume is easily calculated by dividing the molar mass by the density:

$$\text{molar volume} = \frac{\text{Molar mass}}{density}$$

Example 1

The densities of Mg and MgO are 1.74 and 3.58 g/mL respectively. Calculate their molar volumes.

Solution

The molar volumes are given below:

Molar volume of Mg = 24.31 (g/mol) / 1.74 (g/mL) = 14.0 mL / mol
Molar volume of MgO = (24.31+16.00) (g/mol) / 3.58 (g/mL) = 11.3 mL / mol

DISCUSSION

Since the molar volume of the oxide is less than that of the metal, the oxide does not form a protective scale.

Example 2

The densities of Al and Al_2O_3 are 2.702 and 3.965 g/mL respectively. Calculate their volumes per mole of Al.

Solution

The volumes per mole of La are given below:

Molar volume of Al = 26.98 (g/mol) / 2.702 (g/mL) = 9.985 mL / mol
Volume of Al2O3 = (26.98+24.00) (g/mol) / 3.965 (g/mL =12.86 mL / mol

DISCUSSION

It has been a well known fact that aluminum oxide forms a protective scale. These data confirm the fact, and now you have an explanation for corrosion. However, we should realize that sometimes the metal oxide does not form a protective layer even if

the oxide is not under tension.

How does oxidation rate progress on metal surfaces?

A major technological concern of metals is the corrosion due to oxidation. The rate of oxidation is usually expressed in terms of depth of the oxidation layer. Several models have been proposed to express the thickness of the oxide layer *y* as a function of time *t*. In the following discussion, *k* is a rate constant.

The linear rule. When the oxide offers absolutely no protection, the progress of oxidation is a linear relationship with time. This has been called the *rectilinear rate law* by Swaddle.

$$dy = kdt$$

or

$$y = kt$$

When the oxide layer gives some protection, the parabolic law apply. This law is formulated with the consideration,

$$ydy = kdt$$

or

$$y_2 = k't + c$$

with $k' = 2k$ and c is another constant

or

$$y = k\text{''}\ t1/2 + c\text{''}$$

with k" and c" other constants

Oxidation of copper has been shown to follow this rule. The thicker the oxide layer, the more protection the oxide offers in this case. When the oxide layer forms a protective layer, but large flakes crack and leas to faster oxidation as a result. Then, the rate is a combination of the linear rule and the parabolic law.

When the oxide forms a good protective layer, the *logarithmic rate law* and the *inverse logarithmic rate law*) have been applied. Some suggested formulas are:

$$\frac{1}{y} = a\ln(kt + 1)$$

or

$$y = bln(kt + 1)$$

The *a*, *b*, and *k* are just some parameters to be determined by experimental methods. The properties of metals and its oxide play roles in the rate of corrosion. There is no set rate laws, and every case must be studied carefully. So far, we have hinted a few has models for exploration and analysis of corrosion problems.

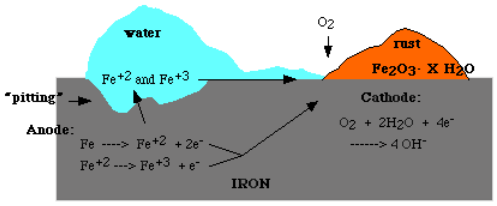
How is iron corroded?

The problem with iron as well as many other metals is that the oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off easily causing "pitting". Extensive pitting eventually causes structural weakness and disintegration of the metal. Most people consider the oxidation of iron results in the formation of a film of iron sesquioxide, which is a term given to red iron(III) oxide, Fe_2O_3, which is also called ferric oxide. In reality, the oxidation and corrosion of iron is a very complicated process.

The corrosion takes place due to oxidation and galvanic actions. The rust formed is generally represented by

\[Fe_2O_3 \cdot *x*H_2O \nonumber \]

where *x* is an unspecific amount of water. Depending on the amount of water, the oxides appear in various colors. The pH of water and electrolytes present in the water affect the rate of iron corrosion, because the presence of electrolytes increases the conductivity of the solution.



What are the major iron oxides and their structures?

As mentioned above, iron can be at oxidation state II or III in the form of Fe^{2+} or Fe^{3+} in its oxides. As a result, iron oxides tends to be somewhat non-stoichiometric.

The common iron oxides are:

ferrous oxide FeO
hematite a-Fe2O3
maghemite g-Fe2O3
magnetite Fe3O4

However, when water is involved, several oxyhydroxides are possible:

goethite a-FeOOH
akaganeite b-FeOOH
lepidocrocite g-FeOOH

There is no need to memorize all these minerals, but you get the idea of varieties of iron oxides and oxyhydroxides.

The basic structures of iron oxides and iron oxy hydroxides can be described as a close packing of oxygen (or hydroxide) with iron ions in the octahedral sites. The structures of goetite and hematite may be describe as an approximate hcp close packing of O^{2-} or HO^{-} ions with some of the octahedral sites occupied by iron ions. Thus, these two types of structures are usually designated as a phases.

The structures of lepidocrocite and maghemite may be described as an approximate ccp (fcc) packing of O^{2-} or HO^{-} ions with some of the octahedral sites occupied by iron ions. Thus, these two types of structures are usually designated as g phases. Some of the iron ions can be replaced by other metal ions, forming solid solutions in a process known as *isomorphous substitution* in terms of structural chemistry.

Questions

1. What is the condition for a metal oxide to form a protective layer to prevent the metal from further oxidation?
2. Which occupies a larger volume, 1 mole of MgO or 1 mole of Mg metal?
3. Which occupies a larger volume, 0.5 mole of Al_2O_3 or 1 mole of Al metal?
4. If the rate of errosion is expressed by the equation,

$$y = b \ln (k t + 1)$$

What is the differential rate law?

Solutions

1. **Hint: The volume of the metal oxide per mole of metal is greater than the molar volume of the metal.**

   Skill -
   Explain protection of metal from corrosion.

2. **Hint: 1 mol of Mg metal.**
3. **Hint: 0.5 mol of Al_2O_3**

   Skill -
   Explain protection of metal from corrosion.

4. **Hint: Work out dy/dt**

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.3.2: Metal Oxides is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Metal Oxides** is licensed CC BY-NC-SA 4.0.

7.1.3.3: Schottky Defects

Lattice structures are not perfect; in fact most of the time they experience defects. Lattice structures (or crystals) are prone to defects especially when their temperature is greater than 0 K [1]. One of these defects is known as the Schottky defect, which occurs when oppositely charged ions vacant their sites [1].

Introduction

Like the human body, lattice structures (most commonly known as crystals) are far from perfection. Our body works hard to keep things proportional but occasionally our right foot is bigger than our left; similarly, crystals may try to arrange it's ions under a strict layout, but occasionally an ion slips to another spot or simply goes missing. Realistically speaking, it should be expected that crystals will depart itself from order (not surprising considering defects occurs at temperature greater than 0 K). There are many ways a crystal can depart itself from order (thus experiences defects); these defects can be grouped in different categories such as Point Defects, Line Defects, Planar Defects, or Volume or Bulk Defects [2]. We will focus on Point Defects, specifically the defect that occurs in ionic crystal structures (i.e. NaCl) called the Schottky Defect.

Point Defects

Lattice structures (or crystals) undergoing point defects experience one of two types:

1. atoms or ions leaving their spot (thus creating vacancies).
2. atoms or ions slipping into the little gaps in between other atoms or ions; those little gaps are known as interstitials--since atoms or ions in the crystals are occupying interstitials, they inherently become (create) interstitials.

By the simplest definition, the Schottky defect is defined by type one, while type two defects are known as the Frenkel defect. The Schottky defect is often visually demonstrated using the following layout of anions and cations:

+	-	+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	(vacant)	+	-
+	-	+	-	+	-	+	-	+	-	+
-	+	-	(vacant)	-	+	-	+	-	+	-
+	-	+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	-	+	-

***Figure* 7.1.3.3.1** *: The positive symbols represents cations (i.e. Na^+) and the negative symbol represents anions (i.e. Cl^-).*

In addition, this layout is applicable only for ionic crystal compounds of the formula MX--layout for ionic crystals with formula MX_2 and M_2X_3 will be discussed later--where M is metal and X is nonmetal. Notice the figure has exactly one cation and one anion vacating their sites; that is what defines a (one) Schottky Defect for a crystal of MX formula--for every cation that vacant its site, the same number of anion will follow suit; essentially the vacant sites come in pairs. This also means the crystal will neither be too positive or too negative because the crystal will always be in equilibrium in respect to the number of anions and cations.

It is possible to approximate the number of Schottky defects (n_s) in a MX ionic crystal compound by using the equation:

$$N = \exp^{-\frac{\Delta H}{2RT}} \tag{7.1.3.3.1}$$

where

- ΔH is the enthalpy of defect formation,
- R is the gas constant,
- T is the absolute temperature (in K), and

N can be calculated by:

$$N = \frac{\text{density of the ionic crystal compound} \times N_A}{\text{molar mass of the ionic crystal compound}} \tag{7.1.3.3.2}$$

From Equation 7.1.3.3.1, it is also possible to calculate the fraction of vacant sites by using the equation:

$$\frac{n_s}{N} = \exp^{-\frac{\Delta H}{2RT}} \tag{7.1.3.3.3}$$

Schottky defects for MX_2 and M_2X_3

As mentioned earlier, a Schottky defect will always result a crystal structure in equilibrium--where no crystal is going to be too positive or too negative; thus in the case of:

- MX_2: one Schottky defect equals one cation and two anion vacancy.
- M_2X_3: one Schottky defect equals two cation and three anion vacancy.

References

1. Housecroft, Catherine. Inorganic Chemistry. Pearson Prentice Hall 2008.
2. Sólyom, J.(Jenö). Fundamentals of the Physics of Solids. Translated by Attila Piróth. New York : Springer, c2007.
3. Tilley, Richard. Understanding Solids. John Wiley & Sons, LTD. 2004.

Problems

1. How does an ionic crystal structure maintain electrical neutrality despite undergoing a Schottky defect?
2. How is a Schottky defect defined for a compound with a MX formula? MX_2? M_2X_3?
3. Given that the enthalpy of defect formation for LiCl is 3.39 x 10^{-19} J and the density of LiCl is 2.068 g/cm^{-3}. Calculate the number of Schottky defect at 873 K.
4. Using the number of Schottky defect solved for question 3, determine the fraction of vacant site for LiCl.
5. If a anion and a cation vacant its site and occupies a space between other anions and cations, is it still a Schottky defect?

Answers

1. For a MX compound: one anion and one cation vacant their sites, so the overall charge will remain balanced. This is the same for MX_2 and M_2X_3 because appropriate numbers of anions and cations vacant their site thus leaving the overall charge neutral.
2. MX compound: one Schottky defect is when one anion and one cation leave their sites. MX_2 compound: one Schottky defect is when one anion and two cations leave their sites. M_2X_3 is when two anions and three cations leave their sites.

7.1.3.3: Schottky Defects is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Schottky Defects** is licensed CC BY-NC-SA 4.0.

7.1.3.4: Solid Defects

Discussion Questions

- What are crystal defects and how are they classified?
- How do impurities affect the structure and properties of a solid?
- What are color centers and how do they affect electric conductivity of solids?

Few, if any, crystals are *perfect* in that all unit cells consist of the ideal arrangement of atoms or molecules and all cells line up in a three dimensional space with no distortion. Some cells may have one or more atoms less whereas others may have one or more atoms than the ideal unit cell. The imperfection of crystals are called **crystal defects**. Crystal defects are results of thermodynamic equilibrium contributed also by the increase in entropy *TS* term of the Gibb's free energy:

$$\Delta G = \Delta H - T\Delta S$$

Only at the unattainable absolute zero K will a crystal be perfect, in other words, no crystals are absolutely perfect. However, the degree of imperfection vary from compound to compound. On the other hand, some solid-like structure called **flickering clusters** also exist in a liquid. For example, the density of water is the highest at 277 K. The flickering clusters increase as temperature drops below 277 K, and the water density decreases as a result. The missing and lacking of atoms or ions in an ideal or imaginary crystal structure or lattice and the misalignment of unit cells in real crystals are called crystal defects or solid defects. Crystal defects occur as points, along lines, or in the form of a surface, and they are called **point, line, or plane defects** respectively.

Point Defects

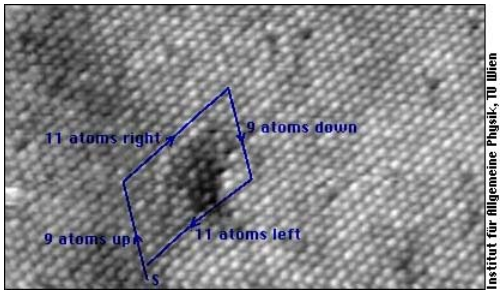
Point defects can be divided into Frenkel defects and **Schottky defects**, and these often occur in ionic crystals. The former are due to misplacement of ions and vacancies. Charges are balanced in the whole crystal despite the presence of interstitial or extra ions and vacancies. On the other hand, when only vacancies of cation and anions are present with no interstitial or misplaced ions, the defects are called Schottky defects.

Point defects are common in crystals with large anions such as AgBr, AgI, $RbAgI_4$. Due to the defects, the ions have some freedom to move about in crystals, making them relatively good conductors. These are called ionic conductors, unlike metals in which electrons are responsible for electric conductivity. Recently, ionic conductors have attracted a lot of attention because the fuel cell and battery technologies require conducting solids to separate the electrodes.

Line Defects

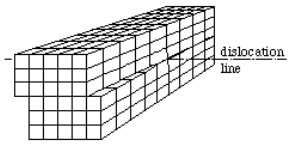
Line defects are mostly due to misalignment of ions or presence of vacancies along a line. When lines of ions are missing in an otherwise perfect array of ions, an **edge dislocation** appeared. Edge dislocation is responsible for the ductility and malleability. In fact the hammering and stretching of materials often involve the movement of edge dislocation. Movements of dislocations give rise to their plastic behavior. Line dislocations usually do not end inside the crystal, and they either form loops or end at the surface of a single crystal.

A dislocation is characterized by its Burgers vector: If you imagine going around the dislocation line, and exactly going back as many atoms in each direction as you have gone forward, you will not come back to the same atom where you have started. The Burgers vector points from start atom to the end atom of your journey (This "journey" is called Burgers circuit in dislocation theory).



In this electron microscope image of the surface of a crystal, you see point defects and a Burger journey around an edge dislocation. The dislocation line is in the crystal, and the image shows its ending at the surface. A Burger vector is approximately perpendicular to the dislocation line, and the missing line of atoms is somewhere within the block of the Buerger journey.

If the misalignment shifts a block of ions gradually downwards or upwards causing the formation of a screw like deformation, a **screw dislocation** is formed. The diagram here shows the idealized screw dislocation.



Line defects weakens the structure along a one-dimensional space, and the defects type and density affects the mechanical properties of the solids. Thus, formation and study of dislocations are particularly important for structural materials such as metals. This link gives some impressive images of dislocations. Chemical etching often reveal pits which are visible under small magnifications.

Example 7.1.3.4.1

The Table of X-ray Crystallographic Data of Minerals (The CRC Handbook of Chemistry and Physics) list the following for bunsenite (NiO): Crystal system: cubic, structure type: rock salt, a = 4.177*10-8 cm. In the table of Physical Constant of Inorganic Compounds, the density of bunsenite (NiO) is 6.67g / cm3. From these values, evaluate the cell volume (volume of the unit cell), sum of Ni and O radii (rNi + rO), 2 Molar volumes, (X-ray) density, and the Schottky defect vacancy rate.

Solution

Actually, most of the required values have been listed in the table, but their evaluations illustrate the methods. These values are evaluated below:

Cell volume = a3
= (4.177*10-8)3
= 72.88*10-24 cm3

$$r_{Ni} + r_O = \frac{a}{2}$$

$$= 2.088 \times 10^{-8}$$

X-ray density = 4*(58.69+16.00) / (6.023*10^{23}*72.88*10^{-24})
= 6.806 g / cm^3,

Compared to the observed density = 6.67 g / cm^3. The molar volumes (58.69+16.00) / density are thus

74.69 / 6.806 = 10.97 cm^3; and 74.69 / 6.67 = 11.20 cm^3

The vacancy rate = 6.806 - 6.67 / 6.806
= 0.02 (or 2%)

DISCUSSION

These methods are hints to assignments.

From the given conditions, we cannot calculate individual radii of Ni and O, but their sum is calculable.

Plane Defects

Plane defects occur along a 2-dimensional surface. The **surface** of a crystal is an obvious imperfection, because these surface atoms are different from those deep in the crystals. When a solid is used as a catalyst, the catalytic activity depends very much on the surface area per unit mass of the sample. For these powdery material, methods have been developed for the determination of unit areas per unit mass.

Another surface defects are along the **grain boundaries**. A grain is a single crystal. If many seeds are formed when a sample starts to crystallize, each seed grow until they meet at the boundaries. Properties along these boundaries are different from the grains. A third plane defects are the **stacking faults**. For example, in the close packing arrangement, the adjancent layers always have the AB relationship. In a ccp (fcc) close packing sequence, ...ABCABC..., one of the layer may suddenly be out of sequence, and become ..ABABCABC.... Similarly, in the hcp sequence, there is a possibility that one of the layer accidentally startes in the C location and resulting in the formation of a grain boundary.

How do impurities affect the structure and properties of a solid?

You already know that to obtain a perfectly pure substance is almost impossible. Purification is a costly process. In general, analytical reagent-grade chemicals are of high purity, and yet few of them are better than 99.9% pure. This means that a foreign atom or molecule is present for every 1000 host atoms or molecules in the crystal. Perhaps the most demanding of purity is in the electronic industry. Silicon crystals of 99.999 (called 5 nines) or better are required for IC chips productions. These crystal are **doped** with nitrogen group elements of P and As or boron group elements B, Al etc to form n- aand p-type semiconductors. In these crystals, the impurity atom substitute atoms of the host crystals.

Presence minute foreign atoms with one electron more or less than the valence four silicon and germanium host atoms is the key of making n- and p-type semiconductors. Having many semiconductors connected in a single chip makes the integrated circuit a very efficient information processor. The electronic properties change dramatically due to these impurities. This is further described in Inorganic Chemistry by Swaddle.

In other bulk materials, the presence of impurity usually leads to a lowering of melting point. For example, Hall and Heroult tried to electrolyze natural aluminum compounds. They discovered that using a 5% mixture of Al_2O_3 (melting point 273 K) in cryolite Na_3AlF_6 (melting point 1273 K) reduced the melting point to 1223 K, and that enabled the production of aluminum in bulk. Recent modifications lowered melting temperatures below 933 K. Some types of glass are made by mixing silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), and sodium oxide (Na_2O). They are softer, but due to lower melting points, they are cheaper to produce.

Color centers and how do they affect electric conductivity of solids?

Color centers are imperfections in crystals that cause color (defects that cause color by absorption of light). Due to defects, metal oxides may also act as semiconductors, because there are many different types of electron traps. Electrons in defect region only absorb light at certain range of wavelength. The color seen are due to lights not absorbed. For example, a diamond with C vacancies (missing carbon atoms) absorbs light, and these centers give green color as shown here. Replacement of Al^{3+} for Si^{4+} in quartz give rise to the color of smoky quartz.

A high temperature phase of ZnO_x, ($x < 1$), has electrons in place of the O^{2-} vacancies. These electrons are color centers, often referred to as *F*-centers (from the German word *farben* meaning color). Similarly, heating of ZnS to 773 K causes a loss of sulfur, and these material fluoresces strongly in ultraviolet light. Some non-stoichiometric solids are engineered to be n-type or p-type semiconductors. Nickel oxide NiO gain oxygen on heating in air, resulting in having Ni^{3+} sites acting as electron trap, a p-type semiconductor. On the other hand, ZnO lose oxygen on heating, and the excess Zn metal atoms in the sample are ready to give electrons. The solid is an n-type semiconductor.

Questions

1. Why does the density of water decreases when the temperature decreases from 277 to 273 K?
2. What type of defects is due to misplaced atoms or ions and vacancies of the same in a crystalline material.
3. What defects reduce the density of a solid?
4. What type of material do the fuel cell and battery technologies need to separate the electrodes?

Solutions

1. **Hint: Due to the formation of flickering clusters.**

   Skill -
   Correlate properties of a material to its structure.

2. **Hint: Frenkel defects.**

   Skill -
   Explain Frendel and Schottky defects.

3. **Hint: Vacancies of Schottky defects reduce the density.**

   Skill -
   Correlate properties of a material to its structure.

4. **Hint: Ionic conductors.**

   Skill -
   Specify the desirable properties of a material.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.3.4: Solid Defects is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Solid Defects** is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

7.1.4: Metal Lattices

Metals are composed of atoms in ordered layers that form a three-dimensional, crystalline structure. That means that the individual units within the solid -- the atoms, in this case -- are organized in a regularly repeating pattern.

Topic hierarchy

7.1.4.1: Structure and Properties of Metals

7.1.4.2: Metal Packing- Layers

7.1.4.3: Metal Packing- Three Dimensions

7.1.4.4: Problems

7.1.4.5: Solutions to Selected Problems

Contributors and Attributions

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 7.1.4: Metal Lattices is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

7.1.4.1: Structure and Properties of Metals

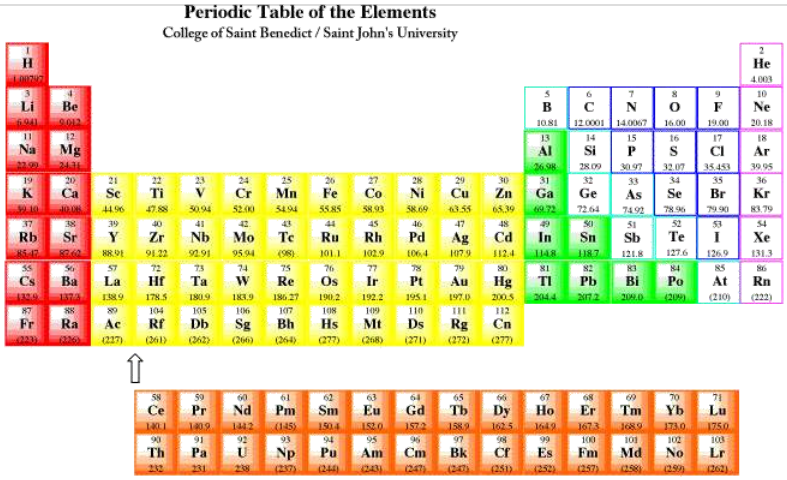


Figure 1.1.7. Symbolic drawing of the longest possible wavelength of an electron that is confined to one atom (left) compared to an electron that is delocalized over a group of atoms (right).

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University) ?

This page titled 7.1.4.1: Structure and Properties of Metals is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **1. Structure and Properties of Metals** by Chris Schaller is licensed CC BY-NC 3.0.

7.1.4.2: Metal Packing- Layers

Figure ME2.6. Packing efficiency has an influence on the strength of interactions between metal nuclei and the electrons in the "electron sea."

For comparison, maybe there is another set of atoms, also in a simple square layer. Suppose they are well-separated from each other; maybe they are far enough apart that you could fit an extra atom between each pair if you wanted to. If the free electron is in the same place -- the middle of the nearest hole -- you can see that it is much farther from the nucleus in this case. The force of attraction is much lower in this case, and the overall energy is not as low.

- Most metals pack very efficiently together to form a solid.
- Efficient packing leads to stronger bonding interactions.

That first case, with atoms packed more tightly together, may be preferable, because of the stronger interaction between the metal nucleus and the free electron. For reasons like this, understanding the packing efficiency in a crystal can be very important.

Contributors and Attributions

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 7.1.4.2: Metal Packing- Layers is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **2. Metal Packing: Layers** by Chris Schaller is licensed CC BY-NC 3.0.

7.1.4.3: Metal Packing- Three Dimensions

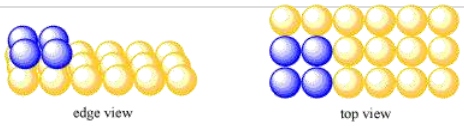


Figure 3.1.15. A final look at cubic close-packing.

Note that this cube has an atom in the center of each face; hence the name, face-centered cubic.

- A cubic close-packed takes the name "cubic" from the presence of a cubic unit cell.
- This cubic unit cell is oriented diagonally to the close-packed layers.
- This cubic unit cell has an atom in the center of each face; it is also called "face-centered cubic".

Contributors and Attributions

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 7.1.4.3: Metal Packing- Three Dimensions is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **3. Metal Packing: Three Dimensions** by Chris Schaller is licensed CC BY-NC 3.0.

7.1.4.4: Problems

Contributors and Attributions

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 7.1.4.4: Problems is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **E. Problems** by Chris Schaller is licensed CC BY-NC 3.0.

7.1.4.5: Solutions to Selected Problems

Contributors and Attributions

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 7.1.4.5: Solutions to Selected Problems is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **S. Solutions to Selected Problems** by Chris Schaller is licensed CC BY-NC 3.0.

SECTION OVERVIEW

7.1.5: Solids

Topic hierarchy

7.1.5.1: Body Centered Packing

7.1.5.2: Metal Structures

7.1.5.3: Simple Cubic

7.1.5.4: Solids

7.1.5.5: Sphere Packing

7.1.5.6: Tetrahedral and Octahedral Sites

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.5: Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1.5.1: Body Centered Packing

The Model for Polonium Crystal Structure

Discussion -

```
O   O  |  If we cut the cube along a face diagonal, the arrangement of
  O    |  atoms look like the diagram on the left.
O   O  |     Thus, bd = 4 R
```

- **If the edge of the cube has a length represented by *a*, and if the radius of the atoms is *R*, express *a* as a function of *R*.**

  Hint: $a = \frac{4R}{\sqrt{3}}$

  Discussion -
  $a = {}^{4\,R}/_{\sqrt{3}}$

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.5.1: Body Centered Packing is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Body Centered Packing** is licensed CC BY-NC-SA 4.0.

7.1.5.2: Metal Structures

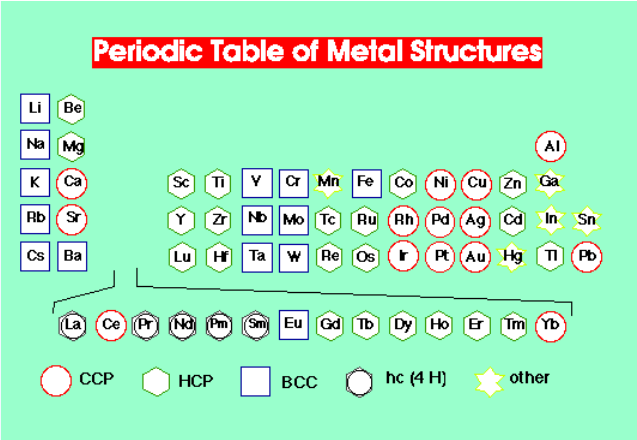


Figure 1: In the above diagram, the ccp (fcc) structures are represented by a red circle, whereas the hcp structures are represented by a black hexagon.

Copper is the most common mentioned metal that has the fcc structure. This element is one of the noble metals. It has been widely used for door knobs and other tools, and has been widely recognized. Yet, most noble metals (Cu, Ag, Au, Ni, Pd, Pt, Rh, and Ir) have fcc type structures. Among the group 2 elements, only Ca and Sr have the fcc structure, whereas Be and Mg have hcp structures. So do Zn, Cd, Sc, Y, Lu, Ti, Zr, Hf, Tc, Re, Ru, Os and most rare earth elements. These are mentioned to bring your attention to these two common types of structures, and you are encouraged to at least be able to give a few examples for each type.

Amazingly, the hcp and fcc structure are very similar in many aspects, but nature knows best. The structures adopted by various metals occur by their design. When crystallization takes place, the atoms arrange themselves according to their structure types.

Exercises 1

a. Copper has a *specific gravity* of 8.92; evaluate its atomic radius.
b. The atomic radius of silver Ag is listed as 145 pm. Evaluate its density.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.5.2: Metal Structures is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Metal Structures** is licensed CC BY-NC-SA 4.0.

7.1.5.3: Simple Cubic

Learning Objectives

- Recognize a unit cell.
- Use geometry to correlate atomic radius with unit cell edge length.
- Calculate parameters relevant to crystal chemistry.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

This page titled 7.1.5.3: Simple Cubic is shared under a not declared license and was authored, remixed, and/or curated by Chung (Peter) Chieh.

- **Simple Cubic** by Chung (Peter) Chieh is licensed CC BY-NC-SA 4.0.

7.1.5.4: Solids

Representation of 3-dimensional structures should usually be made using models, and their representation on a flat surface is difficult. For simplicity, we use a 2-dimensional pattern (plane) to illustrate a 2-dimensional (planar) crystal structure.

```
# @ # @ # @ # @ # @ # @ # @ # @
@ # @ # @ # @ # @ # @ # @ # @ #
# @ # @ # @ # @ # @ # @ # @ # @
@ # @ # @ # @ # @ # @ # @ # @ #
# @ # @ # @ # @ # @ # @ # @ # @
@ # @ # @ # @ # @ # @ # @ # @ #
# @ # @ # @ # @ # @ # @ # @ # @
@ # @ # @ # @ # @ # @ # @ # @ #
```

This pattern or *crystal structure* is generated by using a unit marked by the centers of any four @ or # signs. The choice is up to you in this case. Such a unit is called a primitive unit. The pattern has a square (or rectangular on some screens) appearance, and to preserve the square, we may use a square unit of

```
# @ #           @ # @
@ # @     or    # @ #
# @ #           @ # @
```

as our **unit cell**. Such choices result in having two @ and # per unit cell, and these are called **centered cells**.

Thus, if we know the arrangement of a unit cell, we can use our imagination to build a crystal structure, or use symbols or models to represent a crystal structure. Since each pattern has features shared by many structures, often such a pattern is called a **lattice**. For example, the diamond, zinc blende, wurtzite, and NaCl structures have been called lattices; however, the word lattice has a more formal definition by crystal physics and chemists. The above site gives a gallery of lattices.

Definition: Crystals

Inorganic Chemistry by Swaddle defined crystals as packed regular arrays of atoms, ions, or molecules in a pattern repeated periodically *ad infinitum*.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.5.4: Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Solids** is licensed CC BY-NC-SA 4.0.

7.1.5.5: Sphere Packing

Learning Objectives

- Use the packing of spheres to model the fcc crystal structure.
- Practice solving problems related to crystal structures.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.5.5: Sphere Packing is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Sphere Packing** is licensed CC BY-NC-SA 4.0.

7.1.5.6: Tetrahedral and Octahedral Sites

Learning Objectives

- To construct a model for the tetrahedral and octahedral holes of closest packing.
- To calculate geometric properties of the model.
- Apply these properties to interpret crystal chemistry.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.5.6: Tetrahedral and Octahedral Sites is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Tetrahedral and Octahedral Sites** is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

7.1.6: Thermodynamics of Lattices

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them.

7.1.6.1: Lattice Energy

7.1.6.2: Lattice Energy- The Born-Haber cycle

7.1.6.3: Lattice Enthalpies and Born Haber Cycles

7.1.6.4: The Born-Lande' equation

7.1.6: Thermodynamics of Lattices is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1.6.1: Lattice Energy

Discussion Questions

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, U, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M_aL_b(s) \rightarrow aM^{b+}(g) + bX^{a-}(g)} \tag{7.1.6.1.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 7.1.6.1.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 7.1.6.1.1:

$$\mathrm{aM^{b+}(g) + bX^{a-}(g) \rightarrow M_aL_b(s)}$$

the energy released is called **energy of crystallization** (E_{cryst}). Therefore,

$$U_{lattice} = -E_{cryst}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 7.1.6.1.1 : Comparison of Lattice Energies (U in kJ/mol) of Some Salts

Solid	U	Solid	U	Solid	U	Solid	U
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327

The following trends are obvious at a glance of the data in Table 7.1.6.1.1:

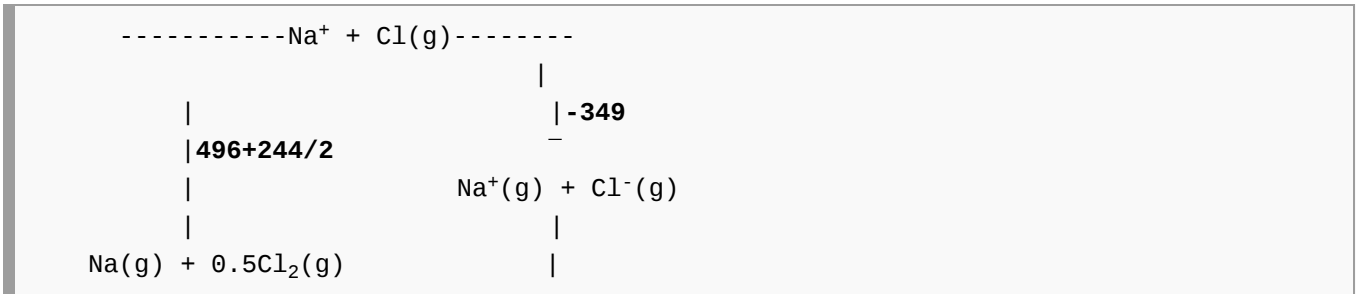
- As the ionic radii of either the cation or anion increase, the lattice energies decrease.
- The solids consists of divalent ions have much larger lattice energies than solids with monovalent ions.

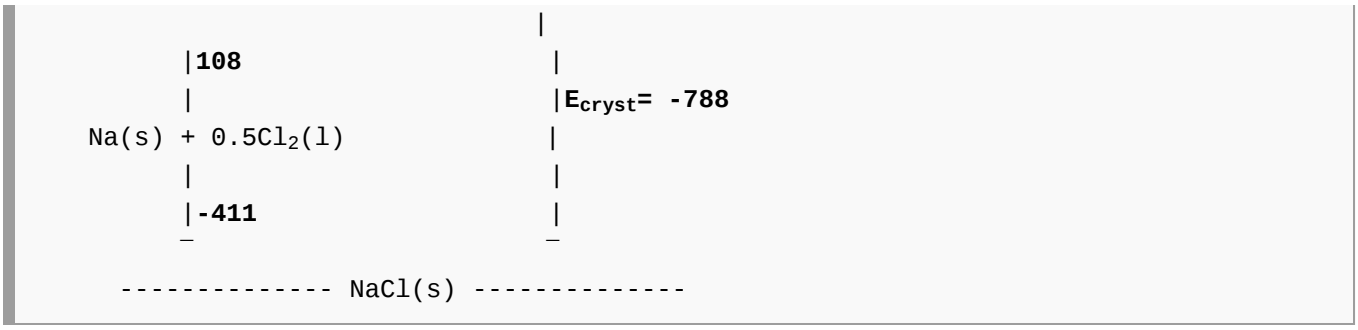
How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:





E_{cryst} = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

Discussion

The value calculated for *U* depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

Na(s) + 0.5 Cl_2(l) ® NaCl(s)	- 411	H_f
Na(g) ® Na(s)	- 108	-H_{sub}
Na^+(g) + e ® Na(g)	- 496	-*IP*
Cl(g) ® 0.5 Cl_2(g)	- 0.5 * 244	-0.5**D*
Cl^-(g) ® Cl(g) + 2 e	349	-*EA*
Add all the above equations leading to		
Na^+(g) + Cl^-(g) ® NaCl(s)	-788 kJ/mol = E_{cryst}	

Lattice Energy is Related to Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulson from ions of opposite charge and ions of the same charge.

As an example, let us consider the the NaCl crystal. In the following discussion, assume *r* be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance 1*r*, 12 Na^+ ions at a distance 2*r*, 8 Cl^- at 3*r*, 6 Na^+ at 4*r*, 24 Na^+ at 5*r*, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \qquad (7.1.6.1.2)$$

The Madelung constant, M, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \qquad (7.1.6.1.3)$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron (1.6022×10^{-19} C),
- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 7.1.6.1.2 : Madelung Constants

Compound	Crystal Lattice	M	A : C	Type
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
$bSiO_2$	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy E_{cryst}, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{7.1.6.1.4}$$

where *N* is the Avogadro's number (6.022x10^{-23}), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

n =	5	7	9	10	12
e.c.	He	Ne	Ar	Kr	Xe

The following values of *n* have been suggested for some common solids:

n =	5.9	8.0	8.7	9.1	9.5
e.c.	LiF	LiCl	LiBr	NaCl	NaBr

Example 7.1.6.1.1

Estimate the energy of crystallization for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by Equation 7.1.6.1.4

$$E_crust = \frac{(6.022\times10^{23}/mol(1.6022\times10^{-19})^2(1.747558)}{4\pi\,(8.854\times10^{-12}C^2/m)(282\times10^{-12}\ m}\left(1-\frac{1}{9.1}\right)$$
$$= -766kJ/mol$$

Discussion

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

Exercise 7.1.6.1.1

Which one of the following has the largest lattice energy? LiF, NaF, CaF_2, AlF_3

Answer

Skill: Explain the trend of lattice energy.

Exercise 7.1.6.1.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, Al_2O_3

Answer

Corrundum Al_2O_3 has some covalent character in the solid as well as the higher charge of the ions.

Exercise 7.1.6.1.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, E_{cryst} for CaO.

Answer

Energy of crystallization is -3527 kJ/mol

Skill: Evaluate the lattice energy and know what values are needed.

Exercise 7.1.6.1.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl (r = 282 pm), and assume the structure to be of the fluorite type (M = 2.512). Evaluate the energy of crystallization, E_{cryst} .

Answer

-515 kJ/mol

Discussion: This number has not been checked. If you get a different value, please let me know.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

7.1.6.1: Lattice Energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Lattice Energy** is licensed CC BY-NC-SA 4.0.

7.1.6.2: Lattice Energy- The Born-Haber cycle

Ionic solids tend to be very stable compounds. The enthalpies of formation of the ionic molecules cannot alone account for this stability. These compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids.

Introduction

This module will introduce the idea of lattice energy, as well as one process that allows us to calculate it: the Born-Haber Cycle. In order to use the Born-Haber Cycle, there are several concepts that we must understand first.

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol.

Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

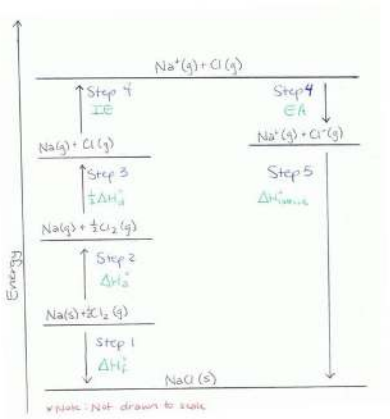
Born-Haber Cycle

There are several important concept to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.
- Sublimation energy is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.
- **Hess's Law** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

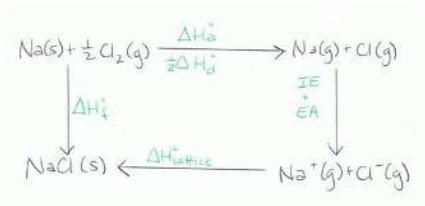
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

References

1. Cheetham, A.K. and P. Day. Solid State Chemistry. Oxford: Clarendon Press, 1992.
2. Jenkins, H. Donald B. "Thermodynamics of the Relationship between Lattice Energy and Lattice Enthalpy." Journal of Chemical Education. Vol. 82, P. 950-952. Coventry, West Midlands, UK: University of Warwick, 2005.
3. Ladd, Mark. Crystal Structures: Lattices and Solids in Stereoview. Chichester: Horwood, 1999.
4. Ladd, Mark. Chemical Bonding in Solids and Fluids. Chichester: Horwood, 1994.
5. Suzuki, Takashi. Free energy and Self-interacting Particles. Boston: Birkhauser, 2005.

Problems

1. Define lattice energy, ionization energy, and electron affinity.
2. What is Hess' Law?
3. Find the lattice energy of KF(s).
   Note: Values can be found in standard tables.
4. Find the lattice energy of $MgCl_2$(s).
5. Which one of the following has the greatest lattice energy?
   a. A) MgO
   b. B) NaC
   c. C) LiCl
   d. D) $MgCl_2$
6. Which one of the following has the greatest Lattice Energy?
   a. NaCl
   b. $CaCl_2$
   c. $AlCl_3$
   d. KCl

Solutions

1. Lattice energy: The difference in energy between the expected experimental value for the energy of the ionic solid and the actual value observed. More specifically, this is the energy gap between the energy of the separate gaseous ions and the energy of the ionic solid.
   Ionization energy: The energy change associated with the removal of an electron from a neutral atom or ion.
   Electron affinity: The release of energy associated with the addition of an electron to a neutral atom or ion.
2. Hess' Law states that the overall energy of a reaction may be determined by breaking down the process into several steps, then adding together the changes in energy of each step.
3. Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**
4. Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**
5. MgO. It has ions with the largest charge.
6. $AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

References

1. Ralph, William, F.Geoffrey, and Jeffry. General Chemistry. Ninth ed. New Jersey:Pearson Education, Inc. 2007. p500;513-515.
2. Combs, Leon. "Lattice Energy". Dr. Leon L. Combs. 1999. erkki.kennesaw.edu/genchem8/ge00002.htm
3. Picture of NaCl diagram intro.chem.okstate.edu/1314f0...BornHaber2.GIF

4. Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. England: Pearson Education Limited, 2008.174-175.

7.1.6.2: Lattice Energy- The Born-Haber cycle is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

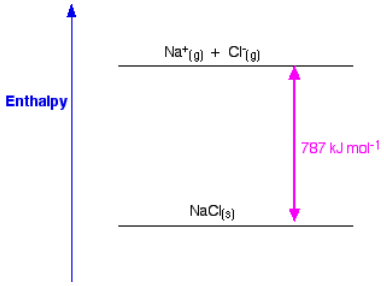
- **Lattice Energy: The Born-Haber cycle** is licensed CC BY-NC-SA 4.0.

7.1.6.3: Lattice Enthalpies and Born Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

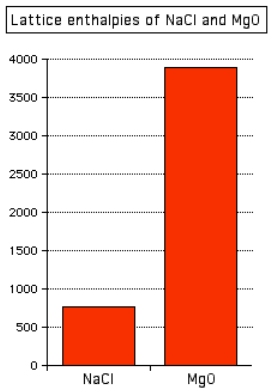
Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

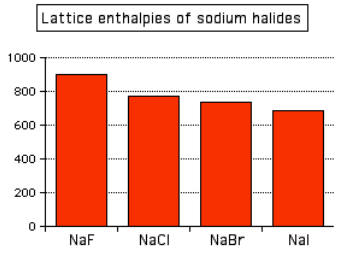


You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

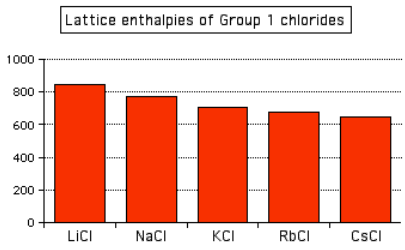
The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:



Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart shows the lattice enthalpies of the Group 1 chlorides.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change

when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\, kJ\, mol^{-1}$$

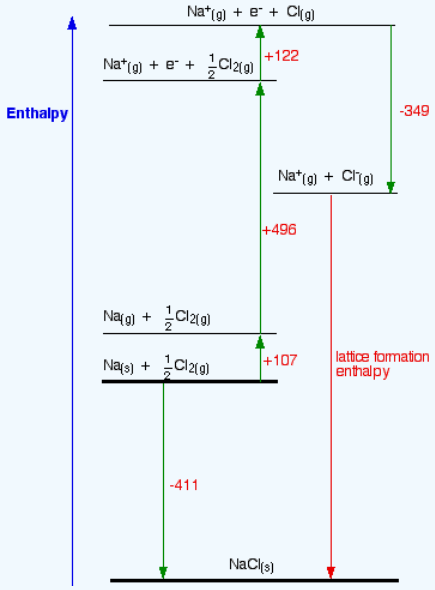
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\, kJ\, mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\, kJ\, mol^{-1}$$

Notice particularly that the "mol^{-1}" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

Example 7.1.6.3.1: Born-Haber Cycle for $NaCl$

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

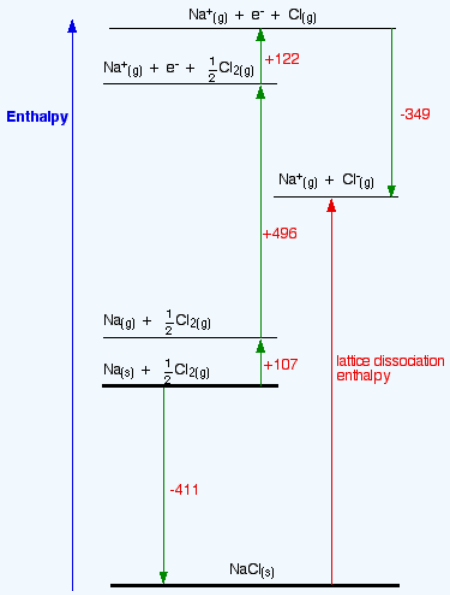
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

Theoretical Estimates of Lattice Energies

Let's assume that a compound is fully ionic. Let's also assume that the ions are point charges - in other words that the charge is concentrated at the center of the ion. By doing physics-style calculations, it is possible to calculate a theoretical value for what you

would expect the lattice energy to be. Calculations of this sort end up with values of *lattice energy*, and not *lattice enthalpy*. If you know how to do it, you can then fairly easily convert between the two.

There are several different equations, of various degrees of complication, for calculating lattice energy in this way. There are two possibilities:

- There is reasonable agreement between the experimental value (calculated from a Born-Haber cycle) and the theoretical value. Sodium chloride is a case like this - the theoretical and experimental values agree to within a few percent. That means that for sodium chloride, the assumptions about the solid being ionic are fairly good.
- The experimental and theoretical values do not agree. A commonly quoted example of this is silver chloride, AgCl. Depending on where you get your data from, the theoretical value for lattice enthalpy for AgCl is anywhere from about 50 to 150 kJ mol^{-1} less than the value that comes from a Born-Haber cycle. In other words, treating the AgCl as 100% ionic underestimates its lattice enthalpy by quite a lot.

The explanation is that silver chloride actually has a significant amount of covalent bonding between the silver and the chlorine, because there is not enough electronegativity difference between the two to allow for complete transfer of an electron from the silver to the chlorine. Comparing experimental (Born-Haber cycle) and theoretical values for lattice enthalpy is a good way of judging how purely ionic a crystal is.

Example 7.1.6.3.2: Born-Haber Cycle for $MgCl_2$

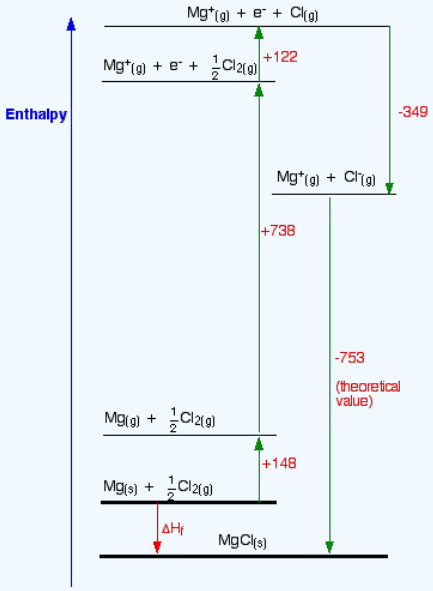
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine.

Let's look at this in terms of Born-Haber cycles of and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$Mg(s) + \frac{1}{2}Cl_2(g) \rightarrow MgCl(s)$$



Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

2. The Born-Haber cycle for $MgCl_2$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)}$$

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

$$Mg(s) + \frac{3}{2}Cl_2(g) \rightarrow MgCl_3(s)$$

So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a 3+ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.
- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of $MgCl_3$ to form!

Look carefully at the reason for this. The lattice enthalpy is the **highest** for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium.

Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so much more energy is needed to remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

Magnesium chloride is $MgCl_2$ because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 7.1.6.3: Lattice Enthalpies and Born Haber Cycles is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Lattice Enthalpies and Born Haber Cycles** by Jim Clark is licensed CC BY-NC 4.0.

7.1.6.4: The Born-Lande' equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. the first is the electrostatic potential energy:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{7.1.6.4.1}$$

with

- M_A is Avogadro's constant (6.022×10^{23})
- M is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10^{-19} C)
- Z^+ is the cation charge
- Z^- is the anion charge
- ϵ_o is the permittivity of free space

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \tag{7.1.6.4.2}$$

with

- B is the repulsion coefficient and
- n is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{7.1.6.4.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example 7.1.6.4.1

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Solution

This question requires basic knowledge of lattice energy. Since F_3 gives the compound a +3 positive charge and the Al gives the compound a -1 negative charge, the compound has large electrostatic attraction. The bigger the electrostatic attraction, the greater the lattice energy.

Example 7.1.6.4.2

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example 7.1.6.4.3

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\,x\,10^{23}}{mole}(1.6022^{-19})\times 1.747}{4\pi \times 8.85\,x\,10^{-12}\frac{c^2}{m}\times 282\,x\,10^{-12}m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
2. Cotton, F. Albert, and F. Albert Cotton. *Advanced Inorganic Chemistry.* New York: Wiley, 1999.

7.1.6.4: The Born-Lande' equation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **The Born-Lande' equation** is licensed CC BY 4.0.

SECTION OVERVIEW

7.2: Solids

Topic hierarchy

7.2.1: Crystalline and Amorphous Solids

7.2.2: Arrangement of Atoms in Crystals

7.2.3: Stucture of Simple Binary Compounds

7.2.4: Crystal Defects

7.2.5: Bonding and Properties of Solids

7.2.6: Metals and Semiconductors

7.2.7: Superconductors

7.2.8: Polymers

7.2.9: Modern Materials

7.2.10: End of Chapter Material

7.2: Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.1: Crystalline and Amorphous Solids

Learning Objective

- To know the characteristic properties of crystalline and amorphous solids.

With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the *positions* of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal latticeA regular repeating three-dimensional structure., thus producing a crystalline solidA solid with a regular repeating three-dimensional structure., or they can aggregate with no particular order, in which case they form an amorphous solidA solid with no particular structural order. (from the Greek *ámorphos*, meaning “shapeless”).

Crystalline solids, or *crystals*, have distinctive internal structures that in turn lead to distinctive flat surfaces, or *faces*. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material (see Section 8.3). The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure 8.1.1), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

Crystalline faces. *The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS_2), or at other angles, as in quartz.*

Cleavage surfaces of an amorphous solid. Obsidian, a volcanic glass with the same chemical composition as granite (typically $KAlSi_3O_8$), tends to have curved, irregular surfaces when cleaved.

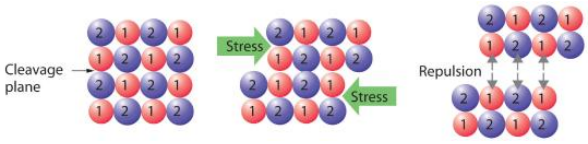
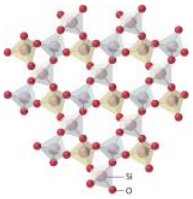


Figure 8.1.1 Cleaving a Crystal of an Ionic Compound along a Plane of Ions *Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.*

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glassAn amorphous, translucent solid. A glass is a solid that has been cooled too

quickly to form ordered crystals.. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of 4×10^{13} K/s, which prevents the atoms from arranging themselves into a regular array.



The lattice of crystalline quartz (SiO_2). *The atoms form a regular arrangement in a structure that consists of linked tetrahedra.*

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Note the Pattern

Crystals have sharp, well-defined melting points; amorphous solids do not.

Summary

Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a **crystal lattice**), which results in a **crystalline solid**, or more or less randomly to produce an **amorphous solid**. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

Key Takeaway

- Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays.

Conceptual Problems

1. Compare the solid and liquid states in terms of
    1. rigidity of structure.
    2. long-range order.
    3. short-range order.
2. How do amorphous solids differ from crystalline solids in each characteristic? Which of the two types of solid is most similar to a liquid?
    1. rigidity of structure
    2. long-range order
    3. short-range order
3. Why is the arrangement of the constituent atoms or molecules more important in determining the properties of a solid than a liquid or a gas?
4. Why are the structures of solids usually described in terms of the positions of the constituent atoms rather than their motion?

5. What physical characteristics distinguish a crystalline solid from an amorphous solid? Describe at least two ways to determine experimentally whether a material is crystalline or amorphous.
6. Explain why each characteristic would or would not favor the formation of an amorphous solid.
    1. slow cooling of pure molten material
    2. impurities in the liquid from which the solid is formed
    3. weak intermolecular attractive forces
7. A student obtained a solid product in a laboratory synthesis. To verify the identity of the solid, she measured its melting point and found that the material melted over a 12°C range. After it had cooled, she measured the melting point of the same sample again and found that this time the solid had a sharp melting point at the temperature that is characteristic of the desired product. Why were the two melting points different? What was responsible for the change in the melting point?

Answers

1.
2.
3. The arrangement of the atoms or molecules is more important in determining the properties of a solid because of the greater persistent long-range order of solids. Gases and liquids cannot readily be described by the spatial arrangement of their components because rapid molecular motion and rearrangement defines many of the properties of liquids and gases.
4.
5.
6.
7. The initial solid contained the desired compound in an amorphous state, as indicated by the wide temperature range over which melting occurred. Slow cooling of the liquid caused it to crystallize, as evidenced by the sharp second melting point observed at the expected temperature.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

7.2.1: Crystalline and Amorphous Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.2: Arrangement of Atoms in Crystals

Learning Objective

- To recognize the unit cell of a crystalline solid.
- To calculate the density of a solid given its unit cell.

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a **crystal lattice**), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cellThe smallest repeating unit of a crystal lattice.. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure 8.2.1. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in part (d) in Figure 8.2.1 is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure 8.2.2 .

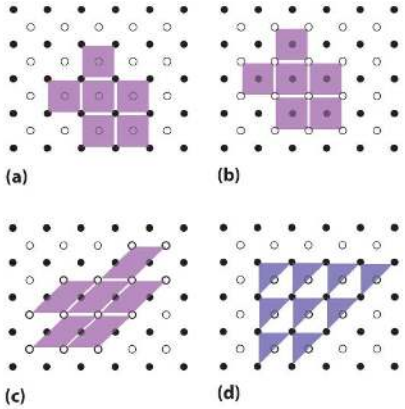


Figure 8.2.1 Unit Cells in Two Dimensions *(a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.*

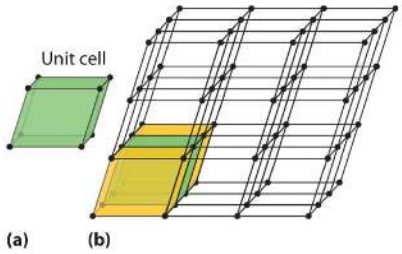


Figure 8.2.2 Unit Cells in Three Dimensions *These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice.*

The Unit Cell

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure 8.2.3). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in which all sides have the same length and all angles are 90°, but the concepts that we introduce also apply to substances whose unit cells are not cubic.

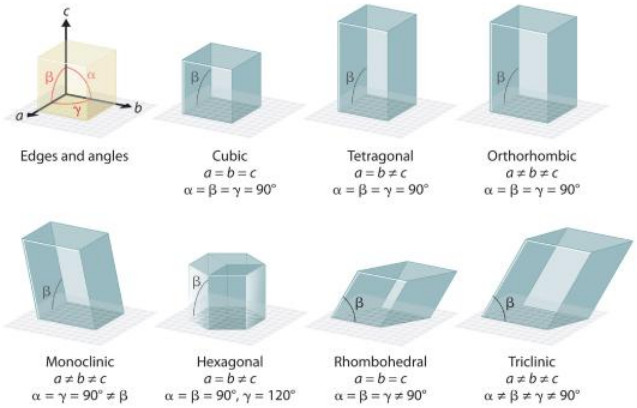


Figure 8.2.3 The General Features of the Seven Basic Unit Cells *The lengths of the edges of the unit cells are indicated by a, b, and c, and the angles are defined as follows: α, the angle between b and c; β, the angle between a and c; and γ, the angle between a and b.*

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubicA cubic unit cell that consists of eight component atoms, molecules, or ions located at the corners of a cube. (part (a) in Figure 8.2.4). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc)A cubic unit cell with eight component atoms, molecules, or ions located at the corners of a cube plus an identical component in the center of the cube. (part (b) in Figure 8.2.4). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc)A cubic unit cell with eight component atoms, molecules, or ions located at the corners of a cube plus an identical component in the center of each face of the cube. (part (c) in Figure 8.2.4).

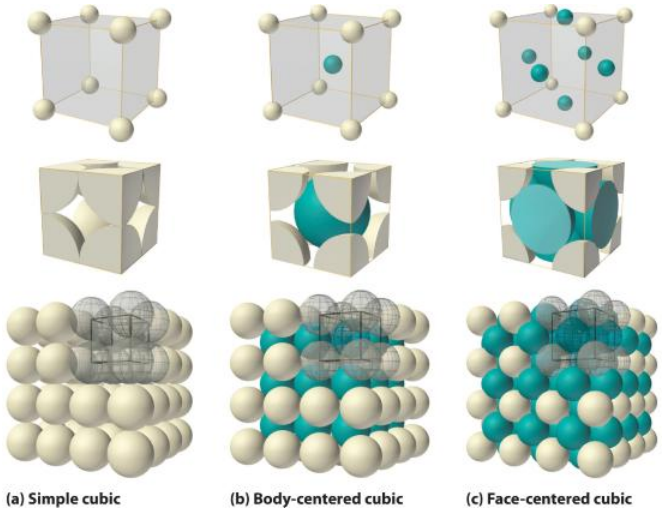


Figure 8.2.4 The Three Kinds of Cubic Unit Cell *For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells.*

As indicated in Figure 8.2.4, a solid consists of a large number of unit cells arrayed in three dimensions. Any intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because **density** is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 8.2.4. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as 1/2 atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes 1/4 atom to each. An atom at a corner of a unit cell is shared by all eight adjacent unit cells and therefore contributes 1/8 atom to each.The statement that atoms lying on an edge or a corner of a unit cell count as 1/4 or 1/8 atom per unit cell, respectively, is true for all unit cells *except* the hexagonal one, in which three unit cells share each vertical edge and six share each

corner (Figure 8.2.3), leading to values of 1/3 and 1/6 atom per unit cell, respectively, for atoms in these positions. In contrast, atoms that lie entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

Note the Pattern

For all unit cells except hexagonal, atoms on the faces contribute 1/2 atom to each unit cell, atoms on the edges contribute 1/4 atom to each unit cell, and atoms on the corners contribute 1/8 atom to each unit cell.

Example 8.2.1

Metallic gold has a face-centered cubic unit cell (part (c) in Figure 8.2.4). How many Au atoms are in each unit cell?

Given: unit cell

Asked for: number of atoms per unit cell

Strategy:

Using Figure 8.2.4 , identify the positions of the Au atoms in a face-centered cubic unit cell and then determine how much each Au atom contributes to the unit cell. Add the contributions of all the Au atoms to obtain the total number of Au atoms in a unit cell.

Solution:

As shown in Figure 8.2.4, a face-centered cubic unit cell has eight atoms at the corners of the cube and six atoms on the faces. Because atoms on a face are shared by two unit cells, each counts as 1/2 atom per unit cell, giving 6 x 1/2 =3 Au atoms per unit cell. Atoms on a corner are shared by eight unit cells and hence contribute only 1/8 atom per unit cell, giving 8 x 1/8 = 1Au atom per unit cell. The total number of Au atoms in each unit cell is thus 3 + 1 = 4.

Exercise

Metallic iron has a body-centered cubic unit cell (part (b) in Figure 8.2.4). How many Fe atoms are in each unit cell?

Answer: two

Now that we know how to count atoms in unit cells, we can use unit cells to calculate the densities of simple compounds. Note, however, that we are assuming a solid consists of a perfect regular array of unit cells, whereas real substances contain impurities and defects that affect many of their bulk properties, including density. Consequently, the results of our calculations will be close but not necessarily identical to the experimentally obtained values.

Example 8.2.2

Calculate the density of metallic iron, which has a body-centered cubic unit cell (part (b) in Figure 8.2.4) with an edge length of 286.6 pm.

Given: unit cell and edge length

Asked for: density

Strategy:

A. Determine the number of iron atoms per unit cell.
B. Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro's number. Then divide the mass by the volume of the cell.

Solution:

A We know from Example 1 that each unit cell of metallic iron contains two Fe atoms.

B The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro's number and then divide the mass by the volume of the cell (making sure to use suitable units to get density in g/cm^3):

$$mass\ of\ Fe = \left(2\ \cancel{atoms}\ Fe\right)\left(\frac{1\ \cancel{mol}}{6.022\times10^{23}\ \cancel{atoms}}\right)\left(\frac{55.85\ g}{\cancel{mol}}\right) = 1.855\times10^{-22}\ g \qquad (7.2.2.1)$$

$$volume = \left[(286.6\ pm)\left(\frac{10^{-12}\ \cancel{m}}{\cancel{pm}}\right)\left(\frac{10^{2}\ cm}{\cancel{m}}\right)\right] = 2.345 \times 10^{-23}\ cm^3 \tag{7.2.2.2}$$

$$density = \frac{1.855 \times 10^{-22}\ g}{2.345 \times 10^{-23}\ cm^3} = 7.880 g/cm^3 \tag{7.2.2.3}$$

This result compares well with the tabulated experimental value of 7.874 g/cm^3.

Exercise

Calculate the density of gold, which has a face-centered cubic unit cell (part (c) in Figure 8.2.4) with an edge length of 407.8 pm.

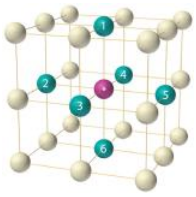
Answer: 19.29 g/cm^3

Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in part (a) in Figure 8.2.4 . Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa.



The arrangement of atoms in a simple cubic unit cell. *Each atom in the lattice has six nearest neighbors in an octahedral arrangement.*

Body-Centered Cubic Structure

The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in part (b) in Figure 8.2.4, the body-centered cubic structure consists of a single layer of spheres in contact with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped “holes” above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in part (a) in Figure 8.2.5 . Each sphere is surrounded by six others in the same plane to produce a hexagonal arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be divided into two sets, labeled B and C in part (a) in Figure 8.2.5. Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

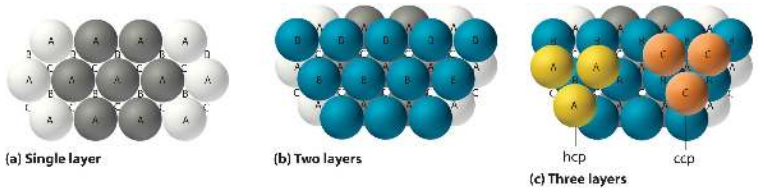


Figure 8.2.5 Close-Packed Layers of Spheres *(a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms at A positions in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure.*

If we place the second layer of spheres at the B positions in part (a) in Figure 8.2.5, we obtain the two-layered structure shown in part (b) in Figure 8.2.5. There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did *not* use for the atoms in the first or second layers (part (c) in Figure 8.2.5). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB…, resulting in a hexagonal close-packed (hcp) structureOne of two variants of the close-packed arrangement—the most efficient way to pack spheres in a lattice—in which the atomic positions alternate from layer to layer in an ABABAB… pattern. (part (a) in Figure 8.2.6). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC…, giving a cubic close-packed (ccp) structureOne of two variants of the close-packed arrangement—the most efficient way to pack spheres in a lattice—in which the atomic positions alter from layer to layer in an ABCABC… pattern. (part (b) in Figure 8.2.6). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in part (b) in Figure 8.2.6, however, simply rotating the structure reveals its cubic nature, which is identical to a fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

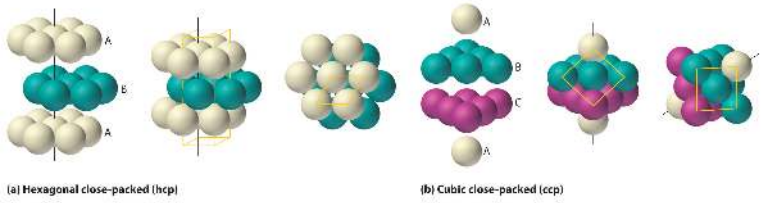


Figure 8.2.6 Close-Packed Structures: hcp and ccp *The illustrations in (a) show an exploded view, a side view, and a top view of the hcp structure. The simple hexagonal unit cell is outlined in the side and top views. Note the similarity to the hexagonal unit cell shown in Figure 8.2.3. The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.*

Table 8.2.1 compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination numberThe number of nearest neighbors in a solid structure.. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

Table 8.2.1 Properties of the Common Structures of Metals

Structure	Percentage of Space Occupied by Atoms	Coordination Number
simple cubic	52	6
body-centered cubic	68	8
hexagonal close packed	74	12

Structure	Percentage of Space Occupied by Atoms	Coordination Number
cubic close packed (identical to face-centered cubic)	74	12

Summary

The smallest repeating unit of a crystal lattice is the **unit cell**. The **simple cubic** unit cell contains only eight atoms, molecules, or ions at the corners of a cube. A **body-centered cubic (bcc)** unit cell contains one additional component in the center of the cube. A **face-centered cubic (fcc)** unit cell contains a component in the center of each face in addition to those at the corners of the cube. Simple cubic and bcc arrangements fill only 52% and 68% of the available space with atoms, respectively. The **hexagonal close-packed (hcp) structure** has an ABABAB… repeating arrangement, and the **cubic close-packed (ccp) structure** has an ABCABC… repeating pattern; the latter is identical to an fcc lattice. The hcp and ccp arrangements fill 74% of the available space and have a **coordination number** of 12 for each atom in the lattice, the number of nearest neighbors. The simple cubic and bcc lattices have coordination numbers of 6 and 8, respectively.

Key Takeaway

- A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure.

Conceptual Problems

1. Why is it valid to represent the structure of a crystalline solid by the structure of its unit cell? What are the most important constraints in selecting a unit cell?
2. All unit cell structures have six sides. Can crystals of a solid have more than six sides? Explain your answer.
3. Explain how the intensive properties of a material are reflected in the unit cell. Are all the properties of a bulk material the same as those of its unit cell? Explain your answer.
4. The experimentally measured density of a bulk material is slightly *higher* than expected based on the structure of the pure material. Propose two explanations for this observation.
5. The experimentally determined density of a material is *lower* than expected based on the arrangement of the atoms in the unit cell, the formula mass, and the size of the atoms. What conclusion(s) can you draw about the material?
6. Only one element (polonium) crystallizes with a simple cubic unit cell. Why is polonium the only example of an element with this structure?
7. What is meant by the term *coordination number* in the structure of a solid? How does the coordination number depend on the structure of the metal?
8. Arrange the three types of cubic unit cells in order of increasing packing efficiency. What is the difference in packing efficiency between the hcp structure and the ccp structure?
9. The structures of many metals depend on pressure and temperature. Which structure—bcc or hcp—would be more likely in a given metal at very high pressures? Explain your reasoning.
10. A metal has two crystalline phases. The *transition temperature*, the temperature at which one phase is converted to the other, is 95°C at 1 atm and 135°C at 1000 atm. Sketch a phase diagram for this substance. The metal is known to have either a ccp structure or a simple cubic structure. Label the regions in your diagram appropriately and justify your selection for the structure of each phase.

Numerical Problems

1. Metallic rhodium has an fcc unit cell. How many atoms of rhodium does each unit cell contain?
2. Chromium has a structure with two atoms per unit cell. Is the structure of this metal simple cubic, bcc, fcc, or hcp?
3. The density of nickel is 8.908 g/cm^3. If the metallic radius of nickel is 125 pm, what is the structure of metallic nickel?
4. The density of tungsten is 19.3 g/cm^3. If the metallic radius of tungsten is 139 pm, what is the structure of metallic tungsten?
5. An element has a density of 10.25 g/cm^3 and a metallic radius of 136.3 pm. The metal crystallizes in a bcc lattice. Identify the element.

6. A 21.64 g sample of a nonreactive metal is placed in a flask containing 12.00 mL of water; the final volume is 13.81 mL. If the length of the edge of the unit cell is 387 pm and the metallic radius is 137 pm, determine the packing arrangement and identify the element.
7. A sample of an alkali metal that has a bcc unit cell is found to have a mass of 1.000 g and a volume of 1.0298 cm^3. When the metal reacts with excess water, the reaction produces 539.29 mL of hydrogen gas at 0.980 atm and 23°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
8. A sample of an alkaline earth metal that has a bcc unit cell is found to have a mass 5.000 g and a volume of 1.392 cm^3. Complete reaction with chlorine gas requires 848.3 mL of chlorine gas at 1.050 atm and 25°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
9. Lithium crystallizes in a bcc structure with an edge length of 3.509 Å. Calculate its density. What is the approximate metallic radius of lithium in picometers?
10. Vanadium is used in the manufacture of rust-resistant vanadium steel. It forms bcc crystals with a density of 6.11 g/cm^3 at 18.7°C. What is the length of the edge of the unit cell? What is the approximate metallic radius of the vanadium in picometers?
11. A simple cubic cell contains one metal atom with a metallic radius of 100 pm.
    1. Determine the volume of the atom(s) contained in one unit cell [the volume of a sphere = 4/3 $\pi $ r^3
    2. What is the length of one edge of the unit cell? (Hint: there is no empty space between atoms.)
    3. Calculate the volume of the unit cell.
    4. Determine the packing efficiency for this structure.
    5. Use the steps in Problem 11 to calculate the packing efficiency for a bcc unit cell with a metallic radius of 1.00 Å.

Answers

1. four
2.
3. fcc
4.
5. molybdenum
6.
7. sodium, unit cell edge = 428 pm, r = 185 pm
8.
9. d = 0.5335 g/cm^3, r =151.9 pm
10.
11.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

7.2.2: Arrangement of Atoms in Crystals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.3: Stucture of Simple Binary Compounds

Learning Objective

- To use the cation:anion radius ratio to predict the structures of simple binary compounds.
- To understand how x-rays are diffracted by crystalline solids.

The structures of most binary compounds can be described using the packing schemes we have just discussed for metals. To do so, we generally focus on the arrangement in space of the largest species present. In ionic solids, this generally means the anions, which are usually arranged in a simple cubic, bcc, fcc, or hcp lattice. Often, however, the anion lattices are not truly “close packed”; because the cations are large enough to prop them apart somewhat, the anions are not actually in contact with one another. In ionic compounds, the cations usually occupy the “holes” between the anions, thus balancing the negative charge. The ratio of cations to anions within a unit cell is required to achieve electrical neutrality and corresponds to the bulk stoichiometry of the compound.

Common Structures of Binary Compounds

As shown in part (a) in Figure 8.3.1, a simple cubic lattice of anions contains only one kind of hole, located in the center of the unit cell. Because this hole is equidistant from all eight atoms at the corners of the unit cell, it is called a cubic holeThe hole located at the center of the simple cubic lattice. The hole is equidistant from all eight atoms or ions at the corners of the unit cell. An atom or ion in a cubic hole has a coordination number of 8.. An atom or ion in a cubic hole therefore has a coordination number of 8. Many ionic compounds with relatively large cations and a 1:1 cation:anion ratio have this structure, which is called the cesium chloride structureThe unit cell for many ionic compounds with relatively large cations and a 1:1 cation:anion ratio. (Figure 8.3.2) because CsCl is a common example.Solid-state chemists tend to describe the structures of new compounds in terms of the structure of a well-known reference compound. Hence you will often read statements such as “Compound X possesses the cesium chloride (or sodium chloride, etc.) structure” to describe the structure of compound X. Notice in Figure 8.3.2 that the z = 0 and the z = 1.0 planes are always the same. This is because the z = 1.0 plane of one unit cell becomes the z = 0 plane of the succeeding one. The unit cell in CsCl contains a single Cs^+ ion as well as $8\times1/8$ Cl^-=1 Cl^- ion, for an overall stoichiometry of CsCl. The cesium chloride structure is most common for ionic substances with relatively large cations, in which the ratio of the radius of the cation to the radius of the anion is in the range shown in Table 8.3.1 .

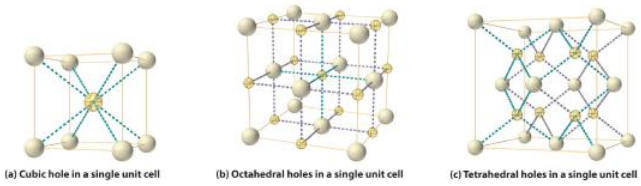


Figure 8.3.1 Holes in Cubic Lattices *The three illustrations show (a) the cubic hole that is in the center of a simple cubic lattice of anions, (b) the locations of the octahedral holes in a face-centered cubic lattice of anions, and (c) the locations of the tetrahedral holes in a face-centered cubic lattice of anions.*

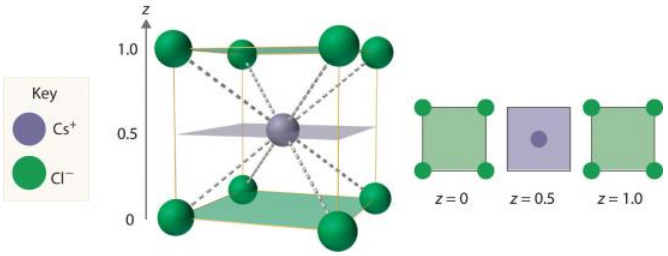


Figure 8.3.2 The Cesium Chloride Structure *The Cs^+ ion occupies the cubic hole in the center of a cube of Cl^- ions. The drawings at the right are horizontal cross-sections through the unit cell at the bottom (z = 0) and halfway between the bottom and top (z = 0.5). A top cross-section (z = 1) is identical to z = 0. Such cross-sections often help us visualize the arrangement of atoms or ions in the unit cell more easily.*

Table 8.3.2 Relationship between the Cation:Anion Radius Ratio and the Site Occupied by the Cations

Approximate Range of Cation:Anion Radius Ratio	Hole Occupied by Cation	Cation Coordination Number
0.225–0.414	tetrahedral	4
0.414–0.732	octahedral	6
0.732–1.000	cubic	8

Note the Pattern

Very large cations occupy cubic holes, cations of intermediate size occupy octahedral holes, and small cations occupy tetrahedral holes in the anion lattice.

In contrast, a face-centered cubic (fcc) array of atoms or anions contains two types of holes: octahedral holesOne of two kinds of holes in a face-centered cubic array of atoms or ions (the other is a tetrahedral hole). One octahedral hole is located in the center of the face-centered cubic unit cell, and there is a shared one in the middle of each edge. An atom or ion in an octahedral hole has a coordination number of 6., one in the center of the unit cell plus a shared one in the middle of each edge (part (b) in Figure 8.3.1, and tetrahedral holesOne of two kinds of holes in a face-centered cubic array of atoms or ions (the other is an octahedral hole). Tetrahedral holes are located between an atom at a corner and the three atoms at the centers of the adjacent faces of the face-centered cubic unit cell. An atom or ion in a tetrahedral hole has a coordination number of 4., located between an atom at a corner and the three atoms at the centers of the adjacent faces (part (c) in Figure 8.3.1). As shown in Table 8.3.1, the ratio of the radius of the cation to the radius of the anion is the most important determinant of whether cations occupy the cubic holes in a cubic anion lattice or the octahedral or tetrahedral holes in an fcc lattice of anions. Very large cations occupy cubic holes in a cubic anion lattice, cations of intermediate size tend to occupy the octahedral holes in an fcc anion lattice, and relatively small cations tend to occupy the tetrahedral holes in an fcc anion lattice. In general, larger cations have higher coordination numbers than small cations.

The most common structure based on a fcc lattice is the sodium chloride structureThe solid structure that results when the octahedral holes of an fcc lattice of anions are filled with cations. (Figure 8.3.3), which contains an fcc array of Cl^- ions with Na^+ ions in all the octahedral holes. We can understand the sodium chloride structure by recognizing that filling all the octahedral holes in an fcc lattice of Cl^- ions with Na^+ ions gives a total of 4 Cl^- ions (one on each face gives 6×/1=3 plus one on each corner gives 8×1/8=1, for a total of 4) and 4 Na^+ ions (one on each edge gives 11×1/4=3 plus one in the middle, for a total of 4). The result is an electrically neutral unit cell and a stoichiometry of NaCl. As shown in Figure 8.3.3, the Na^+ ions in the sodium chloride structure also form an fcc lattice. The sodium chloride structure is favored for substances with two atoms or ions in a 1:1 ratio and in which the ratio of the radius of the cation to the radius of the anion is between 0.414 and 0.732. It is observed in many compounds, including MgO and TiC.

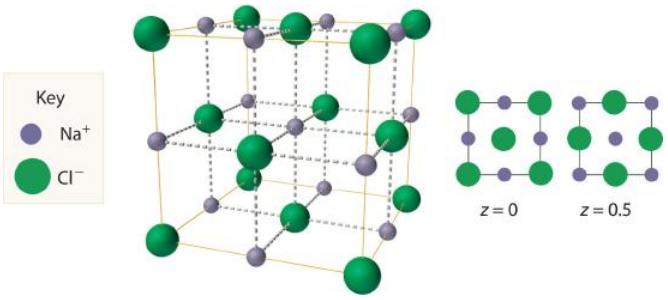


Figure 8.3.3 The Sodium Chloride Structure *In NaCl, the Na^+ ions occupy the octahedral holes in an fcc lattice of Cl^- ions, resulting in an fcc array of Na^+ ions as well.*

The structure shown in Figure 8.3.4 is called the zinc blende structureThe solid structure that results when half of the tetrahedral holes in an fcc lattice of anions are filled with cations with a 1:1 cation:anion ratio and a coordination number of 4., from the common name of the mineral ZnS. It results when the cation in a substance with a 1:1 cation:anion ratio is much smaller than the anion (if the cation:anion radius ratio is less than about 0.414). For example, ZnS contains an fcc lattice of S^{2-} ions, and the cation:anion radius ratio is only about 0.40, so we predict that the cation would occupy either a tetrahedral hole or an octahedral hole. In fact, the relatively small Zn^{2+} cations occupy the tetrahedral holes in the lattice. If all 8 tetrahedral holes in the unit cell were occupied by Zn^{2+} ions, however, the unit cell would contain 4 S^{2-} and 8 Zn^{2+} ions, giving a formula of Zn_2S and a net charge of +4 per unit cell. Consequently, the Zn^{2+} ions occupy *every other* tetrahedral hole, as shown in Figure 8.3.4, giving a total of 4

Zn^{2+} and 4 S^{2-} ions per unit cell and a formula of ZnS. The zinc blende structure results in a coordination number of 4 for each Zn^{2+} ion and a tetrahedral arrangement of the four S^{2-} ions around each Zn^{2+} ion.

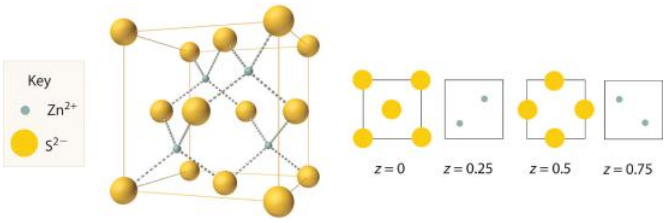


Figure 8.3.4 The Zinc Blende Structure *Zn^{2+} ions occupy every other tetrahedral hole in the fcc array of S^{2-} ions. Each Zn^{2+} ion is surrounded by four S^{2-} ions in a tetrahedral arrangement.*

Example 8.3.1

1. If all the tetrahedral holes in an fcc lattice of anions are occupied by cations, what is the stoichiometry of the resulting compound?
2. Use the ionic radii given in Figure 3.2.7 to identify a plausible oxygen-containing compound with this stoichiometry and structure.

Given: lattice, occupancy of tetrahedral holes, and ionic radii

Asked for: stoichiometry and identity

Strategy:

A Use Figure 8.3.1 to determine the number and location of the tetrahedral holes in an fcc unit cell of anions and place a cation in each.

B Determine the total number of cations and anions in the unit cell; their ratio is the stoichiometry of the compound.

C From the stoichiometry, suggest reasonable charges for the cation and the anion. Use the data in Figure 3.2.7 to identify a cation–anion combination that has a cation:anion radius ratio within a reasonable range.

Solution:

1. **A** Figure 8.3.1 shows that the tetrahedral holes in an fcc unit cell of anions are located entirely within the unit cell, for a total of eight (one near each corner). **B** Because the tetrahedral holes are located entirely within the unit cell, there are eight cations per unit cell. We calculated previously that an fcc unit cell of anions contains a total of four anions per unit cell. The stoichiometry of the compound is therefore M_8Y_4 or, reduced to the smallest whole numbers, M_2Y.
2. **C** The M_2Y stoichiometry is consistent with a lattice composed of M^+ ions and Y^{2-} ions. If the anion is O^{2-} (ionic radius 140 pm), we need a monocation with a radius no larger than about 140 × 0.414 = 58 pm to fit into the tetrahedral holes. According to Figure 3.1.7, none of the monocations has such a small radius; therefore, the most likely possibility is Li^+ at 76 pm. Thus we expect Li_2O to have a structure that is an fcc array of O^{2-} anions with Li^+ cations in all the tetrahedral holes.

Exercise

If only half the octahedral holes in an fcc lattice of anions are filled by cations, what is the stoichiometry of the resulting compound?

Answer: MX_2; an example of such a compound is cadmium chloride ($CdCl_2$), in which the empty cation sites form planes running through the crystal.

We examine only one other structure of the many that are known, the perovskite structureA structure that consists of a bcc array of two metal ions, with one set (M) located at the corners of the cube, and the other set (M′) in the centers of the cube.. *Perovskite* is the generic name for oxides with two different kinds of metal and have the general formula $MM'O_3$, such as $CaTiO_3$. The structure is a body-centered cubic (bcc) array of two metal ions, with one M (Ca in this case) located at the corners of the cube, and the other M′ (in this case Ti) in the centers of the cube. The oxides are in the centers of the square faces (part (a) in Figure 8.3.5). The stoichiometry predicted from the unit cell shown in part (a) in Figure 8.3.5 agrees with the general formula; each unit cell contains 8×18=1 Ca, 1 Ti, and 6×1/2=3 O atoms. The Ti and Ca atoms have coordination numbers of 6 and 12, respectively. We will return to the perovskite structure when we discuss high-temperature superconductors in Section 8.7.

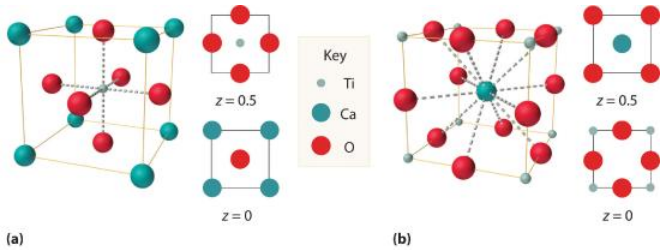


Figure 8.3.5 The Perovskite Structure of $CaTiO_3$ *Two equivalent views are shown: (a) a view with the Ti atom at the center and (b) an alternative view with the Ca atom at the center.*

X-Ray Diffraction

The wavelengths of x-rays are approximately the same magnitude as the distances between atoms in molecules or ions. Consequently, x-rays are a useful tool for obtaining information about the structures of crystalline substances. In a technique called x-ray diffractionAn technique used to obtain information about the structures of crystalline substances by using x-rays., a beam of x-rays is aimed at a sample of a crystalline material, and the x-rays are diffracted by layers of atoms in the crystalline lattice (part (a) in Figure 8.3.6). When the beam strikes photographic film, it produces an x-ray diffraction pattern, which consists of dark spots on a light background (part (b) in Figure 8.3.6). In 1912, the German physicist Max von Laue (1879–1960; Nobel Prize in Physics, 1914) predicted that x-rays should be diffracted by crystals, and his prediction was rapidly confirmed. Within a year, two British physicists, William Henry Bragg (1862–1942) and his son, William Lawrence Bragg (1890–1972), had worked out the mathematics that allows x-ray diffraction to be used to measure interatomic distances in crystals. The Braggs shared the Nobel Prize in Physics in 1915, when the son was only 25 years old. Virtually everything we know today about the detailed structures of solids and molecules in solids is due to the x-ray diffraction technique.

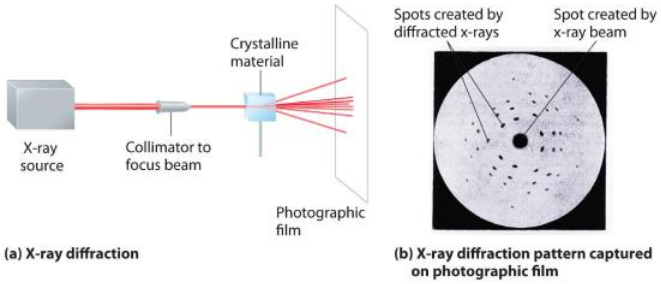


Figure 8.3.6 X-Ray Diffraction *These illustrations show (a) a schematic drawing of x-ray diffraction and (b) the x-ray diffraction pattern of a zinc blende crystalline solid captured on photographic film.*

Recall from Section 2. 2 that two waves that are in phase interfere constructively, thus reinforcing each other and generating a wave with a greater amplitude. In contrast, two waves that are out of phase interfere destructively, effectively canceling each other. When x-rays interact with the components of a crystalline lattice, they are scattered by the electron clouds associated with each atom. As shown in Figure 8.2.4, Figure 8.2.6 , and Figure 8.3.1, the atoms in crystalline solids are typically arranged in planes. Figure 8.3.7 illustrates how two adjacent planes of atoms can scatter x-rays in a way that results in constructive interference. If two x-rays that are initially in phase are diffracted by two planes of atoms separated by a distance *d*, the lower beam travels the extra distance indicated by the lines *BC* and *CD*. The *angle of incidence*, designated as θ, is the angle between the x-ray beam and the planes in the crystal. Because $BC = CD = d \sin \theta$, the extra distance that the lower beam in Figure 8.3.7 must travel compared with the upper beam is $2d \sin \theta$. For these two x-rays to arrive at a detector in phase, the extra distance traveled must be an integral multiple *n* of the wavelength λ:

$$2d\sin\theta = n\lambda \tag{8.3.1}$$

Equation 8.3.1 is the Bragg equationThe equation that describes the relationship between two x-ray beams diffracted from different planes of atoms: $2d \sin\theta = n\lambda$. The structures of crystalline substances with both small molecules and ions or very large biological molecules, with molecular masses in excess of 100,000 amu, can now be determined accurately and routinely using x-ray diffraction and the Bragg equation. Example 4 illustrates how to use the Bragg equation to calculate the distance between planes of atoms in crystals.

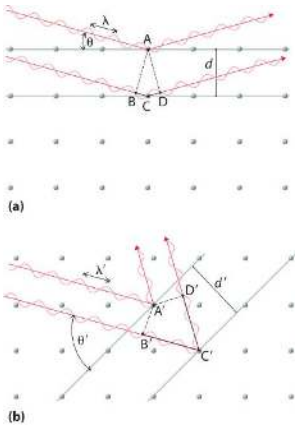


Figure 8.3.7 The Reflection of X-Rays from Two Adjacent Planes of Atoms Can Result in Constructive Interference of the X-Rays *(a) The x-ray diffracted by the lower layer of atoms must travel a distance that is longer by 2d sin θ than the distance traveled by the x-ray diffracted by the upper layer of atoms. Only if this distance (BC plus CD) equals an integral number of wavelengths of the x-rays (i.e., only if λ = 2d sin θ) will the x-rays arrive at the detector in phase. (b) In a solid, many different sets of planes of atoms can diffract x-rays. Each has a different interplanar distance and therefore diffracts the x-rays at a different angle θ, which produces a characteristic pattern of spots.*

Example 8.3.2

X-rays from a copper x-ray tube (λ = 1.54062 Å or 154.062 pm)In x-ray diffraction, the angstrom (Å) is generally used as the unit of wavelength. are diffracted at an angle of 10.89° from a sample of crystalline gold. Assuming that *n* = 1, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to four significant figures.

Given: wavelength, diffraction angle, and number of wavelengths

Asked for: distance between planes

Strategy:

Substitute the given values into the Bragg equation and solve to obtain the distance between planes.

Solution:

We are given *n*, θ, and λ and asked to solve for *d*, so this is a straightforward application of the Bragg equation. For an answer in angstroms, we do not even have to convert units. Solving the Bragg equation for *d* gives

$$d = \frac{n\lambda}{2\ sin\theta} \tag{7.2.3.1}$$

and substituting values gives

$$d = \frac{1 \times 1.54062\ \text{Å}}{2\ sin\ 10.89^{\ o}} = 4.077\ \text{Å} = 407.4\ pm \tag{7.2.3.2}$$

This value corresponds to the edge length of the fcc unit cell of elemental gold.

Exercise

X-rays from a molybdenum x-ray tube (λ = 0.709300 Å) are diffracted at an angle of 7.11° from a sample of metallic iron. Assuming that *n* = 1, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to three significant figures.

Answer: 2.87 Å or 287 pm (corresponding to the edge length of the bcc unit cell of elemental iron)

Summary

The structures of most binary compounds are dictated by the packing arrangement of the largest species present (the anions), with the smaller species (the cations) occupying appropriately sized holes in the anion lattice. A simple cubic lattice of anions contains a single **cubic hole** in the center of the unit cell. Placing a cation in the cubic hole results in the **cesium chloride structure**, with a

1:1 cation:anion ratio and a coordination number of 8 for both the cation and the anion. An fcc array of atoms or ions contains both **octahedral holes** and **tetrahedral holes**. If the octahedral holes in an fcc lattice of anions are filled with cations, the result is a **sodium chloride structure**. It also has a 1:1 cation:anion ratio, and each ion has a coordination number of 6. Occupation of half the tetrahedral holes by cations results in the **zinc blende structure**, with a 1:1 cation:anion ratio and a coordination number of 4 for the cations. More complex structures are possible if there are more than two kinds of atoms in a solid. One example is the **perovskite structure**, in which the two metal ions form an alternating bcc array with the anions in the centers of the square faces. Because the wavelength of x-ray radiation is comparable to the interatomic distances in most solids, **x-ray diffraction** can be used to provide information about the structures of crystalline solids. X-rays diffracted from different planes of atoms in a solid reinforce one another if they are in phase, which occurs only if the extra distance they travel corresponds to an integral number of wavelengths. This relationship is described by the **Bragg equation**: $2d \sin \theta = n\lambda$.

Key Takeaway

- The ratio of cations to anions within a unit cell produces electrical neutrality and corresponds to the bulk stoichiometry of a compound, the structure of which can be determined using x-ray diffraction.

Key Equation

Bragg equation

Equation 8.3.1:

$$2dsin\theta = n\lambda \tag{7.2.3.3}$$

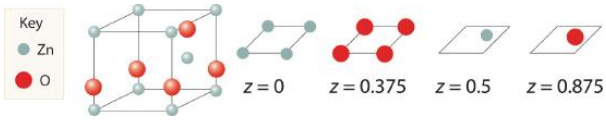
Conceptual Problems

1. Using circles or spheres, sketch a unit cell containing an octahedral hole. Which of the basic structural types possess octahedral holes? If an ion were placed in an octahedral hole, what would its coordination number be?
2. Using circles or spheres, sketch a unit cell containing a tetrahedral hole. Which of the basic structural types possess tetrahedral holes? If an ion were placed in a tetrahedral hole, what would its coordination number be?
3. How many octahedral holes are there in each unit cell of the sodium chloride structure? Potassium fluoride contains an fcc lattice of F^- ions that is identical to the arrangement of Cl^- ions in the sodium chloride structure. Do you expect K^+ ions to occupy the tetrahedral or octahedral holes in the fcc lattice of F^- ions?
4. The unit cell of cesium chloride consists of a cubic array of chloride ions with a cesium ion in the center. Why then is cesium chloride described as having a simple cubic structure rather than a bcc structure? The unit cell of iron also consists of a cubic array of iron atoms with an iron atom in the center of the cube. Is this a bcc or a simple cubic unit cell? Explain your answer.
5. Why are x-rays used to determine the structure of crystalline materials? Could gamma rays also be used to determine crystalline structures? Why or why not?
6. X-rays are higher in energy than most other forms of electromagnetic radiation, including visible light. Why can’t you use visible light to determine the structure of a crystalline material?
7. When x-rays interact with the atoms in a crystal lattice, what relationship between the distances between planes of atoms in the crystal structure and the wavelength of the x-rays results in the scattered x-rays being exactly in phase with one another? What difference in structure between amorphous materials and crystalline materials makes it difficult to determine the structures of amorphous materials by x-ray diffraction?
8. It is possible to use different x-ray sources to generate x-rays with different wavelengths. Use the Bragg equation to predict how the diffraction angle would change if a molybdenum x-ray source (x-ray wavelength = 70.93 pm) were used instead of a copper source (x-ray wavelength = 154.1 pm).
9. Based on the Bragg equation, if crystal A has larger spacing in its diffraction pattern than crystal B, what conclusion can you draw about the spacing between layers of atoms in A compared with B?

Numerical Problems

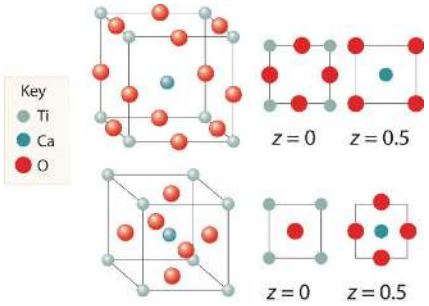
1. Thallium bromide crystallizes in the cesium chloride structure. This bcc structure contains a Tl^+ ion in the center of the cube with Br^- ions at the corners. Sketch an alternative unit cell for this compound.

2. Potassium fluoride has a lattice identical to that of sodium chloride. The potassium ions occupy octahedral holes in an fcc lattice of fluoride ions. Propose an alternative unit cell that can also represent the structure of KF.
3. Calcium fluoride is used to fluoridate drinking water to promote dental health. Crystalline CaF_2 (d = 3.1805 g/cm^3) has a structure in which calcium ions are located at each corner and the middle of each edge of the unit cell, which contains eight fluoride ions per unit cell. The length of the edge of this unit cell is 5.463 Å. Use this information to determine Avogadro's number.
4. Zinc and oxygen form a compound that is used as both a semiconductor and a paint pigment. This compound has the following structure:



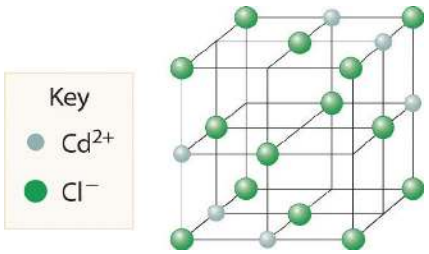
What is the empirical formula of this compound?

5. Here are two representations of the perovskite structure:



Are they identical? What is the empirical formula corresponding to each representation?

6. The salt MX_2 has a cubic close-packed (ccp) structure in which all the tetrahedral holes are filled by anions. What is the coordination number of M? of X?
7. A compound has a structure based on simple cubic packing of the anions, and the cations occupy half of the cubic holes. What is the empirical formula of this compound? What is the coordination number of the cation?
8. Barium and fluoride form a compound that crystallizes in the fluorite structure, in which the fluoride ions occupy all the tetrahedral holes in a ccp array of barium ions. This particular compound is used in embalming fluid. What is its empirical formula?
9. Cadmium chloride is used in paints as a yellow pigment. Is the following structure consistent with an empirical formula of $CdCl_2$? If not, what is the empirical formula of the structure shown?



10. Use the information in the following table to decide whether the cation will occupy a tetrahedral hole, an octahedral hole, or a cubic hole in each case.

Cation Radius (pm)	Anion Radius (pm)
78.0	132
165	133

Cation Radius (pm)	Anion Radius (pm)
81	174

11. Calculate the angle of diffraction when x-rays from a copper tube (λ = 154 pm) are diffracted by planes of atoms parallel to the faces of the cubic unit cell for Mg (260 pm), Zn (247 pm), and Ni (216 pm). The length on one edge of the unit cell is given in parentheses; assume first-order diffraction (n = 1).
12. If x-rays from a copper target (λ = 154 pm) are scattered at an angle of 17.23° by a sample of Mg, what is the distance (in picometers) between the planes responsible for this diffraction? How does this distance compare with that in a sample of Ni for which θ = 20.88°?

Answers

1.
2.
3. d = 3.1805 g/cm^3; Avogadro's number = 6.023 × 10^{23} mol^{-1}
4.
5. Both have same stoichiometry, $CaTiO_3$
6.
7. Stoichiometry is MX_2; coordination number of cations is 8
8.
9. No, the structure shown has an empirical formula of Cd_3Cl_8.
10.
11. Mg: 17.2°, Zn: 18.2°, Ni: 20.9°
12.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

7.2.3: Stucture of Simple Binary Compounds is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.4: Crystal Defects

Learning Objective

- To understand the origin and nature of defects in crystals.

The crystal lattices we have described represent an idealized, simplified system that can be used to understand many of the important principles governing the behavior of solids. In contrast, real crystals contain large numbers of defectsErrors in an idealized crystal lattice. (typically more than 10^4 per milligram), ranging from variable amounts of impurities to missing or misplaced atoms or ions. These defects occur for three main reasons:

1. It is impossible to obtain any substance in 100% pure form. Some impurities are always present.
2. Even if a substance were 100% pure, forming a perfect crystal would require cooling the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the “wrong” place in a lattice or in areas where two lattices that grew separately intersect.
3. Applying an external stress to a crystal, such as a hammer blow, can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment.

In this section, we discuss how defects determine some of the properties of solids. We begin with solids that consist of neutral atoms, specifically metals, and then turn to ionic compounds.

Defects in Metals

Metals can have various types of defects. A point defectA defect in a crystal that affects a single point in the lattice. is any defect that involves only a single particle (a lattice point) or sometimes a very small set of points. A line defectA defect in a crystal that affects a row of points in the lattice. is restricted to a row of lattice points, and a plane defectA defect in a crystal that affects a plane of points in the lattice. involves an entire plane of lattice points in a crystal. A vacancyA point defect that consists of a single atom missing from a site in a crystal. occurs where an atom is missing from the normal crystalline array; it constitutes a tiny void in the middle of a solid (Figure 8.4.1). We focus primarily on point and plane defects in our discussion because they are encountered most frequently.

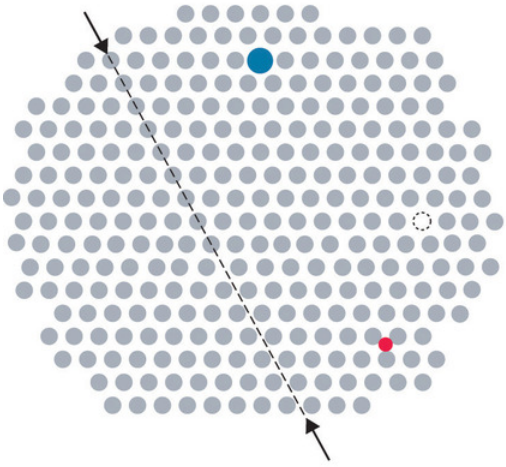


Figure 8.4.1Common Defects in Crystals *In this two-dimensional representation of a crystal lattice containing substitutional and interstitial impurities, vacancies, and line defects, a dashed line and arrows indicate the position of the line defect.*

Impurities

Impurities can be classified as interstitial or substitutional. An interstitial impurityA point defect that results when an impurity atom occupies an octahedral hole or a tetrahedral hole in the lattice between atoms. is usually a smaller atom (typically about 45% smaller than the host) that can fit into the octahedral or tetrahedral holes in the metal lattice (Figure 8.4.1). Steels consist of iron with carbon atoms added as interstitial impurities (Table 8.4.1). The inclusion of one or more transition metals or semimetals can improve the corrosion resistance of steel.

Table 8.4.1Compositions, Properties, and Uses of Some Types of Steel

Name of Steel	Typical Composition*	Properties	Applications
low-carbon	<0.15% C	soft and ductile	wire
mild carbon	0.15%–0.25% C	malleable and ductile	cables, chains, and nails
high-carbon	0.60%–1.5% C	hard and brittle	knives, cutting tools, drill bits, and springs
stainless	15%–20% Cr, 1%–5% Mn, 5%–10% Ni, 1%–3% Si, 1% C, 0.05% P	corrosion resistant	cutlery, instruments, and marine fittings
invar	36% Ni	low coefficient of thermal expansion	measuring tapes and meter sticks
manganese	10%–20% Mn	hard and wear resistant	armor plate, safes, and rails
high-speed	14%–20% W	retains hardness at high temperatures	high-speed cutting tools
silicon	1%–5% Si	hard, strong, and highly magnetic	magnets in electric motors and transformers

*In addition to enough iron to bring the total percentage up to 100%, most steels contain small amounts of carbon (0.5%–1.5%) and manganese (<2%).

In contrast, a substitutional impurityA point defect that results when an impurity atom occupies a normal lattice site. is a different atom of about the same size that simply replaces one of the atoms that compose the host lattice (Figure 8.4.1 \). Substitutional impurities are usually chemically similar to the substance that constitutes the bulk of the sample, and they generally have atomic radii that are within about 15% of the radius of the host. For example, strontium and calcium are chemically similar and have similar radii, and as a result, strontium is a common impurity in crystalline calcium, with the Sr atoms randomly occupying sites normally occupied by Ca.

Note the Pattern

Interstitial impurities are smaller atoms than the host atom, whereas substitutional impurities are usually chemically similar and are similar in size to the host atom.

Dislocations, Deformations, and Work Hardening

Inserting an extra plane of atoms into a crystal lattice produces an edge dislocationA crystal defect that results from the insertion of an extra plane of atoms into part of the crystal lattice.. A familiar example of an edge dislocation occurs when an ear of corn contains an extra row of kernels between the other rows (Figure 8.4.2). An edge dislocation in a crystal causes the planes of atoms in the lattice to deform where the extra plane of atoms begins (Figure 8.4.2). The edge dislocation frequently determines whether the entire solid will deform and fail under stress.

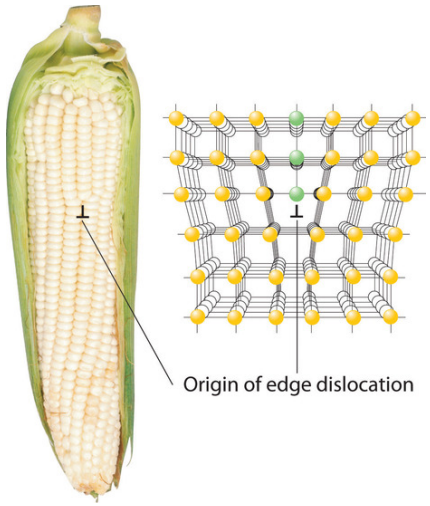


Figure 8.4.2 Edge Dislocations *Shown are two examples of edge dislocations: (a) an edge dislocation in an ear of corn and (b) a three-dimensional representation of an edge dislocation in a solid, illustrating how an edge dislocation can be viewed as a simple line defect arising from the insertion of an extra set of atoms into the lattice. In both cases, the origin of the edge dislocation is indicated by the symbol ⊥*

DeformationA distortion that occurs when a dislocation moves through a crystal. occurs when a dislocation moves through a crystal. To illustrate the process, suppose you have a heavy rug that is lying a few inches off-center on a nonskid pad. To move the rug to its proper place, you could pick up one end and pull it. Because of the large area of contact between the rug and the pad, however, they will probably move as a unit. Alternatively, you could pick up the rug and try to set it back down exactly where you want it, but that requires a great deal of effort (and probably at least one extra person). An easier solution is to create a small wrinkle at one end of the rug (an edge dislocation) and gradually push the wrinkle across, resulting in a net movement of the rug as a whole (part (a) in Figure 8.4.3). Moving the wrinkle requires only a small amount of energy because only a small part of the rug is actually moving at any one time. Similarly, in a solid, the contacts between layers are broken in only one place at a time, which facilitates the deformation process.

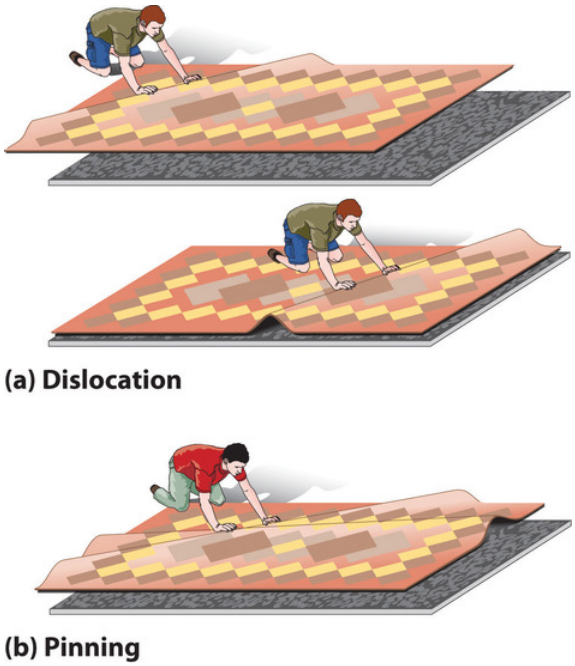


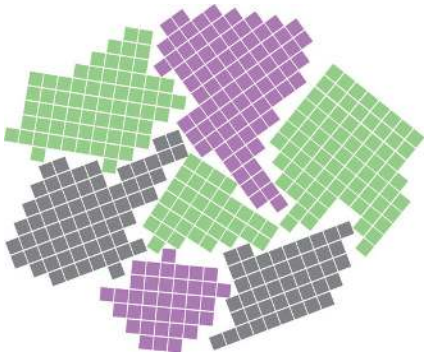
Figure 8.4.3 The Role of Dislocation in the Motion of One Planar Object across Another *(a) Pushing a wrinkle across the rug results in a net movement of the rug with relatively little expenditure of energy because at any given time only a very small amount of the rug is not in contact with the floor. (b) A second intersecting wrinkle prevents movement of the first by "pinning" it.*

If the rug we have just described has a *second* wrinkle at a different angle, however, it is very difficult to move the first one where the two wrinkles intersect (part (b) in Figure 8.4.3); this process is called pinningA process that increases the mechanical strength of a material by introducing multiple defects into a material so that the presence of one defect prevents the motion of another.. Similarly, intersecting dislocations in a solid prevent them from moving, thereby increasing the mechanical strength of the material. In fact, one of the major goals of materials science is to find ways to pin dislocations to strengthen or harden a material.

Pinning can also be achieved by introducing selected impurities in appropriate amounts. Substitutional impurities that are a mismatch in size to the host prevent dislocations from migrating smoothly along a plane. Generally, the higher the concentration of impurities, the more effectively they block migration, and the stronger the material. For example, bronze, which contains about 20% tin and 80% copper by mass, produces a much harder and sharper weapon than does either pure tin or pure copper. Similarly, pure gold is too soft to make durable jewelry, so most gold jewelry contains 75% (18 carat) or 58% (14 carat) gold by mass, with the remainder consisting of copper, silver, or both.

If an interstitial impurity forms polar covalent bonds to the host atoms, the layers are prevented from sliding past one another, even when only a small amount of the impurity is present. For example, because iron forms polar covalent bonds to carbon, the strongest steels need to contain only about 1% carbon by mass to substantially increase their strength (Table 8.4.1).

Most materials are polycrystalline, which means they consist of many microscopic individual crystals called *grains* that are randomly oriented with respect to one another. The place where two grains intersect is called a grain boundaryThe place where two grains in a solid intersect.. The movement of a deformation through a solid tends to stop at a grain boundary. Consequently, controlling the grain size in solids is critical for obtaining desirable mechanical properties; fine-grained materials are usually much stronger than coarse-grained ones.



Grain boundaries. *As a polycrystalline material solidifies, grains with irregular shapes form. The interfaces between grains constitute grain boundaries. (Squares represent unit cells within grains.)*

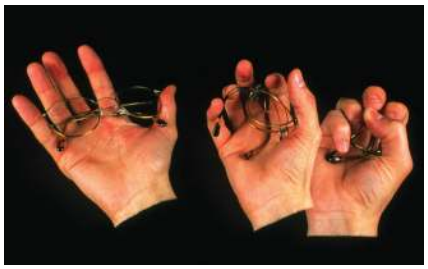
Work hardeningThe practice of introducing a dense network of dislocations throughout a solid, making it very tough and hard. is the introduction of a dense network of dislocations throughout a solid, which makes it very tough and hard. If all the defects in a single 1 cm^3 sample of a work-hardened material were laid end to end, their total length could be 10^6 km! The legendary blades of the Japanese and Moorish swordsmiths owed much of their strength to repeated work hardening of the steel. As the density of defects increases, however, the metal becomes more brittle (less malleable). For example, bending a paper clip back and forth several times increases its brittleness from work hardening and causes the wire to break.

Memory Metal

The compound NiTi, popularly known as “memory metal” or nitinol (*ni*ckel–*ti*tanium *N*aval *O*rdinance *L*aboratory, after the site where it was first prepared), illustrates the importance of deformations. If a straight piece of NiTi wire is wound into a spiral, it will remain in the spiral shape indefinitely, *unless* it is warmed to 50°C–60°C, at which point it will spontaneously straighten out again. The chemistry behind the temperature-induced change in shape is moderately complex, but for our purposes it is sufficient to know that NiTi can exist in two different solid phases.

The high-temperature phase has the cubic cesium chloride structure, in which a Ti atom is embedded in the center of a cube of Ni atoms (or vice versa). The low-temperature phase has a related but kinked structure, in which one of the angles of the unit cell is no longer 90°. Bending an object made of the low-temperature (kinked) phase creates defects that change the pattern of kinks within the structure. If the object is heated to a temperature greater than about 50°C, the material undergoes a transition to the cubic high-

temperature phase, causing the object to return to its original shape. The shape of the object above 50°C is controlled by a complex set of defects and dislocations that can be relaxed or changed only by the thermal motion of the atoms.



Memory metal. *Flexon is a fatigue-resistant alloy of Ti and Ni that is used as a frame for glasses because of its durability and corrosion resistance.*

Memory metal has many other practical applications, such as its use in temperature-sensitive springs that open and close valves in the automatic transmissions of cars. Because NiTi can also undergo pressure- or tension-induced phase transitions, it is used to make wires for straightening teeth in orthodontic braces and in surgical staples that change shape at body temperature to hold broken bones together

Another flexible, fatigue-resistant alloy composed of titanium and nickel is Flexon. Originally discovered by metallurgists who were creating titanium-based alloys for use in missile heat shields, Flexon is now used as a durable, corrosion-resistant frame for glasses, among other uses.

Example 8.4.1

Because steels with at least 4% chromium are much more corrosion resistant than iron, they are collectively sold as “stainless steel.” Referring to the composition of stainless steel in Table 8.4.1 and, if needed, the atomic radii in Figure 3.1.7, predict which type of impurity is represented by each element in stainless steel, excluding iron, that are present in at least 0.05% by mass.

Given: composition of stainless steel and atomic radii

Asked for: type of impurity

Strategy:

Using the data in Table 8.4.1 and the atomic radii in Figure 3.1.7, determine whether the impurities listed are similar in size to an iron atom. Then determine whether each impurity is chemically similar to Fe. If similar in both size and chemistry, the impurity is likely to be a substitutional impurity. If not, it is likely to be an interstitial impurity.

Solution:

According to Table 8.4.1 stainless steel typically contains about 1% carbon, 1%–5% manganese, 0.05% phosphorus, 1%–3% silicon, 5%–10% nickel, and 15%–20% chromium. The three transition elements (Mn, Ni, and Cr) lie near Fe in the periodic table, so they should be similar to Fe in chemical properties and atomic size (atomic radius = 125 pm). Hence they almost certainly will substitute for iron in the Fe lattice. Carbon is a second-period element that is nonmetallic and much smaller (atomic radius = 77 pm) than iron. Carbon will therefore tend to occupy interstitial sites in the iron lattice. Phosphorus and silicon are chemically quite different from iron (phosphorus is a nonmetal, and silicon is a semimetal), even though they are similar in size (atomic radii of 106 and 111 pm, respectively). Thus they are unlikely to be substitutional impurities in the iron lattice or fit into interstitial sites, but they could aggregate into layers that would constitute plane defects.

Exercise

Consider nitrogen, vanadium, zirconium, and uranium impurities in a sample of titanium metal. Which is most likely to form an interstitial impurity? a substitutional impurity?

Answer: nitrogen; vanadium

Defects in Ionic and Molecular Crystals

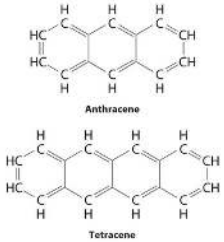
All the defects and impurities described for metals are seen in ionic and molecular compounds as well. Because ionic compounds contain both cations and anions rather than only neutral atoms, however, they exhibit additional types of defects that are not possible in metals.

The most straightforward variant is a substitutional impurity in which a cation or an anion is replaced by another of similar charge and size. For example, Br^- can substitute for Cl^-, so tiny amounts of Br^- are usually present in a chloride salt such as $CaCl_2$ or $BaCl_2$. If the substitutional impurity and the host have *different* charges, however, the situation becomes more complicated. Suppose, for example, that Sr^{2+} (ionic radius = 118 pm) substitutes for K^+ (ionic radius = 138 pm) in KCl. Because the ions are approximately the same size, Sr^{2+} should fit nicely into the face-centered cubic (fcc) lattice of KCl. The difference in charge, however, must somehow be compensated for so that electrical neutrality is preserved. The simplest way is for a second K^+ ion to be lost elsewhere in the crystal, producing a vacancy. Thus substitution of K^+ by Sr^{2+} in KCl results in the introduction of *two* defects: a site in which an Sr^{2+} ion occupies a K^+ position and a vacant cation site. Substitutional impurities whose charges do not match the host's are often introduced intentionally to produce compounds with specific properties.

Virtually all the colored gems used in jewelry are due to substitutional impurities in simple oxide structures. For example, α-Al_2O_3, a hard white solid called *corundum* that is used as an abrasive in fine sandpaper, is the primary component, or *matrix*, of a wide variety of gems. Because many trivalent transition metal ions have ionic radii only a little larger than the radius of Al^{3+} (ionic radius = 53.5 pm), they can replace Al^{3+} in the octahedral holes of the oxide lattice. Substituting small amounts of Cr^{3+} ions (ionic radius = 75 pm) for Al^{3+} gives the deep red color of ruby, and a mixture of impurities (Fe^{2+}, Fe^{3+}, and Ti^{4+}) gives the deep blue of sapphire. True amethyst contains small amounts of Fe^{3+} in an SiO_2 (quartz) matrix. The same metal ion substituted into different mineral lattices can produce very different colors. For example, Fe^{3+} ions are responsible for the yellow color of topaz and the violet color of amethyst. The distinct environments cause differences in *d* orbital energies, enabling the Fe^{3+} ions to absorb light of different frequencies.

The same cation in different environments. *An Fe^{3+} substitutional impurity produces substances with strikingly different colors.*

Substitutional impurities are also observed in *molecular* crystals if the structure of the impurity is similar to the host, and they can have major effects on the properties of the crystal. Pure anthracene, for example, is an electrical conductor, but the transfer of electrons through the molecule is much slower if the anthracene crystal contains even very small amounts of tetracene despite their strong structural similarities.



If a cation or an anion is simply missing, leaving a vacant site in an ionic crystal, then for the crystal to be electrically neutral, there must be a corresponding vacancy of the ion with the opposite charge somewhere in the crystal. In compounds such as KCl, the charges are equal but opposite, so one anion vacancy is sufficient to compensate for each cation vacancy. In compounds such as $CaCl_2$, however, *two* Cl^- anion sites must be vacant to compensate for each missing Ca^{2+} cation. These pairs (or sets) of vacancies are called Schottky defectsA coupled pair of vacancies—one cation and one anion—that maintains the electrical neutrality of an ionic solid. and are particularly common in simple alkali metal halides such as KCl (part (a) in Figure 8.4.4). Many microwave diodes, which are devices that allow a current to flow in a single direction, are composed of materials with Schottky defects.

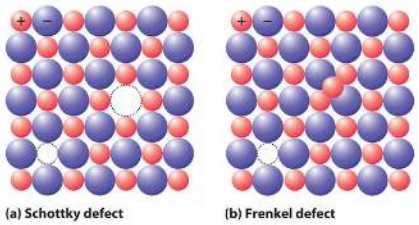


Figure 8.4.4 The Two Most Common Defects in Ionic Solids *(a) A Schottky defect in KCl shows the missing cation/anion pair. (b) A Frenkel defect in AgI shows a misplaced Ag^+ cation.*

Occasionally one of the ions in an ionic lattice is simply in the wrong position. An example of this phenomenon, called a Frenkel defectA defect in an ionic lattice that occurs when one of the ions is in the wrong position., is a cation that occupies a tetrahedral hole rather than an octahedral hole in the anion lattice (part (b) in Figure 8.4.4). Frenkel defects are most common in salts that have a large anion and a relatively small cation. To preserve electrical neutrality, one of the normal cation sites, usually octahedral, must be vacant.

Frenkel defects are particularly common in the silver halides AgCl, AgBr, and AgI, which combine a rather small cation (Ag^+, ionic radius = 115 pm) with large, polarizable anions. Certain more complex salts with a second cation in addition to Ag^+ and Br^- or I^- have so many Ag^+ ions in tetrahedral holes that they are good electrical conductors in the solid state; hence they are called solid electrolytesA solid material with a very high electrical conductivity.. (As you will learn in Chapter 12, most ionic compounds do not conduct electricity in the solid state, although they do conduct electricity when molten or dissolved in a solvent that separates the ions, allowing them to migrate in response to an applied electric field.) In response to an applied voltage, the cations in solid electrolytes can diffuse rapidly through the lattice via octahedral holes, creating Frenkel defects as the cations migrate. Sodium–sulfur batteries use a solid Al_2O_3 electrolyte with small amounts of solid Na_2O. Because the electrolyte cannot leak, it cannot cause corrosion, which gives a battery that uses a solid electrolyte a significant advantage over one with a liquid electrolyte.

Example 8.4.2

In a sample of NaCl, one of every 10,000 sites normally occupied by Na^+ is occupied instead by Ca^{2+}. Assuming that all of the Cl^- sites are fully occupied, what is the stoichiometry of the sample?

Given: ionic solid and number and type of defect

Asked for: stoichiometry

Strategy:

A Identify the unit cell of the host compound. Compute the stoichiometry if 0.01% of the Na^+ sites are occupied by Ca^{2+}. If the overall charge is greater than 0, then the stoichiometry must be incorrect.

B If incorrect, adjust the stoichiometry of the Na^+ ion to compensate for the additional charge.

Solution:

A Pure NaCl has a 1:1 ratio of Na^+ and Cl^- ions arranged in an fcc lattice (the sodium chloride structure). If all the anion sites are occupied by Cl^-, the negative charge is −1.00 per formula unit. If 0.01% of the Na^+ sites are occupied by Ca^{2+} ions, the cation stoichiometry is $Na_{0.99}Ca_{0.01}$. This results in a positive charge of (0.99)(+1) + (0.01)(+2) = +1.01 per formula unit, for a net charge in the crystal of +1.01 + (−1.00) = +0.01 per formula unit. Because the overall charge is greater than 0, this stoichiometry must be incorrect.

B The most plausible way for the solid to adjust its composition to become electrically neutral is for some of the Na^+ sites to be vacant. If one Na^+ site is vacant for each site that has a Ca^{2+} cation, then the cation stoichiometry is $Na_{0.98}Ca_{0.01}$. This results in a positive charge of (0.98)(+1) + (0.01)(+2) = +1.00 per formula unit, which exactly neutralizes the negative charge. The stoichiometry of the solid is thus $Na_{0.98}Ca_{0.01}Cl_{1.00}$.

Exercise

In a sample of MgO that has the sodium chloride structure, 0.02% of the Mg^{2+} ions are replaced by Na^+ ions. Assuming that all of the cation sites are fully occupied, what is the stoichiometry of the sample?

Answer: If the formula of the compound is $Mg_{0.98}Na_{0.02}O_{1-x}$, then x must equal 0.01 to preserve electrical neutrality. The formula is thus $Mg_{0.98}Na_{0.02}O_{0.99}$.

Nonstoichiometric Compounds

The law of multiple proportions, states that chemical compounds contain fixed integral ratios of atoms. In fact, nonstoichiometric compoundsA solid that has intrinsically variable stoichiometries without affecting the fundamental structure of the crystal. contain large numbers of defects, usually vacancies, which give rise to stoichiometries that can depart significantly from simple integral ratios *without affecting the fundamental structure of the crystal*. Nonstoichiometric compounds frequently consist of transition metals, lanthanides, and actinides, with polarizable anions such as oxide (O^{2-}) and sulfide (S^{2-}). Some common examples are listed in Table 8.4.1, along with their basic structure type. These compounds are nonstoichiometric because their constituent metals can exist in multiple oxidation states in the solid, which in combination preserve electrical neutrality.

Table 12.4.1 Some Non-stoichiometric Compounds

Compound	Observed Range of x
Oxides*	
Fe_xO	0.85–0.95
Ni_xO	0.97–1.00
TiO_x	0.75–1.45
VO_x	0.9–1.20
NbO_x	0.9–1.04
Sulfides	
Cu_xS	1.77–2.0
Fe_xS	0.80–0.99
ZrS_x	0.9–1.0
*All the oxides listed have the sodium chloride structure.	

One example is iron(II) oxide (ferrous oxide), which produces the black color in clays and is used as an abrasive. Its stoichiometry is *not* FeO because it always contains less than 1.00 Fe per O^{2-} (typically 0.90–0.95). This is possible because Fe can exist in both the +2 and +3 oxidation states. Thus the difference in charge created by a vacant Fe^{2+} site can be balanced by two Fe^{2+} sites that have Fe^{3+} ions instead [+2 vacancy = (3 − 2) + (3 − 2)]. The crystal lattice is able to accommodate this relatively high fraction of substitutions and vacancies with no significant change in structure.

Note the Pattern

Because a crystal must be electrically neutral, any defect that affects the number or charge of the cations *must be compensated* by a corresponding defect in the number or charge of the anions.

Summary

Real crystals contain large numbers of **defects**. Defects may affect only a single point in the lattice (a **point defect**), a row of lattice points (a **line defect**), or a plane of atoms (a **plane defect**). A point defect can be an atom missing from a site in the crystal (a **vacancy**) or an impurity atom that occupies either a normal lattice site (a **substitutional impurity**) or a hole in the lattice between atoms (an **interstitial impurity**). In an **edge dislocation**, an extra plane of atoms is inserted into part of the crystal lattice. Multiple defects can be introduced into materials so that the presence of one defect prevents the motion of another, in a process called **pinning**. Because defect motion tends to stop at **grain boundaries**, controlling the size of the grains in a material controls its mechanical properties. In addition, a process called **work hardening** introduces defects to toughen metals. **Schottky defects** are a coupled pair of vacancies—one cation and one anion—that maintains electrical neutrality. A **Frenkel defect** is an ion that occupies an incorrect site in the lattice. Cations in such compounds are often able to move rapidly from one site in the crystal to another,

resulting in high electrical conductivity in the solid material. Such compounds are called **solid electrolytes**. **Nonstoichiometric compounds** have variable stoichiometries over a given range with no dramatic change in crystal structure. This behavior is due to a large number of vacancies or substitutions of one ion by another ion with a different charge.

Key Takeaway

- Defects determine the behavior of solids, but because ionic compounds contain both cations and anions, they exhibit additional types of defects that are not found in metals.

Conceptual Problems

1. How are defects and impurities in a solid related? Can a pure, crystalline compound be free of defects? How can a substitutional impurity produce a vacancy?
2. Why does applying a mechanical stress to a covalent solid cause it to fracture? Use an atomic level description to explain why a metal is ductile under conditions that cause a covalent solid to fracture.
3. How does work hardening increase the strength of a metal? How does work hardening affect the physical properties of a metal?
4. Work-hardened metals and covalent solids such as diamonds are both susceptible to cracking when stressed. Explain how such different materials can both exhibit this property.
5. Suppose you want to produce a ductile material with improved properties. Would impurity atoms of similar or dissimilar atomic size be better at maintaining the ductility of a metal? Why? How would introducing an impurity that forms polar covalent bonds with the metal atoms affect the ductility of the metal? Explain your reasoning.
6. Substitutional impurities are often used to tune the properties of material. Why are substitutional impurities generally more effective at high concentrations, whereas interstitial impurities are usually effective at low concentrations?
7. If an O^{2-} ion (ionic radius = 132 pm) is substituted for an F^{-} ion (ionic radius = 133 pm) in an ionic crystal, what structural changes in the ionic lattice will result?
8. How will the introduction of a metal ion with a different charge as an impurity induce the formation of oxygen vacancies in an ionic metal-oxide crystal?
9. Many nonstoichiometric compounds are transition metal compounds. How can such compounds exist, given that their nonintegral cation:anion ratios apparently contradict one of the basic tenets of Dalton's atomic theory of matter?
10. If you wanted to induce the formation of oxygen vacancies in an ionic crystal, which would you introduce as substitutional impurities—cations with a higher positive charge or a lower positive charge than the cations in the parent structure? Explain your reasoning.

Answers

1.
2.
3.
4.
5. Impurity atoms of similar size and with similar chemical properties would be most likely to maintain the ductility of the metal, because they are unlikely to have a large effect on the ease with which one layer of atoms can move past another under mechanical stress. Larger impurity atoms are likely to form "bumps" or kinks that will make it harder for layers of atoms to move across one another. Interstitial atoms that form polar covalent bonds with the metal atoms tend to occupy spaces between the layers; they act as a "glue" that holds layers of metal atoms together, which greatly decreases the ductility.
6.
7. Since O^{2-} and F^{-} are both very similar in size, substitution is possible without disruption of the ionic packing. The difference in charge, however, requires the formation of a vacancy on another F^{-} site to maintain charge neutrality.
8.
9. Most transition metals form at least two cations that differ by only one electron. Consequently, nonstoichiometric compounds containing transition metals can maintain electrical neutrality by gaining electrons to compensate for the absence of anions or the presence of additional metal ions. Conversely, such compounds can lose electrons to compensate for the presence of

additional anions or the absence of metal ions. In both cases, the positive charge on the transition metal is adjusted to maintain electrical neutrality.

10.

Numerical Problems

1. The ionic radius of K^+ is 133 pm, whereas that of Na^+ is 98 pm. Do you expect K^+ to be a common substitutional impurity in compounds containing Na^+? Why or why not?
2. Given Cs (262 pm), Tl (171 pm), and B (88 pm) with their noted atomic radii, which atom is most likely to act as an interstitial impurity in an Sn lattice (Sn atomic radius = 141 pm)? Why?
3. After aluminum, iron is the second most abundant metal in Earth's crust. The silvery-white, ductile metal has a body-centered cubic (bcc) unit cell with an edge length of 286.65 pm.
    1. Use this information to calculate the density of iron.
    2. What would the density of iron be if 0.15% of the iron sites were vacant?
    3. How does the mass of 1.00 cm^3 of iron without defects compare with the mass of 1.00 cm^3 of iron with 0.15% vacancies?
4. Certain ceramic materials are good electrical conductors due to high mobility of oxide ions resulting from the presence of oxygen vacancies. Zirconia (ZrO_2) can be doped with yttrium by adding Y_2O_3. If 0.35 g of Y_2O_3 can be incorporated into 25.0 g of ZrO_2 while maintaining the zirconia structure, what is the percentage of oxygen vacancies in the structure?
5. Which of the following ions is most effective at inducing an O^{2-} vacancy in crystal of CaO? The ionic radii are O^{2-}, 132 pm; Ca^{2+}, 100 pm; Sr^{2+}, 127 pm; F^-, 133 pm; La^{3+}, 104 pm; and K^+, 133 pm. Explain your reasoning.

Answers

1. No. The potassium is much larger than the sodium ion.
2.
3.
    1. 7.8744 g/cm^3
    2. 7.86 g/cm^3
    3. Without defects, the mass is 0.15% greater.
4.
5. The lower charge of K^+ makes it the best candidate for inducing an oxide vacancy, even though its ionic radius is substantially larger than that of Ca^{2+}. Substituting two K^+ ions for two Ca^{2+} ions will decrease the total positive charge by two, and an oxide vacancy will maintain electrical neutrality. For example, if 10% of the Ca^{2+} ions are replaced by K^+, we can represent the change as going from $Ca_{20}O_{20}$ to $K_2Ca_{18}O_{20}$, which has a net charge of +2. Loss of one oxide ion would give a composition of $K_2Ca_{18}O_{19}$, which is electrically neutral.

Contributors

- Anonymous

Memory Metal video is by Mist8K @ YouTube

7.2.4: Crystal Defects is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.5: Bonding and Properties of Solids

Learning Objective

- To understand the correlation between bonding and the properties of solids.

Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as *ionic*, *molecular*, *covalent* (*network*), or *metallic*. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Ionic Solids

You learned in Chapter 4 that an ionic solidA solid that consists of positively and negatively charged ions held together by electrostatic forces. consists of positively and negatively charged ions held together by electrostatic forces. (For more information about ionic solids, see Section 4.2) The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy**, the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase, is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

Molecular solidsA solid that consists of molecules held together by relatively weak forces, such as dipole-dipole interactions, hydrogen bonds, and London dispersion forces. consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these, which were discussed in Chapter 7. The arrangement of the molecules in solid benzene is as follows:

The structure of solid benzene. *In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles.*

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to

optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and *m*-xylene [m-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.

Toluene and *m*-xylene. *The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene.*

Covalent Solids

Covalent solidsA solid that consists of two- or three-dimensional networks of atoms held together by covalent bonds. are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 8.5.1, consists of sp^3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.

Figure 8.5.1The Structures of Diamond and Graphite *(a) Diamond consists of sp^3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.*

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 8.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 8.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure 8.5.1. It contains planar networks of six-membered rings of sp^2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized $2p_z$ orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is

best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 5 . In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons.

Table 8.5.1 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 8.5.1 A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

The Stuctures of Ice

Normal ice has an open hexagonal structure. This explains why the density of liquid water is higher than that of normal ice and why on freezing ice expands. Anyone really interested in the structure of water and ices should reach Martin Chaplin's massive web site at the London South Bank University.

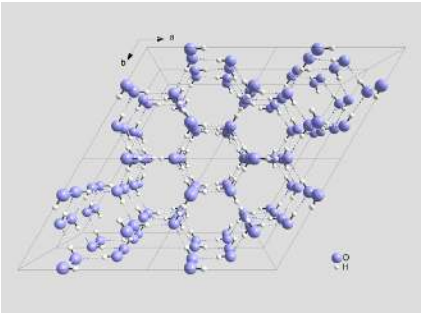


Figure 8.5.2 The Structure of normal ice *Normal ice, called Ice I_h, has an open hexagonal structure held together by hydrogen bonding shown by the dashed lines in this drawing from Wikipedia*

Metallic Solids

Metals are characterized by their ability to reflect light, called lusterThe ability to reflect light. Metals, for instance, have a shiny surface that reflects light (metals are lustrous), whereas nonmetals do not., their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solidsA solid that consists of metal atoms held together by metallic bonds. are dense, with each atom having as many as 12 nearest neighbors.

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds

with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

Note the Pattern

Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the *d* block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron seaValence electrons that are delocalized throughout a metallic solid. (Figure 8.5.3). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. A more complete description of metallic bonding is presented in Section 8.6.

Figure 8.5.3 The Electron-Sea Model of Bonding in Metals *Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.*

Substitutional Alloys

An alloyA solid solution of two or more metals whose properties differ from those of the constituent elements. is a mixture of metals with metallic properties that differ from those of its constituent elements. Brass (Cu and Zn in a 2:1 ratio) and bronze (Cu and Sn in a 4:1 ratio) are examples of substitutional alloysAn alloy formed by the substitution of one metal atom for another of similar size in the lattice., which are metallic solids with large numbers of substitutional impurities. In contrast, small numbers of interstitial impurities, such as carbon in the iron lattice of steel, give an interstitial alloyAn alloy formed by inserting smaller atoms into holes in the metal lattice.. Because scientists can combine two or more metals in varying proportions to tailor the properties of a material for particular applications, most of the metallic substances we encounter are actually alloys. Examples include the low-melting-point alloys used in solder (Pb and Sn in a 2:1 ratio) and in fuses and fire sprinklers (Bi, Pb, Sn, and Cd in a 4:2:1:1 ratio).

The compositions of most alloys can vary over wide ranges. In contrast, intermetallic compoundsAn alloy that consists of certain metals that combine in only specific proportions and whose properties are frequently quite different from those of their constituent elements. consist of certain metals that combine in only specific proportions. Their compositions are largely determined by the relative sizes of their component atoms and the ratio of the total number of valence electrons to the number of atoms present (the *valence electron density*). The structures and physical properties of intermetallic compounds are frequently quite different from those of their constituent elements, but they may be similar to elements with a similar valence electron density. For example, Cr_3Pt is an intermetallic compound used to coat razor blades advertised as "platinum coated"; it is very hard and dramatically lengthens

the useful life of the razor blade. With similar valence electron densities, Cu and PdZn have been found to be virtually identical in their catalytic properties.

Some general properties of the four major classes of solids are summarized in Table 8.5.2.

Table 8.5.2Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

Note the Pattern

The general order of increasing strength of interactions in a solid is molecular solids < ionic solids ≈ metallic solids < covalent solids.

Example 8.5.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.

B Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the *p* block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound $C_6(CH_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a *d*-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

Exercise

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer: C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C_{60}, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. **Ionic solids** consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. **Molecular solids** are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. **Covalent solids** consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. **Metallic solids** have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An **alloy** is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (**substitutional alloys**), by inserting smaller atoms into holes in the metal lattice (**interstitial alloys**), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form **intermetallic compounds** with unique properties.

Key Takeaway

- Solids can be classified as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions is molecular < ionic ≈ metallic < covalent.

Conceptual Problems

1. Four vials labeled A–D contain sucrose, zinc, quartz, and sodium chloride, although not necessarily in that order. The following table summarizes the results of the series of analyses you have performed on the contents:

	A	B	C	D
Melting Point	high	high	high	low
Thermal Conductivity	poor	poor	good	poor
Electrical Conductivity in Solid State	moderate	poor	high	poor
Electrical Conductivity in Liquid State	high	poor	high	poor
Hardness	hard	hard	soft	soft
Luster	none	none	high	none

   Match each vial with its contents.

2. Do ionic solids generally have higher or lower melting points than molecular solids? Why? Do ionic solids generally have higher or lower melting points than covalent solids? Explain your reasoning.
3. The strength of London dispersion forces in molecular solids tends to increase with molecular mass, causing a smooth increase in melting points. Some molecular solids, however, have significantly lower melting points than predicted by their molecular masses. Why?
4. Suppose you want to synthesize a solid that is both heat resistant and a good electrical conductor. What specific types of bonding and molecular interactions would you want in your starting materials?
5. Explain the differences between an interstitial alloy and a substitutional alloy. Given an alloy in which the identity of one metallic element is known, how could you determine whether it is a substitutional alloy or an interstitial alloy?
6. How are intermetallic compounds different from interstitial alloys or substitutional alloys?

Answers

1. 1. NaCl, ionic solid
   2. quartz, covalent solid

3. zinc, metal
4. sucrose, molecular solid

2.
3.
4.

5. In a substitutional alloy, the impurity atoms are similar in size and chemical properties to the atoms of the host lattice; consequently, they simply replace some of the metal atoms in the normal lattice and do not greatly perturb the structure and physical properties. In an interstitial alloy, the impurity atoms are generally much smaller, have very different chemical properties, and occupy holes between the larger metal atoms. Because interstitial impurities form covalent bonds to the metal atoms in the host lattice, they tend to have a large effect on the mechanical properties of the metal, making it harder, less ductile, and more brittle. Comparing the mechanical properties of an alloy with those of the parent metal could be used to decide whether the alloy were a substitutional or interstitial alloy.

6.

Numerical Problems

1. Will the melting point of lanthanum(III) oxide be higher or lower than that of ferrous bromide? The relevant ionic radii are as follows: La^{3+}, 104 pm; O^{2-}, 132 pm; Fe^{2+}, 83 pm; and Br^{-}, 196 pm. Explain your reasoning.
2. Draw a graph showing the relationship between the electrical conductivity of metallic silver and temperature.
3. Which has the higher melting point? Explain your reasoning in each case.
    1. Os or Hf
    2. SnO_2 or ZrO_2
    3. Al_2O_3 or SiO_2
4. Draw a graph showing the relationship between the electrical conductivity of a typical semiconductor and temperature.

Answer

1.
2.
3. 1. Osmium has a higher melting point, due to more valence electrons for metallic bonding.
    2. Zirconium oxide has a higher melting point, because it has greater ionic character.
    3. Aluminum oxide has a higher melting point, again because it has greater ionic character.
4.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

7.2.5: Bonding and Properties of Solids is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.6: Metals and Semiconductors

Learning Objective

- To know the relationship between atomic spectra and the electronic structure of atoms.

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model described in Section 8.5 . The molecular orbital theory we used in Chapter 5 to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^-, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

Band Theory

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of *n* metal atoms, each containing a single electron in an *s* orbital. We use this example to describe an approach to metallic bonding called band theoryA theory used to describe the bonding in metals and semiconductors., which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure 8.6.1 shows the pattern of molecular orbitals that results from the interaction of *ns* orbitals as *n* increases from 2 to 5.

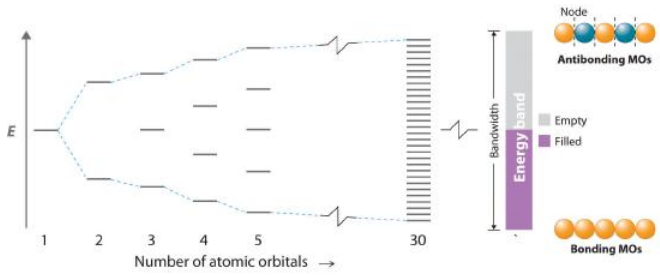


Figure 8.6.1 The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of *n* Atoms, Each of Which Contains a Singly Occupied *s* Orbital. *As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.*

As we saw in Chapter 5, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For $n = 30$, there are still discrete, well-resolved energy levels, but as *n* increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure 8.6.1, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure 8.6.1 is called an energy bandThe continuous set of allowed energy levels generated in band theory when the valence orbitals of the atoms in a solid interact with one another, thus creating a set of molecular orbitals that extend throughout the solid.. The difference in energy between the highest and lowest energy levels is the bandwidthThe difference in energy between the highest and lowest energy levels in an energy band. and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band in Figure 8.6.1 contains *n* energy levels corresponding to the combining

of *s* orbitals from *n* metal atoms. Each of the original *s* orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2*n* electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each *s* orbital, so there are only *n* electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the *bonding* molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only *s* orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in *p* and *d* orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 8.6.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the 1*s*, 2*s*, and 2*p* orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 8.6.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gapThe difference in energy between the highest level of one energy band and the lowest level of the band above it, which represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

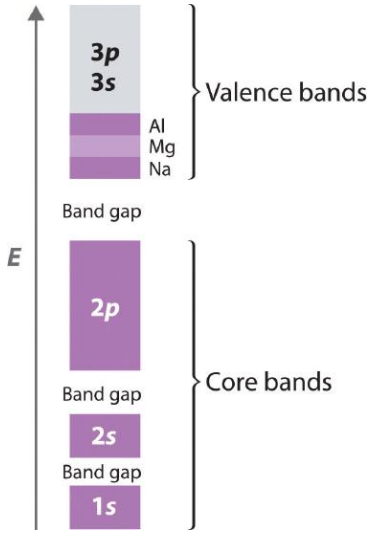


Figure 8.6.2 The Band Structures of the Period 3 Metals Na, Mg, and Al *The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.*

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3*s* and 3*p* in Figure 8.6.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3*s* and 3*p* atomic orbitals are wider than the energy gap between them, so the result is overlapping bandsMolecular orbitals derived from two or more different kinds of valence electrons that have similar energies.. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3*s* and 3*p* bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3*s* orbital and six electrons for each set of 3*p* orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 8.6.2. The partially filled

valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior, it must have a set of delocalized orbitals forming a band of allowed energy levels, and the resulting band must be only partially filled (10%–90%) with electrons. Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Note the Pattern

Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence *ns*, $(n - 1)d$, and *np* orbitals (with a total capacity of 18 electrons per metal atom) or their *ns* and $(n - 1)d$ orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulatorsA material that conducts electricity poorly because its valence bands are full. are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in part (a) in Figure 8.6.3. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2*s* and 2*p* orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

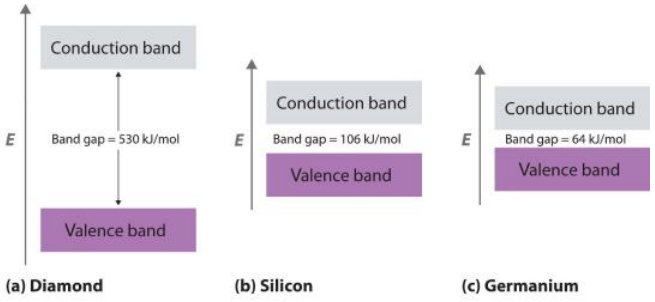


Figure 8.6.3 Energy-Band Diagrams for Diamond, Silicon, and Germanium *The band gap gets smaller from C to Ge.*

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure 8.6.3). Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction bandThe band of empty molecular orbitals in a semiconductor..

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a *positive* charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure 8.6.4). Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductorsA substance such as Si and Ge that has a conductivity between that of metals and insulators.. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure 8.6.5.

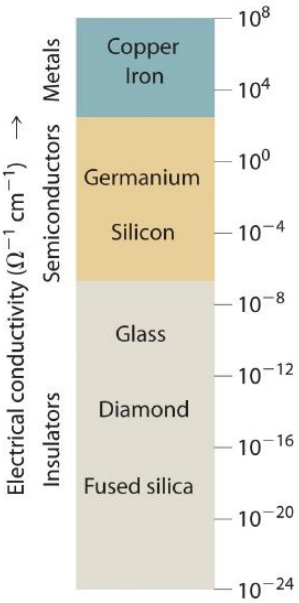


Figure 8.6.4 A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

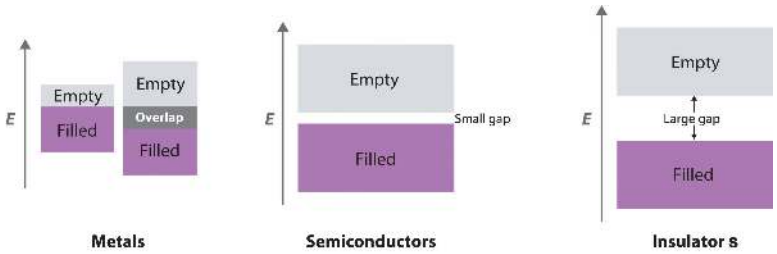


Figure 8.6.5A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators *Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).*

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the *net* motion of the electron through the crystal, and the *lower* the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus *decreasing* the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 8.6.6.

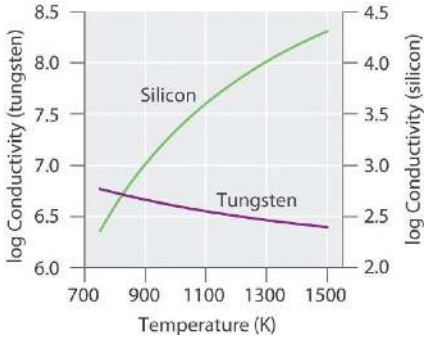


Figure 8.6.6 The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor *The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.*

Note the Pattern

The electrical conductivity of a semiconductor *increases* with increasing temperature, whereas the electrical conductivity of a metal *decreases* with increasing temperature.

n- and *p*-Type Semiconductors

DopingThe process of deliberately introducing small amounts of impurities into commercial semiconductors to tune their electrical properties for specific applications. is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains *more* valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in part (a) in Figure 8.6.7, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an *n*-type semiconductorA semiconductor that has been doped with an impurity that has more valence electrons than the atoms of the host lattice., with the *n* indicating that the added charge carriers are negative (they are electrons).

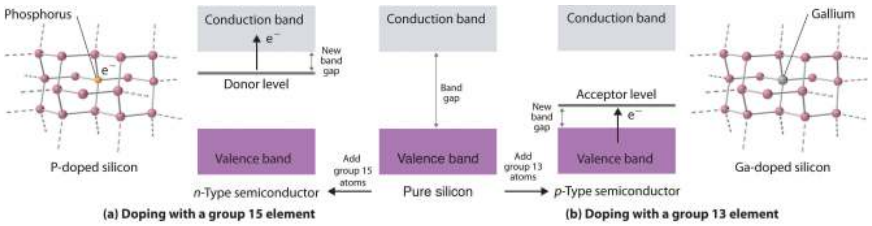


Figure 8.6.7 Structures and Band Diagrams of *n*-Type and *p*-Type Semiconductors *(a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.*

If the impurity atoms contain *fewer* valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in *increased* conductivity because the impurity atoms generate holes in the valence band. As shown in part (b) in Figure 8.6.7, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p*-type semiconductorA semiconductor that has been doped with an impurity that has fewer valence electrons than the atoms of the host lattice., with the *p* standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

Note the Pattern

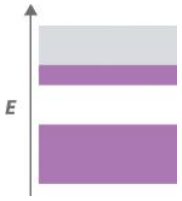
n-Type semiconductors are negative charge carriers; the impurity has *more* valence electrons than the host. *p*-Type semiconductors are positive charge carriers; the impurity has *fewer* valence electrons than the host.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between *n*- and *p*-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced *p*-type semiconductors, whereas doping them with boron and deuterium achieves *n*-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

Example 8.6.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



1. Predict the electrical properties of this solid.
2. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
3. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

A Based on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.

B After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.

C Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

1. **A** The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
2. **B** Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.
3. **C** Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.

1. Predict the electrical properties of the solid.
2. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
3. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

1. The solid has a partially filled band, so it has the electrical properties of a conductor.
2. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
3. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an **energy band**. The difference in energy between the highest and lowest allowed levels within a given band is the **bandwidth**, and the difference in energy between the highest level of one band and the lowest level of the band above it is the **band gap**. If the width of adjacent bands is larger than the energy gap between them, **overlapping bands** result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band

above it (a **conduction band**), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. **Electrical insulators** are poor conductors because their valence bands are full. **Semiconductors** have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by **doping**, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an *n*-**type semiconductor** with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a *p*-**type semiconductor** that also exhibits increased electrical conductivity.

Key Takeaway

- Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid.

Conceptual Problems

1. Can band theory be applied to metals with two electrons in their valence *s* orbitals? with no electrons in their valence *s* orbitals? Why or why not?
2. Given a sample of a metal with 10^{20} atoms, how does the width of the band arising from *p* orbital interactions compare with the width of the band arising from *s* orbital interactions? from *d* orbital interactions?
3. Diamond has one of the lowest electrical conductivities known. Based on this fact, do you expect diamond to be colored? Why? How do you account for the fact that some diamonds are colored (such as “pink” diamond or “green” diamond)?
4. Why do silver halides, used in the photographic industry, have band gaps typical of semiconducting materials, whereas alkali metal halides have very large band gaps?
5. As the ionic character of a compound increases, does its band gap increase or decrease? Why?
6. Why is silicon, rather than carbon or germanium, used in the semiconductor industry?
7. Carbon is an insulator, and silicon and germanium are semiconductors. Explain the relationship between the valence electron configuration of each element and their band structures. Which will have the higher electrical conductivity at room temperature —silicon or germanium?
8. How does doping affect the electrical conductivity of a semiconductor? Draw the effect of doping on the energy levels of the valence band and the conduction band for both an *n*-type and a *p*-type semiconductor.

Answers

1.
2.
3. The low electrical conductivity of diamond implies a very large band gap, corresponding to the energy of a photon of ultraviolet light rather than visible light. Consequently, diamond should be colorless. Pink or green diamonds contain small amounts of highly colored impurities that are responsible for their color.
4.
5. As the ionic character of a compound increases, the band gap will also increase due to a decrease in orbital overlap. Remember that overlap is greatest for orbitals of the same energy, and that the difference in energy between orbitals on adjacent atoms increases as the difference in electronegativity between the atoms increases. Thus, large differences in electronegativity increase the ionic character, decrease the orbital overlap, and increase the band gap.
6.
7.
8.

Numerical Problems

1. Of Ca, N, B, and Ge, which will convert pure silicon into a *p*-type semiconductor when doping? Explain your reasoning.
2. Of Ga, Si, Br, and P, which will convert pure germanium into an *n*-type semiconductor when doping? Explain your reasoning.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Thumbnail from Wikimedia

7.2.6: Metals and Semiconductors is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.7: Superconductors

Learning Objective

- To become familiar with the properties of superconductors.

The phenomenon of superconductivity was discovered by the Danish physicist H. Kamerlingh Onnes (1853–1926; Nobel Prize in Physics, 1913), who found a way to liquefy helium, which boils at 4.2 K and 1 atm pressure. To exploit the very low temperatures made possible by this new cryogenic fluid, he began a systematic study of the properties of metals, especially their electrical properties. Because the electrical resistance of a sample is technically easier to measure than its conductivity, Onnes measured the *resistivity* of his samples. The resistivity and conductivity of a material are inversely proportional:

$$conductivity = \frac{1}{resistivity} \tag{8.7.1}$$

In 1911, Onnes discovered that at about 4 K, the resistivity of metallic mercury (melting point = 234 K) decreased suddenly to essentially zero, rather than continuing to decrease only slowly with decreasing temperature as expected (Figure 8.7.1). He called this phenomenon superconductivityThe phenomenon in which a solid at low temperatures exhibits zero resistance to the flow of electrical current. because a resistivity of zero means that an electrical current can flow forever. Onnes soon discovered that many other metallic elements exhibit superconductivity at very low temperatures. Each of these superconductorsA solid that at low temperatures exhibits zero resistance to the flow of electrical current. has a characteristic superconducting transition temperature (T_c)The temperature at which the electrical resistance of a material drops to zero. at which its resistivity drops to zero. At temperatures less than their T_c, superconductors also completely expel a magnetic field from their interior (part (a) in Figure 8.7.2). This phenomenon is called the Meissner effectThe phenomenon in which a superconductor completely expels a magnetic field from its interior. after one of its discoverers, the German physicist Walther Meissner, who described the phenomenon in 1933. Due to the Meissner effect, a superconductor will actually “float” over a magnet, as shown in part (b) in Figure 8.7.2.

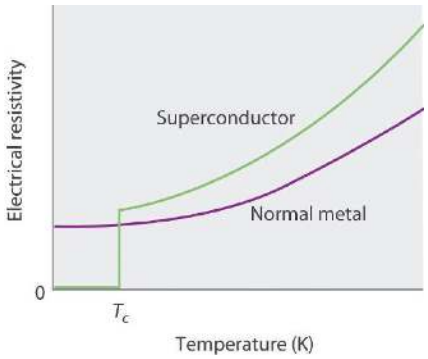


Figure 8.7.1The Temperature Dependence of the Electrical Resistivity of a Normal Metal and a Superconductor *The superconducting transition temperature (T_c) is the temperature at which the resistivity of a superconductor drops to zero.*

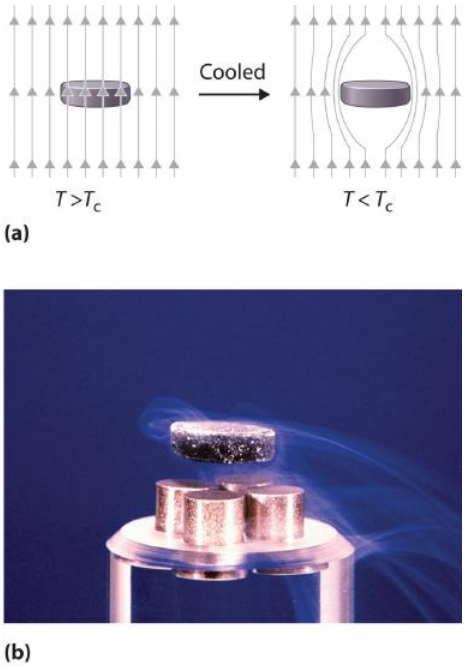


Figure 8.7.2 The Meissner Effect *(a) Below its T_c, a superconductor completely expels magnetic lines of force from its interior. (b) In magnetic levitation, a small magnet "floats" over a disk of a high-temperature superconducting material ($YBa_2Cu_3O_{7-x}$) cooled in liquid nitrogen.*

BCS Theory

For many years, the phenomenon of superconductivity could not be satisfactorily explained by the laws of conventional physics. In the early 1950s, however, American physicists John Bardeen, Leon Cooper, and John Schrieffer formulated a theory for superconductivity that earned them the Nobel Prize in Physics in 1972. According to the BCS theoryA theory used to explain the phenomenon of superconductivity. (named for the initials of their last names), electrons are able to travel through a solid with zero resistance because of attractive interactions involving two electrons that are at some distance from each other. As one electron moves through the lattice, the surrounding nuclei are attracted to it. The motion of the nuclei can create a transient (short-lived) hole that pulls the second electron in the same direction as the first. The nuclei then return to their original positions to avoid colliding with the second electron as it approaches. The pairs of electrons, called Cooper pairsPairs of electrons that migrate through a superconducting material as a unit., migrate through the crystal as a unit. The electrons in Cooper pairs change partners frequently, like dancers in a ballet.

According to the BCS theory, as the temperature of the solid increases, the vibrations of the atoms in the lattice increase continuously, until eventually the electrons cannot avoid colliding with them. The collisions result in the loss of superconductivity at higher temperatures.

The phenomenon of superconductivity suggested many exciting technological applications. For example, using superconducting wires in power cables would result in zero power losses, even over distances of hundreds of miles. Additionally, because superconductors expel magnetic fields, a combination of magnetic rails and superconducting wheels (or vice versa) could be used to produce *magnetic levitation* of, for example, a train over the track, resulting in friction-free transportation.

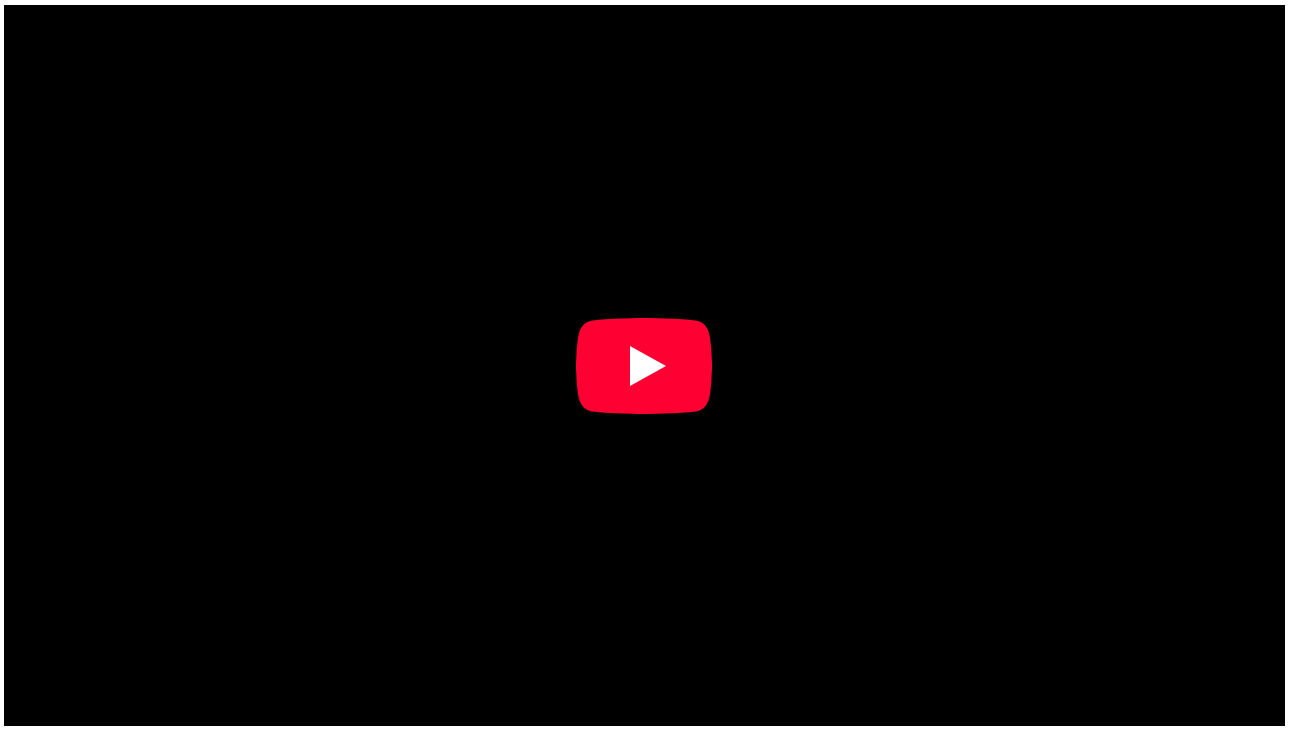
Unfortunately, for many years the only superconductors known had serious limitations, especially the need for very low temperatures, which required the use of expensive cryogenic fluids such as liquid He. In addition, the superconducting properties of many substances are destroyed by large electrical currents or even moderately large magnetic fields, making them useless for applications in power cables or high-field magnets. The ability of materials such as NbTi, NbSn, Nb_3Si, and Nb_3Ge to tolerate rather high magnetic fields, however, has led to a number of commercial applications of superconductors, including high-field magnets for nuclear magnetic resonance (NMR) spectrometers and magnetic resonance imaging (MRI) instruments in medicine, which, unlike x-rays, can detect small changes in soft tissues in the body.

High-Temperature Superconductors

Because of these limitations, scientists continued to search for materials that exhibited superconductivity at temperatures greater than 77 K (the temperature of liquid nitrogen, the least expensive cryogenic fluid). In 1986, Johannes G. Bednorz and Karl A. Müller, working for IBM in Zurich, showed that certain mixed-metal oxides containing La, Ba, and Cu exhibited superconductivity above 30 K. These compounds had been prepared by French workers as potential solid catalysts some years earlier, but their electrical properties had never been examined at low temperatures. Although initially the scientific community was extremely skeptical, the compounds were so easy to prepare that the results were confirmed within a few weeks. These high-temperature superconductorsA material that becomes a superconductor at temperatures greater than 30 K. earned Bednorz and Müller the Nobel Prize in Physics in 1987. Subsequent research has produced new compounds with related structures that are superconducting at temperatures as high as 135 K. The best known of these was discovered by Paul Chu and Maw-Kuen Wu Jr. and is called the "Chu–Wu phase" or the 1-2-3 superconductor.

The formula for the 1-2-3 superconductor is $YBa_2Cu_3O_{7-x}$, where x is about 0.1 for samples that superconduct at about 95 K. If $x \approx 1.0$, giving a formula of $YBa_2Cu_3O_6$, the material is an electrical insulator. The superconducting phase is thus a nonstoichiometric compound, with a fixed ratio of metal atoms but a variable oxygen content. The overall equation for the synthesis of this material is as follows:

$$Y_2O_3\,(s) + 4BaCO_3\,(s) + 6CuO\,(s) + \frac{1}{2}O_2\,(g) \xrightarrow{\Delta} 2YBa_2Cu_3O_{7(s)} + 4CO_2\,(g) \tag{8.7.2}$$



If we assume that the superconducting phase is really stoichiometric $YBa_2Cu_3O_7$, then the average oxidation states of O, Y, Ba, and Cu are −2, +3, +2, and +7/3 respectively. The simplest way to view the average oxidation state of Cu is to assume that two Cu atoms per formula unit are present as Cu^{2+} and one is present as the rather unusual Cu^{3+}. In $YBa_2Cu_3O_6$, the insulating form, the oxidation state of Cu is+5/3 so there are two Cu^{2+} and one Cu^{+} per formula unit.

As shown in Figure 8.7.3, the unit cell of the 1-2-3 superconductor is related to the unit cell of the simple perovskite structure (part (b) in Figure 8.7.3). The only difference between the superconducting and insulating forms of the compound is that an O atom has been removed from between the Cu^{3+} ions, which destroys the chains of Cu atoms and leaves the Cu in the center of the unit cell as Cu^{+}. The chains of Cu atoms are crucial to the formation of the superconducting state.

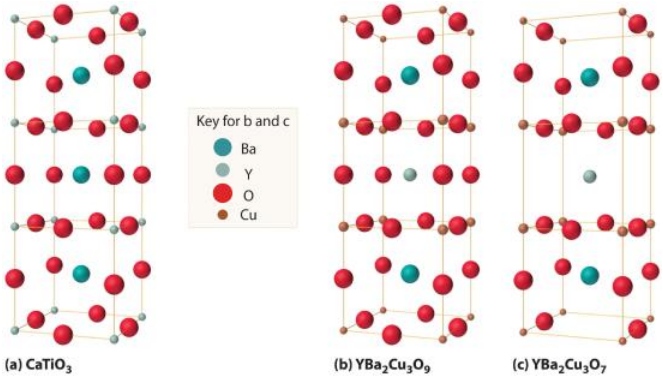


Figure 8.7.3 The Relationship of the Structure of a Superconductor Consisting of Y-Ba-Cu-O to a Simple Perovskite Structure *(a) Stacking three unit cells of the Ca-centered $CaTiO_3$ perovskite structure (part (b) in Figure 8.3.4) together with (b) replacement of all Ti atoms by Cu, replacement of Ca in the top and bottom cubes by Ba, and replacement of Ca in the central cube by Y gives a $YBa_2Cu_3O_9$ stoichiometry. (c) The removal of two oxygen atoms per unit cell gives the nominal $YBa_2Cu_3O_7$ stoichiometry of the superconducting material.*

Table 8.7.1 lists the ideal compositions of some of the known high-temperature superconductors that have been discovered in recent years. Engineers have learned how to process the brittle polycrystalline 1-2-3 and related compounds into wires, tapes, and films that can carry enormous electrical currents. Commercial applications include their use in infrared sensors and in analog signal processing and microwave devices.

Table 8.7.1 The Composition of Various Superconductors

Compound	T_c (K)
$Ba(Pb_{1-x}Bi_x)O_3$	13.5
$(La_{2-x}Sr_x)CuO_4$	35
*Nominal compositions only. Oxygen deficiencies or excesses are common in these compounds.	

Compound	T_c (K)
$YBa_2Cu_3O_{7-x}$	95
$Bi_2(Sr_{2-x}Ca_x)CuO_6$*	80
$Bi_2Ca_2Sr_2Cu_3O_{10}$*	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$*	125
$HgBa_2Ca_2Cu_3O_8$*	133
K_3C_{60}	18
Rb_3C_{60}	30
*Nominal compositions only. Oxygen deficiencies or excesses are common in these compounds.	

Example 8.7.1

Calculate the average oxidation state of Cu in a sample of $YBa_2Cu_3O_{7-x}$ with x = 0.5. How do you expect its structure to differ from those shown in Figure 8.7.3 for $YBa_2Cu_3O_9$ and $YBa_2Cu_3O_7$?

Given: stoichiometry

Asked for: average oxidation state and structure

Strategy:

A Based on the oxidation states of the other component atoms, calculate the average oxidation state of Cu that would make an electrically neutral compound.

B Compare the stoichiometry of the structures shown in Figure 8.7.3 with the stoichiometry of the given compound to predict how the structures differ.

Solution:

A The net negative charge from oxygen is (7.0 − 0.5) (−2) = −13, and the sum of the charges on the Y and Ba atoms is [1 × (+3)] + [2 × (+2)] = +7. This leaves a net charge of −6 per unit cell, which must be compensated for by the three Cu atoms, for a net charge of +6/3=+2 per Cu.

B The most likely structure would be one in which every other O atom between the Cu atoms in the Cu chains of $YBa_2Cu_3O_7$ has been removed.

Exercise

Calculate the average oxidation state of Cu in a sample of $HgBa_2Ca_2Cu_3O_8$. Assume that Hg is present as Hg^{2+}.

Answer: +2

Summary

Superconductors are solids that at low temperatures exhibit zero resistance to the flow of electrical current, a phenomenon known as **superconductivity**. The temperature at which the electrical resistance of a substance drops to zero is its **superconducting transition temperature (T_c)**. Superconductors also expel a magnetic field from their interior, a phenomenon known as the **Meissner effect**. Superconductivity can be explained by the **BCS theory**, which says that electrons are able to travel through a solid with no resistance because they couple to form pairs of electrons (Cooper pairs). **High-temperature superconductors** have T_c values greater than 30 K.

Key Takeaway

- Superconductivity can be described using the BCS theory, in which Cooper pairs of electrons migrate through the crystal as a unit.

Conceptual Problems

1. Why does the BCS theory predict that superconductivity is not possible at temperatures above approximately 30 K?
2. How does the formation of Cooper pairs lead to superconductivity?

Answer

1. According to BCS theory, the interactions that lead to formation of Cooper pairs of electrons are so weak that they should be disrupted by thermal vibrations of lattice atoms above about 30 K.
2.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Video from Wisconsin MRSEC @ YouTube

7.2.7: Superconductors is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.8: Polymers

Learning Objective

- To understand polymer synthesis.
- To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called polymersA giant molecule that consists of many basic structural units (monomers) connected in a chain or network by covalent bonds. (from the Greek *poly* and *meros*, meaning “many parts”). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses. They consist of basic structural units called monomersThe basic structural unit of a polymer., which are repeated many times in each molecule. As shown schematically in Figure 8.8.1 , polymerizationA process by which monomers are connected into chains or networks by covalent bonds. is the process by which monomers are connected into chains or networks by covalent bonds. Polymers can form via a *condensation reaction*, in which two monomer molecules are joined by a new covalent bond and a small molecule such as water is eliminated, or by an *addition reaction*, a variant of a condensation reaction in which the components of a species AB are added to adjacent atoms of a multiple bond. Many people confuse the terms *plastics* and *polymers*. PlasticThe property of a material that allows it to be molded into almost any shape. is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

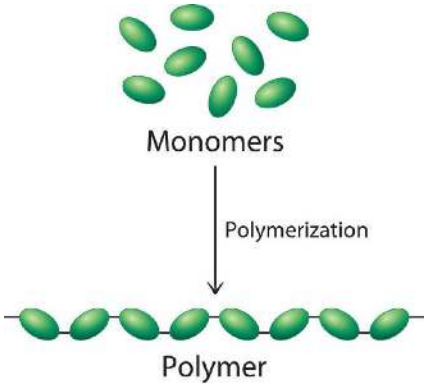


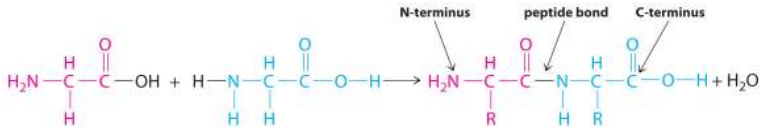
Figure 8.8.1 Polymer formation during a polymerization reaction, *a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

Note the Pattern

Polymers are formed via condensation or addition reactions.

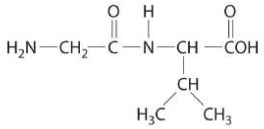
Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where H_2O is eliminated:



In the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-*

terminus). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:



Glycyl-valine

The most important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. Chains with less than about 50 amino acid residues are called peptidesBiological polymers with less than about 50 amino acid residues., whereas those with more than about 50 amino acid residues are called proteinsBiological polymers with more than 50 amino acid residues linked together by amide bonds.. Many proteins are enzymesCatalysts that occur naturally in living organisms and that catalyze biological reactions., which are catalysts that increase the rate of a biological reaction.

Note the Pattern

Synthetic polymers usually contain only a few different monomers, whereas biological polymers can have many kinds of monomers, such as amino acids arranged in different orders.

Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain. Other important peptides are the hormones vasopressin and oxytocin. Although their structures and amino acid sequences are similar, vasopressin is a blood pressure regulator, whereas oxytocin induces labor in pregnant women and milk production in nursing mothers. Oxytocin was the first biologically active peptide to be prepared in the laboratory by Vincent du Vigneaud (1901–1978), who was awarded the Nobel Prize in Chemistry in 1955.

Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion (For more information on corrosion, see Section 17.6.) In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 8.8.2). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibersA particle of a synthetic polymer that is more than 100 times longer than it is wide. that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible –CH_2– units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

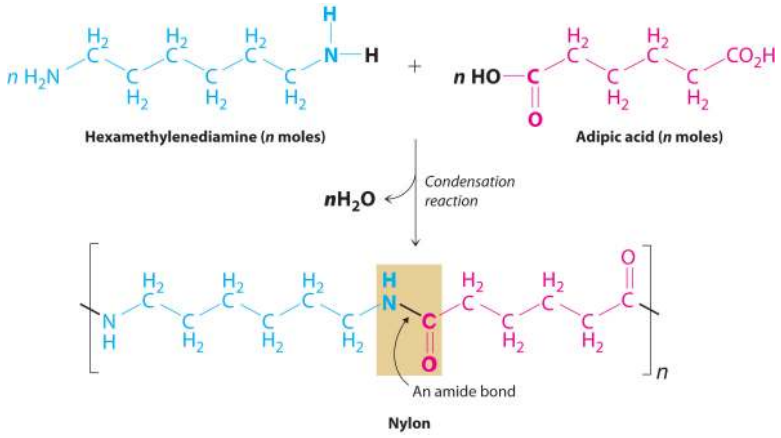


Figure 8.8.2 The Synthesis of Nylon *Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.*

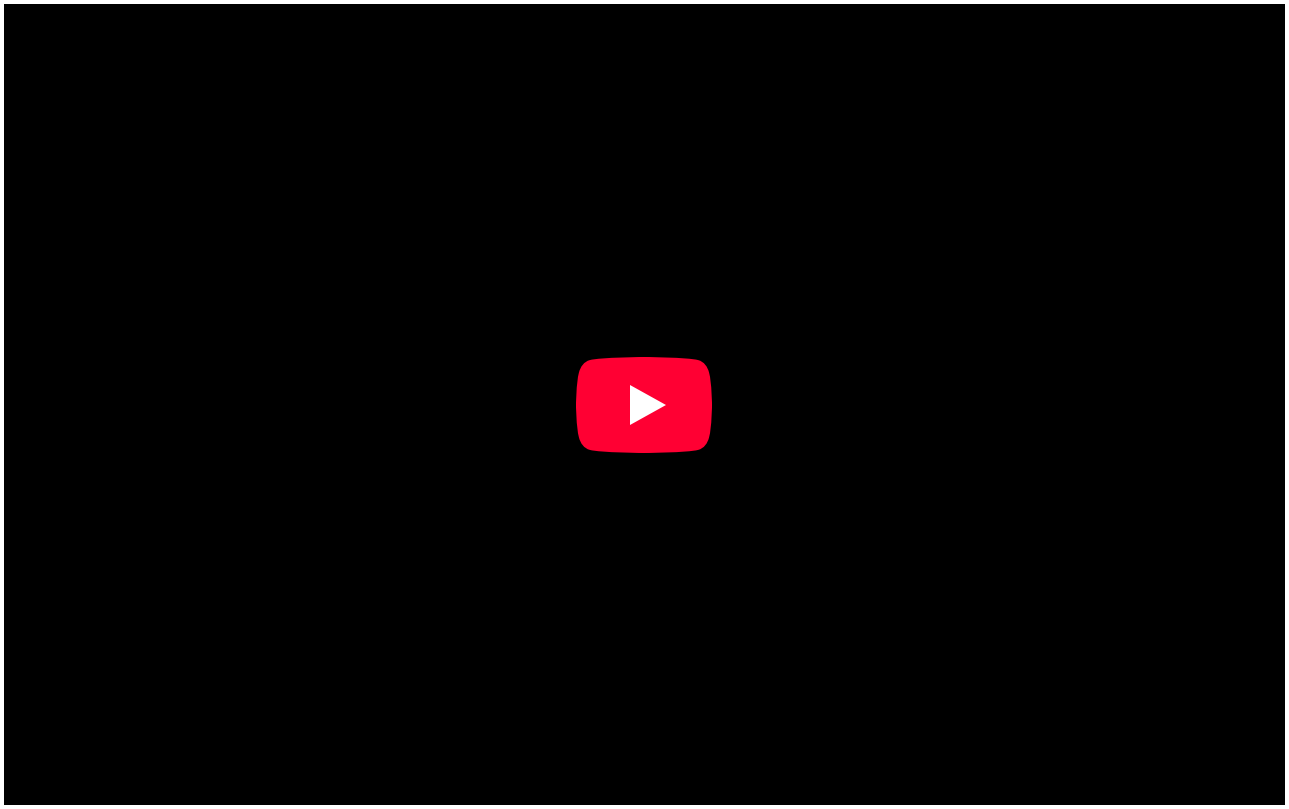


Figure 8.8.3 Synthesis of Nylon: *A video showing the synthesis of nylon 6,10 by Mabakken*

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel.

Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene (CH_2=CH_2), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene

(LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.

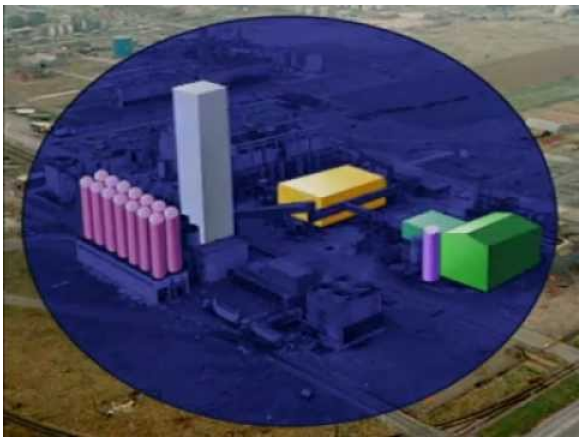


Figure 8.8.4 Commercial Polyethene production: *A video discussing the commercial production of polyethene from the Royal Society of Chemistry*

Because most synthetic fibers are neither soluble nor low melting, multistep processes are required to manufacture them and form them into objects. Graphite fibers are formed by heating a precursor polymer at high temperatures to decompose it, a process called pyrolysisA high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.. The usual precursor for graphite is polyacrylonitrile, better known by its trade name—Orlon. A similar approach is used to prepare fibers of silicon carbide using an organosilicon precursor such as polydimethylsilane $\{[–(CH_3)_2Si–]_n\}$. A new type of fiber consisting of carbon nanotubes, hollow cylinders of carbon just one atom thick, is lightweight, strong, and impact resistant. Its performance has been compared to that of Kevlar, and it is being considered for use in body armor, flexible solar panels, and bombproof trash bins, among other uses.

Because there are no good polymer precursors for elemental boron or boron nitride, these fibers have to be prepared by time-consuming and costly indirect methods. Even though boron fibers are about eight times stronger than metallic aluminum and 10% lighter, they are significantly more expensive. Consequently, unless an application requires boron's greater resistance to oxidation, these fibers cannot compete with less costly graphite fibers.

Example 8.8.1

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

Given: type of polymer

Asked for: application

Strategy:

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

Solution:

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

Exercise

Which products are manufactured from LDPE and which from HPDE?

1. lawn chair frames
2. rope
3. disposable syringes
4. automobile protective covers

Answer:

1. HDPE
2. LDPE
3. HDPE
4. LDPE

Summary

Polymers are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

Key Takeaway

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or synthetic polymers.

Conceptual Problems

1. How are amino acids and proteins related to monomers and polymers? Draw the general structure of an amide bond linking two amino acid residues.
2. Although proteins and synthetic polymers (such as nylon) both contain amide bonds, different terms are used to describe the two types of polymer. Compare and contrast the terminology used for the
    1. smallest repeating unit.
    2. covalent bond connecting the units.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Nylon synthesis from MA Bakken @ YouTube

Polyethylene production from Royal Society of Chemistry @ YouTube

7.2.8: Polymers is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.9: Modern Materials

Learning Objective

- To become familiar with the properties of some contemporary materials.

In addition to polymers, other materials, such as ceramics, high-strength alloys, and composites, play a major role in almost every aspect of our lives. Until relatively recently, steel was used for any application that required an especially strong and durable material, such as bridges, automobiles, airplanes, golf clubs, and tennis rackets. In the last 15 to 20 years, however, graphite or boron fiber golf clubs and tennis rackets have made wood and steel obsolete for these items. Likewise, a modern jet engine now is largely composed of Ti and Ni by weight rather than steel (Table 8.9.1). The percentage of iron in wings and fuselages is similarly low, which indicates the extent to which other materials have supplanted steel. The Chevrolet Corvette introduced in 1953 was considered unusual because its body was constructed of fiberglass, a composite material, rather than steel; by 1992, Jaguar fabricated an all-aluminum limited-edition vehicle. In fact, the current models of many automobiles have engines that are made mostly of aluminum rather than steel. In this section, we describe some of the chemistry behind three classes of contemporary materials: ceramics, superalloys, and composites.

Table 8.9.1 The Approximate Elemental Composition of a Modern Jet Engine

Element	Percentage by Mass
titanium	38
nickel	37
chromium	12
cobalt	6
aluminum	3
niobium	1
tantalum	0.025

Ceramics

A ceramicAny nonmetallic inorganic solid that is strong eneough to be used in structural applications. is any nonmetallic, inorganic solid that is strong enough for use in structural applications. Traditional ceramics, which are based on metal silicates or aluminosilicates, are the materials used to make pottery, china, bricks, and concrete. Modern ceramics contain a much wider range of components and can be classified as either *ceramic oxides*, which are based on metal oxides such as alumina (Al_2O_3), zirconia (ZrO_2), and beryllia (BeO), or *nonoxide ceramics*, which are based on metal carbides such as silicon carbide (carborundum, SiC) and tungsten carbide (WC), or nitrides like silicon nitride (Si_3N_4) and boron nitride (BN).

All modern ceramics are hard, lightweight, and stable at very high temperatures. Unfortunately, however, they are also rather brittle, tending to crack or break under stresses that would cause metals to bend or dent. Thus a major challenge for materials scientists is to take advantage of the desirable properties of ceramics, such as their thermal and oxidative stability, chemical inertness, and toughness, while finding ways to decrease their brittleness to use them in new applications. Few metals can be used in jet engines, for example, because most lose mechanical strength and react with oxygen at the very high operating temperatures inside the engines (approximately 2000°C). In contrast, ceramic oxides such as Al_2O_3 cannot react with oxygen regardless of the temperature because aluminum is already in its highest possible oxidation state (Al^{3+}). Even nonoxide ceramics such as silicon and boron nitrides and silicon carbide are essentially unreactive in air up to about 1500°C. Producing a high-strength ceramic for service use involves a process called sinteringA process that fuses the grains of a ceramic into a dense, strong material. Sintering is used to produce high-strength ceramics., which fuses the grains into a dense and strong material (Figure 8.9.2).

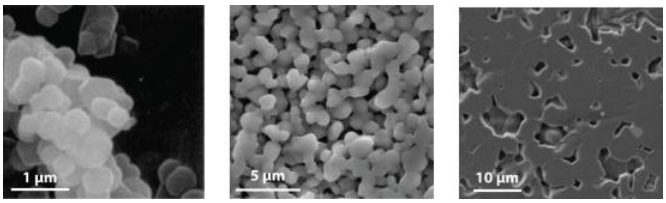


Figure 8.9.2 Sintering *These photos show the effects of sintering magnesium oxide grains: (a) the microstructure before sintering; (b) the microstructure of the ceramic after sintering for two hours at 1250°C; and (c) the microstructure after sintering for two hours at 1450°C. During the sintering process, the grains fuse, forming a dense and strong material.*

Note the Pattern

Ceramics are hard, lightweight, and able to withstand high temperatures, but they are also brittle.

One of the most widely used raw materials for making ceramics is clay. Clay minerals consist of hydrated alumina (Al_2O_3) and silica (SiO_2) that have a broad range of impurities, including barium, calcium, sodium, potassium, and iron. Although the structures of clay minerals are complicated, they all contain layers of metal atoms linked by oxygen atoms. Water molecules fit between the layers to form a thin film of water. When hydrated, clays can be easily molded, but during high-temperature heat treatment, called *firing*, a dense and strong ceramic is produced.

Because ceramics are so hard, they are easily contaminated by the material used to grind them. In fact, the ceramic often grinds the metal surface of the mill almost as fast as the mill grinds the ceramic! The sol-gel processA process used to manufacture ceramics by producing fine powders of ceramic oxides with uniformly sized particles. was developed to address this problem. In this process, a water-soluble precursor species, usually a metal or semimetal alkoxide [$M(OR)_n$] undergoes a hydrolysis reaction to form a cloudy aqueous dispersion called a *sol*. The sol contains particles of the metal or semimetal hydroxide [$M(OH)_n$], which are typically 1–100 nm in diameter. As the reaction proceeds, molecules of water are eliminated from between the $M(OH)_n$ units in a condensation reaction, and the particles fuse together, producing oxide bridges, M–O–M. Eventually, the particles become linked in a three-dimensional network that causes the solution to form a *gel*, similar to a gelatin dessert. Heating the gel to 200°C–500°C causes more water to be eliminated, thus forming small particles of metal oxide that can be amazingly uniform in size. This chemistry starts with highly pure $SiCl_4$ and proceeds via the following reactions starting with the alkoxide formation

$$SiCl_4\,(s) + 4CH_3CH_2OH\,(l) + 4NH_3\,(g) \rightarrow SiO(OCH_2CH_3)_4\,(s) + 4NH_4Sl\,(s) \tag{12.8.1}$$

and then the hydrolysis of the alkoxide

$$SiO(OCH_2CH_3)_4\,(s) + 4H_2O\,(l) \rightarrow (HO)_3Si - OH\,(s) + 4CH_3CH_2OH\,(aq) \tag{12.8.2}$$

ending with the condensation

$$(HO_3)\,Si - OH\,(s) + nHO - Si(OH)_3\,(s) \rightarrow (HO_3)\,Si\,(-O - Si(OH)_3)_n\,(s) + nH_2O\,(l) \tag{12.8.3}$$

Nature uses the same process to create opal gemstones.

Superalloys

SuperalloysA high-strength alloy based on cobalt, nickel, and iron, often of complex composition, that is used in applications that require mechanical strength, high surface stability, and resistance to high temperatures. are high-strength alloys, often with a complex composition, that are used in systems requiring mechanical strength, high surface stability (minimal flaking or pitting), and resistance to high temperatures. The aerospace industry, for example, requires materials that have high strength-to-weight ratios to improve the fuel efficiency of advanced propulsion systems, and these systems must operate safely at temperatures greater than 1000°C.

Note the Pattern

Superalloys are used in systems requiring mechanical strength, minimal flaking or pitting, and high-temperature resistance.

Although most superalloys are based on nickel, cobalt, or iron, other metals are used as well. Pure nickel or cobalt is relatively easily oxidized, but adding small amounts of other metals (Al, Co, Cr, Mo, Nb, Ti, and W) results in an alloy that has superior properties. Consequently, most of the internal parts of modern gas turbine jet engines are now made of superalloys based on either

nickel (used in blades and disks) or cobalt (used in vanes, combustion chamber liners, and afterburners). The cobalt-based superalloys are not as strong as the nickel-based ones, but they have excellent corrosion resistance at high temperatures.

Other alloys, such as aluminum–lithium and alloys based on titanium, also have applications in the aerospace industry. Because aluminum–lithium alloys are lighter, stiffer, and more resistant to fatigue at high temperatures than aluminum itself, they are used in engine parts and in the metal "skins" that cover wings and bodies. Titanium's high strength, corrosion resistance, and lightweight properties are equally desirable for applications where minimizing weight is important (as in airplanes). Unfortunately, however, metallic titanium reacts rapidly with air at high temperatures to form TiN and TiO_2. The welding of titanium or any similar processes must therefore be carried out in an argon or inert gas atmosphere, which adds significantly to the cost. Initially, titanium and its alloys were primarily used in military applications, but more recently, they have been used as components of the airframes of commercial planes, in ship structures, and in biological implants.

Composite Materials

Composite materialsA material that consists of at least two distinct phases: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix. have at least two distinct components: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix and limit the growth of cracks by pinning defects in the bulk material (Figure 8.9.3). The resulting material is stronger, tougher, stiffer, and more resistant to corrosion than either component alone. Composites are thus the nanometer-scale equivalent of reinforced concrete, in which steel rods greatly increase the mechanical strength of the cement matrix, and are extensively used in the aircraft industry, among others. For example, the Boeing 777 is 9% composites by weight, whereas the newly developed Boeing 787 is 50% composites by weight. Not only does the use of composite materials reduce the weight of the aircraft, and therefore its fuel consumption, but it also allows new design concepts because composites can be molded. Moreover, by using composites in the Boeing 787 multiple functions can be integrated into a single system, such as acoustic damping, thermal regulation, and the electrical system.

Three distinct types of composite material are generally recognized, distinguished by the nature of the matrix. These are polymer-matrix composites, metal-matrix composites, and ceramic-matrix composites.

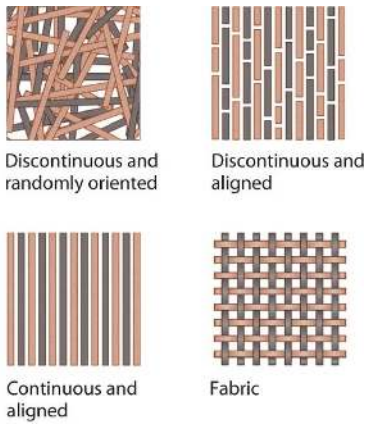


Figure 8.9.3 Some Possible Arrangements of Fibers in Fiber-Reinforced Composite Materials *The arrangements shown range from discontinuous and randomly oriented to continuous and aligned. The fibers limit the growth of cracks by pinning defects within the matrix.*

Note the Pattern

Composites are stronger, tougher, stiffer, and more resistant to corrosion than their components alone.

Fiberglass is a polymer-matrix compositeA compositie that consists of reinforcing fibers embedded in a polymer matrix. that consists of glass fibers embedded in a polymer, forming tapes that are then arranged in layers impregnated with epoxy. The result is a strong, stiff, lightweight material that is resistant to chemical degradation. It is not strong enough, however, to resist cracking or puncturing on impact. Stronger, stiffer polymer-matrix composites contain fibers of carbon (graphite), boron, or polyamides such as Kevlar. High-tech tennis rackets and golf clubs as well as the skins of modern military aircraft such as the "stealth" F-117A fighters and B-2 bombers are made from both carbon fiber–epoxy and boron fiber–epoxy composites. Compared with metals, these materials are 25%–50% lighter and thus reduce operating costs. Similarly, the space shuttle payload bay doors and panels are made

of a carbon fiber–epoxy composite. The structure of the Boeing 787 has been described as essentially one giant macromolecule, where everything is fastened through cross-linked chemical bonds reinforced with carbon fiber.

Metal-matrix compositesA composite that consists of reinforcing fibers embedded in a metal or a metal alloy matrix. consist of metals or metal alloys reinforced with fibers. They offer significant advantages for high-temperature applications but pose major manufacturing challenges. For example, obtaining a uniform distribution and alignment of the reinforcing fibers can be difficult, and because organic polymers cannot survive the high temperatures of molten metals, only fibers composed of boron, carbon, or ceramic (such as silicon carbide) can be used. Aluminum alloys reinforced with boron fibers are used in the aerospace industry, where their strength and lightweight properties make up for their relatively high cost. The skins of hypersonic aircraft and structural units in the space shuttle are made of metal-matrix composites.

Ceramic-matrix compositesA composite consisting of reinforcing fibers embedded in a ceramic matrix. contain ceramic fibers in a ceramic matrix material. A typical example is alumina reinforced with silicon carbide fibers. Combining the two very high-melting-point materials results in a composite that has excellent thermal stability, great strength, and corrosion resistance, while the SiC fibers reduce brittleness and cracking. Consequently, these materials are used in very high-temperature applications, such as the leading edge of wings of hypersonic airplanes and jet engine parts. They are also used in the protective ceramic tiles on the space shuttle, which contain short fibers of pure SiO_2 mixed with fibers of an aluminum–boron–silicate ceramic. These tiles are excellent thermal insulators and extremely light (their density is only about 0.2 g/cm^3). Although their surface reaches a temperature of about 1250°C during reentry into Earth's atmosphere, the temperature of the underlying aluminum alloy skin stays below 200°C.

Example 8.9.1

An engineer is tasked with designing a jet ski hull. What material is most suited to this application? Why?

Given: design objective

Asked for: most suitable material

Strategy:

Determine under what conditions the design will be used. Then decide what type of material is most appropriate.

Solution:

A jet ski hull must be lightweight to maximize speed and fuel efficiency. Because of its use in a marine environment, it must also be resistant to impact and corrosion. A ceramic material provides rigidity but is brittle and therefore tends to break or crack under stress, such as when it impacts waves at high speeds. Superalloys provide strength and stability, but a superalloy is probably too heavy for this application. Depending on the selection of metals, it might not be resistant to corrosion in a marine environment either. Composite materials, however, provide strength, stiffness, and corrosion resistance; they are also lightweight materials. This is not a high-temperature application, so we do not need a metal-matrix composite or a ceramic-matrix composite. The best choice of material is a polymer-matrix composite with Kevlar fibers to increase the strength of the composite on impact.

Exercise

In designing a new generation of space shuttle, National Aeronautics and Space Administration (NASA) engineers are considering thermal-protection devices to protect the skin of the craft. Among the materials being considered are titanium- or nickel-based alloys and silicon-carbide ceramic reinforced with carbon fibers. Why are these materials suitable for this application?

Answer: Ti- or Ni-based alloys have a high strength-to-weight ratio, resist corrosion, and are safe at high temperatures. Reinforced ceramic is lightweight; has high thermal and oxidative stability; and is chemically inert, tough, and impact resistant.

Summary

Ceramics are nonmetallic, inorganic solids that are typically strong; they have high melting points but are brittle. The two major classes of modern ceramics are ceramic oxides and nonoxide ceramics, which are composed of nonmetal carbides or nitrides. The production of ceramics generally involves pressing a powder of the material into the desired shape and sintering at a temperature just below its melting point. The necessary fine powders of ceramic oxides with uniformly sized particles can be produced by the **sol-gel process**. **Superalloys** are new metal phases based on cobalt, nickel, or iron that exhibit unusually high temperature stability and resistance to oxidation. **Composite materials** consist of at least two phases: a matrix that constitutes the bulk of the material and fibers or granules that act as a reinforcement. **Polymer-matrix composites** have reinforcing fibers embedded in a polymer

matrix. **Metal-matrix composites** have a metal matrix and fibers of boron, graphite, or ceramic. **Ceramic-matrix composites** use reinforcing fibers, usually also ceramic, to make the matrix phase less brittle.

Key Takeaway

- Materials that have contemporary applications include ceramics, high-strength alloys, and composites, whose properties can be modified as needed.

Conceptual Problems

1. Can a compound based on titanium oxide qualify as a ceramic material? Explain your answer.
2. What features make ceramic materials attractive for use under extreme conditions? What are some potential drawbacks of ceramics?
3. How do composite materials differ from the other classes of materials discussed in this chapter? What advantages do composites have versus other materials?
4. How does the matrix control the properties of a composite material? What is the role of an additive in determining the properties of a composite material?

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

7.2.9: Modern Materials is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2.10: End of Chapter Material

Template:HideTOC

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

7.2.10: End of Chapter Material is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

8: Coordination Chemistry

Coordination compounds are molecules that poses one or multiple metal centers that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighboring counter-ions. A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds and in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands.

8.1: Introduction and History of Coordination Compounds
8.1.1: History of Coordination Compounds
8.2: Structure and Nomenclature of Coordination Compounds
8.2.1: Intro to Coordination Chemistry
8.2.2: Coordination Numbers and Geometry
8.2.2.1: Jahn-Teller Distortions
8.2.2.2: Molecular Examples
8.2.3: Introduction to Coordination Chemistry
8.2.4: Isomers
8.2.4.1: Optical Isomers in Inorganic Complexes
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes
8.2.4.1.3: Polarimetry
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.5: Stereoisomers of Complex Metal Complexes
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
8.2.5: Ligands
8.2.5.1: EDTA
8.2.5.2: The Irving-Williams Series
8.2.6: What is a Complex Ion?
8.2.7: Nomenclature of Coordination Complexes
8.3: Complex Ion Chemistry
8.3.1: Acidity of the Hexaaqua Ions
8.3.2: Geometry of Complex Ions
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.4: Ligand Exchange Reactions (Thermodynamics)
8.3.5: Nomenclature of Complex Ions
8.3.6: Origin of Color in Complex Ions
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
8.3.10: Stereoisomerism in complex ions

8.4: Complex Ion Equilibria
8.4.1: Chelation
8.4.2: Complex-Ion Equilibria
8.4.3: Complex Equilibrium
8.4.4: Hard and Soft Acids and Bases
8.4.5: Stability of Metal Complexes and Chelation

8: Coordination Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.1: Introduction and History of Coordination Compounds

8.1: Introduction and History of Coordination Compounds is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.1.1: History of Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

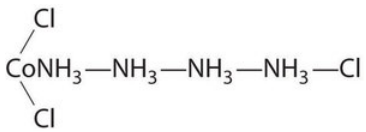
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning “to bind”), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called “double salts” were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the “Chattanooga choo-choo” model for $CoCl_3 \cdot 4NH_3$ shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different “adducts” of ammonia with $PtCl_4$ were known at the time: $PtCl_4 \cdot nNH_3$ (n = 2–6). Some of Werner’s original data on these compounds are shown in Table 8.1.1.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of “free” chloride ions present. For example, Werner’s data on $PtCl_4 \cdot 6NH_3$ in Table 8.1.1.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4 \cdot 2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 8.1.1.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)$$
$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)$$
$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)$$
$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)$$
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure 8.1.1.1*a*). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure 8.1.1.1*b*). His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

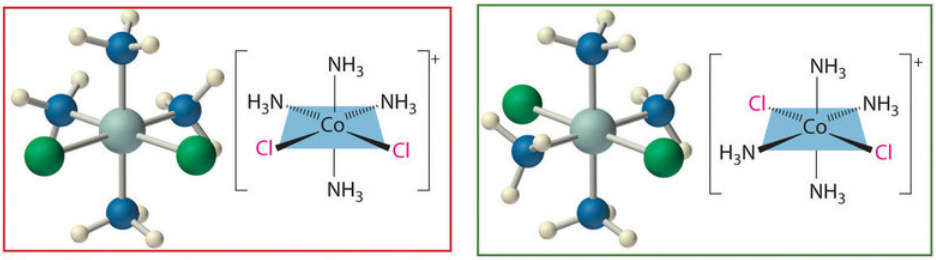


Figure 8.1.1.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 8.1.1.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

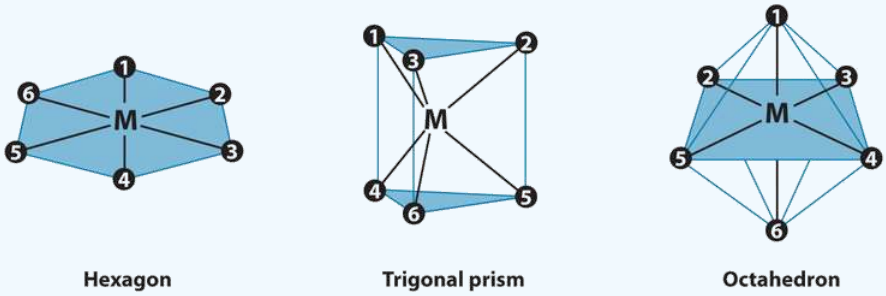
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 8.1.1.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

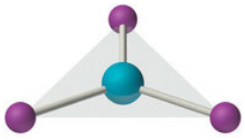
Coordination Number 2

Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.

Linear ML_2

Coordination Number 3

Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.

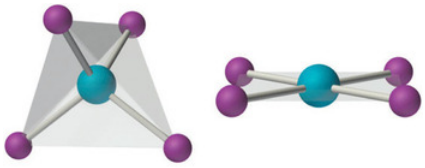


Trigonal planar ML_3

Coordination Number 4

Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row

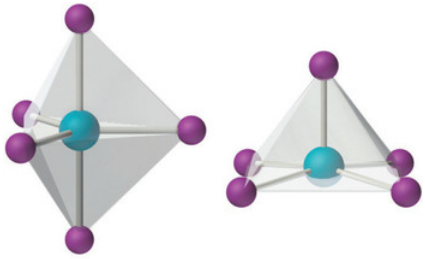
transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

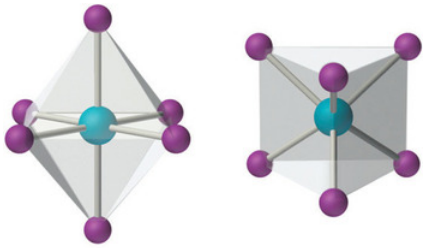
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

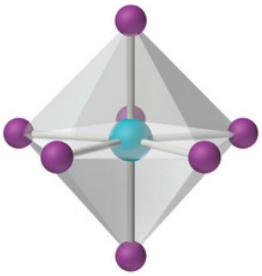
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

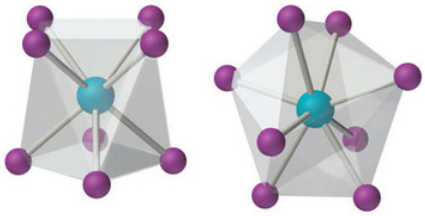
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

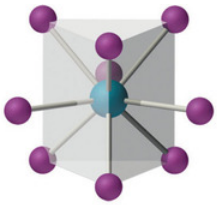
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

8.1.1: History of Coordination Compounds is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **24.1: Werner's Theory of Coordination Compounds** by Anonymous is licensed CC BY-NC-SA 4.0.

8.2: Structure and Nomenclature of Coordination Compounds

Coordination chemistry is the study of compounds formed between metal ions and other neutral or negatively charged molecules such as $[Co(NH_2CH_2CH_2NH_2)_2ClNH_3]^{2+}$ Cl_2^{2-}. In this formulation, $Co(NH_2CH_2CH_2NH_2)_2ClNH_3]^{2+}$ is known as a metal complex, which is a charged species consisting of metal ion bonded to one or more groups of molecules. The bonded molecules are called ligand. The little picture shown here depicts a structure of a 6-coordinated complex.

8.2: Structure and Nomenclature of Coordination Compounds is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.2.1: Intro to Coordination Chemistry

Discussion Questions

- How did the study of coordination compounds started?
- How can the number of isomers be used to determine the structure of a coordination compound?

Coordination chemistry is the study of the compounds that form between metals and **ligands**, where a ligand is any molecule or ion that binds to the metal. A metal **complex** is the unit containing the metal bound to its ligands. For example, $[PtCl_2(NH_3)_2]$ is the neutral metal complex where the Pt^{+2} metal is bound to two Cl^- ligands and two NH_3 ligands. If a complex is charged, it is called a **complex ion** (ex. $[Pt(NH_3)_4]^{+2}$ is a complex cation). A complex ion is stabilized by formation of a **coordination compound** with ions of opposite charge (ex. $[Pt(NH_3)_4]Cl_2$). It is convention to write the formula of a complex or complex ion inside of square brackets, while counterions are written outside of the brackets. In this convention, it is understood that ligands inside the brackets are bound directly to the metal ion, in the metal's *first coordination sphere* (a.k.a inner coordination sphere). Ions written outside of the brackets are assumed to be in the *second coordination sphere*, and they are not directly bound to the metal.

- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Complex Cation: $[CO(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Coordination Compound: $K_4[Fe(CN)_6]$

A common metal complex is $Ag(NH_3)_2^+$, formed when Ag^+ ions are mixed with neutral ammonia molecules.

$$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+ \tag{8.2.1.1}$$

A complex $Ag(S_2O_3)_2^{3-}$ is formed between silver ions and negative thiosulfate ions:

$$Ag^+ + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} \tag{8.2.1.2}$$

The geometry and arrangement of ligands around the metal center affect the properties of a coordination compounds. Compounds with the same molecular formula can appear as **isomers** with very different properties. Isomers are molecules that have identical chemical formulas, but have different arrangements of atoms in space. Isomers with different geometric arrangements of ligands are called **geometric isomers**. Isomers whose structures are mirror images of each other are called **optical isomers**.

How did the study of coordination compounds started?

The coordination chemistry was pioneered by Nobel Prize winner Alfred Werner (1866-1919). He received the Nobel Prize in 1913 for his coordination theory of transition metal-amine complexes. At the start of the 20th century, inorganic chemistry was not a prominant field until Werner studied the metal-amine complexes such as $[Co(NH_3)_6Cl_3]$. Werner recognized the existence of several forms of cobalt-ammonia chloride. These compounds have different color and other characteristics. The chemical formula has three chloride ions per mole, but the number of chloride ions that precipitate with Ag^+ ions per formula is not always three. He thought only **ionized chloride ions** will form precipitate with silver ion. In the following table, the number below the **Ionized Cl^-** is the number of ionized chloride ions per formula. To distinguish ionized chloride from the coordinated chloride, Werner formulated the **Complex formula** and explained structure of the cobalt complexes.

Figure 1: Proposed Structure of Cobalt Ammonia Complexes from Number of Ionized Chloride

Solid	Color	Ionized Cl^-	Complex formula
$CoCl_36NH_3$	Yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_35NH_3$	Purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_34NH_3$	Green	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_34NH_3$	Violet	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

The structures of the complexes were proposed based on a coordination sphere of 6. The 6 ligands can be ammonia molecules or chloride ions. Two different structures were proposed for the last two compounds, the *trans* compound has two chloride ions on

opposite vertices of an octahedral, whereas the the two chloride ions are adjacent to each other in the *cis* compound. The *cis* and *trans* compounds are known as geometric isomers.

Other cobalt complexes studied by Werner are also interesting. It has been predicted that the complex $Co(NH_2CH_2CH_2NH_2)_2ClNH_3]^{2+}$ should exist in two forms, which are mirror images of each other. Werner isolated solids of the two forms, and structural studies confirmed his interpretations. The ligand $NH_2CH_2CH_2NH_2$ is ethylenediamine (en) often represented by en.

Example 1

Sketch the structures of isomers $Co(en)_3^{3+}$ complex ion to show that they are mirror images of each other.

Solution

The images are shown on page 242 *Inorganic Chemistry* by Swaddle. If the triangular face of the end-amino group lie on the paper, you can draw lines to represent the en bidentate ligand. These lines will show that the two images are similar to the left-hand and right-hand screws.

From the description above, sketch the structures.

Exercise 1

- How many isomers does the complex $Co(NH_2CH_2CH_2NH_2)_2ClNH_3]^{2+}$ have? Draw the structures of the isomers.
- How many isomers does $Co(en)_2Cl_2^+$ have? Sketch the structures of the isomers.
- How many isomers does $Co(NH_3)_4Cl_2^+$ have? Sketch the structures of the isomers.

How are coordination compounds named?

Structures of coordination compounds can be very complicated, and their names long because the ligands may already have long names. Knowing the rules of nomenclature not only enable you to understand what the complex is, but also let you give appropriate names to them.

Often, several groups of the ligand are involved in a complex. The number of ligand molecules per complex is indicated by a Greek prefix: mono-, di- (or bis), tri-, tetra-, penta-, hexa, hepta-, octa-, nona-, (ennea-), deca- etc for 1, 2, 3, ... 10 etc. If the names of ligands already have one of these prefixes, the names are placed in parentheses. The prefices for the number of ligands become bis-, tris-, tetrakis, pentakis- etc.

For neutral ligands, their names are not changed, except the following few:

- H_2O: aqua
- NH_3: ammine (not two m's, amine is for organic compounds)
- CO: carbonyl
- NO: nitrosyl

Normal names that will not change

- C5H5N, pyradine
- NH2CH2CH2NH2, ethylenediamine
- C5H4N-C5H4N, dipyridyl
- P(C6H5)3, triphenylphosphine
- NH2CH2CH2NHCH2CH2NH2, diethylenetriamine

The last "e" in names of negative ions are changed to "o" in names of complexes. Sometimes "ide" is changed to "o". Note the following:

- Cl-, chloride -> chloro
- OH-, hydroxide -> hydroxo
- O2-, oxide -> oxo
- O2- peroxide, -> peroxo
- CN-, cyanide -> cyano
- N3-, azide -> axido

- N3-, nitride -> nitrido
- NH2-, amide -> amido
- CO32-, carbonate -> carbonato
- -ONO2-, nitrate -> nitrato (when bonded through O)
- -NO3-, nitrate -> nitro (when bonded through N)
- S2-, sulfide -> sulfido
- SCN-, thiocyanate -> thiocyanato-S
- NCS-, thiocyanate -> thiocyanato-N
- -(CH2-N(CH2COO-)2)2, ethylenediaminetetraacetato (EDTA)

The names of complexes start with the ligands, the anionic ones first, followed with neutral ligands and the metal. If the complex is negative, the name ends with "ate". At the very end are some Roman numerals representing the oxidation state of the metal.

To give and remember all rules of nomenclature are hard to do. Pay attention to the names whenever you encounter any complexes is the way to learn.

- [Co(NH3)5Cl]Cl2, Chloropentaamminecobalt(III) chloride
- [Cr(H2O)4Cl2]Cl, Dichlorotetraaquochromium(III) chloride
- K[PtCl3NH3], Potassiumtrichloroammineplatinate(II)
- PtCl2(NH3)2, Dichlorodiammineplatinum
- Co(en)3Cl3, tris(ethylenediamine)cobalt(III)chloride
- Ni(PF3)4, tetrakis(phosphorus(III)fluoride)nickel(0)

A bridging ligand is indicated by placing a m- before its name. The m- should be repeated for every bridging ligand. For example,

(H3N)3Co(OH)3Co(NH3)3, Triamminecobalt(III)-m-trihydroxotriamminecobalt(III)

Example 2

Give the structural formula for chlorotriphenylphosphinepalladium(II)- m-dichlorochlorotriphenylphosphinepalladium(II).

Solution

The structure is

Exercise 2

- How many ionized chloride ions are there per formula?
- How many chloride ions act as bridges per formula in this complex?
- How many types of chloride ligands are there in this complex?

Example 3

Name the complex:

Solution

The name is Bis(ethylenediamine)cobalt(III)-m- imido-m-hydroxobis(ethylenediamine)cobalt(III) ion.

DISCUSSION

When this compound dissolves in water, is the solution a conductor? What are the ions present in the solution of this compound? How many moles of chloride ions are present per mole of the compound?

When potassiumtrichloroammineplatinate(II) dissolves in water, what ions are produced? What about chloropentaamminecobalt(III) chloride?

How the number of isomers be used to determine the structure of a coordination compound?

Before modern structure determination methods were developed, the study of complexes were mostly done by chemical methods and deduction. The fact that CoCl2(NH3)4Cl has only two isomer suggests that

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

8.2.1: Intro to Coordination Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.2.2: Coordination Numbers and Geometry

The total number of points of attachment to the central element is termed the **coordination number** and this can vary from 2 to as many as 16, but is usually 6. In simple terms, the coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion.

Introduction

Based on the radius ratio, it can be seen that the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate. It is important to recognize that every geometry has a specific coordination number, but every complex wish a specific coordination number will have a choice of several possible geometries (i.e., there is not a one-to-one correspondance between coordination number and geometry).

Coordination Number 2

This arrangement is not very common for first row transition metal ion complexes and some of the best known examples are for Silver(I). In this case we have a low charge and an ion at the right hand side of the d-block indicating smaller size

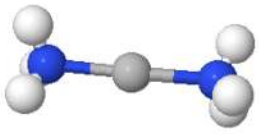


Figure 1: The linear $[Ag(NH_3)_2]^+$ ion

Coordination Number 3

Once again, this is not very common for first row transition metal ions. Examples with three different geometries have been identified:

- **Trigonal planar Geometry**: Well known for main group species like CO_3^{2-} etc., this geometry has the four atoms in a plane with the bond angles between the ligands at 120 degrees.

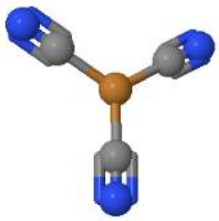


Figure 2: The Trigonal planar $[Cu(CN)_3]^{2-}$ system

- **Trigonal pyramid Geometry**: More common with main group ions.
- **T-shaped**: The first example of a rare T-shaped molecule was found in 1977.

Coordination Number 4

Two different geometries are possible. The tetrahedron is the more common while the square planar is found almost exclusively with metal ions having a d^8 electronic configuration.

- **Tetrahedral Geometry**: The chemistry of molecules centered around a tetrahedral C atom is covered in organic courses. To be politically correct, please change all occurrences of C to Co. There are large numbers of tetrahedral Cobalt(II) complexes known.

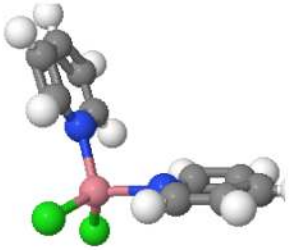


Figure 3: $CoCl_2pyr_2$

- **Square Planar Geometry:** This is fairly rare and is included only because some extremely important molecules exist with this shape.

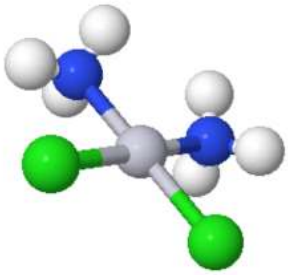


Figure 4: cisplatin - cis-$PtCl_2(NH_3)_2$

Coordination Number 5

- **Square pyramid Geometry:** Oxovanadium salts (Vanadyl, VO^{2+}) often show square pyramidal geometry, for example, $VO(acac)_2$. Note that the Vanadium(IV) can be considered coordinatively unsaturated and addition of pyridine leads to the formation of an octahedral complex.
- **Trigonal Bipyramid Geometry:** The structure of $[Cr(en)_3][Ni(CN)_5]$ 1.5 H_2O was reported in 1968 to be a remarkable example of a complex exhibiting both types of geometry in the same crystal. The reaction of cyanide ion with Ni^{2+} proceeds via several steps:

$$Ni^{2+} + 2CN^- \rightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2CN^- \rightarrow \underset{\text{orange-red}}{[Ni(CN)_4]^{2-}}$$

with $\log(\beta_4) = 30.1$

$$[Ni(CN)_4]^{2-} + CN^- \rightarrow \underset{\text{deep red}}{[Ni(CN)_5]^{3-}}$$

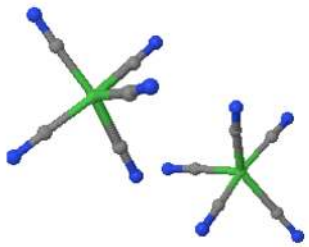


Figure 5: $[Ni(CN)_5]^{3-}$

Coordination Number 6

- **Hexagonal planar Geometry**: Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.

- **Trigonal prism Geometry**: Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.
- **Octahedral (Oh):** The most common geometry found for first row transition metal ions, including all aqua ions. In some cases distortions are observed and these can sometimes be explained in terms of the Jahn-Teller Theorem.

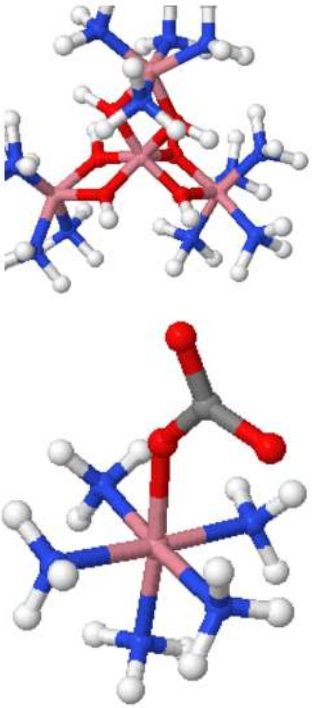


Figure 6: $[Co(en)_3]Cl_3$(left) and $[CoCO_3(NH_3)_5]^+$ (right)

Coordination Number 7

Not very common for 1st row complexes and the energy difference between the structures seems small and distortions occur so that prediction of the closest "idealized" shape is generally difficult. Three geometries are possible:

- **Capped octahedron (C_{3v}) Geometry**

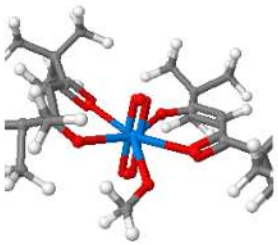


Figure 7: $K_3[NbOF_6]$

- **Capped trigonal prism (C_{2v})**
- **Pentagonal Bipyramid (D_{5h})**

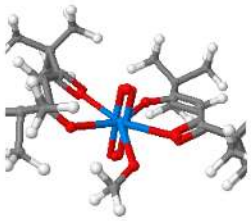


Figure 8: bis-(tert-butylacac)$_2$(DMSO)di-oxoUranium

Coordination Number 8

- **Dodecahedron (D_{2d}) Geometry**
- **Cube (O_h) Geometry**
- **Square antiprism (D_{4d}) Geometry**
- **Hexagonal bipyramid (D_{6h}) Geometry**

Coordination Number 9

- **Three-face centered trigonal prism (D_{3h}) Geometry**

Coordination Number 10

- **Bicapped square antiprism (D_{4d}) Geometry**

Coordination Number 11

- **All-faced capped trigonal prism (D_{3h}) Geometry: This is not a common stereochemistry.**

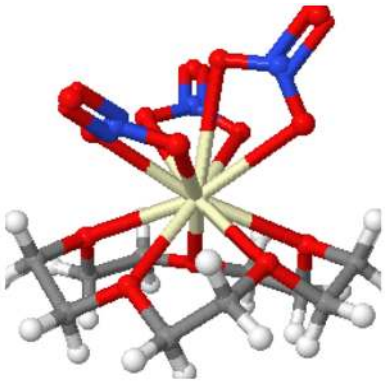


***Figure 9**: aqua-(12-crown-4)-tris(nitrato-O,O')-cerium(III) (12-crown-4) solvate and (15-crown-5)-tris(nitrato-O,O')-cerium(III) the Cerium ion is 11 coordinate.*

Coordination Number 12

- **cuboctahedron (O_h) Geometry**

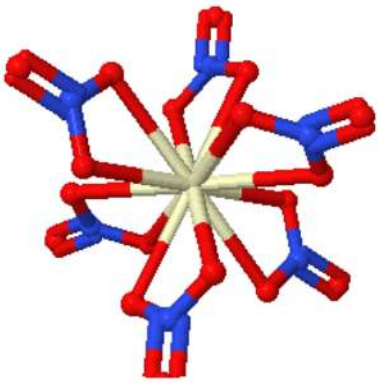


Figure 10: Ceric ammonium nitrate -$(NH_4)_2Ce(NO_3)_6$

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.2: Coordination Numbers and Geometry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.2.2.1: Jahn-Teller Distortions

The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.

Introduction

In 1937, Hermann Jahn and Edward Teller postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," in regards to its electronic state.[1] This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecroft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy."[2] This is most commonly observed with transition metal octahedral complexes, however, it can be observed in tetrahedral compounds as well.

For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_{2g} (d_{xz}, d_{yz}, d_{xy}) and e_g (d_{z^2} and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure 8.2.2.1.1below:

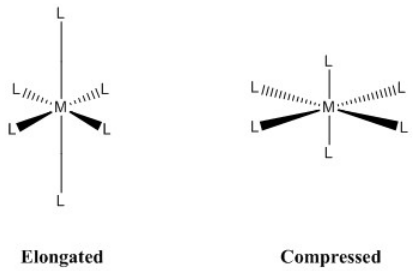


Figure 8.2.2.1.1 : Jahn-Teller distortions for an octahedral complex.

When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, while the orbitals without a z component are destabilized (higher in energy) as shown in Figure 8.2.2.1.2 below:

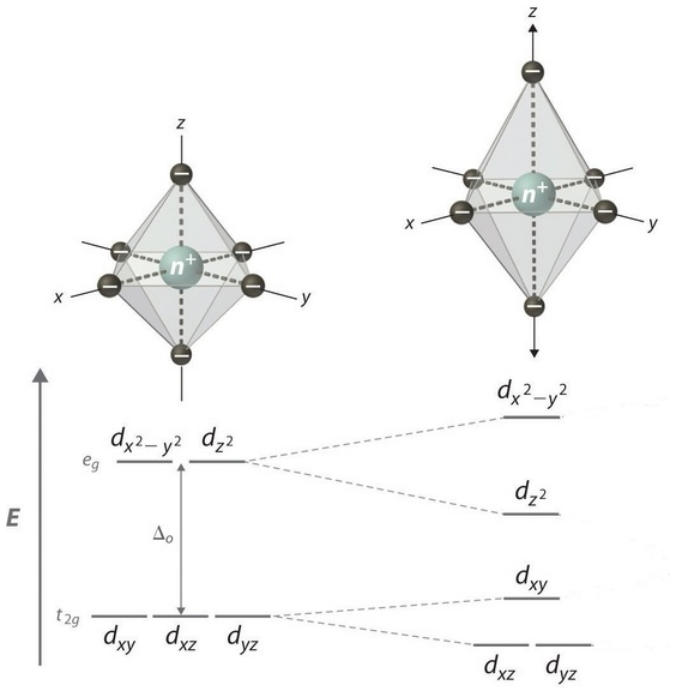


Figure 8.2.2.1.2 : Illustration of tetragonal distortion (elongation) for an octahedral complex.

This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due to the interactions. Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure 8.2.2.1.3

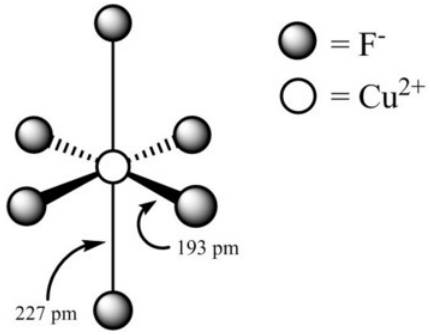


Figure 8.2.2.1.3 : Structure of octahedral copper(II) fluoride.[3]

Notice that the two axial bonds are both elongated and the four shorter equatorial bonds are the same length as each other. According the theorem, the orbital degeneracy is eliminated by distortion, making the molecule more stable based on the model presented in Figure 8.2.2.1.2

Compression

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals *without* a z component, while the orbitals with a z component are destabilized (higher in energy) as shown in Figure 8.2.2.1.4 below:

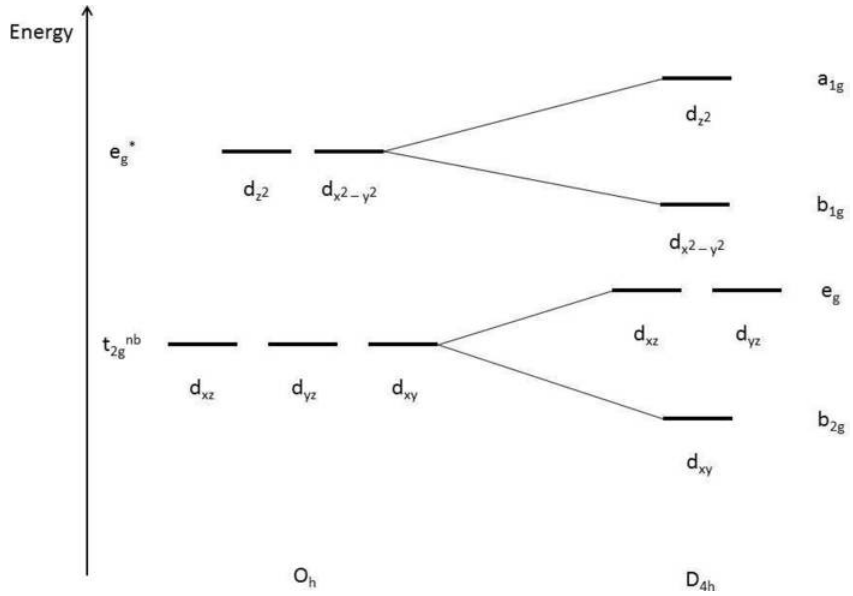


Figure 8.2.2.1.4 : Illustration of tetragonal distortion (compression) for an octahedral complex.

This is due to the *z*-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d_{z^2} orbital is antibonding, it is expected to increase in energy due to compression. The d_{xz} and d_{yz} orbitals are still nonbonding, but are destabilized due to the interactions.

Electronic Configurations

For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the t_{2g} or e_g orbitals. The electronic states of octahedral complexes depend on the number of d-electrons and the splitting energy, Δ. When Δ is large and is greater than the energy required to pair electrons, electrons pair in t_{2g} before occupying e_g. On the other hand, when $Delta$ small and is less than the pairing energy, electrons will occupy e_g before pairing in t_{2g}. The Δ of an octahedral complex is dictated by the chemical environment (ligand identity), and the identity and charge of the metal ion. If there electron configurations for any d-electron count is different depending on Δ, the configuration with more paired electrons is called low spin while the one with more unpaired electrons is called high spin.

The electron configurations diagrams for d1 through d10 with large and small δ are illustrated in the figures below. Notice that the electron configurations for d^1, d^2, d^3, d^8, d^9, and d^{10} are the same no matter what the magnitude of Δ. Low spin and high spin configurations exist only for the electron counts d^4, d^5, d^6, and d^7.

Large Δ

Figure 8.2.2.1.5 (below) shows the various electronic configurations for octahedral complexes with large Δ, including the low-spin configurations of d^4, d^5, d^6, and d^7:

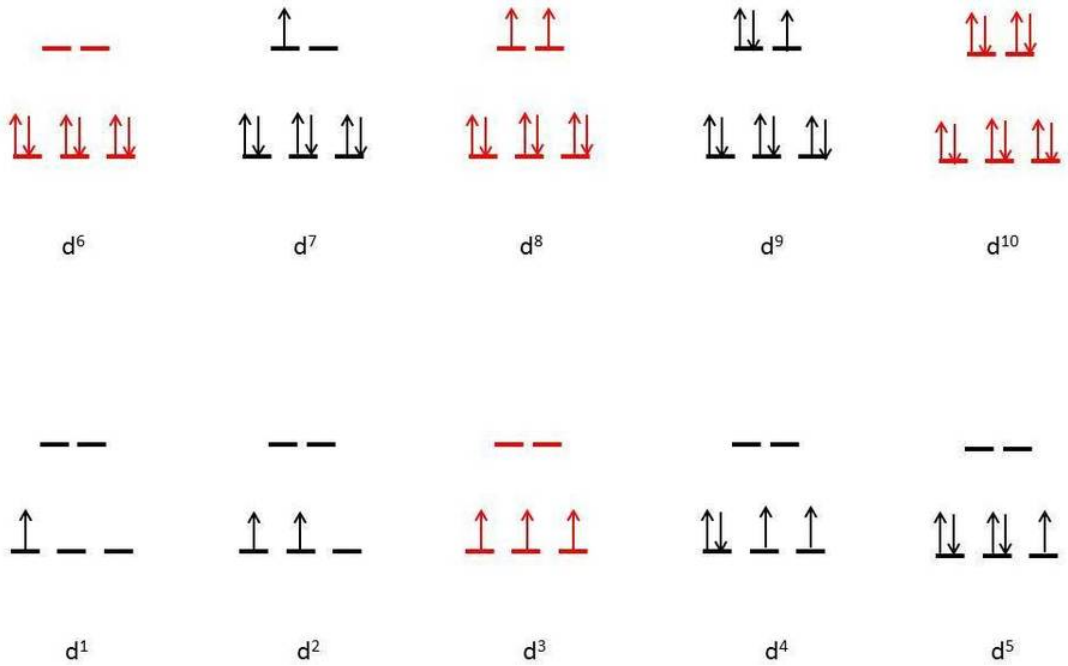


Figure 8.2.2.1.5: Electron configuration diagram of octahedral complexes (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of large Δ. The electron configurations highlighted in red (d^3, low spin d^6, d^8, and d^{10}) **do not** exhibit Jahn-Teller distortions. On the other hand d^1, d^2, low spin d^4, low spin d^5, low spin d^7, and d^9, would be expected to exhibit Jhan-Teller distortion. These electronic configurations correspond to a variety of transition metals. Some common examples include Cr^{3+}, Co^{3+}, and Ni^{2+}.

Small Δ

Figure 8.2.2.1.6(below) shows the various electronic configurations for octahedral complexes with small Δ, including the high-spin configurations of d^4, d^5, d^6, and d^7::

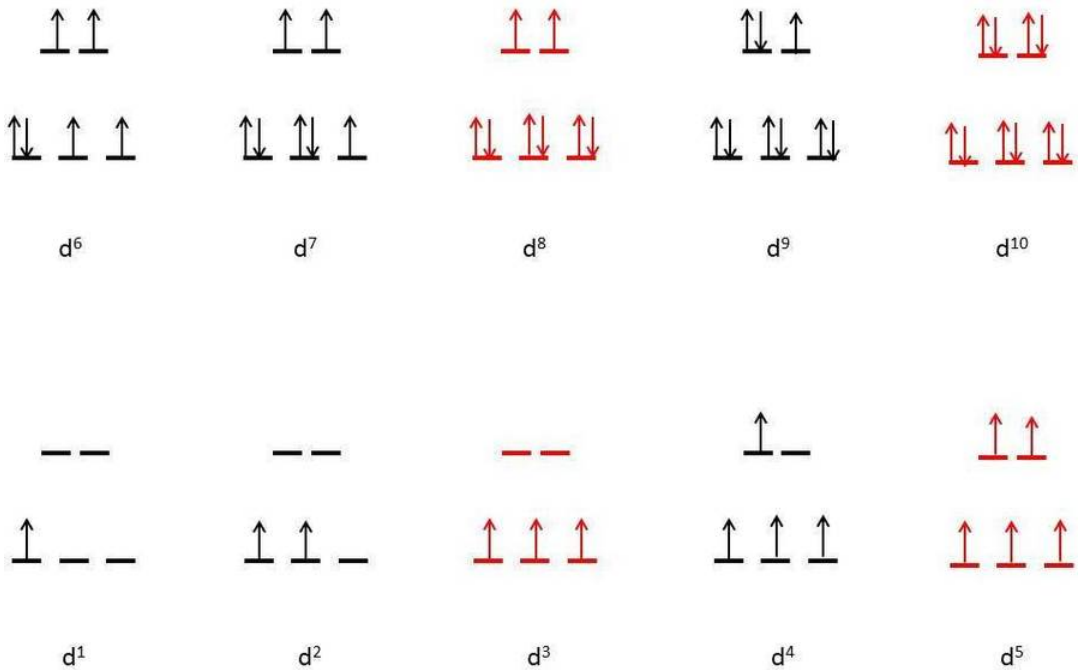


Figure 8.2.2.1.6: High spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of small Δ. The electron configurations highlighted in red (d^3, high spin d^5, d^8, and d^{10}) **do not** exhibit Jahn-Teller distortions. In general, degenerate electronic states occupying the e_g orbital set tend to show stronger Jahn-Teller effects. This is primarily caused by the occupation of these high energy orbitals. Since the system is more stable with a lower energy configuration, the degeneracy of the e_g set is broken, the symmetry is reduced, and occupations at lower energy orbitals occur.

Spectroscopic Observation

Jahn-Teller distortions can be observed using a variety of spectroscopic techniques. In UV-VIS absorption spectroscopy, distortion causes splitting of bands in the spectrum due to a reduction in symmetry (O_h to D_{4h}). Consider a hypothetical molecule with octahedral symmetry showing a single absorption band. If the molecule were to undergo Jahn-Teller distortion, the number of bands would increase as shown in Figure 8.2.2.1.7below:

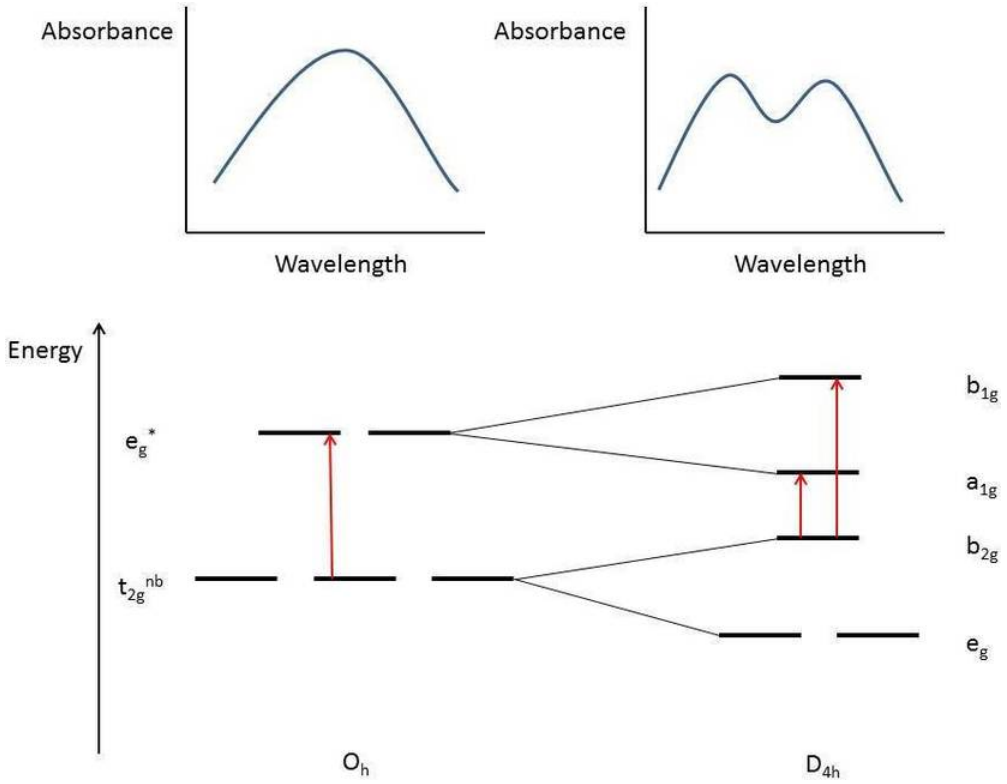


Figure 8.2.2.1.7: Hypothetical absorption spectra of an octahedral molecule (left) and the same molecule with Jahn-Teller elongation (right). The red arrows indicate electronic transitions.

A similar phenomenon can be seen with IR and Raman vibrational spectroscopy. The number of vibrational modes for a molecule can be calculated using the 3n - 6 rule (or 3n - 5 for linear geometry) rule. If a molecule exhibits an O_h symmetry point group, it will have fewer bands than that of a Jahn-Teller distorted molecule with D_{4h} symmetry. Thus, one could observe Jahn-Teller effects through either IR or Raman techniques. This effect can also be observed in EPR experiments as long as there is at least one unpaired electron.

Table 8.2.2.1.1: Examples of Jahn-Teller distorted complexes

$CuBr_2$	4 Br at 240 pm 2 Br at 318 pm
$CuCl_2$	4 Cl at 230 pm 2 Cl at 295 pm
$CuCl_2.2H_2O$	2 O at 193 pm 2 Cl at 228 pm 2 Cl at 295 pm
$CsCuCl_3$	4 Cl at 230 pm 2 Cl at 265 pm
CuF_2	4 F at 193 pm 2 F at 227 pm
$CuSO_4.4NH_3.H_2O$	4 N at 205 pm 1 O at 259 pm 1 O at 337 pm
K_2CuF_4	4 F at 191 pm 2 F at 237 pm

$KCuAlF_6$	2 F at 188 pm 4 F at 220 pm
CrF_2	4 F at 200 pm 2 F at 243 pm
$KCrF_3$	4 F at 214 pm 2 F at 200 pm
MnF_3	2 F at 209 pm 2 F at 191 pm 2 F at 179 pm

The Jahn-Teller Theorem predicts that distortions should occur for *any degenerate state*, including degeneracy of the t_{2g} level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the e_g level.

References

1. Jahn, H. A.; Teller, E. *Proc. R. Soc. London A*, **1937**, *161*, 220-235. DOI: 10.1098/rspa.1937.0142
2. Housecroft, C.; Sharpe, A. G. *Inorganic Chemistry*. Prentice Hall, 3rd Ed., 2008, p. 644. ISBN: 978-0-13-175553-6
3. Billy, C.; Haendler, H. A. *J. Am. Chem. Soc.*, **1957**, *79*, 1049–1051. DOI: 10.1021/ja01562a011

References

- Janes, R.; Moore, E. A. *Metal-ligand bonding*. The Open University, 2004, p. 23. ISBN 0-85404-979-7
- P.T.Miller, P.G.Lenhert and M.D.Joesten, *Inorg. Chem.*, 11, 2221, 1972.
- J.S.Wood, C.P.Keijzers and R.O.Day, *Acta Crystallogr., Sect.C (Cr. Str. Comm.)*, 40, 404, 1984.
- M.D.Joesten, M.S.Hussain and P.G.Lenhert, *Inorg. Chem.*, 9, 151, 1970.

Practice Questions

1. Why do d^3 complexes not show Jahn-Teller distortions?
2. Does the spin system (high spin v. low spin) of a molecule play a role in Jahn-Teller effects?
3. What spectroscopic method would one utilize in order to observe Jahn-Teller distortions in a diamagnetic molecule?
4. What spectroscopic method(s) would one utilize in order to observe Jahn-Teller distortions in a paramagnetic molecule?
5. Why are Jahn-Teller effects most prevalent in inorganic (transition metal) compounds?

Answers

1. Complexes with d^3 electron configurations do not show Jahn-Teller distortions because there is no ground state degeneracy.
2. Yes. Examining the d^5 electron configuration, one finds that the high spin scenario contains all singly occupied d orbitals (no degeneracy). However, the low spin d^5 electron configuration shows degeneracy, which then leads to possible Jahn-Teller effects.
3. UV-VIS absorption spectroscopy is one of the most common techniques for observing these effects. In general, it is independent of magnetism (diamagnetic v. paramagnetic). Thus, one would see the effect in the spectrum of UV-VIS absorption analysis. Note that EPR requires at least one unpaired electron, and therefore not EPR active.
4. Inorganic, specifically transition metal, complexes are most prevalent in showing Jahn-Teller distortions due to the availability of d orbitals. The most common geometry that the Jahn-Teller effect is observed is in octahedral complexes (see **Figures 2, 4, 5** and **6** above) due to the splitting of d orbitals into two degenerate sets. Due to stabilization, the degeneracies are removed, making a lower symmetry and lower energy molecule.
5. In addition to UV-VIS absorption, one can also employ EPR spectroscopy if a molecule possesses and unpaired electron.

Contributors and Attributions

- Kamran Ghiassi (UC Davis)
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.2.1: Jahn-Teller Distortions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Jahn-Teller Distortions** is licensed CC BY-NC-SA 4.0.

8.2.2.2: Molecular Examples

UndefinedNameError: reference to undefined name 'jmol' (click for details)

Coordination Number 2

The linear $[Ag(NH_3)_2]^+$ ion

Although $[Ag(en)]ClO_4$ involves a normally bidentate ligand, in this case the structure is polymeric and the silver ion still retains a CN=2 with the N atoms (from different ligands) at ~180 degrees to each other.

Coordination Number 3

Trigonal planar - D_{3h}

$[Cu(CN)_3]^{2-}$

$[Cu(PPh_3)_2Br]$

To help view more easily, the H atoms are turned off.

Trigonal pyramid

T-shaped

$[Rh(PPh_3)_3]^+$

To help view more easily, the H atoms are turned off.

Coordination Number 4

Tetrahedral

$Copyr_2Cl_2$

Square Planar

cisplatin - cis-$Pt(NH_3)_2Cl_2$

The *cis*- isomer is a powerful anti-cancer drug whereas the *trans*- is inactive.

Coordination Number 5

Square pyramid

Trigonal Bipyramid

$[Ni(CN)_5]^{3-}$

Coordination Number 6

Hexagonal planar

Trigonal prism

tris(cis-1,2-diphenylethene-1,2-dithiolato)rhenium

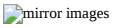
The ReS6 geometry is perfectly trigonal prismatic.

Octahedral

Hexol

The first 'truly' inorganic complex to be resolved into its optical isomers.

$[Co(en)_3]Cl_3$



The classic example of optical isomerism in octahedral coordination complexes (H atoms not shown).

$[Co(NH_3)_5CO_3]^+$

Coordination Number 7

Capped octahedron (C_{3v})

$K_3[NbOF_6]$

Capped trigonal prism (C_{2v})

$[V(III)(Hedta)(H_2O)]H_2O$

Pentagonal Bipyramid (D_{5h})

bis-(tert-butylacac)$_2$(DMSO)di-oxoUranium

The UO7 geometry fits a pentagonal bipyramid.

Coordination Number 8

Dodecahedron (D_{2d})

$Zr(acac)_2(NO_3)_2$

$[Zr(C_2O_4)_4]^{4-}$ is reported to have this shape as well.

Cube (O_h)

Square antiprism (D_{4d})

$U(acac)_4$

Hexagonal bipyramid (D_{6h})

$UO_2(OAc)_3$

Coordination Number 9

Three-face centred trigonal prism (D_{3h})

Hydrated salts of the lanthanide elements eg $Eu(H_2O)_9]^{3+}$

Coordination Number 10

Bicapped square antiprism (D_{4d})

Tetrakis(nitrato-O,O')-bis(triphenylphosphine oxide) cerium(IV)

Another example is $[Ce(NO_3)_5]^{2-}$

Coordination Number 11

All-faced capped trigonal prism (D_{3h})

This is not a common stereochemistry.
In aqua-(12-crown-4)-tris(nitrato-O,O')-cerium(III) (12-crown-4) solvate and (15-crown-5)-tris(nitrato-O,O')-cerium(III) the Cerium ion is 11 coordinate.

Coordination Number 12

cuboctahedron (Oh)

Ceric ammonium nitrate -$(NH_4)_2Ce(NO_3)_6$

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.2.2: Molecular Examples is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Molecular Examples** is licensed CC BY-NC-SA 4.0.

8.2.3: Introduction to Coordination Chemistry

Complexes or **coordination compounds** are molecules that posess a metal center that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighboring counter-ions.

Introduction

Coordination chemistry emerged from the work of Alfred Werner, a Swiss chemist who examined different compounds composed of cobalt (III) chloride and ammonia. Upon the addition of hydrochloric acid, Werner observed that ammonia could not be completely removed. He then proposed that the ammonia must be bound more tightly to the central cobalt ion. However, when aqueous silver nitrate was added, one of the products formed was solid silver chloride. The amount of silver chloride formed was related to the number of ammonia molecules bound to the cobalt (III) chloride. For example, when silver nitrate was added to $CoCl_3 \cdot 6NH_3$, all three chlorides were converted to silver chloride. However, when silver nitrate was added to $CoCl_3 \cdot 5NH_3$, only 2 of the 3 chlorides formed silver chloride. When $CoCl_3 \cdot 4NH_3$ was treated with silver nitrate, one of the three chlorides precipitated as silver chloride.

The resulting observations suggested the formation of **complex** or **coordination compounds**. In the **inner coordination sphere**, which is also referred to in some texts as the **first sphere**, ligands are directly bound to the central metal. In the **outer coordination sphere**, sometimes referred to as the **second sphere**, other ions are attached to the complex ion. Werner was awarded the Nobel Prize in 1913 for his coordination theory. The following table is a summary of Werner's observations:

Initial compound	Resulting compounds upon adding $AgNO_3$
$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]^{3+}(Cl^-)_3$
$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]^{2+}(Cl^-)_2$
$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]^{+}(Cl^-)$
$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$

As the table above shows, the complex ion $[Co(NH_3)_6]^{3+}$ is countered by the three chloride ions. The multi-level binding of coordination complexes play an important role in determining the dissociation of these complexes in aqueous solution. For example, $[Co(NH_3)_5Cl]Cl_2$ dissociates into three ions while $[Co(NH_3)_4Cl_2]Cl$ dissociates into two ions. By applying a current through the aqueous solutions of the resulting complex compounds, Werner measured the electrical conductivity and thus the dissociation properties of the complex compounds. The results confirmed his hypothesis of the formation of complex compounds. It is important to note that the above compounds have a coordination number of 6, which is a common coordination number for many inorganic complexes. Coordination numbers for complex compounds typically range from 1 to 16.

Properties of Coordination Complexes

Some methods of verifying the presence of complex ions include studying its chemical behavior. This can be achieved by observing the compounds' color, solubility, absorption spectrum, magnetic properties, etc. The properties of complex compounds are separate from the properties of the individual atoms. By forming coordination compounds, the properties of both the metal and the ligand are altered.

Metal-ligand bonds are typically thought of Lewis acid-base interactions. The metal atom acts as an electron pair acceptor (Lewis acid), while the ligands act as electron pair donors (Lewis base). The nature of the bond between metal and ligand is stronger than intermolecular forces because they form directional bonds between the metal ion and the ligand, but are weaker than covalent bonds and ionic bonds.

Common Ligands

Monodentate ligands donate one pair of electrons to the central metal atoms. An example of these ligands are the halide ions (F^-, Cl^-, Br^-, I^-). Polydentate ligands, also called chelates or chelating agents, donate more than one pair of electrons to the metal atom forming a stronger bond and a more stable complex. A common chelating agent is ethylenediamine (en), which, as the name

suggests, contains two ammines or :NH_2 sites which can bind to two sites on the central metal. An example of a tridentate ligand is bis-diethylenetriamine. An example of such a coordination complex is bis-diethylenetriamine cobalt(III).

Complex compound/ion	Coordination number	Oxidation State of Metal Atom
$[Fe(CN)_6]^{4-}$	6	2+
$[Co(NH_3)_4SO_4]^-$	5	1+
$[Pt(NH_3)_4]^{2+}$	4	2+
$[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$	6	2+

Complex ions can form many compounds by binding with other complex ions in multiple ratios. This leads to many combinations of coordination compounds. The structures of certain coordination compounds can also have isomers, which can change their interactions with other chemical agents. The binding between metal and ligands is studied in metals, tetrahedral, and octahedral structures. There are many pharmaceutical and biological applications of coordination complexes and their isomers.

References

1. Kleinberg, J.; Argersinger, W J; Grisworld E. Inorganic Chemistry.; D. C. Heath and Company: Boston, MA, 1960; Chapter 6.
2. Martell, Arthur E. Chemistry of the metal chelate compounds.; Prentice-Hall inc: New York, NY, 1952.
3. Oxtoby, David W.; Gillis H. P.; Campion, Alan. Principles of Modern Chemistry, 6th ed.; Thomson Brooks/Cole: Belmont, CA, 2008; Chapter 8.
4. Myers, Thomas R. "Rules for coordination number of metal ions (CEC)." *J. Chem. Educ.* **1981**, *58*, 681.
5. Syamal, A. "Some improper terms in coordination chemistry." *J. Chem. Educ.* **1985**, *62*, 143.
6. Toma, Henrique E.; Araki, Koiti; Dovidauskas, Sergio. "A Cyclic Voltammetry Experiment Illustrating Redox Potentials, Equilibrium Constants, and Substitution Reactions in Coordination Chemistry." *J. Chem. Educ.* **2000** *77* 1351.
7. Toofan, Jahansooz. "A Simple Expression between Critical Radius Ratio and Coordination Number." *J. Chem. Educ.* **1994**, *71*, 147.
8. Woolf, A. A. "Coordination and radius ratio: A graphical representation." *J. Chem. Educ.* **1989**, *66*, 509.

Contributors and Attributions

- Anushweta Asthana (UCD)

8.2.3: Introduction to Coordination Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Introduction to Coordination Chemistry** is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

8.2.4: Isomers

There are several types of this isomerism frequently encountered in coordination chemistry and the following represents some of them. Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination*, and *linkage* and two types of stereoisomers: *geometric and optical.*

Structural isomers, as their name implies, differ in their structure or bonding, which are separate from **stereoisomers** that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, you look at: (1) the ligands that are bonded to the central metal, and (2) which atom of the ligands attach to the central metal. Below is a quick look at the different types of structural isomers. The highlighted ions are the ions that switch or change somehow to make the type of structural isomer it is.

8.2.4.1: Optical Isomers in Inorganic Complexes

8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands

8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes

8.2.4.1.3: Polarimetry

8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin

8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes

8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II

8.2.4.5: Stereoisomers of Complex Metal Complexes

8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes

8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes

8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes

---

8.2.4: Isomers is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.2.4.1: Optical Isomers in Inorganic Complexes

Optical activity refers to whether or not a compound has optical isomers. A coordinate compound that is optically active **has** optical isomers and a coordinate compound that is not optically active does **not have** optical isomers. As we will discuss later, optical isomers have the unique property of rotating light. When light is shot through a polarimeter, optical isomers can rotate the light so it comes out in a different direction on the other end. Armed with the knowledge of symmetry and mirror images, optical isomers should not be very difficult. There are two ways optical isomers can be determined: using mirror images or using planes of symmetry.

Optical isomers do not exhibit symmetry and do not have identical mirror images. Let's go through a quick review of symmetry and mirror images. A *mirror image* of an object is that object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry on the other hand refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

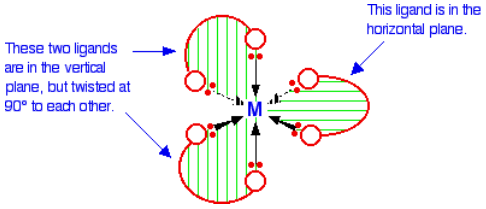
Method 1: The "Mirror Image Method"

The mirror images method uses a mirror image of the molecule to determined whether optical isomers exist or not. If the mirror image **can** be rotated in such a way that it looks identical to the original molecule, then the molecule is said to be superimposable and has no optical isomers. On the other hand, if the mirror image **cannot** be rotated in any way such that it looks identical to the original molecule, then the molecule is said to be non-superimposable and the molecule has optical isomers. Once again, if the mirror image is superimposable, then no optical isomers but if the mirror image is non-superimposable, then optical isomers exist.

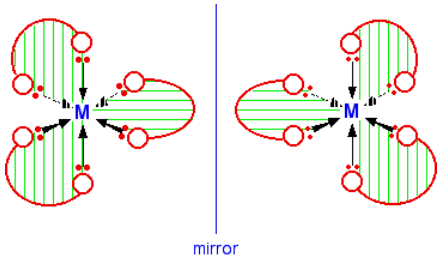
Definition: Non-superimposable

Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another. This means that no matter how the structure is rotated, it cannot be put on top of another with all points matching. An example of this is your hands. Both left and right hands are identical, but they cannot be put on top of each other with all points matching.

The examples you are most likely to need occur in octahedral complexes which contain bidentate ligands - ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$. The diagram below shows a simplified view of one of these ions. Essentially, they all have the same shape - all that differs is the nature of the "headphones".



A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarised light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:



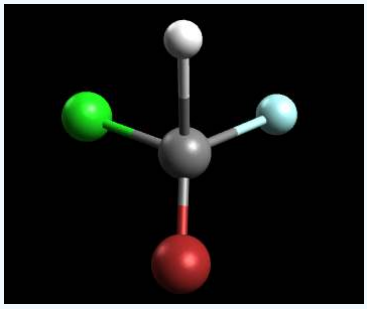
You may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one. As long as you draw the isomers carefully, with the second one a true reflection of the first, the two structures will be different.

Method 2: The "Plane of Symmetry Method"

The plane of symmetry method uses symmetry, as it's name indicates, to identify optical isomers. In this method, one tries to see if such a plane exists which when cut through the coordinate compound produces two exact images. In other words, one looks for the existence of a plane of symmetry within the coordinate compound. If a plane of symmetry exists, then no optical isomers exist. On the other hand, if there is no plane of symmetry, the coordinate compound has optical isomers. Furthermore, if a plane of symmetry exists around the central atom, then that molecule is called **achiral** but if a plane of symmetry does not exist around the central molecule, then that molecule has chiral center.

Example 8.2.4.1.1: CHBrClF

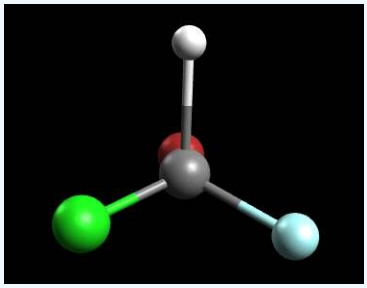
Consider the tetrahedral molecule, CHBrClF (note the color scheme: grey=carbon, white=hydrogen, green=chlorine, blue=fluorine, red=bromine)



Is this molecule optically active? In other words, does this molecule have optical isomers?

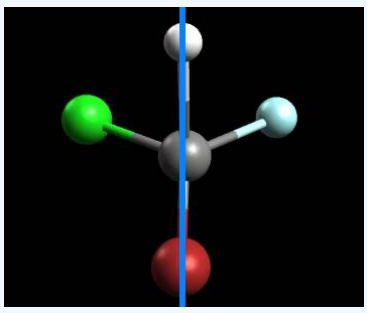
Solution

First take the Mirror-image method. The mirror image of the molecule is:



Note that this mirror image is not superimposable. In other words, the mirror image above cannot be rotated in any such way that it looks identical to the original molecule. Remember, if the mirror image is not superimposable, then optical isomers exist. Thus we know that this molecule has optical isomers.

Let's try approaching this problem using the symmetry method. If we take the original molecule and draw an axis or plane of symmetry down the middle, this is what we get:



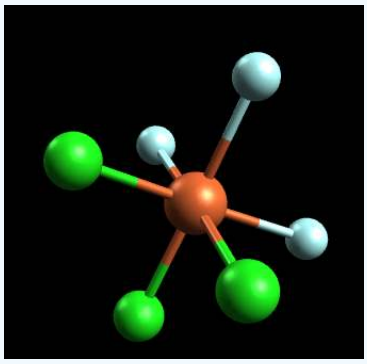
Since the left side is not identical to the right, this molecule does not have a symmetrical center and thus can be called chiral.Additionally, because it does not have a symmetrical center, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that has 4 different ligands, optical isomers will exist most of the time.

No matter which method you use, the answer will end up being the same.

Optical isomers because they have no plane of symmetry. In the organic case, for tetrahedral complexes, this is fairly easy to recognize the possibility of this by looking for a center atom with **four** different things attached to it. Unfortunately, this is not quite so easy with more complicated geometries!

Example 8.2.4.1.1: $PFeCl_3F_3$

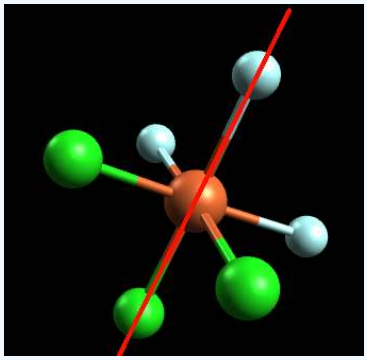
This time we will be analyzing the octahedral compound $FeCl_3F_3$. Is this molecule optically active?



(note the color scheme: orange=iron, blue=fluorine, green=chlorine):

Solution

If we try to attempt this problem using the mirror image method, we notice that the mirror image is essentially identical to the original molecule. In other words, the mirror image can be placed on top of the original molecule and is thus superimposable. Since the mirror image is superimposable, this molecule does not have any optical isomers. Let's attempt this same problem using the symmetry method. If we draw an axis or plane of symmetry, this is what we get:



Since the left side is identical to the right side, this molecule has a symmetrical center and is an achiral molecule. Thus, it has no optical isomers.

What is a Polarimeter?

A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance. Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the *angle of rotation*. The angle of rotation is basically known as observed angle.

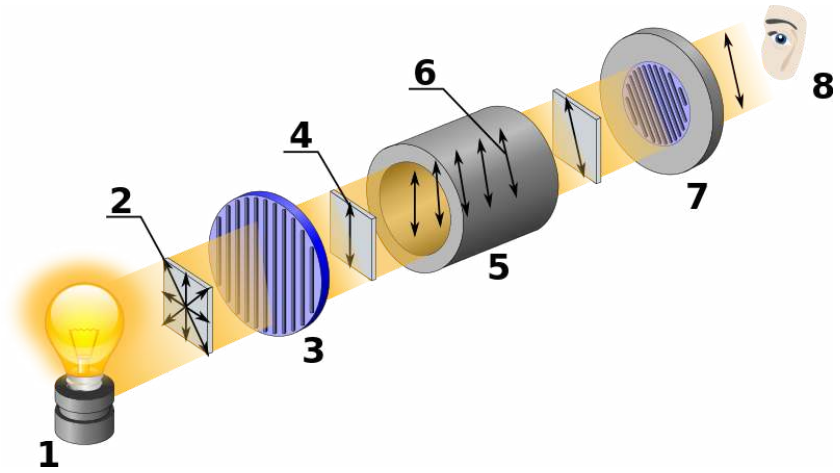


Figure 8.2.4.1.1 : Schematic of a polarimeter showing the principles behind it's operation. Unpolarized light is passed through a polarizing filter before traveling through a sample. The degree of rotation of polarization is determined by a second, rotatable filter. (CC AS 3.0; Kaidor).

The polarimeter is made up of a polarizer (#3 on Figure 8.2.4.1.1) and an analyzer (#7 on Figure 8.2.4.1.1). The polarizer allows only those light waves which move in a single plane. This causes the light to become plane polarized. When the analyzer is also placed in a similar position it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle no waves can pass through the right angle and the field appears to be dark. If now a glass tube containing an optically active solution is placed between the polarizer and analyzer the light now rotates through the plane of polarization through a certain angle, the analyzer will have to be rotated in same angle.

Nomenclature of Optical Isomers

Various methods have been used to denote the absolute configuration of optical isomers such as R or S, Λ or Δ, or C and A. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use and that for bis and tris bidentate complexes the absolute configuration be designated Lambda Λ (left-handed) and Delta Δ (right-handed).

Priorities are assigned for mononuclear coordination systems based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog (CIP rules). These rules use the coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number (smallest CIP number). For example the hypothetical complex [Co Cl Br I NH_3 NO_2 SCN]$^{2-}$ would assign the I- as 1, Br as 2, Cl as 3, SCN as 4, NO_2 as 5 and NH_3 as 6.

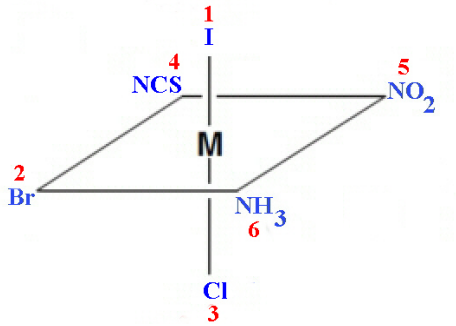
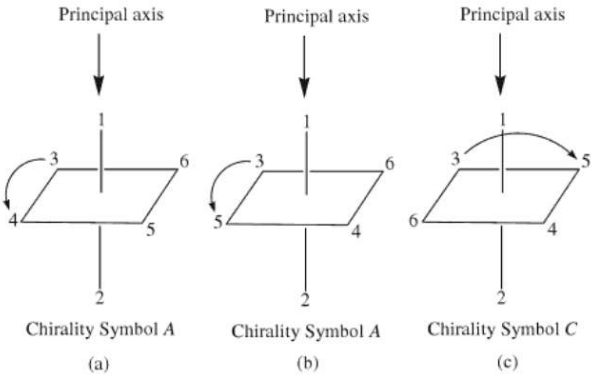


Figure* 8.2.4.1.2 *: *Here is one isomer where the I and Cl, and Br and NO_2 were found to be trans- to each other.*

The reference axis for an octahedral center is that axis containing the ligating atom of CIP priority 1 and the trans ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference. In the example shown above this would be C.



The two optical isomers of $[Co(en)_3]^{3+}$ have identical chemical properties and just denoting their absolute configuration does NOT give any information regarding the direction in which they rotate plane-polarised light. This can ONLY be determined from measurement and then the isomers are further distinguished by using the prefixes (-) and (+) depending on whether they rotate left or right.

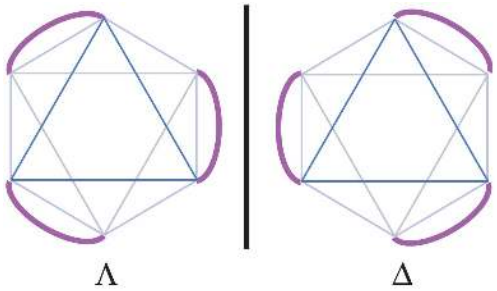


Figure 8.2.4.1.3 : left-handed Λ isomer (left) and right-handed Δ isomer (right)

To add to the confusion, when measured at the sodium D line (589 nm), the tris(1,2-diaminoethane)M(III) complexes (M= Rh(III) and Co(III)) with **IDENTICAL** absolute configuration, rotate plane polarized light in **OPPOSITE** directions! The left-handed (Λ)-$[Co(en)_3]^{3+}$ isomer gives a rotation to the right and therefore corresponds to the (+) isomer. Since the successful resolution of an entirely inorganic ion (containing no C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers e.g. $(NH_4)_2Pt(S_5)_3.2H_2O$.

For tetrahedral complexes, R and S would be used in a similar method to tetrahedral Carbon species and although it is predicted that tetrahedral complexes with 4 different ligands should be able to give rise to optical isomers, in general they are too labile and can not be isolated.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)
- Jim Clark (Chemguide.co.uk)

8.2.4.1: Optical Isomers in Inorganic Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Optical Isomers in Inorganic Complexes** is licensed CC BY-NC-SA 4.0.

8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands

Enantiomers are another kind of isomer that occur in octahedral metal complexes. Like the square planar platinum complexes seen before, these compounds consist of metal ions with other atoms or groups bound to them. More information about the binding of ligands to metals is found in the section on Lewis acids and bases. These groups that bind to metal ions are called ligands. One example of a type of octahedral compounds that can form enantiomers is bidentate complexes. In bidentate complexes (from the Greek two teeth) or chelating complexes (from the Greek crab), a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand.

Figure SC18a: Ethylenediamine (sometimes abbreviated en).

Bidentate ligands bind very tightly to a metal because they form two bonds with it, rather than just one.

> *In an octahedral complex, the two donor atoms in a bidentate ligand bind **cis** to each other. They **cannot** reach all the way around the molecule to bind trans to each other.*

The spatial relationship between the metal and the two atoms connected to it from the same ligand forms a plane. If more than one bidentate ligand is connected to the metal, the relative orientation of one plane to another creates the possibility of mirror images. A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller.

Figure SC18b. A left-handed propeller shape (left) is seen in Λ isomers of octahedral enantiomers. A right-handed propeller (right) is seen in Δ isomers of octahedral enantiomers.

These shapes are alternatively described as a left-handed screw and a right handed screw. If you can picture turning the shape so that it screws into the page behind it, which direction would you turn the screwdriver? If you would twist the screwdriver clockwise, then you have a right handed screw. If you would twist the screwdriver counter-clockwise, then you have a left handed screw.

What do we know about enantiomers?

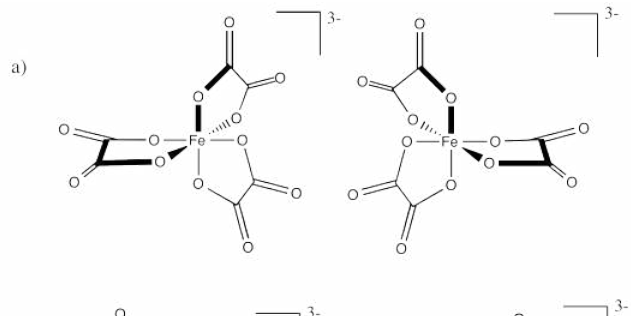
- enantiomers have identical physical properties, except...
- enantiomers have opposite optical rotation.

These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, early 20th century workers such as Alfred Werner were able to rule out some competing ideas about the structures of metal compounds. Today, we know that metal complexes play important roles in enzymes in biology, and Werner's work on metal complexes laid the groundwork for how we think about these complexes.

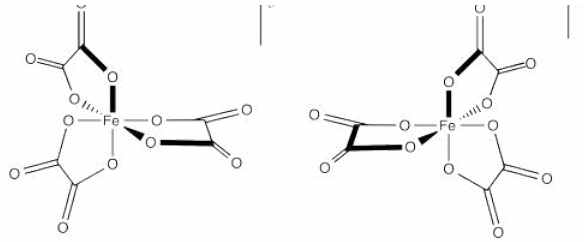
In addition, stereochemistry in metal complexes became very important in the late 20th century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, in order to maximize pharmaceutical effectiveness and minimize side effects.

Problem SC18.1.

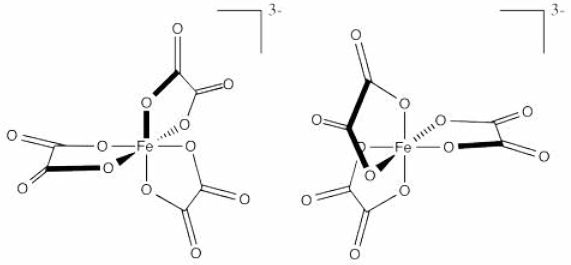
Identify the relationships between the following pairs of iron(III) oxalate ions.



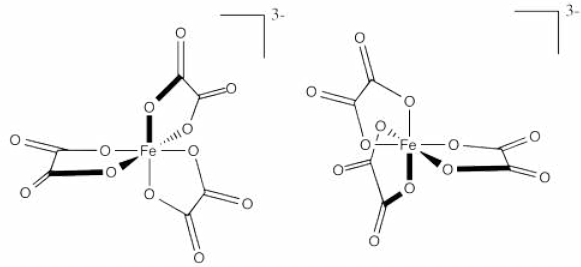
b)



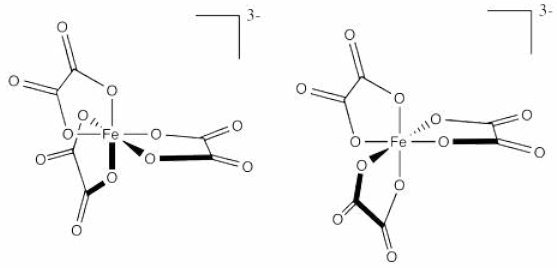
c)



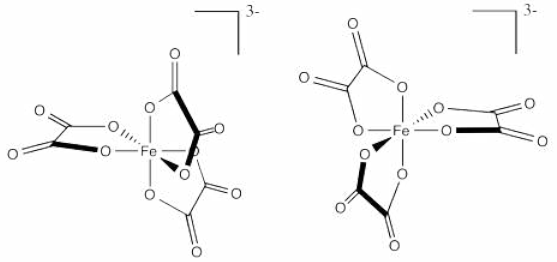
d)



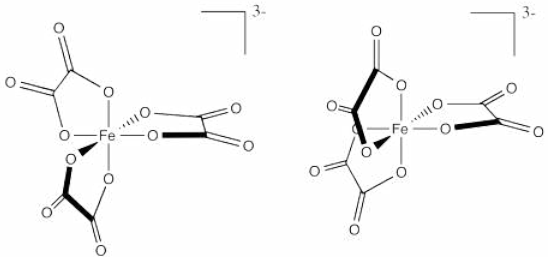
e)



f)

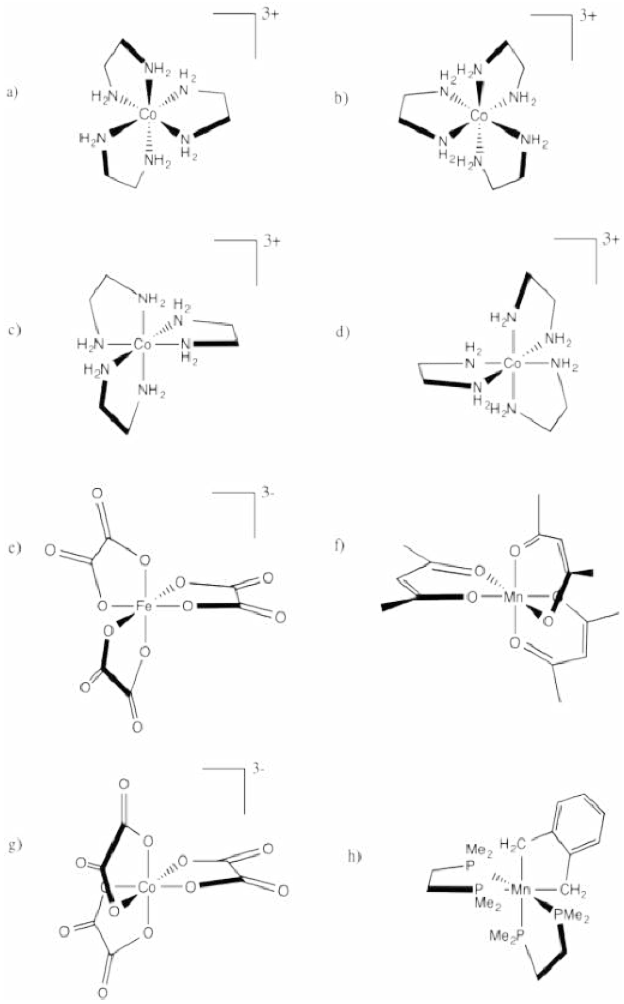


g)



Problem SC18.2.

Indicate whether each of the following compounds is the Δ or Λ isomer and draw its enantiomer.



Exercise: How many stereoisomers does an octahedral complex have? (contribution from B.J. Johnson)

This page titled 8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **Enantiomers in Octahedral Complexes with Bidentate Ligands** by Chris Schaller is licensed CC BY-NC 3.0.

8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes

The symmetry of a molecule is determined by the existence of **symmetry operations** performed with respect to **symmetry elements**. A symmetry element is a line, a plane or a point in or through an object, about which a rotation or reflection leaves the object in an orientation indistinguishable from the original. A plane of symmetry and the reflection operation is the coincidence of atoms on one side of the plane with corresponding atoms on the other side, as though reflected in a mirror.

Nine Planes of Potential Symmetry

Identifying planes of symmetry in an octahedral geometry can be daunting in evaluating if a molecule is chiral or not. There is a simple approach, which requires identying and testing six possible planes of symmetry that may exist for this geometry. To demonstrated this, we will consider the $[\mathrm{Cr(CO)_6}]$ complex in Figure 8.2.4.1.2.1

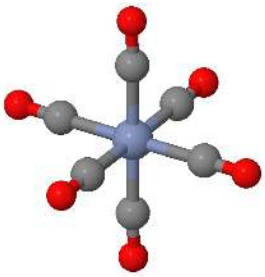


Figure 8.2.4.1.2.1: Octahedral Structure of the $[Cr(CO_6]$ complex. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

While you can no doubt recognize at least one plane of symmetry to confirm that this is an achiral complex, let's identify all six of them. First we have the three planes that include the Cr metal center (as they all do) and four of the attached ligands (Figure 8.2.4.1.2.2). These are often the easy planes to identify.

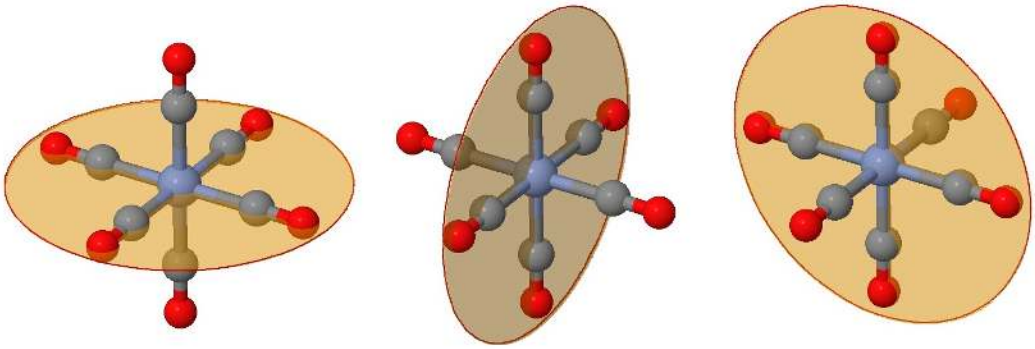


Figure 8.2.4.1.2.2: Three potential planes of symmetry for an octahedral complex. These planes have four ligands on the plane and two off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbeins University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

The next six planes are harder to identify and can be viewed as rotations of those in Figure 8.2.4.1.2.2by 45°. These planes bisect one angle between ligands, but still have two ligands on the plane (instead of four in the planes of Figure 8.2.4.1.2.2).

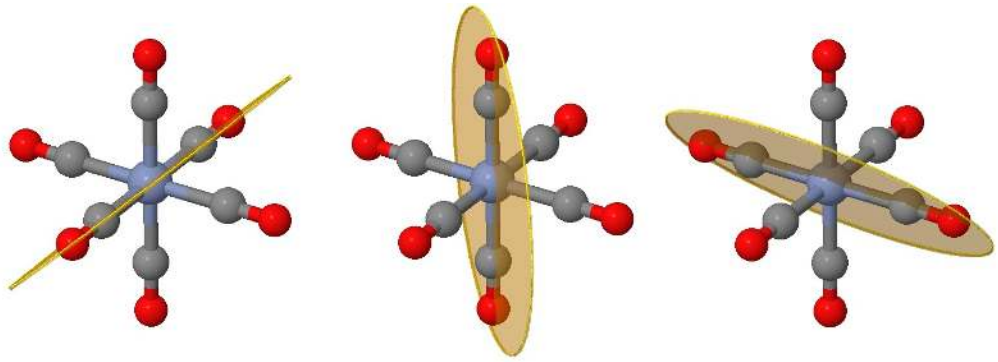


Figure 8.2.4.1.2.3 : Three potential planes of symmetry for an octahedral complex. These planes have two ligands on the plane and four off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

The next three planes are even harder to view on the same perspective but are also rotations of those in Figure 8.2.4.1.2.2by 45° in the perpendicular direction. These planes bisect an angle between ligands, but still have two ligands on the plane.

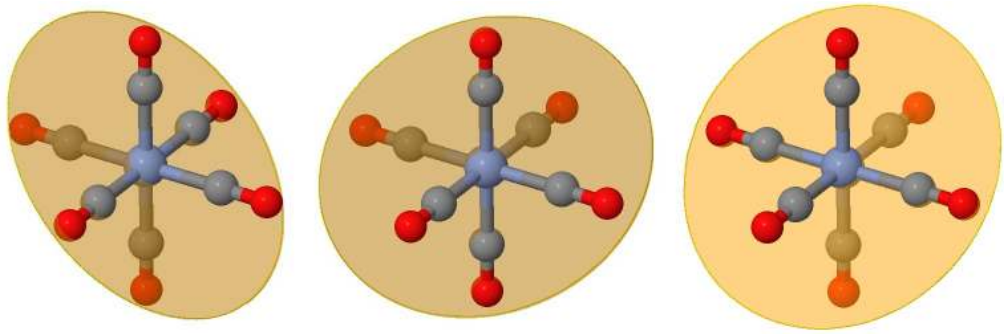


Figure 8.2.4.1.2.4 : Three potential planes of symmetry for an octahedral complex. These planes have two ligands on the plane and four off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

All nine planes, in each of planes are combined in the images below.

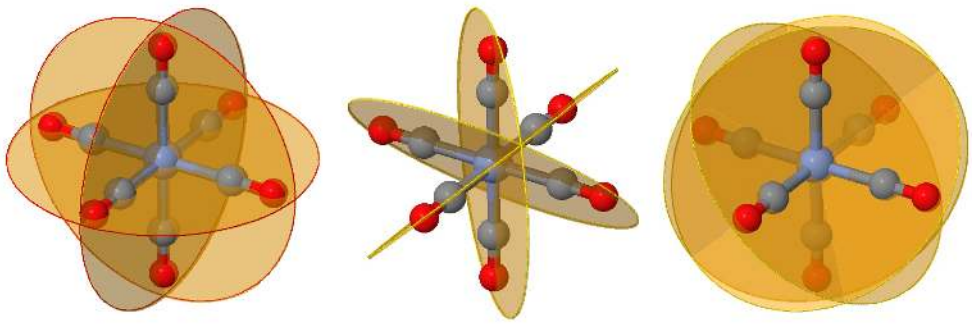


Figure 8.2.4.1.2.4 have two ligands on the plane and four off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

Now that can you identify these nine planes that may be mirror planes in an octahedral complex, you have to evaluate if they truly are mirror planes. That is simply asking if the ligand fields above the plane is IDENTICAL to the ligand field below. For the $[\mathrm{Cr(CO)}]$ complex discussed above, all nine planes are indeed mirror planes. However, in other complexes that may not be the case. Fortunately, to determine if a complex is chiral (optically active), then only one plane needs to be identified.

Contributors and Attributions

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Identifying Planes of Symmetry in Octahedral Complexes** is licensed CC BY-NC-SA 4.0.

8.2.4.1.3: Polarimetry

In measuring optical rotation, plane-polarized light travels down a long tube containing the sample. If it is a liquid, the sample may be placed in the tube as a pure liquid (its is sometimes called a neat sample). Usually, the sample is dissolved in a solvent and the resulting solution is placed in the tube. There are important factors affecting the outcome of the experiment.

- Optical rotation depends on the number of molecules encountered by the light during the experiment.
- Two factors can be controlled in the experiment and must be accounted for when comparing an experimental result to a reported value.

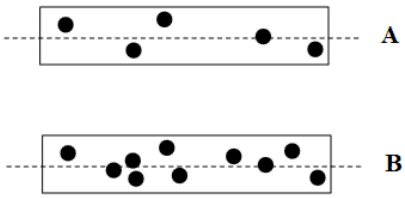


Figure 8.2.4.1.3.1 : The effect of concentration on optical rotation.

- The more concentrated the sample (the more molecules per unit volume), the more molecules will be encountered.
- Concentrated solutions and neat samples will have higher optical rotations than dilute solutions.
- The value of the optical rotation must be corrected for concentration.

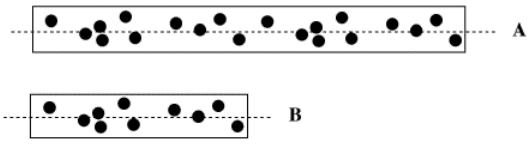


Figure 8.2.4.1.3.2 : The effect of path length on optical rotation.

- The longer the path of light through a solution of molecules, the more molecules will be encountered by the light, and the greater the optical rotation.
- The value of the optical rotation must be corrected for the length of the cell used to hold the sample.

Summary

$$[\alpha] = \frac{\alpha}{cl}$$

- α is the measured optical rotation.
- c is the sample concentration in grams per deciliter (1 dL = 10 mL), that is, c = m / V (m = mass in g, V = volume in dL).
- l is the cell length in decimeters (1 dm = 10 cm = 100 mm)
- The square brackets mean the optical rotation has been corrected for these variables.

? Exercise 8.2.4.1.3.1

Apr 14, 2018, 10:50 AM

Problem SC7.1.

A pure sample of the naturally-occurring, chiral compound A (0.250 g) is dissolved in acetone (2.0 mL) and the solution is placed in a 0.5 dm cell. Three polarimetry readings are recorded with the sample: 0.775º, 0.806º, 0.682º.

1. What is [a]?
2. What would be the [a] value of the opposite enantiomer?

Answer

TBA

Exercise 8.2.4.1.3.2

Apr 14, 2018, 10:50 AM

Problem SC7.2.

A pure sample of the (+) enantiomer of compound B shows [a] = 32°. What would be the observed a if a solution of the sample was made by dissolving 0.150 g in 1.0 mL of dichloromethane and was then placed in a 0.5 dm cell?

Answer

TBA

Contributors and Attributions

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 8.2.4.1.3: Polarimetry is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **Polarimetry** by Chris Schaller is licensed CC BY-NC 3.0.

8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

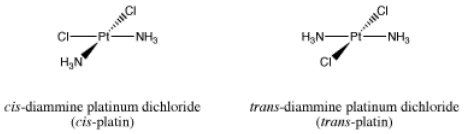


Figure SC2.1. Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

Exercise SC2.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

Exercise SC2.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

Contributors and Attributions

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

This page titled 8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **Stereoisomers: Geometric Isomers in cis-platin** by Chris Schaller is licensed CC BY-NC 3.0.

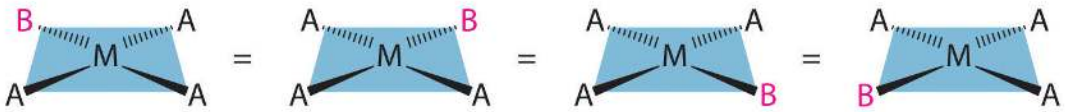
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

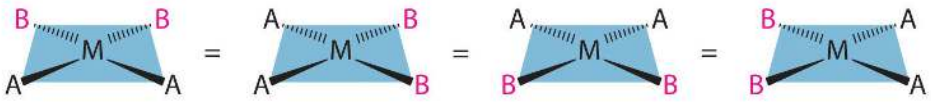
Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

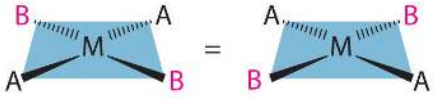


MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

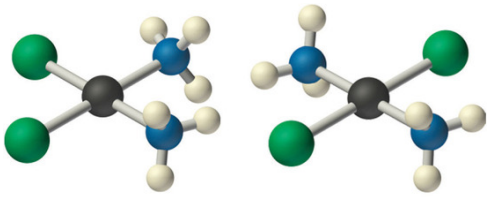


MA_2B_2 square planar complex, *cis* isomer



MA_2B_2 square planar complex, *trans* isomer

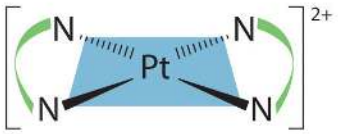
Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

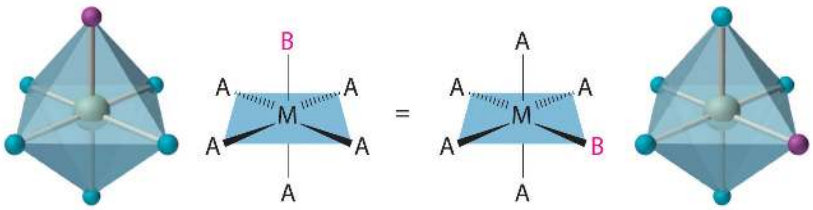
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

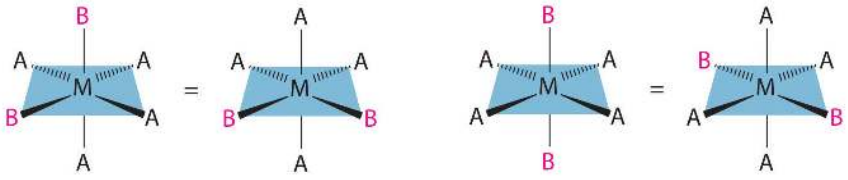
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four "in-plane" ligands are different from the two "axial" ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



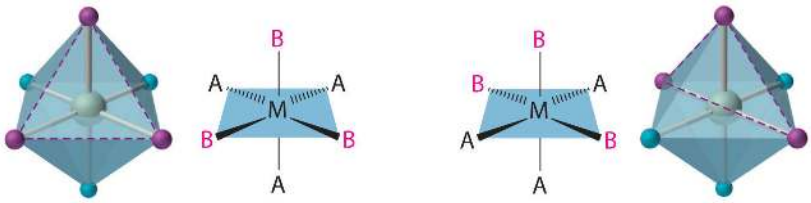
MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer

MA_3B_3 octahedral complex, *mer* isomer

Example 8.2.4.3.1

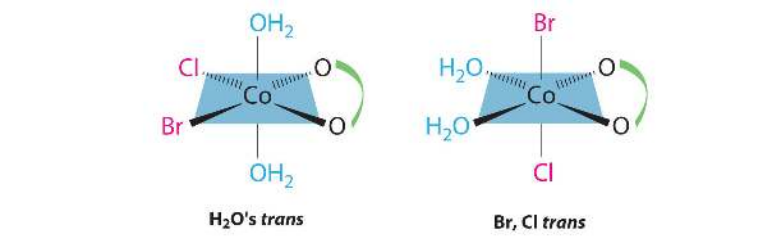
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

Asked for: structures of geometrical isomers

Solution

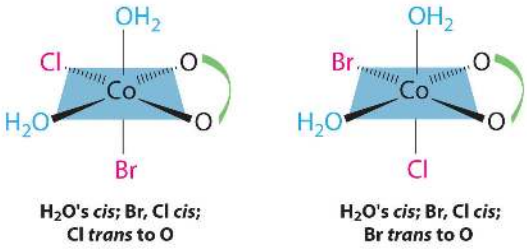
This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



H_2O's *trans*

Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O

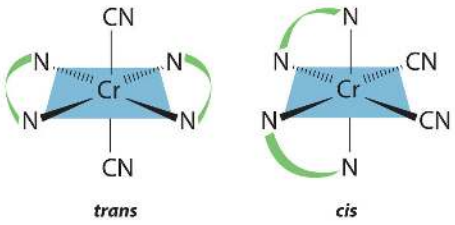
H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

This complex can therefore exist as four different geometrical isomers.

Exercise 8.2.4.3.1

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer



Two geometrical isomers are possible: trans and cis.

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Stereoisomers: Geometric Isomers in Transition Metal Complexes** is licensed CC BY-NC-SA 4.0.

8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II

Geometric Isomers are isomers that differ in the arrangement of the ligands around the metal or the central atom. In other words, these isomers differ from each other based on where the ligands are placed in the coordinate compound. This will be much easier to understand as examples will be considered. There are 2 main types of geometric isomers:

- Cis-Trans Isomers (referencing the spatial arrangement of two species)
- Mer-Fac Isomers (referencing the spatial arrangement of three species)

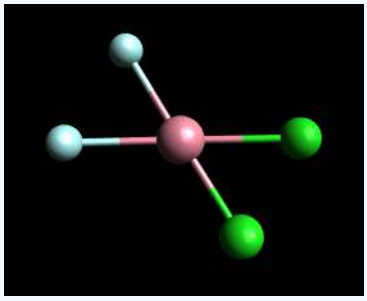
Cis-Trans Isomers

Cis-Trans Isomers are isomers that differ in the arrangement of two ligands in square planar and octahedral geometry. Cis isomers are isomers where the two ligands are 90 degrees apart from one another in relation to the central molecule. This is because Cis isomers have a bond angle of 90º, between two same atoms. Trans isomers, on the other hand, are isomers where the two ligands are on opposite sides in a molecule because trans isomers have a bond angle of 180º, between the two same atoms. When naming cis or trans isomers, the name begins either with cis or trans, whichever applies, followed by a hyphen and then the name of a molecule. For example a cis isomer of $CoCl_2F_2$ would be called cis-$CoCl_2F_2$. Finally, the last thing to keep in mind when examining cis and trans isomers is that **only square planar and octahedral** geometries can have cis or trans isomers. Examples of both isomers are provided below.

Example 8.2.4.4.1: cis Isomer

$CoCl_2F_2$:

(Color scheme: pink=cobalt, blue=fluorine, green=chlorine)



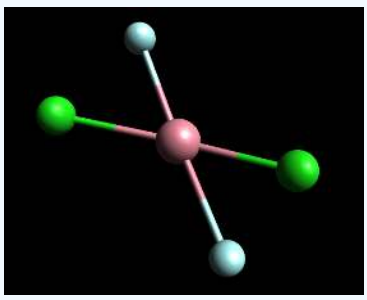
This above is an example of the molecule cis-$CoCl_2F_2$ or cis-dichlorodifluorocobalt (IV). The molecule pictured above is a cis isomer because both fluorine and chlorine ligands, respectively, are on the same side of the molecule. Additionally, one can approximate that the bond angle between each of the chlorine atoms and between each of the fluorine atoms is 90º.

Isomer

$CoCl_2F_2$:

(Color scheme: pink=cobalt, blue=fluorine, green=chlorine)

(Note, the differences in the length of the bond between the two pictures are not intentional and have nothing to do with cis-trans isomerism)

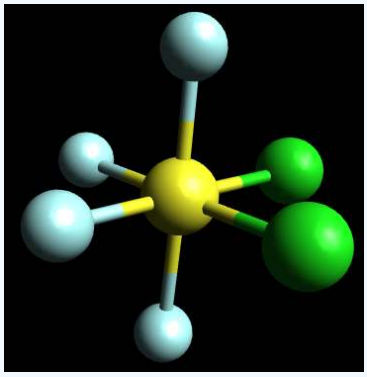


This above is an example of the molecule trans-$CoCl_2F_2$ or trans-dichlorodifluorocobalt (IV).

We know the above molecule is a trans isomer because the two same chlorine atoms and the two same fluorine atoms are opposite each other. Furthermore, the bond angle between the two chlorine atoms and between the two fluorine atoms is 180°. The above examples were all for square planar geometry but as the examples below illustrate, cis-trans isomerism can also occur in octahedral geometry. Both the molecules below are isomers of the molecule SCl_2F_4 (color scheme: yellow=sulfur, blue=fluorine, green=chlorine).

Example 8.2.4.4.3: Octahedral cis Isomer

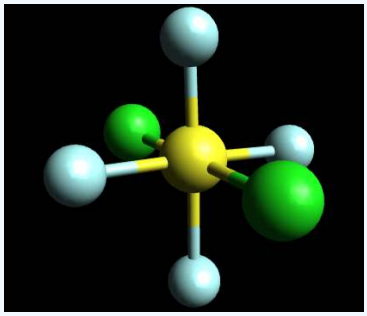
SCl_2F_4:



We know this isomer above is a cis isomer because both the chlorine ligands are on the same side and the bond angle between the chlorine atoms appears to be 90°.

Example 8.2.4.4.4: Octahedral trans Isomer

SCl_2F_4:



The isomer above is a trans isomer because the chlorine ligands are on opposite sides and the bond angle between the chlorine atoms is 180°. All other isomers are essentially just rotations of these two isomers. Once again when trying to find cis and trans isomers look at the arrangement of the ligands. If two same ligands are on the same side, it is a cis isomer and if the ligands are on opposite sides, it is a trans isomer. Another way to tell the isomers apart is the bond angles: cis isomers have a 90° bond angle whereas trans isomers have a 180° bond angle.

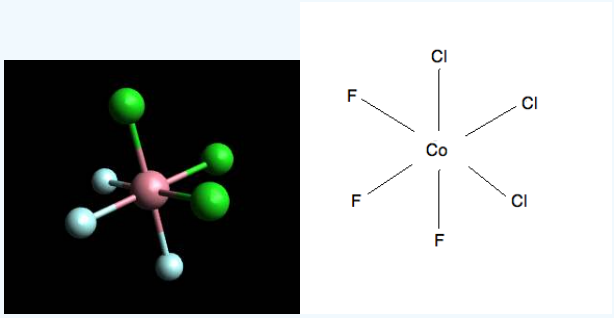
Mer-Fac Isomers

Mer-Fac isomers are easier to notice than cis-trans isomers in the sense that they only exist in octahedral geometry. Just like cis-trans isomers, mer-fac isomers are determined based on whether or not the ligands exist on the same side. Instead of dealing with 2 ligands, mer-fac isomers deal with 3 ligands. If the 3 ligands are all on the same side, the isomer is called a fac-isomer. Another way to identify fac isomers is to look at the bond angle between the ligands because fac isomers have a 90° bond angle between each of the 3 atoms. The mer isomer on the other hand is where only 2 of the 3 ligands are on the same side. In mer isomers, there exists a 90°-90°-180° bond angle between the 3 same ligands. In terms of nomenclature, mer-fac isomers follow the same rule as

cis-trans isomers where you put the isomer type, followed by a hyphen, followed by the molecular formula. Examples have been provided below.

Example 8.2.4.4.5: fac Isomer

Below is an example of the fac isomer, fac-$CoCl_3F_3$:

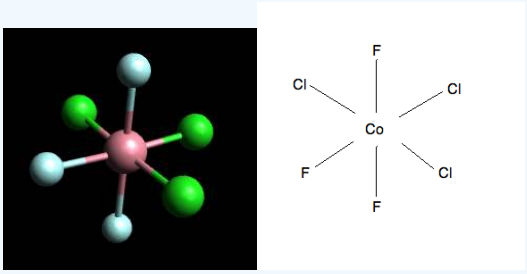


(note the color scheme: pink=cobalt, green=chlorine, blue=fluorine)

Through the 2d version, it is easier to see how the ligands are all on the same side. Nonetheless, in the 3D version, one can observe that the bond angle between the 3 same ligands is 90º, thus making this isomer a fac-isomer.

Example 8.2.4.4.6: mer Isomer

Below is an example of the mer isomer, mer-$CoCl_3F_3$:



(note the color scheme: pink=cobalt, green=chlorine, blue=fluorine)

Its hard to tell in the 3D version but in the 2D version, one can easily tell how the same ligands are not on the same side. Additionally, one can approximate that the bond angle between the three chlorine atoms and between the three fluorine atoms is 90º-90º-180º, thus making the above molecule a mer isomer.

Contributors and Attributions

Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Stereoisomers: Geometric Isomers in Transition Metal Complexes II** is licensed CC BY-NC-SA 4.0.

8.2.4.5: Stereoisomers of Complex Metal Complexes

Stereoisomers are isomers that have the same molecular formula and ligands, but differ in the arrangement of those ligands in 3D space.

Contributors and Attributions

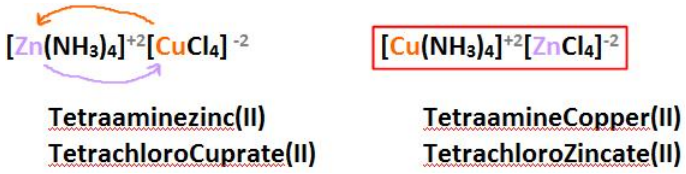
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)
- Angad Oberoi (UCD)

8.2.4.5: Stereoisomers of Complex Metal Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Stereoisomers of Complex Metal Complexes** is licensed CC BY-NC-SA 4.0.

8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes

Coordination isomerism occurs in compounds containing complex anionic and cationic parts and can be viewed as the interchange of one or more ligands between the cationic complex ion and the anionic complex ion. For example, $[Co(NH_3)_6][Cr(CN)_6]$ is a coordination isomer with $[Cr(NH_3)_6][Co(CN)_6]$. Alternatively, coordination isomers may be formed by switching the metals between the two complex ions like $[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.



? Exercise 8.2.4.6.1

Are $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$ coordination isomers?

Solution

Here, both the cation and anion are complex ions. In the first isomer, NH_3 is attached to the copper and the Cl^- are attached to the platinum. In the second isomer, they have swapped.

Yes, they are coordination isomers.

? Exercise 8.2.4.6.2

What is one coordination isomer of $[Co(NH_3)_6][Cr(C_2O_4)_3]$?

Solution

Coordination isomers involve swapping the species from the inner coordination sphere to one metal (e.g, cation) to inner coordination sphere of a different metal (e.g., the anion) in the compound. One isomer is completely swapping the ligand sphere, e.g, $[Co(C_2O_4)_3][Cr(NH_3)_6]$.

Alternative coordination isomers are $[Co(NH_3)_4(C_2O_4)][Cr(NH_3)_2(C_2O_4)_2]$ and $[Co(NH_3)_2(C_2O_4)_2][Cr(NH_3)_4(C_2O_4)]$.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Structural Isomers: Coordination Isomerism in Transition Metal Complexes** is licensed CC BY-NC-SA 4.0.

8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes

Coordination isomerism is a form of structural isomerism in which the composition of the complex ion varies. In a coordination isomer the total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. Ionization isomers can be thought of as occurring because of the formation of different ions in solution.

Introduction

Ionization isomers are identical except for a ligand has exchanged places with an anion or neutral molecule that was originally outside the coordination complex. The central ion and the other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different.

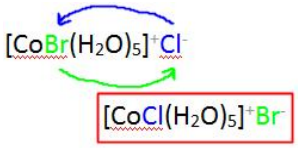


Figure 8.2.4.7.1 : Two Ionization isomers. The two isomers differ only which ligands are actually bound to the center metal. These two isomers are called pentaaqua**bromo**cobaltate(II) **chloride** and pentaaqua**chloro**cobaltate(II) **bromide**.

The difference between the ionization isomers can be viewed within the context of the ions generated when each are dissolved in solution.

For example, when pentaaquabromocobaltate(II)chloride is dissolved in water, Cl^- ions are generated:

$$CoBr(H_2O)_5Cl(s) \rightarrow CoBr(H_2O)_5^+(aq) + Cl^+(aq)$$

whereas when pentaaquachlorocobaltate(II)bromide is dissolved, Br^- ions are generated:

$$CoCl(H_2O)_5Br(s) \rightarrow CoCl(H_2O)_5^+(aq) + Br^+(aq).$$

Note

If one dissolved $[PtBr(NH_3)_3]NO_2$ and $[Pt(NO_2)(NH_3)_3]Br$ into solution, then two different set of ions will be general.

- Dissolving $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would have the following reaction

$$[PtBr(NH_3)_3]NO_2(s) \rightarrow [PtBr(NH_3)_3]^+(aq) + NO_2^-(aq) \quad (8.2.4.7.1)$$

- Dissolving of $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would be

$$[Pt(NO_2)(NH_3)_3]Br(s) \rightarrow [Pt(NO_2)(NH_3)_3]^+(aq) + Br^-(aq) \quad (8.2.4.7.2)$$

Notice that these two ionization isomers differ in that one ion is directly attached to the central metal, but the other is not.

Equations 8.2.4.7.1 and 8.2.4.7.2 are valid under the assumption that the platinum-ligand bonds of the complexes are stable (i.e., not labile). Otherwise, they may break and other ligands (e.g., water) may bind.

Example 8.2.4.7.1

Are $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ coordination isomers?

Solution

First, we need confirm that each compound has the same number of atoms of the respective elements (this requires viewing both cations and anions of each compound).

Element	number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	number of atoms in $[Cr(NH_3)_5Br]SO_4$

Element	number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	number of atoms in $[Cr(NH_3)_5Br]SO_4$
Cr	1	1
N	5	5
H	15	15
O	4	4
S	1	1
Br	1	1

Now, let's look at what these two compounds look like (Figure 8.2.4.7.2). The sulfate group is a ligand with a dative bond to the chromium atom and the bromide counter ion ($[Cr(NH_3)_5(OSO_3)]Br$). For $[Cr(NH_3)_5Br]SO_4$, this is the the reverse.

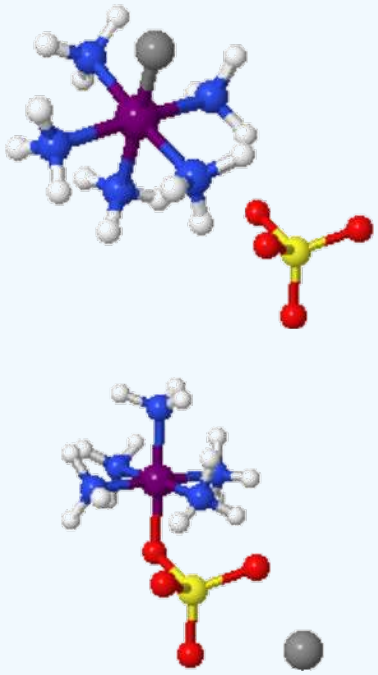


Figure 8.2.4.7.2: $[Cr(NH_3)_5(OSO_3)]Br$ (left) and $[Cr(NH_3)_5Br]SO_4$ (right) are coordination isomers.

Yes, $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ are coordination isomers.

? Exercise 8.2.4.7.1

Are $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$ ionization isomers?

Solution

In the first isomer, SO_4 is attached to the Cobalt and is part of the complex ion (the cation), with Br as the anion. In the second isomer, Br is attached to the cobalt as part of the complex and SO_4 is acting as the anion.

A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.

Solvate or Hydrate Isomerization: A Special kind of Ionization Isomer

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*). In the case of water, this is called *Hydrate isomerism*. The best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Structural Isomers - Ionization Isomerism in Transition Metal Complexes** is licensed CC BY-NC-SA 4.0.

8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^-/NCS^- and NO_2^-/ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a *polydentate* rather than an *ambidentate* ligand.

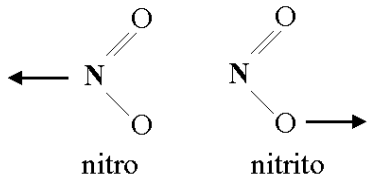
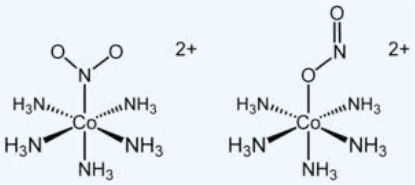


Figure 8.2.4.8.1 : Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

The names used to specify the changed ligands are changed as well. For example, the (NO_2^-) ion is called *nitro* when it binds with the N atom and is called *nitrito* when it binds with the O atom.

Example 8.2.4.8.1: Nitro- vs. Nitrito- Linkage Isomers

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.



(left) The nitro isomer (Co-NO_2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro-* complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito-* complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers

- $[Co(ONO)(NH_3)_5]Cl$: the *nitrito* isomer -O attached
- $[Co(NO_2)(NH_3)_5]Cl$: the *nitro* isomer - N attached.

The formula of the complex is unchanged, but the properties of the complex may differ.

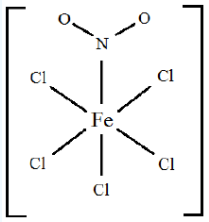
Another example of an ambidentate ligans is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Polyfunctional ligands can bond to a metal center through different ligand atoms to form various isomers. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, SO_3^{2-}.

Exercise 8.2.4.8.1

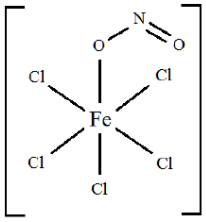
Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ linkage isomers?

Solution

Here, the difference is in how the ligand bonds to the metal. In the first isomer, the ligand bonds to the metal through an electron pair on the nitrogen. In the second isomer, the ligand bonds to the metal through an electron pair on one of the oxygen atoms. It's easier to see it:



$[FeCl_5(NO_2)]^{3-}$



$[FeCl_5(ONO)]^{3-}$

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Structural Isomers: Linkage Isomerism in Transition Metal Complexes** is licensed CC BY-NC-SA 4.0.

8.2.5: Ligands

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom.

The term ligand come from the latin word *ligare* (which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. Ligands can be anions, cations, or neutral molecules. Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion.

Monodentate Ligands

The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the center through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

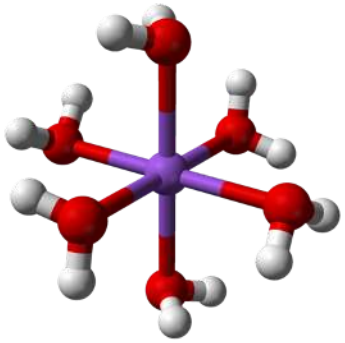


Figure 8.2.5.1: Central atom with six monodentate ligands attached. (Image courtesy of Wikimedia Commons.)

Bidentate Ligands

Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Common examples of bidentate ligands are ethylenediamine (en), and the oxalate ion (ox). Shown below is a diagram of ethylenediamine: the nitrogen (blue) atoms on the edges each have two free electrons that can be used to bond to a central metal atom or ion.

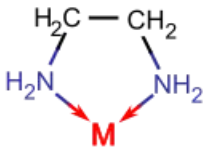


Figure 8.2.5.2: Ethylenediamine (en) is an example of a bidentate ligand. (Image courtesy of Wikimedia Commons.). Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M

Polydentate Ligands

Polydentate ligands range in the number of atoms used to bond to a central metal atom or ion. EDTA, a hexadentate ligand, is an example of a polydentate ligand that has six donor atoms with electron pairs that can be used to bond to a central metal atom or ion.

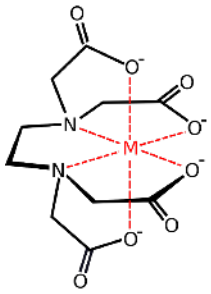
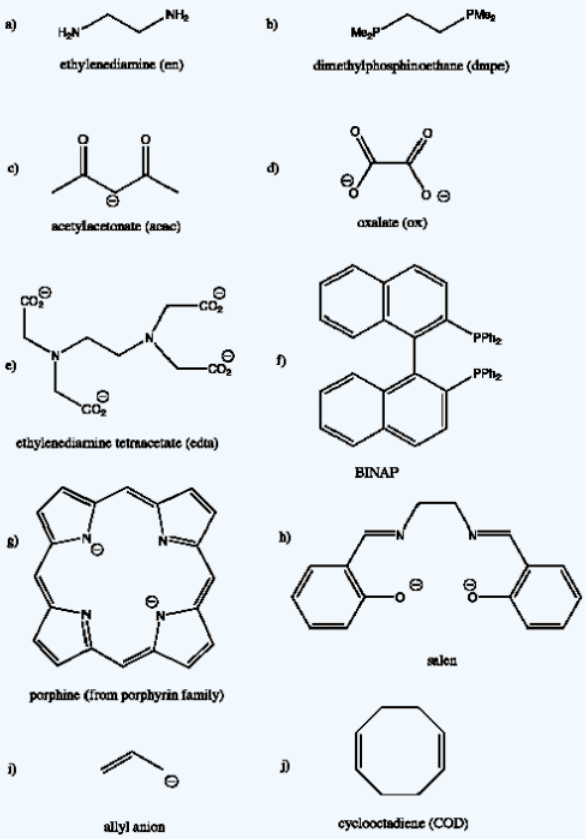


Figure 8.2.5.3: Ethylenediaminetetraaceticacid acid (EDTA) is a hexadentate ligand and can bind a Metal via multiple "teeth" (left) Unbound EDTA ion and (right) EDTA bound to a generic transition metal. (Images courtesy of Wikimedia Commons.)

Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. A good example of this is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom.

Example 8.2.5.1

Draw metal complexes using the ligands below and metal ions of your choice.



Chelation

Chelation is a process in which a polydentate ligand bonds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent. The term chelate was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew, who stated: "The adjective chelate, derived from the great claw or chela (chely- Greek) of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." As the name implies, chelating ligands have high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands. Both Ethylenediamine (Figure 8.2.5.2) and Ethylenediaminetetraaceticacid acid (Figure 8.2.5.3) are examples of chelating agents, but many others are commonly found in the inorganic laboratory.

The Chelate Effect

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "pre-organized" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand that strongly complexes transition metal ions, including Fe^{+2} in hemogloben (Figure 8.2.5.4).

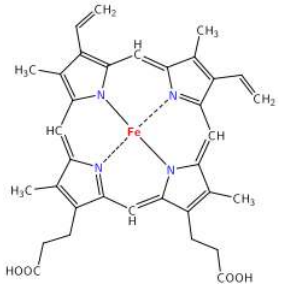
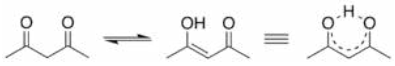


Figure 8.2.5.4: Heme b macrocyclic ligand that binds iron in hemoglobin

Some other common chelating and cyclic ligands are shown below:

- **Acetylacetonate** ($acac^-$, top) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



- **2,2'-Bipyridine 2,2'-Bipyridine** (Figure 8.2.5.5 left) and related bidentate ligands such as 1,10-phenanthroline form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis.
- **Crown ethers** such as 18-crown-6 **2,2'-Bipyridine** (Figure 8.2.5.5 center) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.
- The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (**2,2'-Bipyridine** (Figure 8.2.5.5 right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.

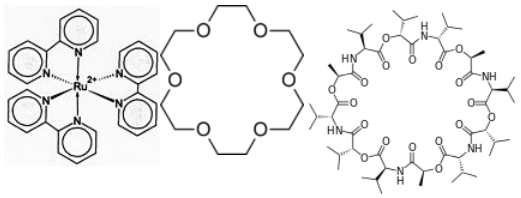


Figure 8.2.5.5: (let) 2,2'-Bipyridine, (center) 18-crown-6 2,2'-Bipyridine (right) valinomycin

References

1. Petrucci, Harwood, Herring, Madura. General Chemistry Principles & Modern Applications. Prentice Hall. New Jersey, 2007
2. Cox, Tony. (2004). Instant notes in inorganic chemistry. Oxford, UK: Taylor & Francis.
3. Libraries, Association, Robert Williams, and J. Silva. Bringing chemistry to life. Oxford University Press, USA, 1999. Print.
4. Moeller, Therald, Douville, Judith, & Libraries, Association. (1988). Inorganic Chemistry: A Modern Introduction. Amer Library Assn.
5. Bowker, R., Warmus, Mieczysław, Muzzy, Adrienne, LOCALIZADO, AUTOR, Hopkinson, Barbara, Saur, K, Izod, Irene, Hopkinson, Barbara, Saur, K, Books, K, & Company, K. (1994). Inorganic Chemistry Concepts. K G Saur Verlag Gmbh & Co.
6. Porterfield, William. (1984). Inorganic chemistry. Addison Wesley Publishing Company.

Contributors and Attributions

- Harjeet Bassi (UCD)
- Adapted from the Wikibook constructed by Chemistry 310 students at Penn State University.

8.2.5: Ligands is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.2: Ligands** is licensed CC BY-SA 4.0.

8.2.5.1: EDTA

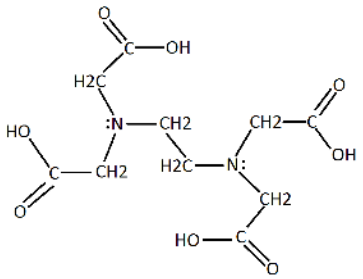


Figure 2: An EDTA molecule binds a total of six times to a generic central metal, labeled M. Notice that the atoms with the unpaired electrons (the two nitrogens and four oxygens) make these coordinate covalent bonds. Credits go to Wikipedia for picture.

Contributors and Attributions

- Allen Zeng, UC Davis, SSReno, Parul Jandir, UC Davis

8.2.5.1: EDTA is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

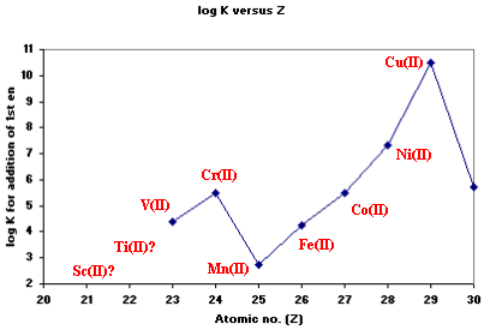
- **EDTA** is licensed CC BY-NC-SA 4.0.

8.2.5.2: The Irving-Williams Series

The general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is:

$$\mathrm{Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)}$$

This trend is essentially independent of the ligand. In the case of 1,2-diaminoethane (en), the first step-wise stability constants ($\log K_1$) for M(II) ions are shown below.



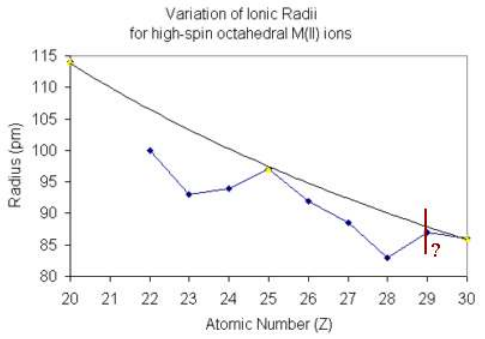
> The Irving-Williams sequence is generally quoted ONLY for Mn(II) to Zn(II) since there is little data available for the other first row transition metal ions because their M(II) oxidation states are not very stable. The position of Cu(II) is considered out-of-line with predictions based on Crystal Field Theory and is probably a consequence of the fact that Cu(II) often forms Jahn-Teller distorted octahedral complexes.

One explanation

Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the **charge to radius ratio**. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block.

For free metal ions in the gaseous phase it might be expected that the ionic radius of each ion on progressing across the d-block should show a gradual decrease in size. This would come about due to the incomplete screening of the additional positive charge by the additional electron, as is observed in the Lanthanide Contraction.

For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t_{2g} orbitals before filling the e_g orbitals since for octahedral complexes, the t_{2g} subset are directed in between the incoming ligands whilst the e_g subset are directed towards the incoming ligands and cause maximum repulsion.



For d^1-d^3 (and d^6-d^8) the addition of the electrons to the t_{2g} orbitals will mean that the screening of the increasing attractive nuclear charge is not very effective and the radius should be smaller than for the free ion.

The position of d^4 and d^9 on the plot is difficult to ascertain with certainty since six-coordinate complexes are expected to be distorted due to the Jahn-Teller Theorem. Cr(II) is not very stable so few measurements are available. For Cu(II) however, most complexes are found to have 4 short bonds and 2 long bonds although 2 short and 4 long bonds is feasible. The radii are expected to show an increase over the d^3 and d^8 situation since electrons are being added to the e_g subset. The reported values have been found to lie on both sides of the predicted value.

For d^0, d^5 and d^{10} the screening expected is essentially that of a spherical arrangement equivalent to the absence of a crystal field. The plot above shows that these points return to the line drawn showing a gradual decrease of the radius on moving across the d-block.

Once the decrease in radius with Z pattern is understood, it is a small step to move to a pattern for q/r since this only involves taking the reciprocal of the radius and holding the charge constant. The radius essentially decreases with increasing Z, therefore 1/r must increase with increasing Z.

For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be

$$\mathrm{Mn(II)} < \mathrm{Fe(II)} < \mathrm{Co(II)} < \mathrm{Ni(II)} > \mathrm{Cu(II)} > \mathrm{Zn(II)}$$

Apart from the position of Cu(II), this corresponds to the Irving-Williams series (Eqution 1). The discrepancy is once again accounted for by the fact that copper(II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory.

Contributors and Attributions

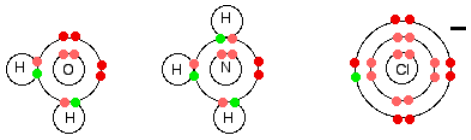
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

This page titled 8.2.5.2: The Irving-Williams Series is shared under a not declared license and was authored, remixed, and/or curated by Robert J. Lancashire.

- **The Irving-Williams Series** by Robert J. Lancashire is licensed CC BY-NC-SA 4.0.

8.2.6: What is a Complex Ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (although in some cases, the bonding is actually more complicated than that.) The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as Lewis bases.

Bonding in Simple Complex Ions

We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $Al(H_2O)_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

Example 8.2.6.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

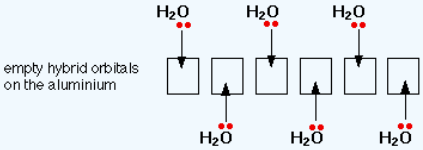
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

When it forms an Al^{3+} ion it loses the 3-level electrons to leave

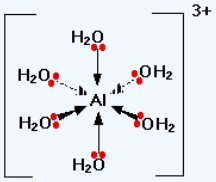
$$1s^2 2s^2 2p^6$$

That means that all the 3-level orbitals are now empty. The aluminum uses of six of these to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules it is possible to fit around an aluminum ion (and most other metal ions). By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

Example 8.2.6.2is chosen because it is very similar to the last one - except that it involves a transition metal.

Example 8.2.6.2: $Fe(H_2O)_6^{3+}$

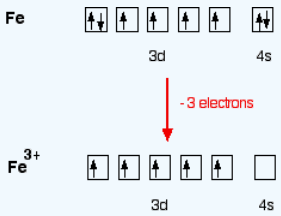
Iron has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$$

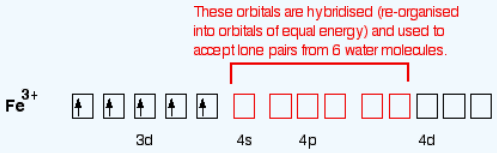
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$$

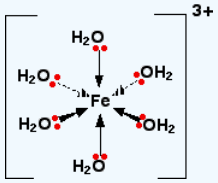
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminum ion.



Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

Example 8.2.6.3demonstrates the formation of a complex ion with a negative charge.

Example 8.2.6.3: $CuCl_4^{2-}$

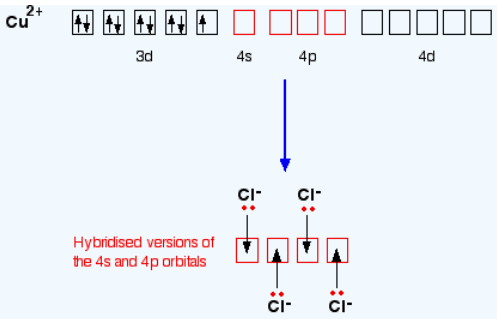
Copper has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

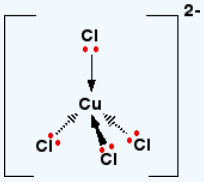
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridised form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



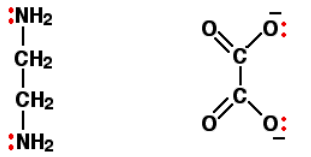
The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Complex metal ions containing more complicated ligands

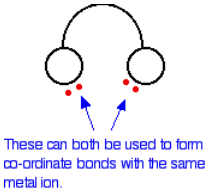
In the examples we've already looked at, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).



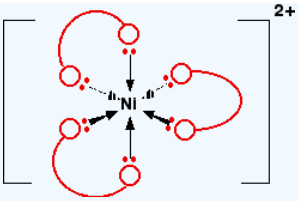
In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



Example 8.2.6.4: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$.

The structure of the ion looks like this:



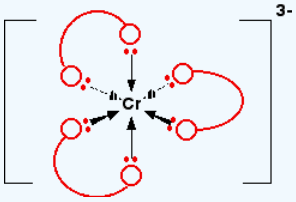
In this case, the "ear pieces" are the nitrogen atoms of the NH_2 groups - and the "bit that goes over your head " is the - CH_2CH_2- group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other. Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the **number of bonds**, not the number of ligands.

Example 8.2.6.5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried 2-. (3+) + (3 x 2-) = 3-.

The structure of the ion looks like this:

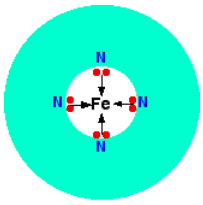


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

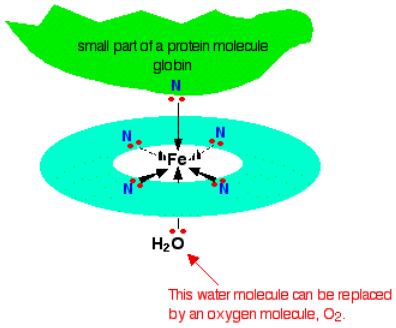
A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the haem, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

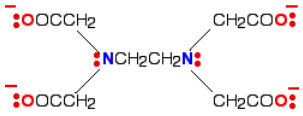


Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds. The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

> You probably know that carbon monoxide is poisonous because it reacts with haemoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that haemoglobin molecule useless for any further oxygen transfer.

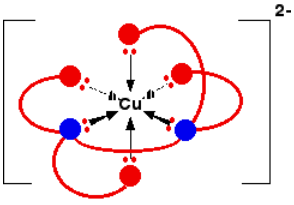
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA, which is used as a negative ion - $EDTA^{4-}$. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the $EDTA^{4-}$ ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the $[Cu(EDTA)]^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.2.6: What is a Complex Ion? is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **What is a Complex Ion?** by Jim Clark is licensed CC BY-NC 4.0.

8.2.7: Nomenclature of Coordination Complexes

Learning Objectives

- To learn the basis for complex ion and compound nomenclature

Coordination complexes have their own classes of isomers, different magnetic properties and colors, and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal ligands]$^{\pm Charge}$, while names are written Prefix Ligands Metal (Oxidation State).

Introduction

According to the Lewis Acid-Base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. **Coordination complexes** consist of a ligand and a metal center cation and their charge can be positive, negative, or neutral. **Coordination compounds** are neutral compounds that contain at least one complex ions. Example of coordination complexes and compounds are:

- Complex Cation: $[Co(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is **monodentate** or **polydentate**.

Rules to Complex Ion Nomenclature

To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rule 1: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table 8.2.7.1: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 2: Neutral Ligands

Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table 8.2.7.2: Select Neutral Monodentate Ligands. Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table 8.2.7.3: Select Polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis* (for two ligands), *tris* (for three ligands), and *tetrakis* (for four ligands).

Table 8.2.7.4: Prefixes for indicating number of ligands in a complex.

Number of Ligands	Monodentate Ligands	Polydentate Ligands
1	mono	-
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron(III) ion. Remember that ligands are always named first, before the metal is.

Example 8.2.7.1

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4 aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

Exercise 8.2.7.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Answer

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that *en* is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "di", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Rule 4: The Metals

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis. For example, in the problems above, chromium and cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as copper(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate(II). The following change to their Latin names when part of an anion complex:

Table 8.2.7.5: Latin terms for Select Metal Ion

Transition Metal	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. This is not necessary if it is neutral or part of a coordination compound (Example 8.2.7.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

Example 8.2.7.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

Exercise 8.2.7.2

What is the name of $[CuCl_4]^{2-}$?

Answer

tetrachlorocuprate(II) ion

A last little side note: when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Foe xample, for $NaCl$. The the positive Na cation comes first and the negative Cl^- anion follows.

Example 8.2.7.3

What is the name of $[Pt(NH_3)_4][Pt(Cl)_4]$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

Exercise 8.2.7.3: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

Answer

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Writing Formulas of Coordination Complexes

While chemistry typically follow the nomenclature rules for naming complexes and compounds, there is disagreement with the rules for constructing formulas of inorganic complexes. For example, the order of ligand names in their formula has been ambiguous with different conventions being used (charged vs neutral, number of each ligand, etc.). In 2005, IUPAC adopted the recommendation that all ligand names in formulas be listed **alphabetically** (in the same way as in the naming convention) irrespective of the charge or number of each ligand type.

However, this rule is not adhered to in many chemistry laboratories. For practice, the order of the ligands in chemical formulas does not matter as long as you write the transition metal first, which is the stance taken here.

Examples 8.2.7.4

Write the chemical formulas for:

a. Amminetetraaquachromium(II) ion
b. Amminesulfatochromium(II)

Solution

a. Amminetetraaquachromium(II) ion could be written as $[Cr(H_2O)_4(NH_3)]^{+2}$ or $[Cr(NH_3)(H_2O)_4]^{+2}$.
b. Amminesulfatochromium (II) could be written as $[Cr(SO_4)(NH_3)]$ or $[Cr(NH_3)(SO_4)]$.

Exercise 8.2.7.4

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer

a. Amminetetraaquachromium (II) sulfate can be written as $[Cr(H_2O)_4(NH_3)]SO_4$. Although $[Cr(NH_3)(H_2O)_4]SO_4$ is also acceptable.
b. Potassium hexacyanoferrate (III) is be written as $K_3[Fe(CN)_6]$

8.2.7: Nomenclature of Coordination Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **23.3: Nomenclature of Coordination Chemistry** by Justin Hosung Lee, Sophia Muller is licensed CC BY-NC-SA 4.0.

SECTION OVERVIEW

8.3: Complex Ion Chemistry

An introduction to the complex ions formed by transition and other metals. Includes bonding, shapes and names, and a simple look at the origin of color. Looks in detail at various ligand exchange reactions and the chemistry of common hexaaqua ions.

8.3.1: Acidity of the Hexaaqua Ions

8.3.2: Geometry of Complex Ions

8.3.3: Ligand Exchange Reactions (Introduction)

8.3.4: Ligand Exchange Reactions (Thermodynamics)

8.3.5: Nomenclature of Complex Ions

8.3.6: Origin of Color in Complex Ions

8.3.7: Reactions of the Hexaaqua Ions with Ammonia

8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions

8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions

8.3.10: Stereoisomerism in complex ions

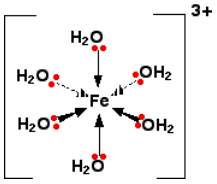
This page titled 8.3: Complex Ion Chemistry is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

8.3.1: Acidity of the Hexaaqua Ions

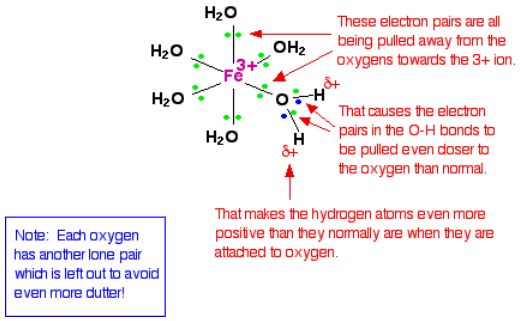
This page explains why complex ions of the type $[M(H_2O)_6]^{n+}$ are acidic.

The Charge Distribution within Complex Ion

The pH's of solutions containing hexaaqua ions vary a lot from one metal to another (assuming you are comparing solutions of equal concentrations). However, the underlying explanation is the same for all of them. We'll take the hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$ as typical. The structure of the ion is:



Each of the six water molecules are attached to the central iron(III) ion via a co-ordinate bond using one of the lone pairs on the oxygen. We'll choose one of these water molecules at random (it doesn't make any difference which one!), and look at the bonding in a bit more detail - showing all the bonds around the oxygen. Imagine for the moment that the 3+ charge is located entirely on the iron.



When the lone pairs on the oxygens form co-ordinate bonds with the iron, there is obviously a movement of electrons towards the iron. That has an effect on the electrons in the O-H bonds. These electrons, in turn, get pulled towards the oxygen even more than usual. That leaves the hydrogen nuclei more exposed than normal. The overall effect is that each of the hydrogen atoms is more positive than it is in ordinary water molecules. The 3+ charge is no longer located entirely on the iron but spread out over the whole ion - much of it on the hydrogen atoms.

The effect of dissolving this ion in water

The hydrogen atoms attached to the water ligands are sufficiently positive that they can be pulled off in a reaction involving water molecules in the solution. The first stage of this process is:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+ \tag{8.3.1.1}$$

The complex ion is acting as an (Arrhenius) acid by donating a hydrogen ion to water molecules in the solution. The water is, of course, acting as a (Arrhenius) base by accepting the hydrogen ion. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify Equation 8.3.1.1:

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \tag{8.3.1.2}$$

However, if you write it like this, remember that the hydrogen ion is not just falling off the complex ion. It is being pulled off by a water molecule in the solution. Whenever you write "$H^+(aq)$" what you really mean is a hydroxonium ion, H_3O^+.

The hexaaquairon(III) ion is quite strongly acidic giving solutions with pH's around 1.5, depending on concentration. You can get further loss of hydrogen ions as well, from a second and a third water molecule since the complex ion is a polyprotic acid.

Losing a second hydrogen ion:

$$[Fe(H_2O)_5(OH)]^{2+}(aq) \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+}(aq) + H^+(aq) \tag{8.3.1.3}$$

and a third one:

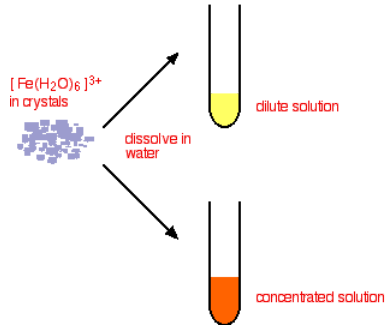
$$[Fe(H_2O)_4(OH)_2]^+(aq) \rightleftharpoons [Fe(H_2O)_3(OH)_3](s) + H^+(aq) \tag{8.3.1.4}$$

This time you end up with a neutral complex and because it has no charge, it does not dissolve to any extent in water, and a precipitate is formed.

In practice

What do you actually get in solution if you dissolve an iron(III) salt in water? In fact you get a mixture of all the complexes that you have seen in the equations above. These reactions are all equilibria, so everything will be present. The proportions depend on how concentrated the solution is.

The color of the solution is very variable and depends in part on the concentration of the solution. Dilute solutions containing iron(III) ions can be pale yellow. More concentrated ones are much more orange, and may even produce some orange precipitate. None of these colors represents the true color of the $[Fe(H_2O)_6]^{3+}$ ion - which is a very pale lilac color and is only really easy to see in solids containing the ion.

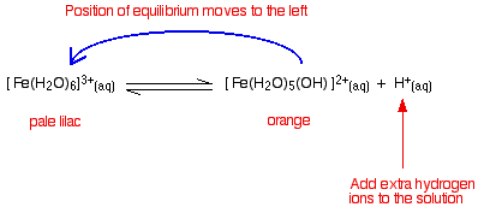


Looking at the equilibrium showing the loss of the first hydrogen ion:

$$\underbrace{Fe(H_2O)_6^{3+}}_{\text{pale lilac}} + H_2O \rightleftharpoons \underbrace{Fe(H_2O)_5(OH)^{2+}}_{\text{orange}} + H_3O^+$$

The color of the new complex ion on the right-hand side is so strong that it completely masks the color of the hexaaqua ion. In concentrated solutions, the equilibrium position will be even further to the right-hand side (Le Chatelier's Principle), and so the color darkens. You will also get significant loss of other hydrogen ions (Equation 8.3.1.3and 8.3.1.4) leading to some formation of the neutral complex and thus some precipitate.

The position of this equilibrium can be shifted by adding extra hydrogen ions from a concentrated acid (e.g., by adding concentrated nitric acid to a solution of iron(III) nitrate). The new hydrogen ions push the position of the equilibrium to the left so that you can see the color of the hexaaqua ion. This is slightly easier to follow if you write the simplified version of the equilibrium (Equation 8.3.1.2).



3+ Ions are More Acidic than 2+ ions

Solutions containing 3+ hexaaqua ions tend to have pH's in the range from 1 to 3. Solutions containing 2+ ions have higher pH's - typically around 5 - 6, although they can go down to about 3. Remember that the reason that these ions are acidic is because of the pull of the electrons towards the positive central ion. An ion with 3+ charges on it is going to pull the electrons more strongly than one with only 2+ charges.

In 3+ ions, the electrons in the O-H bonds will be pulled further away from the hydrogens than in 2+ ions. That means that the hydrogen atoms in the ligand water molecules will have a greater positive charge in a 3+ ion, and so will be more attracted to water molecules in the solution. If they are more attracted, they will be more readily lost - and so the 3+ ions are more acidic.

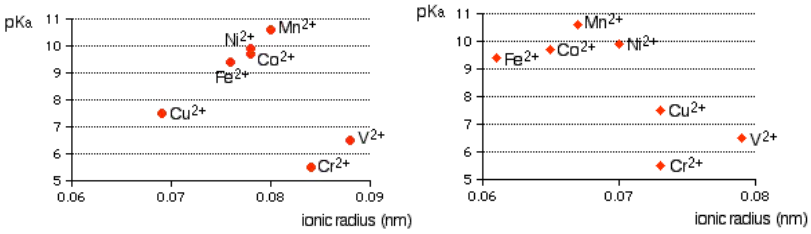
The Effect of ionic radius on acidity

If you have ions of the same charge, it seems reasonable that the smaller the volume this charge is packed into, the greater the distorting effect on the electrons in the O-H bonds. Ions with the same charge but in a smaller volume (a higher charge density) would be expected to be more acidic. You would therefore expect to find that the smaller the radius of the metal ion, the stronger the acid. Unfortunately, it's not that simple!

Unfortunately, almost every data source that you refer to quotes different values for ionic radii. This is because the radius of a metal ion varies depending on what negative ion it is associated with. We are interested in what happens when the metal ion is bonded to water molecules, so haven't got simple ions at all! Whatever values we take are unlikely to represent the real situation. In the graphs which follow I have taken values for ionic radii from two common sources so that you can see what a lot of difference it makes to the argument.

The graphs

If it is true that the smaller the ionic radius, the stronger the acidity of the hexaaqua ion, you would expect some sort of regular increase in pK_a (showing weaker acids) as ionic radius increases. The following graphs plot pK_a against ionic radii for the 2+ ions of the elements in the first transition series from vanadium to copper. The first graph plots pK_a against ionic radii taken from Chemistry Data Book by Stark and Wallace.



You can see that there is a trend for several of the ions, but it is completely broken by vanadium and chromium. The second graph uses ionic radii taken from the Nuffield Advanced Science Book of Data.

There probably is a relationship between ionic radius and acid strength, but that it is nothing like as simple and straightforward as most books at this level pretend. The problem is that there are other more important effects operating as well (quite apart from differences in charge) that can completely swamp the effect of the changes in ionic radius. You have to look in far more detail at the bonding in the hexaaqua ions and the product ions.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.1: Acidity of the Hexaaqua Ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

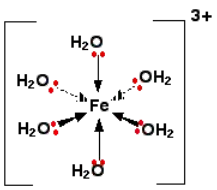
- **Acidity of the Hexaaqua Ions** by Jim Clark is licensed CC BY-NC 4.0.

8.3.2: Geometry of Complex Ions

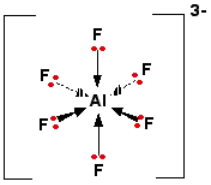
This page describes the shapes of some common complex metal ions. These shapes are for complex ions formed using monodentate ligands - ligands which only form one bond to the central metal ion. You will probably be familiar with working out the shapes of simple compounds using the electron pair repulsion theory. Unfortunately that does not work for most complex metal ions involving transition metals.

6-coordinated Complex Ions

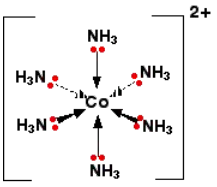
These are complex ions in which the central metal ion is forming six bonds. In the simple cases we are talking about, that means that it will be attached to six ligands. These ions have an octahedral shape. Four of the ligands are in one plane, with the fifth one above the plane, and the sixth one below the plane. The diagram shows four fairly random examples of octahedral ions.



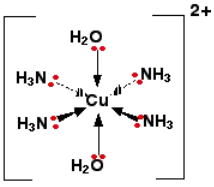
[$Fe(H_2O)_6$]$^{3+}$



[AlF_6]$^{3-}$



[$Co(NH_3)_6$]$^{2+}$



[$Cu(NH_3)_4(H_2O)_2$]$^{2+}$

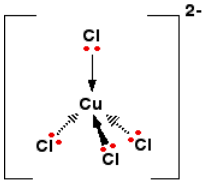
It does not matter the nature of the ligands. If you have six of them, this is the shape they will take up. Easy!

4-coordinated Complex Ions

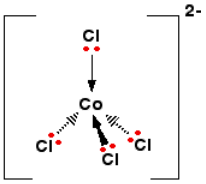
These are far less common, and they can take up one of two different shapes.

Tetrahedral ions

There are two very similar ions which crop up commonly at this level: $[CuCl_4]^{2-}$ and $[CoCl_4]^{2-}$. The copper(II) and cobalt(II) ions have four chloride ions bonded to them rather than six, because the chloride ions are too big to fit any more around the central metal ion.



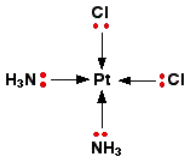
[$CuCl_4$]$^{2-}$



[$CoCl_4$]$^{2-}$

A square planar complex

Occasionally a 4-coordinated complex turns out to be square planar. There is no easy way of predicting that this is going to happen. The only one you might possibly come across at this level is cisplatin which is used as an anti-cancer drug. Cisplatin is a neutral complex, $Pt(NH_3)_2Cl_2$. It is neutral because the 2+ charge of the original platinum(II) ion is exactly canceled by the two negative charges supplied by the chloride ions.



$Pt(NH_3)_2Cl_2$

The platinum, the two chlorines, and the two nitrogens are all in the same plane. We will have more to say about cisplatin immediately below.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.2: Geometry of Complex Ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

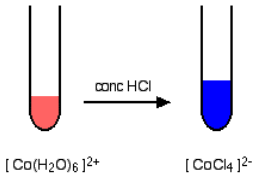
- **Geometry of Complex Ions** by Jim Clark is licensed CC BY-NC 4.0.

8.3.3: Ligand Exchange Reactions (Introduction)

This page describes some common ligand exchange (substitution) reactions involving complex metal ions. It assumes that you are familiar with basic ideas about complex ions. A *ligand exchange reaction* involves the substitution of one or more ligands in a complex ion with one or more different ligands.

Replacing aqua with chloro ligands

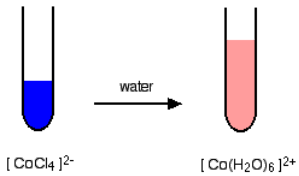
If you add concentrated hydrochloric acid to a solution containing hexaaquacobalt(II) ions (for example, cobalt(II) chloride solution), the solution turns from its original pink color to a dark rich blue. The six aqua molecules are replaced by four chloro ions.



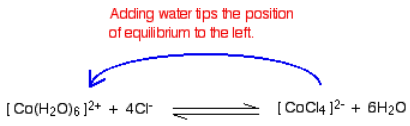
The reaction taking place is reversible.

$$[Co(H_2O)_6]^{2+} + 4\,Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6\,H_2O$$

Concentrated hydrochloric acid is used as the source of chloride ions because it provides a very high concentration compared to what is possible with, say, sodium chloride solution. Concentrated hydrochloric acid has a chloride ion concentration of approximately 10 mol dm^{-3}. The high chloride ion concentration pushes the position of the equilibrium to the right according to Le Chatelier's Principle.

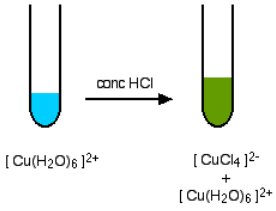


Notice the change in the co-ordination of the cobalt. Chloride ions are bigger than water molecules, and there isn't room to fit six of them around the central cobalt ion. This reaction can be easily reversed by adding water to the solution. Adding water to the right-hand side of the equilibrium has the effect of moving the position of equilibrium to the left. The pink color of the hexaaquacobalt(II) ion is produced again (only paler, of course, because it is more dilute).



Replacing the water in the hexaaquacopper(II) ion

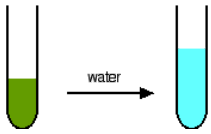
In terms of the chemistry, this is exactly the same as the last example - all that differs are the colors. Unfortunately, these are not quite so straightforward. The color of the tetrachlorocuprate(II) ion is almost always seen mixed with that of the original hexaaqua ion. What you normally see is:



The reaction taking place is reversible, and you get a mixture of colors due to both of the complex ions.

$$[Cu(H_2O)_6]^{2+} \rightleftharpoons [CuCl_4]^{2-} + 6\,H_2O$$

You may find the color of the tetrachlorocuprate(II) ion variously described as olive-green or yellow. Adding water to the green solution, replaces the chloro ligands by water molecules again, and returns the solution to blue.



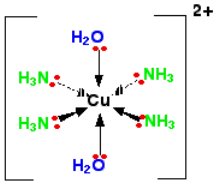
Replacing water molecules by ammonia

Water molecules and ammonia molecules are very similar in size, and so there is no change in co-ordination this time. Unfortunately, the reactions aren't quite so straightforward to describe. Ammonia solution can react with hexaaqua metal ions in two quite distinct ways, because it can act as a base as well as a ligand.

If you add a small amount of ammonia solution you get precipitates of the metal hydroxide - the ammonia is acting as a base. In some cases, these precipitates redissolve when you add more ammonia to give solutions in which a ligand exchange reaction has occurred. In the diagrams below, both steps are shown, but we are only going to consider the chemistry of the overall ligand exchange reaction. The precipitates dissolve because of a complicated series of equilibrium shifts, and we shan't worry about that for the moment.

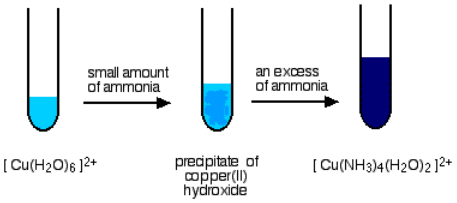
Replacing the water in the hexaaquacopper(II) ion

This is a slightly untypical case, because only four of the six water molecules get replaced to give the tetraamminediaquacopper(II) ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.



the tetraamminediaquacopper(II) ion

Notice that the four ammonias all lie in one plane, with the water molecules above and below. What you see in a test tube is:



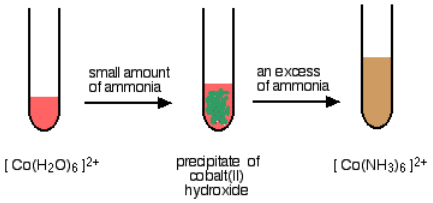
The main equilibrium involved in the ligand exchange reaction is:

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O$$

The color of the deep blue complex is so strong that this reaction is used as a sensitive test for copper(II) ions in solution. Even if you try to reverse the change by adding large amounts of water to the equilibrium, the strength of the deep blue (even highly diluted) always masks the pale blue of the aqua ion.

Replacing the water in the hexaaquacobalt(II) ion

This time, all the water molecules get replaced.



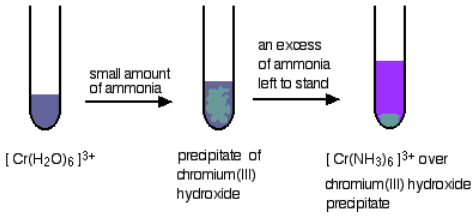
$$[Co(H_2O)_6]^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6\,H_2O$$

The straw colored solution formed changes color very rapidly on standing to a deep reddish brown. The hexaamminecobalt(II) ions are oxidised by the air to hexaamminecobalt(III) ions. However, that is a quite separate reaction, and is not a part of the ligand exchange reaction.

Replacing the water in the hexaaquachromium(III) ion

Again, all the agua ligands are replaced by ammine ligands. The difference this time is that the reaction is incomplete. The precipitate has to be left to stand in the presence of excess concentrated ammonia solution for some time to get the fully substituted ammine complex. Even so, you still get left with some unreacted precipitate.

$$[Cr(H_2O)_6]^{3+} + 6\,NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 6\,H_2O$$

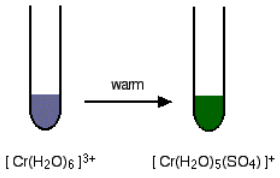


Two more replacements of the water in the hexaaquachromium(III) ion

The color of the hexaaquachromium(III) ion has been shown as a "difficult to describe" violet-blue-grey in all the diagrams above. In practice, when it is produced during a reaction in a test tube, it is often green. A typical example of this is the use of acidified potassium dichromate(VI) as an oxidising agent. Whenever this is used, the orange solution turns green and we nearly always describe the green ion as being $Cr^{3+}_{(aq)}$ - implying the hexaaquachromium(III) ion. That's actually an over-simplification. What happens is that one or more of the ligand water molecules get replaced by a negative ion in the solution - typically sulfate or chloride.

Replacement of the water by sulfate ions

You can do this simply by warming some chromium(III) sulfate solution.



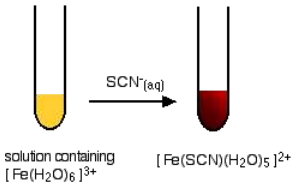
One of the water molecules is replaced by a sulfate ion. Notice the change in the charge on the ion. Two of the positive charges are canceled by the presence of the two negative charges on the sulfate ion.

Replacement of the water by chloride ions

In the presence of chloride ions (for example with chromium(III) chloride), the most commonly observed color is green. This happens when two of the water molecules are replaced by chloride ions to give the tetraaquadichlorochromium(III) ion - $[Cr(H_2O)_4Cl_2]^+$. Once again, notice that replacing water molecules by chloride ions changes the charge on the ion.

A ligand exchange reaction in the test for iron(III) ions

This provides an extremely sensitive test for iron(III) ions in solution. If you add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.



Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.3: Ligand Exchange Reactions (Introduction) is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Ligand Exchange Reactions (Introduction)** by Jim Clark is licensed CC BY-NC 4.0.

8.3.4: Ligand Exchange Reactions (Thermodynamics)

This page explains what is meant by a stability constant for a complex ion, and goes on to look at how its size is governed in part by the entropy change during a ligand exchange reaction.

Replacing aqua ligands with ammine ligands

If you add ammonia solution to a solution containing hexaaquacopper(II) ions, $[Cu(H_2O)_6]^{2+}$, four of the water molecules are eventually replaced by ammonia molecules to give $[Cu(NH_3)_4(H_2O)_2]^{2+}$. This can be written as an equilibrium reaction to show the overall effect:

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O \tag{8.3.4.1}$$

In fact, the water molecules get replaced one at a time, and so this is made up of a series of part-reactions:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O \tag{8.3.4.2}$$

$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O \tag{8.3.4.3}$$

$$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O \tag{8.3.4.4}$$

$$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O \tag{8.3.4.5}$$

Although this can look a bit daunting at first sight, all that is happening is that first you have one, then two, then three, then four water molecules in total replaced by four ammine ligands.

Individual stability constants

Let's take a closer look at the first of these equilibria (Equation 8.3.4.2). Like any other equilibrium, this one has an equilibrium constant, K_c - except that in this case, we call it a stability constant. Because this is the first water molecule to be replaced, we call it K_1 and is given by this expression:

$$K_1 = \frac{[[Cu(NH_3)(H_2O)_5]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]}$$

There are two points of possible confusion here - one minor, one more important!

- First, the square brackets have changed their meaning! Square brackets are often used to keep everything in a complex ion together and tidy. Here, they have reverted to their other use, which implies concentrations in mol dm^{-3}.
- In order to avoid complete confusion, the square brackets keeping the complexes together have been removed entirely.
- More importantly, if you compare the equilibrium constant expression with the equation, you will see that the water on the right-hand side hasn't been included. That is normal practice with these expressions.
- Because everything is dissolved in water, the water is present as a huge excess. Generating a little bit more during the reaction is going to make no effective difference to the total concentration of the water in terms of moles of water per dm^3.
- The concentration of the water is approximately constant. The equilibrium constant is defined so that you avoid having an extra unnecessary constant in the expression.

With that out of the way, let's go back to where we were - but introduce a value for K_1:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$$

$$K_1 = \frac{[Cu(NH_3)(H_2O)_5^{2+}]}{[Cu(H_2O)_6^{2+}]\,[NH_3]} = 1.78 \times 10^4 \text{ mol}^{-1}\text{ dm}^3$$

The value of the equilibrium constant is fairly large, suggesting that there is a strong tendency to form the ion containing an ammonia molecule. A high value of a stability constant shows that the ion is easily formed. Each of the other equilibria above also has its own stability constant, K_2, K_3 and K_4. For example, K_2 is given by:

$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O$$

$$K_2 = \frac{[Cu(NH_3)_2(H_2O)_4^{2+}]}{[Cu(NH_3)(H_2O)_5^{2+}]\,[NH_3]}$$
$$= 4.07 \times 10^3 \ \text{mol}^{-1}\,\text{dm}^3$$

The ion with two ammonias is even more stable than the ion with one ammonia. You could keep plugging away at this and come up with the following table of stability constants:

ion	K_n	value (mol^{-1} dm^3)	log K_n
$[Cu(NH_3)(H_2O)_5]^{2+}$	K_1	1.78×10^4	4.25
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	K_2	4.07×10^3	3.61
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	K_3	9.55×10^2	2.98
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_4	1.74×10^2	2.24

You will often find these values quoted as log K_1. All this does is tidy the numbers up so that you can see the patterns more easily. The ions keep on getting more stable as you replace up to 4 water molecules, but notice that the equilibrium constants are gradually getting less big as you replace more and more waters. This is common with individual stability constants.

Overall Formation constants

The overall stability constant is simply the equilibrium constant for the total reaction:

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O$$

It is given by this expression:

$$\text{overall } K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2^{2+}]}{[Cu(H_2O)_6^{2+}]\,[NH_3]^4}$$
$$= 1.20 \times 10^{13} \ \text{mol}^{-4}\,\text{dm}^{12}$$

You can see that overall this is a very large equilibrium constant, implying a high tendency for the ammonias to replace the waters. The "log" value is 13.1. This overall value is found by multiplying together all the individual values of K_1, K_2 and so on. To find out why that works, you will need a big bit of paper and some patience! Write down expressions for all the individual values (the first two are done for you above), and then multiply those expressions together. You will find that all the terms for the intermediate ions cancel out to leave you with the expression for the overall stability constant.

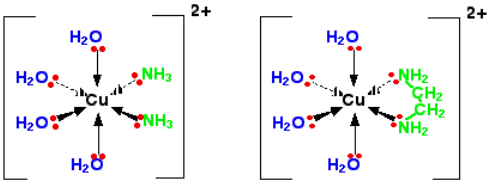
Summary

Whether you are looking at the replacement of individual water molecules or an overall reaction producing the final complex ion, a stability constant is simply the equilibrium constant for the reaction you are looking at. The **larger** the value of the stability constant, the further the reaction lies to the **right**. That implies that complex ions with large stability constants are more stable than ones with smaller ones.

Stability constants tend to be very large numbers. In order to simplify the numbers a "log" scale is often used. Because of the way this works, a difference of 1 in the log value comes from a 10 times difference in the stability constant. A difference of 2 comes from a 100 (in other words, 10^2) times difference in stability constant - and so on.

Stability constants and entropy - the chelate effect

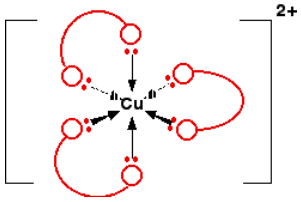
The chelate effect is an effect which happens when you replace water (or other simple ligands) around the central metal ion by multidentate ligands like 1,2-diaminoethane (often abbreviated to "en") or EDTA. Compare what happens if you replace two water molecules around a $[Cu(H_2O)_6]^{2+}$ ion with either 2 ammonia molecules or one molecule of 1,2-diaminoethane.



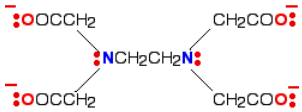
This second structure is known as a chelate from a Greek word meaning a crab's claw. You can picture the copper ion as being nipped by the claw of the 1,2-diaminoethane molecule. Chelates are much more stable than complex ions formed from simple monodentate ligands. The overall stability constants for the two ions are:

ion	log K
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.86
$[Cu(H_2O)_4(en)]^{2+}$	10.6

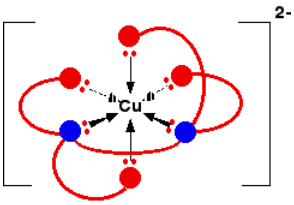
The reaction with the 1,2-diaminoethane could eventually go on to produce a complex ion $[Cu(en)_3]^{2+}$. Simplifying the structure of this:



The overall stability constant for this (as log K) is 18.7. Another copper-based chelate comes from the reaction with EDTA.



the $EDTA^{4-}$ ion

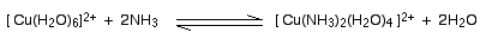


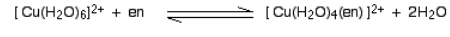
the $[Cu(EDTA)]^{2-}$ ion

This also has a high stability constant - log K is 18.8. However many examples you take, you always find that a chelate (a complex ion involving multidentate ligands) is more stable than ions with only monodentate ligands. This is known as the chelate effect.

The reason for the chelate effect

If you compare the two equilibria below, the one with the 1,2-diaminoethane ("en") has the higher equilibrium (stability) constant (for values, see above).





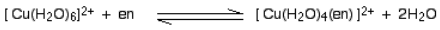
The enthalpy changes of the two reactions are fairly similar. You might expect this because in each case you are breaking two bonds between copper and oxygen atoms and replacing them by two bonds between copper and nitrogen atoms.

If the enthalpy changes are similar, what causes the difference in the extent to which the two reactions happen?

You need to think about the entropy change during each reaction.

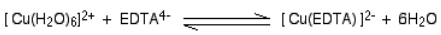
Entropy is most easily thought of as a measure of disorder. Any change which increases the amount of disorder increases the tendency of a reaction to happen.

If you look again at the two equiilbria, you might notice that the 1,2-diaminoethane equilibrium does lead to an increase in the entropy. There are only two species on the left-hand side of the equation, but three on the right.



You can obviously get more entropy out of three species than out of only two. Compare that with the other equilibrium. In this case, there is no change in the total number of species before and after reaction, and so no useful contribution to an increase in entropy.

In the case of the complex with EDTA, the increase in entropy is very pronounced.



Here, we are increasing the number of species present from two on the left-hand side to seven on the right. You can get a major amount of increase in disorder by making this change.

Reversing this last change is going to be far more difficult in entropy terms. You would have to move from a highly disordered state to a much more ordered one. That isn't so likely to happen, and so the copper-EDTA complex is very stable.

Summary

Complexes involving multidentate ligands are more stable than those with only monodentate ligands. The underlying reason for this is that each multidentate ligand displaces more than one water molecule. This leads to an increase in the number of species present in the system, and therefore an increase in entropy. An increase in entropy makes the formation of the chelated complex more favorable.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.4: Ligand Exchange Reactions (Thermodynamics) is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Ligand Exchange Reactions (Thermodynamics)** by Jim Clark is licensed CC BY-NC 4.0.

8.3.5: Nomenclature of Complex Ions

This page explains how to name some common complex metal ions. Although the names of complex ions can look long and worrying, the formulae are simply being coded in much the same way that organic names are coded. Once you have sorted out that code, the names are entirely descriptive.

Naming the ligands

The table shows some common ligands and the code for them in the name of a complex ion. The old names sometimes differ by a letter or so, but never enough for it to be confusing.

ligand	coded by	(old name)
H_2O	aqua	aquo
NH_3	ammine	ammino
OH^-	hydroxo	hydroxy
Cl^-	chloro	
F^-	fluoro	
CN^-	cyano	

Take care with the code for ammonia as a ligand - it has 2 "m"s in its name. If you miss one of these out so that you are left with "amine" or "amino", you are refering to the NH_2 group in an organic compound. This is probably the only point of confusion with these names.

Coding for the number of ligands

The normal prefixes apply if there is more than one ligand.

no of ligands	coded by
2	di
3	tri
4	tetra
5	penta
6	hexa

Putting this together

For a complex ion containing only one type of ligand, there is no problem. For example:

$[Cu(H_2O)_6]^{2+}$ is called the hexaaquacopper(II) ion.

(Don't worry about the copper(II) bit for the moment.) The fact that there are two "a"s next to each other in the name is OK.

With more than one type of ligand in an ion, the ligands are named in alphabetical order - ignoring the prefixes. For example:

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ is called the tetraamminediaquacopper(II) ion.

The "ammine" is named before the "aqua" because "am" comes before "aq" in the alphabet. The "tetra" and "di" are ignored.

Naming the metal

You might have thought that this was fairly obvious, but it isn't necessarily. It depends on whether the complex ion ends up as positively or negatively charged.

For positively charged complex ions

A positively charged complex ion is called a cationic complex. A cation is a positively charged ion. The metal in this is named exactly as you would expect, with the addition of its oxidation state. Going back to a previous example, $[Cu(H_2O)_6]^{2+}$ is called the hexaaquacopper(II) ion because the copper's oxidation state is +2.

Copper's oxidation is +2 because the original uncomplexed ion was Cu^{2+} - NOT because the complex carries 2+ charges.

The oxidation state is frequently left out if a metal only ever has one oxidation state. For example, in its compounds aluminium always has an oxidation state of +3. $[Al(H_2O)_6]^{3+}$ is usually just called the hexaaquaaluminium ion rather than the hexaaquaaluminium(III) ion.

For negatively charged complex ions

A negatively charged complex ion is called an anionic complex. An anion is a negatively charged ion. In this case the name of the metal is modified to show that it has ended up in a negative ion. This is shown by the ending **-ate**.

With many metals, the basic name of the metal is changed as well - sometimes drastically! Common examples include:

metal	changed to
cobalt	cobaltate
aluminium	aluminate
chromium	chromate
vanadium	vanadate
copper	cuprate
iron	ferrate

So, for example, suppose you bond 4 chloride ions around a Cu^{2+} ion to give $[CuCl_4]^{2-}$.

The name shows the 4 (tetra) chlorines (chloro) around a copper in an overall negative ion (cuprate). The copper has on oxidation state of +2. This is the tetrachlorocuprate(II) ion.

Similarly, $[Al(H_2O)_2(OH)_4]^-$ is called the diaquatetrahydroxoaluminate ion. Take the name to pieces so that you can see exactly what refers to what. Don't forget that the two different ligands are named in alphabetical order - aqua before hydroxo - ignoring the prefixes, di and tetra. The oxidation state of the aluminum could be shown, but is not absolutely necessary because aluminum only has the one oxidation state in its compounds. The full name is the diaquatetrahydroxoaluminate(III) ion.

Contributors and Attributions

Jim Clark (Chemguide.co.uk)

This page titled 8.3.5: Nomenclature of Complex Ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Nomenclature of Complex Ions** by Jim Clark is licensed CC BY-NC 4.0.

8.3.6: Origin of Color in Complex Ions

This page is going to take a simple look at the origin of color in complex ions - in particular, why so many transition metal ions are colored.

White light and Colors

If you pass white light through a prism it splits into all the colors of the rainbow. Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred metersfor radio waves. Visible light has wavelengths from about 400 to 750 nm. (1 nanometer = 10-9 meters.)

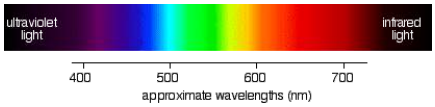
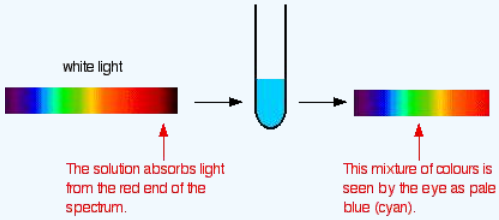


Figure: The diagram shows an approximation to the spectrum of visible light.

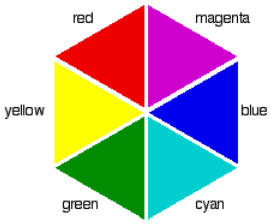
Example 1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.

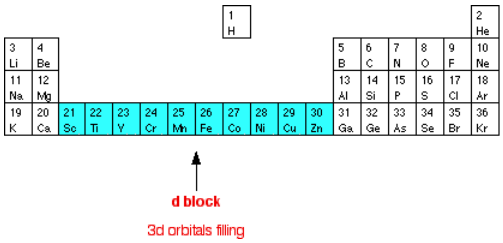


Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You wouldn't have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

If you arrange some colors in a circle, you get a "color wheel". The diagram shows one possible version of this.



colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum. Cyan is the complementary color of red.



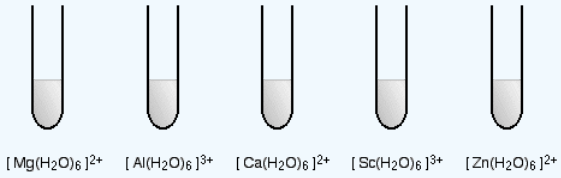
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). This shortened version of the Periodic Table shows the first row of the d block, where the 3d orbitals are being filled.

> *The usual definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] $3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^14s^2$) does not really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. Technically, the Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.*

Example 2: Hexaaqua Metal Ions

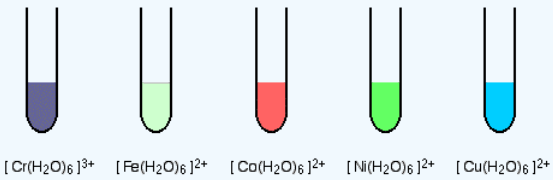
The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[\ M(H_2O)_6\ ]^{n+}$. The charge on these ions is typically 2+ or 3+.

Non-transition metal ions



These ions are all colorless.

Transition metal ions



The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

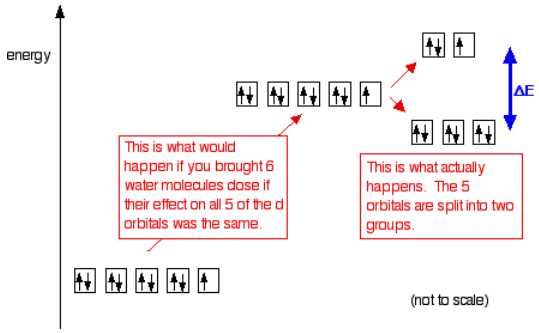
So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion?

The Origin of Color in Complex Ions containing transition metals

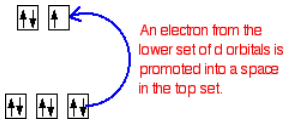
Complex ions containing transition metals are usually colored, whereas the similar ions from non-transition metals are not. That suggests that the partly filled d orbitals must be involved in generating the color in some way. Remember that transition metals are defined as having partly filled d orbitals.

Octahedral Complexes

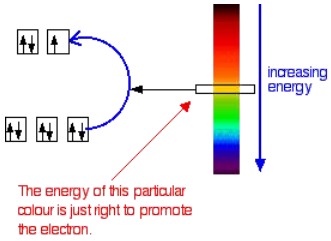
For simplicity we are going to look at the octahedral complexes which have six simple ligands arranged around the central metal ion. The argument is not really any different if you have multidentate ligands. When the ligands bond with the transition metal ion, there is repulsion between the electrons in the ligands and the electrons in the d orbitals of the metal ion. That raises the energy of the d orbitals. However, because of the way the d orbitals are arranged in space, it doesn't raise all their energies by the same amount. Instead, it splits them into two groups. The diagram shows the arrangement of the d electrons in a Cu^{2+} ion before and after six water molecules bond with it.



Whenever 6 ligands are arranged around a transition metal ion, the d orbitals are always split into 2 groups in this way - 2 with a higher energy than the other 3. The size of the energy gap between them (shown by the blue arrows on the diagram) varies with the nature of the transition metal ion, its oxidation state (whether it is 3+ or 2+, for example), and the nature of the ligands. When white light is passed through a solution of this ion, some of the energy in the light is used to promote an electron from the lower set of orbitals into a space in the upper set.



Each wavelength of light has a particular energy associated with it. Red light has the lowest energy in the visible region. Violet light has the greatest energy. Suppose that the energy gap in the d orbitals of the complex ion corresponded to the energy of yellow light.



The yellow light would be absorbed because its energy would be used in promoting the electron. That leaves the other colors. Your eye would see the light passing through as a dark blue, because blue is the complementary color of yellow.

Tetrahedral Complexes

Simple tetrahedral complexes have four ligands arranged around the central metal ion. Again the ligands have an effect on the energy of the d electrons in the metal ion. This time, of course, the ligands are arranged differently in space relative to the shapes of the d orbitals. The net effect is that when the d orbitals split into two groups, three of them have a greater energy, and the other two a lesser energy (the opposite of the arrangement in an octahedral complex). Apart from this difference of detail, the explanation for the origin of color in terms of the absorption of particular wavelengths of light is exactly the same as for octahedral complexes.

What about non-transition metal complex ions?

Non-transition metals do not have partly filled d orbitals. Visible light is only absorbed if some energy from the light is used to promote an electron over exactly the right energy gap. Non-transition metals do not have any electron transitions which can absorb wavelengths from visible light. For example, although scandium is a member of the d block, its ion (Sc^{3+}) hasn't got

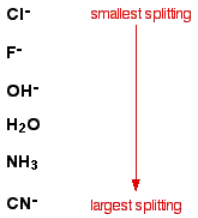
any d electrons left to move around. This is no different from an ion based on Mg^{2+} or Al^{3+}. Scandium(III) complexes are colorless because no visible light is absorbed. In the zinc case, the 3d level is completely full - there are not any gaps to promote an electron in to. Zinc complexes are also colorless.

Factors Affecting the Color of Transition Metal complexes

In each case we are going to choose a particular metal ion for the center of the complex, and change other factors. color changes in a fairly haphazard way from metal to metal across a transition series.

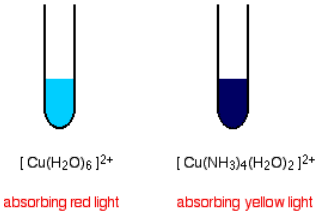
The nature of the ligand

Different ligands have different effects on the energies of the d orbitals of the central ion. Some ligands have strong electrical fields which cause a large energy gap when the d orbitals split into two groups. Others have much weaker fields producing much smaller gaps. Remember that the size of the gap determines what wavelength of light is going to get absorbed. The list shows some common ligands. Those at the top produce the smallest splitting; those at the bottom the largest splitting.



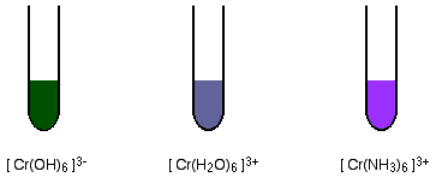
The greater the splitting, the more energy is needed to promote an electron from the lower group of orbitals to the higher ones. In terms of the color of the light absorbed, greater energy corresponds to shorter wavelengths. That means that as the splitting increases, the light absorbed will tend to shift away from the red end of the spectrum towards orange, yellow and so on.

There is a fairly clear-cut case in copper(II) chemistry. If you add an excess of ammonia solution to hexaaquacopper(II) ions in solution, the pale blue (cyan) color is replaced by a dark inky blue as some of the water molecules in the complex ion are replaced by ammonia.



The first complex must be absorbing red light in order to give the complementary color cyan. The second one must be absorbing in the yellow region in order to give the complementary color dark blue. Yellow light has a higher energy than red light. You need that higher energy because ammonia causes more splitting of the d orbitals than water does.

It is not often as simple to see as this, though! Trying to sort out what is being absorbed when you have murky colors not on the simple color wheel further up the page is much more of a problem. The diagrams show some approximate colors of some ions based on chromium(III).

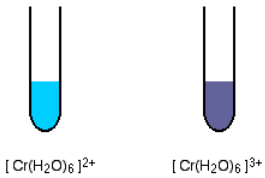


It is obvious that changing the ligand is changing the color, but trying to explain the colors in terms of our simple theory is not easy.

The oxidation state of the metal

As the oxidation state of the metal increases, so also does the amount of splitting of the d orbitals. Changes of oxidation state therefore change the color of the light absorbed, and so the color of the light you see. Taking another example from chromium

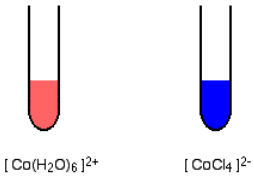
chemistry involving only a change of oxidation state (from +2 to +3):



The 2+ ion is almost the same color as the hexaaquacopper(II) ion, and the 3+ ion is the hard-to-describe violet-blue-grey color.

The coordination of the Ion

Splitting is greater if the ion is octahedral than if it is tetrahedral, and therefore the color will change with a change of co-ordination. The problem is that an ion will normally only change co-ordination if you change the ligand - and changing the ligand will change the color as well. Hence, you cannot isolate out the effect of the co-ordination change. For example, a commonly quoted case comes from cobalt(II) chemistry, with the ions $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$.



The difference in the colors is going to be a combination of the effect of the change of ligand, and the change of the number of ligands.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.6: Origin of Color in Complex Ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Origin of Color in Complex Ions** by Jim Clark is licensed CC BY-NC 4.0.

8.3.7: Reactions of the Hexaaqua Ions with Ammonia

This page describes and explains the reactions between complex ions of the type $[M(H_2O)_6]^{n+}$ and ammonia solution.Reactions of the hexaaqua ions with ammonia solution are complicated by the fact that the ammonia can have two quite different functions. It can act as a base (in the Brønsted-Lowry sense), but it is also a possible ligand which can replace water molecules around the central metal ion. When it acts as a ligand, it is acting as a Lewis base. We need to look at these two functions separately.

Ammonia acting as a (Brønsted-Lowry) base

This is what happens when you only add small amounts of dilute ammonia solution to any of the hexaaqua ions. The ligand effect only happens with an excess of ammonia or with concentrated ammonia - and with some metals you don't even see it then.

We'll talk through what happens if you add a small amount of dilute ammonia solution to a solution containing a 2+ hexaaqua ion. These have the formula $[M(H_2O)_6]^{2+}$, and they are acidic. Their acidity is shown in the reaction of the hexaaqua ions with water molecules from the solution:

$$[M(H_2O)_6]^{2+}(aq) + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$$

They are acting as acids by donating hydrogen ions to water molecules in the solution. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

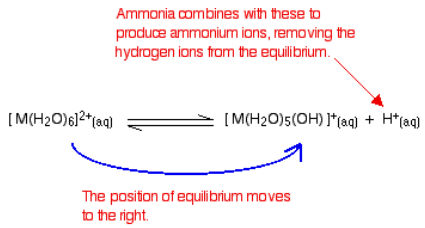
$$[M(H_2O)_6]^{2+}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H^{+}(aq)$$

Adding ammonia solution to this equilibrium - stage 1

There are two possible reactions.

1. Reaction of ammonia with the hydroxonium ions (hydrogen ions)
2. Ammonia will react with these to produce ammonium ions.

According to Le Chatelier's Principle, the position of equilibrium will move to the right, producing more of the new complex ion.



Reaction of ammonia with the hexaaqua ion

Statistically, there is far more chance of an ammonia molecule hitting a hexaaqua metal ion than of hitting a hydrogen ion. There are far more hexaaqua ions present. If that happens, you get exactly the same new complex ion formed as above.

$$[M(H_2O)_6]^{2+}(aq) + NH_3 \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + NH_4^{+}(aq)$$

Notice that this is still a reversible change (unlike the corresponding change when you add hydroxide ions). Ammonia is only a weak base.

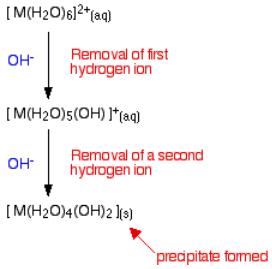
The second stage of the reaction

Whichever of the above reactions happens, you end up with $[M(H_2O)_5(OH)]^{+}$ ions in solution. These are also acidic, and can lose hydrogen ions from another of the water ligands. Taking the easier version of the equilibrium:

$$[M(H_2O)_5(OH)]^{+}(aq) \rightleftharpoons [M(H_2O)_4(OH)_2](s) + H^{+}(aq)$$

Adding ammonia again tips the equilibrium to the right - either by reacting with the hydrogen ions, or by reacting directly with the complex on the left-hand side. When this happens, the new complex formed no longer has a charge - this is a "neutral complex". It is insoluble in water - and so a precipitate is formed. This precipitate is often written without including the remaining water ligands. In other words we write it as $M(OH)_2$. A precipitate of the metal hydroxide has been formed.

Summarizing what has happened



You can also usefully write the complete change as an overall equilibrium reaction. This will be important for later on.

$$[M(H_2O)_6]^{2+}(aq) + 2\,NH_3 \rightleftharpoons [M(H_2O)_4(OH)_2](s) + 2\,NH_4^+(aq)$$

If you did the same reaction with a 3+ ion, the only difference is that you would have to remove a total of 3 hydrogen ions in order to get to the neutral complex. That would give the overall equation:

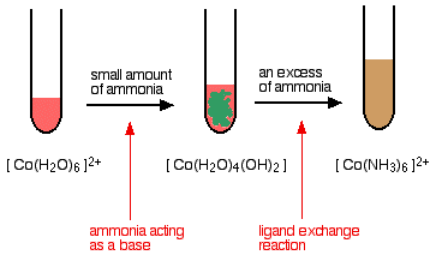
$$[M(H_2O)_6]^{3+}(aq) + 3\,NH_3 \rightleftharpoons [M(H_2O)_3(OH)_3](s) + 4\,NH_4^+(aq)$$

Ions of specific metals

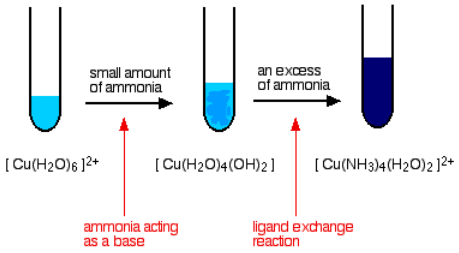
Remember that we are concentrating for the moment on the ammonia acting as a base - in other words, on the formation of hydroxide precipitates when you add small amounts of ammonia solution to solutions containing hexaaqua metal The diagrams, however, will show the complete change so I don't have to repeat them later on. Ignore the cases where the precipitate dissolves in excess ammonia for the moment.

2+ ions

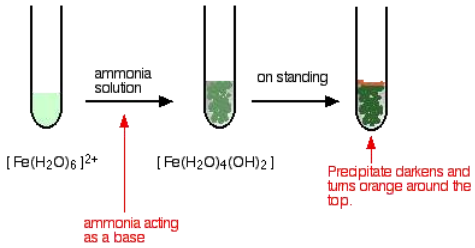
hexaaquacobalt(II)



hexaaquacopper(II)

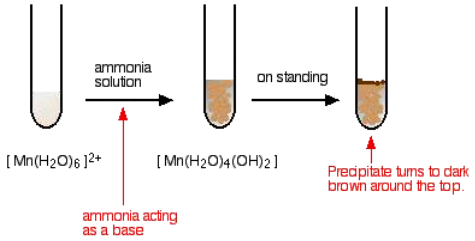


hexaaquairon(II)



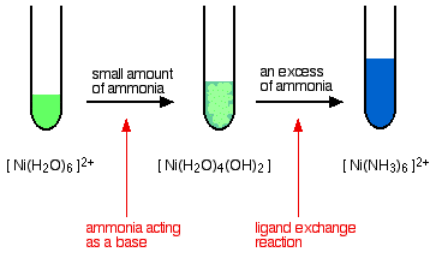
Iron is very easily oxidized under alkaline conditions. Oxygen in the air oxidizes the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect. This is NOT a ligand exchange reaction.

hexaaquamanganese(II)

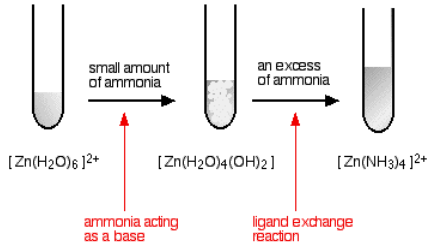


I have shown the original solution as very pale pink (the palest I can produce!), but in fact it is virtually colorless. The pale brown precipitate is oxidized to darker brown manganese(III) oxide in contact with oxygen from the air. Again, this isn't a ligand exchange reaction.

hexaaquanickel(II)



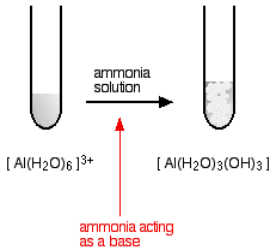
hexaaquazinc



You start and finish with colourless solutions, producing a white precipitate on the way.

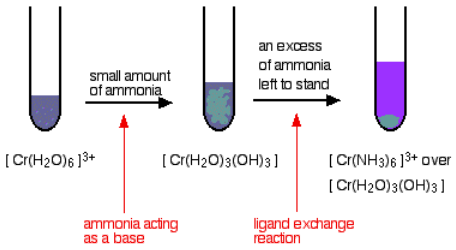
3+ ions

hexaaquaaluminium

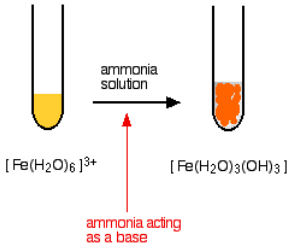


Starting from a colorless solution, you get a white precipitate.

hexaaquachromium(III)



hexaaquairon(III)



Summary of the effect of adding small amounts of ammonia solution

In each case you get a precipitate of the neutral complex - the metal hydroxide. Apart from minor differences in the exact shade of color you get, these are almost all exactly the same as the precipitates you get when you add a little sodium hydroxide solution to the solutions of the hexaaqua ions. The only real difference lies in the color of the cobalt precipitate.

Ammonia acting as a ligand

The ligand exchange reaction

In some cases, ammonia replaces water around the central metal ion to give another soluble complex. This is known as a ligand exchange reaction, and involves an equilibrium such as this one:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The formation of this new soluble complex causes the precipitate to dissolve. The ammonia attaches to the central metal ion using the lone pair of electrons on the nitrogen atom. Because it is a lone pair donor, it is acting as a Lewis base.

Explaining why the precipitate dissolves

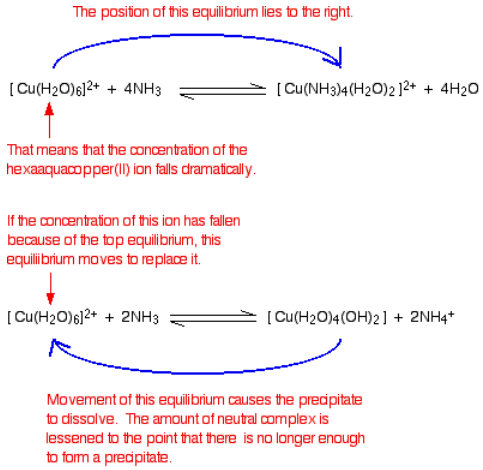
Almost all text books leave the argument at this point, assuming that it is obvious why the formation of the complex causes some precipitates to dissolve - it is not! Consider the copper case as typical of any of them. There are two equilibria involved in this. The first is the one in which ammonia is acting as a base and producing the precipitate:

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

The other one is the ligand exchange reaction:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

Notice that the hexaaqua ion appears in both of these. There is now an interaction between the two equilibria:



Looking at it like this is helpful in explaining why some precipitates dissolve in excess ammonia while others don't. It depends on the positions of the equilibria. To get the precipitate to dissolve, you obviously need the ligand exchange equilibrium to lie well to the right, but you need the acid-base equilibrium to be easy to pull back to the left.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.7: Reactions of the Hexaaqua Ions with Ammonia is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Reactions of the Hexaaqua Ions with Ammonia** by Jim Clark is licensed CC BY-NC 4.0.

8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions

This page describes and explains the reactions between complex ions of the type $[M(H_2O)_6]^{n+}$ and carbonate ions from, for example, sodium carbonate solution. There is a difference in the reactions depending on whether the metal at the center of the hexaaqua ion carries a 2+ or a 3+ charge. We need to look at each cases separately.

3+ ions reacting with carbonate ions

The 3+ hexaaqua ions are sufficiently acidic to react with carbonate ions to release carbon dioxide gas and precipitate a metal hydroxide.

The acidity of the 3+ hexaaqua ions

These have the formula $[M(H_2O)_6]^{3+}$, and they are fairly acidic. They react with water molecules from the solution:

$$[M(H_2O)_6]^{3+}(aq) + H_2O \rightleftharpoons [M(H_2O)_6]^{2+}(aq) + H_3O^+(aq)$$

They are acting as acids by donating hydrogen ions to water molecules in the solution. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

$$[M(H_2O)_6]^{3+}(aq) \rightleftharpoons [M(H_2O)_6]^{2+}(aq) + H^+(aq)$$

Carbonate ions acting as a base

Carbonate ions combine with hydrogen ions in two stages - first to make hydrogencarbonate ions, and then to give carbon dioxide and water.

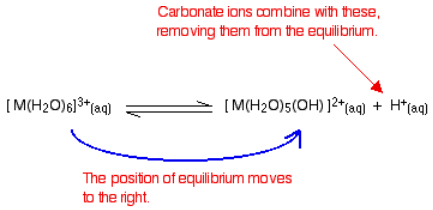
$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_2(g) + H_2O(l)$$

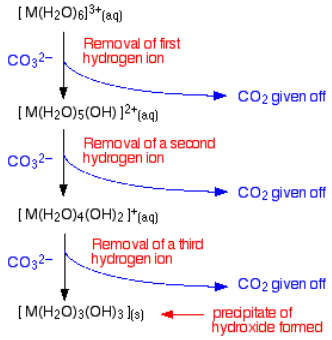
Reacting carbonate ions with the 3+ hexaaqua ions

Provided the proportions are right, the 3+ hexaaqua ions are sufficiently acidic for the reactions to go all the way to carbon dioxide. There are two possible reactions.

1. Reaction of carbonate ions with the hydroxonium ions (hydrogen ions). According to Le Chatelier's Principle, as the hydrogen ions are removed, the position of equilibrium will move to the right, producing more of the new complex ion.



2. Reaction of carbonate ions with the hexaaqua ion. Statistically, there is far more chance of a carbonate ion hitting a hexaaqua metal ion than of hitting a hydrogen ion. It removes a hydrogen ion directly from the hexaaqua complex. If that happens, you get exactly the same new complex ion formed as above. But it doesn't stop there. Carbonate ions keep on removing hydrogen ions from the complex until you end up with a neutral complex. You see that as a precipitate of the metal hydroxide.



You can also usefully write the complete change as an overall reaction.

$$2\,[M(H_2O)_6]^{3+}(aq) + 3\,CO_3^{2-} \longrightarrow 2\,[M(H_2O)_3(OH)_3](s) + 3\,CO_2(g) + 3\,H_2O(l)$$

2+ ions reacting with carbonate ions

The 2+ hexaaqua ions aren't strongly acidic enough to release carbon dioxide from carbonates. In these cases, you still get a precipitate - but it is a precipitate of what is loosely described as the "metal carbonate".

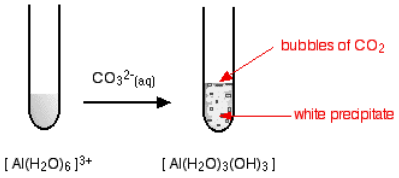
$$M^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MCO_3(s)$$

Looking at the ions of specific metals

We'll look at the reactions of three 3+ ions and three 2+ ions. The important ones are the 3+ ions.

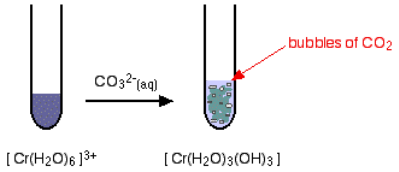
The 3+ ions

hexaaquaaluminium



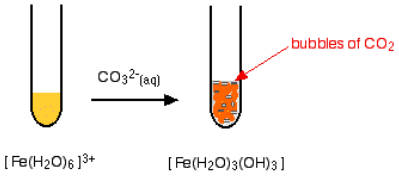
Starting from a colourless solution, you get a white precipitate - but with bubbles of gas as well. The precipitate is identical to the one you get if you add small amounts of either sodium hydroxide or ammonia solutions to a solution of the hexaaquaaluminium ions.

hexaaquachromium(III)



Again, the precipitate is just the same as if you had added small amounts of either sodium hydroxide or ammonia solution.

hexaaquairon(III)



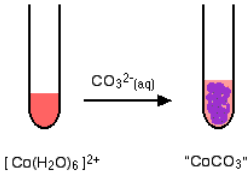
. . . and again, exactly the same precipitate as if you had added any other base.

Summary

In each case you get a precipitate of the neutral complex - the metal hydroxide. This is exactly the same precipitate that you get if you add small amounts of either sodium hydroxide solution or ammonia solution to solutions of these ions. Bubbles of carbon dioxide are also given off.

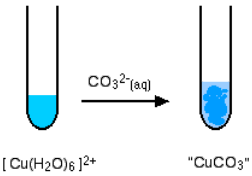
2+ ions

hexaaquacobalt(II)



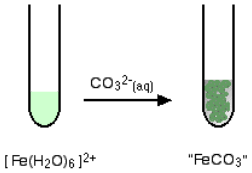
No gas this time - just a precipitate of "cobalt(II) carbonate".

hexaaquacopper(II)



Again, there isn't any carbon dioxide - just a precipitate of the "copper(II) carbonate".

hexaaquairon(II)



You get a precipitate of the "iron(II) carbonate", but no carbon dioxide.

Summary

Hexaaqua ions with a 2+ charge aren't sufficiently acidic to liberate carbon dioxide from carbonate ions. Instead you get a precipitate which you can think of as being the metal carbonate.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Reactions of the Hexaaqua Ions with Carbonate Ions** by Jim Clark is licensed CC BY-NC 4.0.

8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions

This page describes and explains the reactions between complex ions of the type $[M(H_2O)_6]^{n+}$ and hydroxide ions from, for example, sodium hydroxide solution. It assumes that you know why these ions are acidic, and are happy about the equilibria involved.

The general case

Although there are only minor differences, for simplicity we will look at 2+ ions and 3+ ions separately.

Adding hydroxide ions to 2+ hexaaqua ions

These have the form $[M(H_2O)_6]^{2+}$. Their acidity is shown in the reaction of the hexaaqua ions with water molecules from the solution:

$$[M(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$$

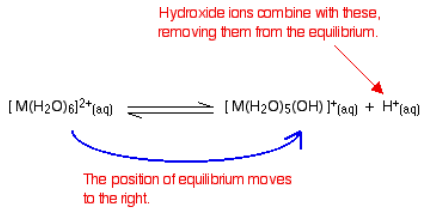
They are acting as acids by donating hydrogen ions to water molecules in the solution. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

$$[M(H_2O)_6]^{2+}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H^{+}(aq)$$

Disturbing this equilibrium by adding hydroxide ions - stage 1

What happens if you add hydroxide ions to this equilibrium? There are two possible reactions.

1. Reaction of hydroxide ions with the hydroxonium ions (hydrogen ions). According to Le Chatelier's Principle, the position of equilibrium will move to the right, producing more of the new complex ion.



2. Reaction of hydroxide ions with the hexaaqua ion. Statistically, there is far more chance of a hydroxide ion hitting a hexaaqua metal ion than of hitting a hydrogen ion. There are far more hexaaqua ions present. If that happens, you get exactly the same new complex ion formed as above.

$$[M(H_2O)_6]^{2+}(aq) + OH^{-}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_2O(l)$$

Notice that this isn't a ligand exchange reaction. The hydroxide ion has removed a hydrogen ion from one of the ligand water molecules. The reaction has also become essentially irreversible.

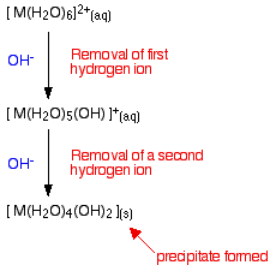
The second stage of the reaction

Whichever of the above reactions happens, you end up with $[M(H_2O)_5(OH)]^{+}$ ions in solution. These are also acidic, and can lose hydrogen ions from another of the water ligands. Taking the easier version of the equilibrium:

$$[M(H_2O)_5(OH)]^{+}(aq) \rightleftharpoons [M(H_2O)_4(OH)_2](s) + H^{+}(aq)$$

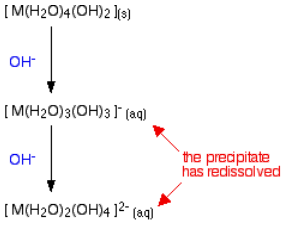
Adding hydroxide ions again tips the equilibrium to the right - either by reacting with the hydrogen ions, or by reacting directly with the complex on the left-hand side. When this occurs, the new complex formed no longer has a charge - we describe it as a "neutral complex". In all the cases we are looking at, this neutral complex is insoluble in water - and so a precipitate is formed. This precipitate is often written without including the remaining water ligands. In other words we write it as $M(OH)_2$. A precipitate of the metal hydroxide has been formed.

Summarizing what has happened so far



Going further

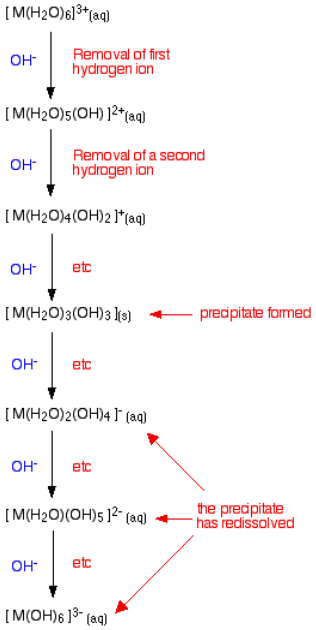
There is no logical reason why the removal of hydrogen ions from the complex should stop at this point. Further hydrogen ions can be removed by hydroxide ions to produce anionic complexes - complexes carrying negative charges. Whether this actually happens in the test tube to any extent varies from metal to metal.



In fact, if you do this using sodium hydroxide solution of the usual concentrations, most of the 2+ ions that you will meet at this level don't go beyond the precipitate. The only one you are likely to come across is the zinc case - and that has a complication. The final ion is $[Zn(OH)_4]^{2-}$ - a tetrahedral ion which has lost the remaining 2 water ligands.

Adding hydroxide ions to 3+ hexaaqua ions

The argument here is exactly as before - the only difference is the number of hydrogen ions which have to be removed from the original hexaaqua complex to produce the neutral complex. Going beyond the neutral complex is also rather more common with 3+ than with 2+ ions, and may go as far as having a hydrogen ion removed from each of the six water molecules. This is summarized in the same sort of flow scheme as before:



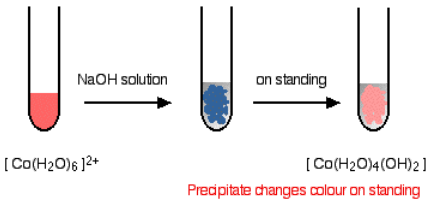
Looking at the ions of specific metals

In each case the formula of the precipitate will be given as if it were the simple neutral complex. In fact, these "hydroxide" precipitates sometimes rearrange by losing water from combinations of the attached OH groups. This produces oxides closely

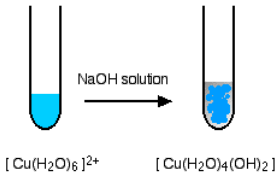
associated with the lost water. These changes are beyond the scope of this site.

2+ ions

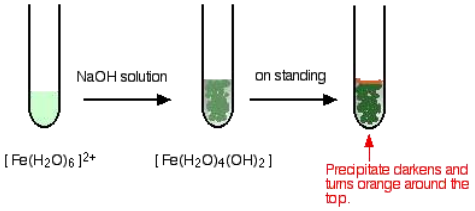
hexaaquacobalt(II)



hexaaquacopper(II)

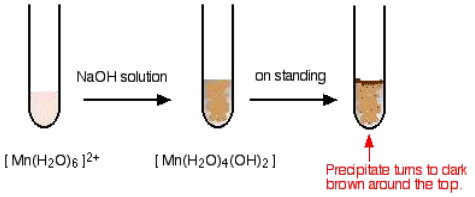


hexaaquairon(II)



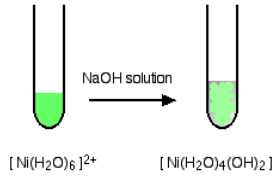
Iron is very easily oxidized under alkaline conditions. Oxygen in the air oxidizes the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect.

hexaaquamanganese(II)

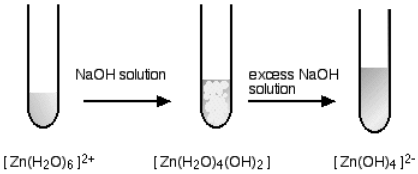


I have shown the original solution as very pale pink (the palest I can produce!), but in fact it is virtually colourless. The pale brown precipitate is oxidized to darker brown manganese(III) oxide in contact with oxygen from the air.

hexaaquanickel(II)



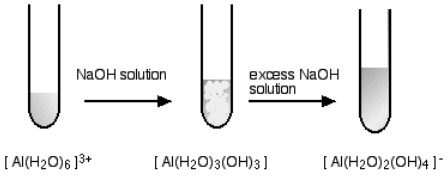
hexaaquazinc



You start and finish with colorless solutions, producing a white precipitate on the way.

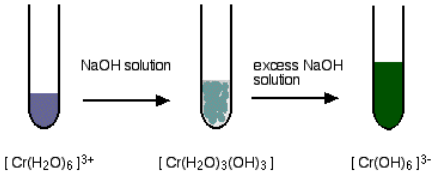
3+ ions

hexaaquaaluminium

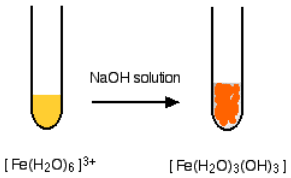


This looks exactly the same in the test test as the corresponding zinc reaction above - but beware the different formulae of the precipitate and the final solution.

hexaaquachromium(III)



hexaaquairon(III)



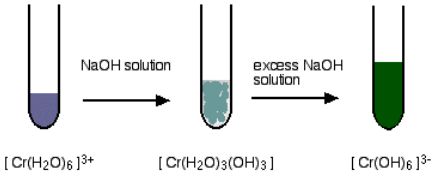
Reversing the process

If adding hydroxide ions removes hydrogen ions from the hexaaqua complex one at a time, it doesn't seem unreasonable that you could put them back again by adding an acid. That's just what happens!

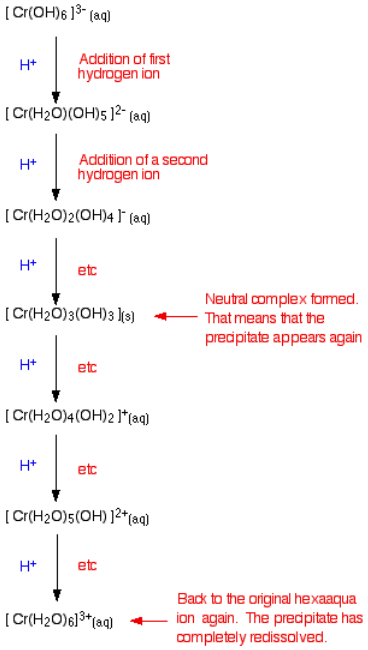
We'll look in detail at what happens in the chromium(III) case, but exactly the same principle applies to all the other examples we've looked at - whether for 2+ or 3+ ions. As long as you understand what is happening, you can work out the details if you need to

Adding acid to hexahydroxochromate(III) ions

These are the ions formed at the end of the sequence in which you add hydroxide ions to a solution containing hexaaquachromium(III) ions. Their formula is $[Cr(OH)_6]^{3-}$. A reminder of the color changes when you add sodium hydroxide solution to a solution containing hexaaquachromium(III) ions:



If you add an acid (dilute sulphuric acid, for example), the hydrogen ions get put back on one at a time.



You already know the colors of the significant stages (the beginning, the end, and the neutral complex). It isn't a separate bit of learning! You can apply this to any case. If you know the colors as you remove hydrogen ions, you automatically know them as you put the hydrogen ions back on again. It also doesn't matter where you start from either - whether, for example, you add acid to an ionic complex like $[Cr(OH)_6]^{3-}$, or a neutral one like $[Fe(H_2O)_4(OH)_2]$.

You will know that the $[Fe(H_2O)_4(OH)_2]$ is a dirty green precipitate. When you add the hydrogen ions back to it, it will revert to the very pale green solution of the $[Fe(H_2O)_6]^{2+}$ ion. None of this is a new bit of learning - you just have to re-arrange what you already know!

Amphoteric hydroxides

An amphoteric substance has both acidic and basic properties. In other words, it will react with both bases and acids. Some of the metal hydroxides we've been looking at are doing exactly that.

Chromium(III) hydroxide as an amphoteric hydroxide

"Chromium(III) hydroxide" is a simple way of naming the neutral complex $[Cr(H_2O)_3(OH)_3]$. You have seen that it reacts with bases (hydroxide ions) to give $[Cr(OH)_6]^{3-}$. It also reacts with acids (hydrogen ions) to give $[Cr(H_2O)_6]^{3+}$. This is a good example of amphoteric behavior.

Other examples of amphoteric hydroxides are zinc hydroxide and aluminium hydroxide.

Copper(II) hydroxide as a basic oxide

Quite a lot of metal hydroxides won't react any further with hydroxide ions if you use sodium hydroxide solution at the sort of concentrations normally used in the lab. That means that they don't have any significant acidic nature.

"Copper(II) hydroxide" is what we would normally call the neutral complex $[Cu(H_2O)_4(OH)_2]$. This doesn't dissolve in sodium hydroxide solution at any concentration normally used in the lab. It doesn't show any acidic character.

On the other hand, it will react with acids - replacing the lost hydrogen ions on the water ligands. Because it is accepting hydrogen ions, it is acting as a base. Hydroxides like this (which react with acids, but not bases) are not amphoteric - they are just simple bases.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

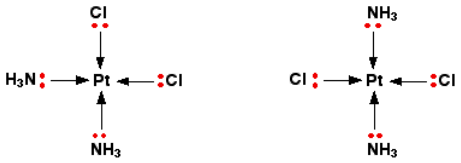
- **Reactions of the Hexaaqua Ions with Hydroxide Ions** by Jim Clark is licensed CC BY-NC 4.0.

8.3.10: Stereoisomerism in complex ions

Some complex ions can show either optical or geometric isomerism.

Geometric Isomerism

This occurs in planar complexes like the $Pt(NH_3)_2Cl_2$ we've just looked at. There are two completely different ways in which the ammonias and chloride ions could arrange themselves around the central platinum ion:



the "**cis**" form the "**trans**" form

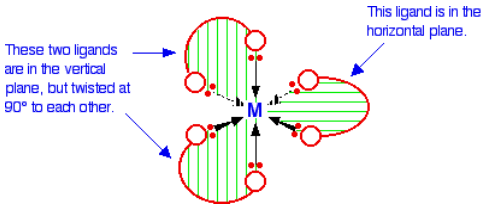
The two structures drawn are isomers because there is no way that you can just twist one to turn it into the other. The complexes are both locked into their current forms.

The terms *cis* and *trans* are used in the same way as they are in organic chemistry. Trans implies "opposite" - notice that the ammine ligands are arranged opposite each other in that version, and so are the chloro ligands. Cis means "on the same side" - in this instance, that just means that the ammine and chloro ligands are next door to each other.

Optical isomerism

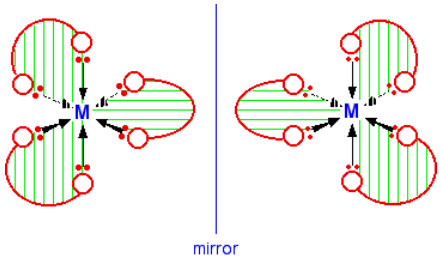
You recognize optical isomers because they have no plane of symmetry. In the organic case, it is fairly easy to recognize the possibility of this by looking for a carbon atom with four different things attached to it. It isn't qute so easy with the complex ions - either to draw or to visualize! The examples you are most likely to need occur in octahedral complexes which contain bidentate ligands - ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$.

The diagram below shows a simplified view of one of these ions. Essentially, they all have the same shape - all that differs is the nature of the "headphones". The charges are left off the ion, because obviously they will vary from case to case. The shape shown applies to any ion of this kind.



If your visual imagination will cope, you may be able to see that this ion has no plane of symmetry. If you find this difficult to visualize, the only solution is to make the ion out of a lump of plasticene (or a bit of clay or dough) and three bits of cardboard cut to shape.

A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarized light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:



If you have a really impressive visual imagination, you may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 8.3.10: Stereoisomerism in complex ions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Stereoisomerism in complex ions** by Jim Clark is licensed CC BY-NC 4.0.

SECTION OVERVIEW

8.4: Complex Ion Equilibria

Complex ions typically exist in complex equilibrium involving its central metal ion and the ligands.

Topic hierarchy

8.4.1: Chelation

8.4.2: Complex-Ion Equilibria

8.4.3: Complex Equilibrium

8.4.4: Hard and Soft Acids and Bases

8.4.5: Stability of Metal Complexes and Chelation

8.4: Complex Ion Equilibria is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.4.1: Chelation

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it.

Introduction

Many complexes are relatively unreactive species remaining unchanged throughout a sequence of chemical or physical operations and can often be isolated as stable solids or liquid compounds. Other complexes have a much more transient existence and may exist only in solution or be highly reactive and easily converted to other species. All metals form complexes, although the extent of formation and nature of these depend very largely on the electronic structure of the metal. The concept of a metal complex originated in the work of Alfred Werner, who in 1913 was awarded the first Nobel Prize in Inorganic chemistry.

Complexes may be non-ionic (neutral) or cationic or anionic, depending on the charges carried by the central metal ion and the coordinated groups. The total number of points of attachment to the central element is termed the coordination number and this can vary from 2 to greater than 12, but is usually 6. The term ligand come from the latin word *ligare*, which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. The first use of the term in a British journal was by H. Irving and R.J.P. Williams in *Nature*, 1948, 162, 746 in their paper describing what is now called the Irving-Williams series.

Ligands can be further characterised as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. The term **chelate** was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew [*J. Chem. Soc.*, 1920, 117, 1456], who stated: "The adjective chelate, derived from the great claw or **chela (chely- Greek)** of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings."

Metal complexation is of widespread interest. It is studied not only by inorganic chemists, but by physical and organic chemists, biochemists, pharmacologists, molecular biologists and environmentalists.

Thermodynamic Stability

The "stability of a complex in solution" refers to the degree of association between the two species involved in the state of equilibrium. Qualitatively, the greater the association, the greater the stability of the compound. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightarrow ML_4$$

then the larger the stability constant, the higher the proportion of ML_4 that exists in the solution. Free metal ions rarely exist in solution so that M, will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For example in water:

$$M(H_2O)_4 + L \rightleftharpoons M(H_2O)_3L + H_2O$$

$$M(H_2O)_3L + L \rightleftharpoons M(H_2O)_2L_2 + H_2O$$

However, for simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

$M + L \rightarrow ML$ with

$$K_1 = \frac{[ML]}{[M][L]}$$

$ML + L \rightarrow ML_2$ with

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

$ML_2 + L \rightarrow ML_3$ with

$$K_3 = \frac{[ML3]}{[ML_2][L]}$$

$ML_3 + L \rightarrow ML_4$ with

$$K_4 = \frac{[ML_4]}{[ML_3][L]}$$

where K_1, K_2 etc. are referred to as "stepwise stability constants." Alternatively, the "Overall Stability Constant" can be constructed

$$M + 4L \rightarrow ML_4 \beta_4 = \frac{[ML_4]}{[M][L]^4}$$

The stepwise and overall stability constants are therefore related as follows:

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$$

or more generally,

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times \ldots K_n$$

Table E4 outlines the sequential formation constants for a range of metal-ligand complexes.

Example 8.4.1.1: The Cuprammonium Ion

Consider the four steps involved in the formation of the cuprammonium ion $Cu(NH_3)_4^{2+}$:

STEP 1:

$$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+}$$

with

$$K_1 = \frac{[Cu(NH_3)^{2+}]}{[Cu^{2+}][NH_3]}$$

STEP 2:

$$CuNH_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+}$$

with

$$K_2 = \frac{[Cu(NH_3)_2^{2+}]}{[Cu(NH_3)^{2+}][NH_3]}$$

STEP 3:

$$Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{2+}$$

with

$$K_3 = \frac{[Cu(NH_3)_3^{2+}]}{[Cu(NH_3)_2^{2+}][NH_3]}$$

STEP 4:

$$Cu(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

with

$$K_4 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu(NH_3)_3^{2+}][NH_3]}$$

where the $\{K\}$ constants are the *stepwise stability constants*. Also:

$$\beta_4 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$$

The addition of the four ammine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

$$\log K_1 = 4.0,$$

$$\log K_2 = 3.2,$$

$$\log K_3 = 2.7,$$

$$\log K_4 = 2.0 \text{ or } \log \beta_4 = 11.9$$

Pay attention to definitions: a number of texts may refer to β_4 as the **instability constant** or the **dissociation constant** of coordination complexes (e.g., termed β_4' below) , which corresponds to the **reciprocal** of the formation constant (K_4), since the reactions referred to are those where fully formed complexes break down to the aqua ion and free ligands. For example,

$$\beta_4' = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]}$$

However, this is not definition use here (Table E4) and should be compared with the equation for the formation constant given earlier.

It is usual to represent the metal-binding process by a series of stepwise equilibria which lead to stability constants that may vary numerically from hundreds to enormous values such as 10^{35} and more. That is

100,000,000,000,000,000,000,000,000,000,000,000.0

For this reason, they are commonly reported as logarithms. So $\log_{10}$ (β) = $\log_{10}$ (10^{35}) = 35. It is additionally useful to use logarithms, since log(K) is directly proportional to the free energy of the reaction.

$$\Delta G^o = -RT \ln(\beta)$$

$$\Delta G^o = -2.303RT \log_{10}(\beta)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Below are three tables of the formation constants and thermodynamics properties of example ligand-metal complexes; a more complete table can be found in Table E4.

Table 8.4.1.1: Reaction of ammonia and 1,2-diaminoethane with Cd^{2+}.

# of ligands	ΔG° (kJmol^{-1})	ΔH° (kJmol^{-1})	ΔS° (JK-1mol^{-1})	log β
2 NH_3(1 en)	-28.24 (-33.30)	-29.79 (-29.41)	-5.19 (+13.05)	4.95 (5.84)
4 NH_3(2 en)	-42.51 (-60.67)	-53.14 (-56.48)	-35.50 (+13.75)	7.44 (10.62)

Table 8.4.1.2: Reaction of pyridine and 2,2'-bipyridine with Ni^{2+}.

# of ligands	log β	ΔG° (kJmol^{-1})
2 py (1 bipy)	3.5 (6.9)	-20 (-39)
4 py (2 bipy)	5.6 (13.6)	-32 (-78)

# of ligands	log β	ΔG° (kJmol^{-1})
6 py (3 bipy)	9.8 (19.3)	-56 (-110)

Table 8.4.1.3: Reaction of ammonia and 1,2-diaminoethane with Ni^{2+}.

# of ligands	log β	ΔG° (kJmol^{-1})
1 NH_3	2.8	-16
2 NH_3 (1 en)	5.0 (7.51)	-28.5 (-42.8)
3 NH_3	6.6	-37.7
4 NH_3 (2 en)	7.87 (13.86)	-44.9 (-79.1)
5 NH_3	8.6	-49.1
6 NH_3 (3 en)	8.61 (18.28)	-49.2 (-104.4)

The Chelate Effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is **much more thermodynamically stable**. This can be seen by looking at the values for adding two monodentates compared with adding one bidentate, or adding four monodentates compared to two bidentates, or adding six monodentates compared to three bidentates.

A number of points should be highlighted from the formation constants in Table E4. In Table 8.4.1.1, it can be seen that the ΔH° values for the formation steps are almost identical, that is, heat is evolved to about the same extent whether forming a complex involving monodentate ligands or bidentate ligands. What is seen to vary significantly is the ΔS° term which changes from negative (unfavorable) to positive (favorable). Note as well that there is a dramatic increase in the size of the ΔS° term for adding two compared to adding four monodentate ligands. (-5 to -35 JK^{-1}mol^{-1}). What does this imply, if we consider ΔS° to give a measure of disorder?

In the case of complex formation of Ni^{2+} with ammonia or 1,2-diaminoethane, by rewriting the equilibria, the following equations are produced.

$$\begin{array}{lcl} [Ni(H_2O)_6]^{2+} + 6\,NH_3 \overset{\beta_6}{\Leftrightarrow} [Ni(NH_3)_6]^{2+} & & \textbf{1f} \\ [Ni(NH_3)_6]^{2+} \Leftrightarrow [Ni(H_2O)_6]^{2+} + 6\,NH_3 & & \textbf{1d} \\ [Ni(H_2O)_6]^{2+} + 3\,en \overset{\beta_3}{\Leftrightarrow} [Ni(en)_3]^{2+} & & \textbf{2f} \\ \hline [Ni(NH_3)_6]^{2+} + 3\,en \Leftrightarrow [Ni(en)_3]^{2+} + 6NH_3 & & \textbf{3} \end{array}$$

Using the equilibrium constant for the reaction (3 above) where the *three* bidentate ligands replace the *six* monodentateligands, we find that at a temperature of 25° C:

$$\Delta G^\circ = -2.303\,RT\,\log_{10} K$$
$$= -2.303\,RT\,(18.28 - 8.61)$$
$$= -54\ \text{kJ mol}^{-1}$$

Based on measurements made over a range of temperatures, it is possible to break down the ΔG° term into the enthalpy and entropy components.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The result is that: $\Delta H^\circ = -29 kJmol^{-1}$

$$- T\Delta S° = -25 \text{ kJ mol}^{-1}$$

and at 25C (298K)

$$\Delta S° = +88 \text{ J K}^{-1} \text{ mol}^{-1}$$

For many years, these numbers have been **incorrectly recorded** in textbooks. For example, the third edition of "Basic Inorganic Chemistry" by F.A. Cotton, G. Wilkinson and P.L. Gaus, John Wiley & Sons, Inc, 1995, on page 186 gives the values as:

$$\Delta G° = -67 \text{ kJ mol}^{-1}$$
$$\Delta H° = -12 \text{ kJ mol}^{-1}$$
$$-T\Delta S° = -55 \text{ kJ mol}^{-1}$$

The conclusion they drew from these incorrect numbers was that the chelate effect was essentially an entropy effect, since the $T\Delta S°$ contribution was nearly 5 times bigger than $\Delta H°$.

In fact, the breakdown of the $\Delta G°$ into $\Delta H°$ and $T\Delta S°$ shows that the two terms are nearly equal (-29 and -25 kJ mol^{-1}, respectively) with the $\Delta H°$ term a little bigger! The entropy term found is still much larger than for reactions involving a non-chelating ligand substitution at a metal ion. How can we explain this enhanced contribution from entropy? One explanation is to count the number of species on the left and right hand side of the equation above.

It will be seen that on the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species, that is a net gain of 3 species occurs as the reaction proceeds. This can account for the increase in entropy since it represents an increase in the disorder of the system. An alternative view comes from trying to understand how the reactions might proceed. To form a complex with 6 monodentates requires 6 separate favorable collisions between the metal ion and the ligand molecules. To form the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm but remember that the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring.

If you consider dissociation steps, then when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again. **Both** conditions favor the formation of the complex with bidentate groups rather than monodentate groups.

References

1. For a fascinating review of the origin and dissemination of the term 'ligand' in chemistry see: W.H. Brock, K.A Jensen, C.K. Jorgensen and G.B. Kauffman, *Polyhedron*, 2, 1983, 1-7.
2. Gilbert T. Morgan and H.D.K. Drew, *J. Chem. Soc.*, 1920, 117, 1456
3. H. Irving and R.J.P. Williams, *Nature*, 1948, 162, 746
4. A description of his Alfred Werner's life and the influence his work played in the development of coordination chemistry is given by G.B. Kauffman in "*Inorganic Coordination Compounds*", Heyden & Son Ltd, 1981.

Problems

Calculate the entropy changes at 25°C, for the following reactions:

$$Zn^{2+} + 2NH_3 <=> [Zn(NH_3)_2]^{2+}$$

$$\Delta H = -28.03 \text{ kJ mol}^{-1} \text{ and } \log_{10} \beta_2 = 5.01$$

$$Zn^{2+} + en <=> [Zn(en)]^{2+}$$

$$\Delta H = -27.6 \text{ kJ mol}^{-1} \text{ and } \log_{10} \beta = 6.15 \text{ (NB R=8.314 JK}^{-1}\text{mol}^{-1}\text{)}$$

Solution

The calculations make use of the equations:

$$\mathbf{\Delta G° = RT\ln\beta}$$
$$\mathbf{\Delta G° = 2.303RT\log_{10}\beta}$$
$$\mathbf{\Delta G° = \Delta H° - T\Delta S°}$$

First it is necessary to calculate the ΔG values from the given formation constants and temperature 25C = 298K.

For the ammonia complex, ΔG = -8.314 * 298 * 2.303 * 5.01 $kJmol^{-1}$, that is -28.6 $kJmol^{-1}$.

For the 1,2-diaminoethane complex, ΔG= -8.314 * 298 * 2.303 * 6.15 $kJmol^{-1}$ which corresponds to -35.1 $kJmol^{-1}$.

This makes use of the relation between Ln and log10 such that ln(x) = 2.303 log10 (x).

Then using the second relationship above, ΔS can be found.

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

For the ammonia complex this gives 1.9 $JK^{-1}mol^{-1}$ and for the 1,2-diaminoethane complex 25.2 $JK^{-1}mol^{-1}$, which are the values given as answer 2.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

This page titled 8.4.1: Chelation is shared under a not declared license and was authored, remixed, and/or curated by Robert J. Lancashire.

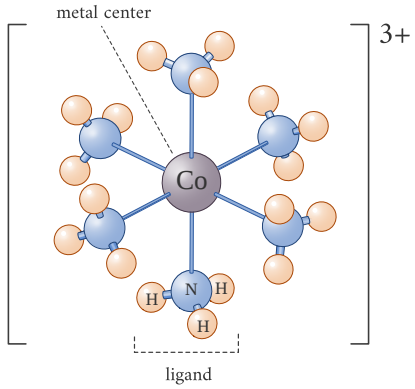
- **Chelation** by Robert J. Lancashire is licensed CC BY-NC-SA 4.0.

8.4.2: 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.



$[Co(NH_3)_6]^{3+}$

Figure 8.4.2.1: 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.

$$x\mathrm{M(aq)} + y\mathrm{L(aq)} \rightleftharpoons \mathrm{M}_x\mathrm{L}_y(aq)$$

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

$$\mathrm{Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)}$$

and the resulting formation constant expression:

$$\begin{aligned} K_f &= \frac{[\mathrm{Ag(CN)_2^-}]}{[\mathrm{Ag^+}][\mathrm{CN^-}]^2} \\ &= 5.6 \times 10^{18} \end{aligned}$$

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:

$$\begin{aligned} K_d &= \frac{1}{K_f} \\ &= \frac{[\mathrm{Ag^+}][\mathrm{CN^-}]^2}{[\mathrm{Ag(CN)_2}]^-} \\ &= 1.8 \times 10^{-19} \end{aligned}$$

In logarithm form K_f and K_d would be:

$$\begin{aligned} \log K_f &= \log(5.6 \times 10^{18}) = 18.7 \\ \log K_d &= \log(1.8 \times 10^{-19}) = -18.7 \end{aligned}$$

Example 8.4.2.1: 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:

$$[\mathrm{Cu(H_2O)_4}]^{2+}(\mathrm{aq}) + 4\,\mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}(\mathrm{aq}) + 4\,\mathrm{H_2O(l)}$$

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:

$$[\mathrm{Cu(H_2O)_4}]^{2+}(\mathrm{aq}) + \mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Cu(H_2O)_3(NH_3)}]^{2+}(\mathrm{aq}) + \mathrm{H_2O(l)} \qquad (\text{step } 1)$$

$$K_1 = \frac{[[\mathrm{Cu(H_2O)_3(NH_3)}]^{2+}]}{[[\mathrm{Cu(H_2O)_4}]^{2+}][\mathrm{NH_3}]} = 1.9 \times 10^4$$

Ligand Exchange Step 2:

$$[\mathrm{Cu(H_2O)_3(NH_3)}]^{2+}(\mathrm{aq}) + \mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Cu(H_2O)_2(NH_3)_2}]^{2+}(\mathrm{aq}) + \mathrm{H_2O(l)} \qquad (\text{step } 2)$$

$$K_2 = \frac{[[\mathrm{Cu(H_2O)_2(NH_3)_2}]^{2+}]}{[[\mathrm{Cu(H_2O)_3(NH_3)}]^{2+}][\mathrm{NH_3}]} = 3.9 \times 10^3$$

Ligand Exchange Step 3:

$$[\mathrm{Cu(H_2O)_2(NH_3)_2}]^{2+}(\mathrm{aq}) + \mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Cu(H_2O)(NH_3)_3}]^{2+}(\mathrm{aq}) + \mathrm{H_2O(l)} \qquad (\text{step } 3)$$

$$K_3 = \frac{[[\mathrm{Cu(H_2O)(NH_3)_3}]^{2+}]}{[[\mathrm{Cu(H_2O)_2(NH_3)_2}]^{2+}][\mathrm{NH_3}]} = 1.0 \times 10^3$$

Ligand Exchange Step 4:

$$[\mathrm{Cu(H_2O)(NH_3)_3}]^{2+}(\mathrm{aq}) + \mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}(\mathrm{aq}) + \mathrm{H_2O(l)} \qquad (\text{step } 4)$$

$$K_4 = \frac{[[\mathrm{Cu(NH_3)_4}]^{2+}]}{[[\mathrm{Cu(H_2O)(NH_3)_3}]^{2+}][\mathrm{NH_3}]} = 1.5 \times 10^2$$

Total

$$
\begin{aligned}
K_f &= K_1 \times K_2 \times K_3 \times K_4 \\
&= \frac{[[Cu(H_2O)_3(NH_3)]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]} \times \frac{[[Cu(H_2O)_2(NH_3)_2]^{2+}]}{[[Cu(H_2O)_3(NH_3)]^{2+}][NH_3]} \times \frac{[[Cu(H_2O)(NH_3)_3]^{2+}]}{[[Cu(H_2O)_2(NH_3)_2]^{2+}][NH_3]} \\
&\quad \times \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)(NH_3)_3]^{2+}][NH_3]} \\
&= \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]^4} \\
&= 1.1 \times 10^{13}
\end{aligned}
$$

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 8.4.2.2: 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 8.4.2.2). 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.

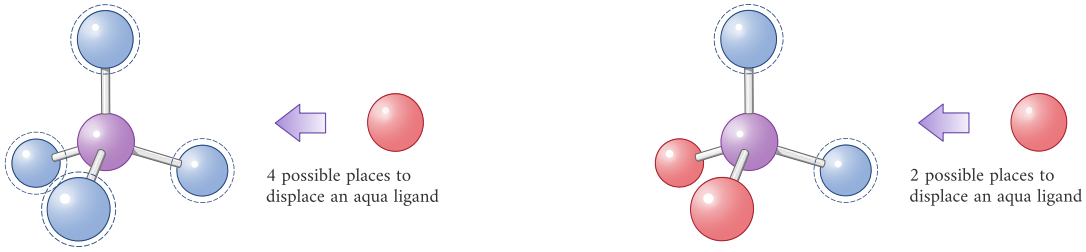


Figure 8.4.2.2: Ligand exchange in the tetrahedral complex. The first exchange step can occur with four ligands, while the third step has only two possible ligands to replace. (CC BY 4.0 Unported; Ümit Kaya via LibreTexts)

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 8.4.2.3

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 8.4.2.4

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.

8.4.2: Complex-Ion Equilibria is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Complex-Ion Equilibria** by Christopher May, Gianna Navarro, Katherine Barrett is licensed CC BY-NC-SA 4.0.

8.4.3: Complex Equilibrium

The lone pairs of electrons in water molecules make water an excellent ligand. Metal ions in any body of water in the environment usually are coordinated to 6 water molecules, e.g. $Ag(H_2O)_6^+$, $Cu(H_2O)_6^{2+}$, and $Cr(H_2O)_6^{2+}$, etc. In the literature, these ions are represented by $Ag^+(aq)$, $Cu^{2+}(aq)$, and $Cr^{3+}(aq)$ and very often the (aq) notation is also omitted (although probably should not be).

When a stronger coordinating ligand such as NH_3 is present, its molecules compete with water for the coordination site.

$$Ag(H_2O)_6^+ + NH_3 \rightleftharpoons Ag(NH_3)(H_2O)_5^+$$

$$Ag(NH_3)(H_2O)_5^+ + NH_3 \rightleftharpoons Ag(NH_3)_2(H_2O)_4^+$$

And these are simply represented by the following with the equilibrium constant as indicated.

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_1 = 2.0 \times 10^3$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2 = 8.0 \times 10^3$$

K_1 and K_2 are called **stepwise equilibrium constants** as opposed to the **overall equilibrium constants**, β_1 and β_2. Note, however, that

$$K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]}$$

with

$$\beta_1 = K_1$$

and

$$K_2 = \frac{[Ag(NH_3)^{+2}]}{[Ag(NH_3)^+][NH_3]}$$

with

$$\beta_2 = \frac{[Ag(NH_3)^{+2}]}{[Ag^+][NH_3]^2} = K_1 K_2$$

A mole fraction (X) distribution diagram for various complexes of silver can be used to show their variations. The total concentration of silver-ion-containing species C_0 is,

$$\begin{aligned} C_0 &= [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] \\ &= [Ag^+]\left(1 + \beta_1[NH_3] + \beta_2[NH_3]^2\right) \end{aligned}$$

And the mole fraction, X, of a species A, $X(A)$ is easily calculated using the following equations.

$$\begin{aligned} X(Ag^+) &= \frac{[Ag^+]}{C_0} \\ &= \frac{1}{1 + \beta_1[NH_3] + \beta_2[NH_3]^2} \end{aligned}$$

$$\begin{aligned} X(Ag(NH_3)^+) &= \frac{[Ag(NH_3)^+]}{C_0} \\ &= \beta_1 \frac{[NH3]}{1 + \beta_1[NH_3] + \beta_2[NH_3]^2} \\ &= \beta_1[NH_3]X(Ag^+) \end{aligned}$$

$$X(\mathrm{Ag(NH_3)^{2+}}) = \frac{[\mathrm{Ag(NH_3)_2^+}]}{C_0}$$
$$= \beta_2 \frac{[\mathrm{NH_3}]^2}{1 + \beta_1[\mathrm{NH_3}] + \beta_2[\mathrm{NH_3}]^2}$$
$$= \beta_2[\mathrm{NH_3}]^2 X(\mathrm{Ag^+})$$

Example 1

Evaluate $X(\mathrm{Ag^+})$, $X(\mathrm{Ag(NH_3)^+})$, and $X(\mathrm{Ag(NH_3)^{2+}})$ for a solution containing 0.20 M$\mathrm{Ag^+}$ ions mixed with an equal volume of 2.00 M $\mathrm{NH_3}$ solution.

Solution

Assume the volume doubles when the solutions are mixed. We have,

- $\beta_1 = K_1 = 2.0 \times 10^3$
- $\beta_2 = K_1 K_2 = 1.6 \times 10^7$
- $[\mathrm{NH_3}] = 1.00\ M$
- $C_0 = [\mathrm{Ag^+}] = 0.10\ M$

Now it is an application of the mole fraction equations outlined above:

$$X(\mathrm{Ag^+}) = \frac{1}{1 + \beta_1[\mathrm{NH_3}] + \beta_2[\mathrm{NH_3}]^2}$$
$$= \frac{1}{1.6 \times 10^7}$$
$$= 6.25 \times 10^{-8}$$
$$X(\mathrm{Ag(NH_3)^+}) = \beta_1[\mathrm{NH_3}]X(\mathrm{Ag^+})$$
$$= 1.25 \times 10^{-4}$$
$$X(\mathrm{Ag(NH_3)_2^+}) = \beta_2[NH_3]_2 X(\mathrm{Ag^+})$$
$$= 1$$

DISCUSSION

More precisely $[\mathrm{NH_3}] = 0.80\ M$, but the results are not changed. Since $[\mathrm{NH_3}] \gg [\mathrm{Ag^+}]$, the complex with the highest number of ligands is the dominating species.

Example 2

What are the concentrations of $\mathrm{NH_3}$ when

- $[\mathrm{Ag^+}]$=$[\mathrm{Ag(NH_3)^+}]$
- $[\mathrm{Ag(NH_3)^+}]$=$[\mathrm{Ag(NH_3)_2^+}]$

These are cross points for the mole fraction distribution lines.

Solution

Early on, we have derived these relationships.

$$X(\mathrm{Ag(NH_3)^+}) = \beta_1[\mathrm{NH_3}]X(\mathrm{Ag^+})$$
$$X(\mathrm{Ag(NH_3)_2^+}) = \beta_2[\mathrm{NH_3}]^2 X(\mathrm{Ag^+})$$

When the mole fractions are equal, their concentrations are also equal. Thus, when the mole fraction of $\mathrm{Ag^+}$ is the same as the mole fraction of $\mathrm{Ag(NH_3)^+}$,

$$X(\mathrm{Ag^+}) = X(\mathrm{Ag(NH_3)^+})$$

We have

$$\beta_1 [\mathrm{NH_3}] = 1$$

$$[\mathrm{NH_3}] = \frac{1}{\beta_1}$$

By the same arguments, the cross point of $X(\mathrm{Ag(NH_3)^+})$ line and $X(\mathrm{Ag(NH_3)_2^+})$ line occur when

$$[\mathrm{NH_3}] = \frac{1}{\sqrt{\beta_2}}$$

DISCUSSION

Note that $[\mathrm{NH_3}]$ refers to the concentration of the free ligand, not the total concentration of $\mathrm{NH_3}$. For a chemical engineering application, much more details must be revealed in order to understand the complexity of coordination equilibrium. Here is a case for a simulation model either implemented using spread sheet or programming.

The Cupric Complexes

In the case of $\mathrm{Cu^{2+}}$ ions, the equilibria are more complicated, because the coordination number of ligands can be as high as 6. Consider the following data:

$$\mathrm{Cu^{2+} + NH_3 \rightarrow Cu(NH_3)^{2+}}$$

with $K_1 = 1.1 \times 10^4$.

$$\mathrm{Cu(NH_3)^{2+} + NH_3 \rightarrow Cu(NH_3)_2^{2+}}$$

with $K_2 = 2.7 \times 10^3$.

$$\mathrm{Cu(NH_3)_2^{2+} + NH_3 \rightarrow Cu(NH_3)_3^{2+}}$$

with $K_3 = 6.3 \times 10^2$.

$$\mathrm{Cu(NH_3)_3^{2+} + NH_3 \rightarrow Cu(NH_3)_4^{2+}}$$

with $K_4 = 30$.

At high concentration of $\mathrm{NH_3}$ more of $\mathrm{Cu(NH_3)_4^{2+}}$ complexes are formed. The higher the number of ammonia is coordinated to the cupric ion, the deeper is the color blue. What we have done for the silver ion complexes can be applied to the cupric complexes, and the calculation is a little more complicated. However, the theory and method are the same, and you may applied the discussion on silver ion to that of the cupric ion cases.

8.4.3: Complex Equilibrium is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Complex-Ion Equilibrian II** by Chung (Peter) Chieh is licensed CC BY-NC-SA 4.0.

8.4.4: Hard and Soft Acids and Bases

The thermodynamic stability of a metal complex depends greatly on the properties of the ligand and the metal ion and on the type of bonding. Metal–ligand interaction is an example of a Lewis acid–base interaction. Lewis bases can be divided into two categories:

- hard bases contain small, relatively nonpolarizable donor atoms (such as N, O, and F), and
- soft bases contain larger, relatively polarizable donor atoms (such as P, S, and Cl).

Metal ions with the highest affinities for hard bases are hard acids, whereas metal ions with the highest affinity for soft bases are soft acids. Some examples of hard and soft acids and bases are given in Table 8.4.4.1. Notice that hard acids are usually cations of electropositive metals; consequently, they are relatively nonpolarizable and have higher charge-to-radius ratios. Conversely, soft acids tend to be cations of less electropositive metals; consequently, they have lower charge-to-radius ratios and are more polarizable. Chemists can predict the relative stabilities of complexes formed by the d-block metals with a remarkable degree of accuracy by using a simple rule: hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.

Table 8.4.4.1: Examples of Hard and Soft Acids and Bases

	Acids	Bases
hard	H^+	NH_3, RNH_2, N_2H_4
	Li^+, Na^+, K^+	H_2O, ROH, R_2O
	Be^{2+}, Mg^{2+}, Ca^{2+}, VO^{2+}	OH^-, F^-, Cl^-, $CH_3CO_2^-$
	Al^{3+}, Sc^{3+}, Cr^{3+}	CO_3^{2-}
	Ti^{4+}	PO_4^{3-}
soft	BF_3, Al_2Cl_6, CO_2, SO_3	
	Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}	H^-
	Pd^{2+}, Pt^{2+}, Hg^{2+}	CN^-, SCN^-, I^-, RS^-
	$GaCl_3$, $GaBr_3$, GaI_3	CO, R_2S

> *Hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.*

Because the interaction between hard acids and hard bases is primarily electrostatic in nature, the stability of complexes involving hard acids and hard bases increases as the positive charge on the metal ion increases and as its radius decreases. For example, the complex of Al^{3+} (r = 53.5 pm) with four fluoride ligands (AlF_4^-) is about 10^8 times more stable than InF_4^-, the corresponding fluoride complex of In^{3+} (r = 80 pm). In general, the stability of complexes of divalent first-row transition metals with a given ligand varies inversely with the radius of the metal ion, as shown in Table 8.4.4.2 The inversion in the order at copper is due to the anomalous structure of copper(II) complexes, which will be discussed shortly.

Table 8.4.4.2

complex stability	Mn^{2+}	< Fe^{2+}	< Co^{2+}	< Ni^{2+}	< Cu^{2+}
ionic radius (pm)	83	78	74.5	69	73

Because a hard metal interacts with a base in much the same way as a proton, by binding to a lone pair of electrons on the base, the stability of complexes of hard acids with hard bases increases as the ligand becomes more basic. For example, because ammonia is a stronger base than water, metal ions bind preferentially to ammonia. Consequently, adding ammonia to aqueous solutions of many of the first-row transition-metal cations results in the formation of the corresponding ammonia complexes.

In contrast, the interaction between soft metals (such as the second- and third-row transition metals and Cu^+) and soft bases is largely covalent in nature. Most soft-metal ions have a filled or nearly filled d subshell, which suggests that metal-to-ligand π bonding is important. Complexes of soft metals with soft bases are therefore much more stable than would be predicted based on electrostatic arguments.

The hard acid–hard base/soft acid–soft base concept also allows us to understand why metals are found in nature in different kinds of ores. Recall that most of the first-row transition metals are isolated from oxide ores but that copper and zinc tend to occur naturally in sulfide ores. This is consistent with the increase in the soft character of the metals across the first row of the transition metals from left to right. Recall also that most of the second- and third-row transition metals occur in nature as sulfide ores, consistent with their greater soft character.

This page titled 8.4.4: Hard and Soft Acids and Bases is shared under a not declared license and was authored, remixed, and/or curated by Robert J. Lancashire.

8.4.5: Stability of Metal Complexes and Chelation

Ligands like chloride, water, and ammonia are said to be monodentate (one-toothed, from the Greek mono, meaning “one,” and the Latin dent-, meaning “tooth”): they are attached to the metal via only a single atom. Ligands can, however, be bidentate (two-toothed, from the Greek di, meaning “two”), tridentate (three-toothed, from the Greek tri, meaning “three”), or, in general, polydentate (many-toothed, from the Greek poly, meaning “many”), indicating that they are attached to the metal at two, three, or several sites, respectively. Ethylenediamine ($H_2NCH_2CH_2NH_2$, often abbreviated as en) and diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, often abbreviated as dien) are examples of a bidentate and a tridentate ligand, respectively, because each nitrogen atom has a lone pair that can be shared with a metal ion. When a bidentate ligand such as ethylenediamine binds to a metal such as Ni^{2+}, a five-membered ring is formed. A metal-containing ring like that shown is called a chelate ring (from the Greek chele, meaning “claw”). Correspondingly, a polydentate ligand is a chelating agent, and complexes that contain polydentate ligands are called chelate complexes.

A chelate complex

Experimentally, it is observed that metal complexes of polydentate ligands are significantly more stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the chelate effect. For example, the complex of Ni^{2+} with three ethylenediamine ligands, $[Ni(en)_3]^{2+}$, should be chemically similar to the Ni^{2+} complex with six ammonia ligands, $[Ni(NH_3)_6]^{2+}$. In fact, the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ is almost 10 orders of magnitude larger than the equilibrium constant for the formation of $[Ni(NH_3)_6]^{2+}$ (Table E4):

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O(l) \quad K_f = 4 \times 10^8 \tag{8.4.5.1}$$

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 2 \times 10^{18} \tag{8.4.5.2}$$

The formation constants are formulated as ligand exchange reactions with aqua ligands being displaced by new ligands (NH_3 or en) in the examples above.

> *Chelate complexes are more stable than the analogous complexes with monodentate ligands.*

The stability of a chelate complex depends on the size of the chelate rings. For ligands with a flexible organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings, which are in turn much more stable than complexes with four- or seven-membered rings. For example, the complex of nickel (II) with three ethylenediamine ligands is about 363,000 times more stable than the corresponding nickel (II) complex with trimethylenediamine ($H_2NCH_2CH_2CH_2NH_2$, abbreviated as tn):

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 6.76 \times 10^{17} \tag{8.4.5.3}$$

$$[Ni(H_2O)_6]^{2+} + 3tn \rightleftharpoons [Ni(tn)_3]^{2+} + 6H_2O(l) \quad K_f = 1.86 \times 10^{12} \tag{8.4.5.4}$$

*The above measurements were done in a solution of ionic strength 0.15 at 25° C.

Example 8.4.5.1

Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

Given: four Cr(III) complexes

Asked for: relative stabilities

Strategy:

A Determine the relative basicity of the ligands to identify the most stable complexes.

B Decide whether any complexes are further stabilized by a chelate effect and arrange the complexes in order of increasing stability.

Solution

A The metal ion is the same in each case: Cr^{3+}. Consequently, we must focus on the properties of the ligands to determine the stabilities of the complexes. Because the stability of a metal complex increases as the basicity of the ligands increases, we need to determine the relative basicity of the four ligands. Our earlier discussion of acid–base properties suggests that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability expected due to ligand basicity is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}.$$

B Because of the chelate effect, we expect ethylenediamine to form a stronger complex with Cr^{3+} than ammonia. Consequently, the likely order of increasing stability is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}.$$

? Exercise 8.4.5.1

Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

Answer: $[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

The Chelate Effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is **much more thermodynamically stable**. This can be seen by looking at the values for adding two monodentates compared with adding one bidentate, or adding four monodentates compared to two bidentates, or adding six monodentates compared to three bidentates.

> *The Chelate Effect is that complexes resulting from coordination with the chelating ligand is much more thermodynamically stable than complexes with non-chelating ligands.*

A number of points should be highlighted from the formation constants in Table E4. In Table 8.4.5.1, it can be seen that the ΔH° values for the formation steps are almost identical, that is, heat is evolved to about the same extent whether forming a complex involving monodentate ligands or bidentate ligands. What is seen to vary significantly is the ΔS° term which changes from negative (unfavorable) to positive (favorable). Note as well that there is a dramatic increase in the size of the ΔS° term for adding two compared to adding four monodentate ligands. (-5 to -35 $JK^{-1}mol^{-1}$). What does this imply, if we consider ΔS° to give a measure of disorder?

In the case of complex formation of Ni^{2+} with ammonia or 1,2-diaminoethane, by rewriting the equilibria, the following equations are produced.

$$\begin{array}{lcl} [Ni(H_2O)_6]^{2+} + 6\,NH_3 \overset{\beta_6}{\Leftrightarrow} [Ni(NH_3)_6]^{2+} & & \textbf{1f} \\ [Ni(NH_3)_6]^{2+} \Leftrightarrow [Ni(H_2O)_6]^{2+} + 6\,NH_3 & & \textbf{1d} \\ [Ni(H_2O)_6]^{2+} + 3\,en \overset{\beta_3}{\Leftrightarrow} [Ni(en)_3]^{2+} & & \textbf{2f} \\ \hline [Ni(NH_3)_6]^{2+} + 3\,en \Leftrightarrow [Ni(en)_3]^{2+} + 6NH_3 & & \textbf{3} \end{array}$$

Using the equilibrium constant for the reaction (3 above) where the *three* bidentate ligands replace the *six* monodentateligands, we find that at a temperature of 25° C:

$$\begin{aligned} \Delta G^\circ &= -2.303\,RT\,\log_{10} K \\ &= -2.303\,RT\,(18.28 - 8.61) \\ &= -54\ \text{kJ mol}^{-1} \end{aligned}$$

Based on measurements made over a range of temperatures, it is possible to break down the ΔG° term into the enthalpy and entropy components.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The result is that: $\Delta H^\circ = -29 kJ mol^{-1}$

$$- T\Delta S^\circ = -25 \text{ kJ mol}^{-1}$$
and at 25C (298K)
$$\Delta S^\circ = +88 \text{ J K}^{-1} \text{ mol}^{-1}$$

For many years, these numbers have been **incorrectly recorded** in textbooks. For example, the third edition of "Basic Inorganic Chemistry" by F.A. Cotton, G. Wilkinson and P.L. Gaus, John Wiley & Sons, Inc, 1995, on page 186 gives the values as:

$$\Delta G^\circ = -67 \text{ kJ mol}^{-1}$$
$$\Delta H^\circ = -12 \text{ kJ mol}^{-1}$$
$$-T\Delta S^\circ = -55 \text{ kJ mol}^{-1}$$

The conclusion they drew from these incorrect numbers was that the chelate effect was essentially an entropy effect, since the $T\Delta S^\circ$ contribution was nearly 5 times bigger than ΔH°.

In fact, the breakdown of the ΔG° into ΔH° and $T\Delta S^\circ$ shows that the two terms are nearly equal (-29 and -25 kJ mol^{-1}, respectively) with the ΔH° term a little bigger! The entropy term found is still much larger than for reactions involving a non-chelating ligand substitution at a metal ion. How can we explain this enhanced contribution from entropy? One explanation is to count the number of species on the left and right hand side of the equation above.

It will be seen that on the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species, that is a net gain of 3 species occurs as the reaction proceeds. This can account for the increase in entropy since it represents an increase in the disorder of the system. An alternative view comes from trying to understand how the reactions might proceed. To form a complex with 6 monodentates requires 6 separate favorable collisions between the metal ion and the ligand molecules. To form the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm but remember that the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring.

If you consider dissociation steps, then when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again. **Both** conditions favor the formation of the complex with bidentate groups rather than monodentate groups.

This page titled 8.4.5: Stability of Metal Complexes and Chelation is shared under a not declared license and was authored, remixed, and/or curated by Robert J. Lancashire.

- **Stability of Metal Complexes and Chelation** by Robert J. Lancashire is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

9: Crystal Field Theory

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. Crystal field theory (CFT) is a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature.

9.1: Colors of Coordination Complexes
9.2: Crystal Field Stabilization Energy
9.3: Crystal Field Theory
9.4: High Spin and Low Spin Complexes
9.5: Introduction to Crystal Field Theory
9.6: Magnetic Moments of Transition Metals
9.7: Magnetism
9.8: Metals, Tetrahedral and Octahedral
9.9: Non-octahedral Complexes
9.10: Octahedral vs. Tetrahedral Geometries
9.11: Orgel Diagrams
9.11.1: Qualitative Orgel Diagrams
9.12: Tanabe-Sugano Diagrams
9.13: Thermodynamics and Structural Consequences of d-Orbital Splitting

Template:HideTOC

9: Crystal Field Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.1: Colors of Coordination Complexes

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 9.1.1), and when all the wavelengths are present, it appears as white light.

Figure 9.1.1: 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 9.1.2, 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 9.1.2, 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.

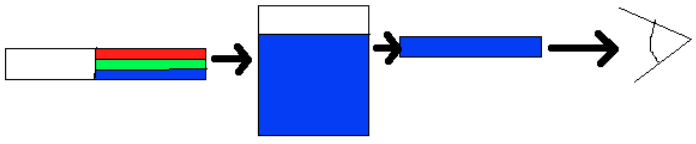


Figure 9.1.2: Subtractive mixing

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 9.1.3; the "o" subscript on the Δ indicates that the complex has octahedral geometry.

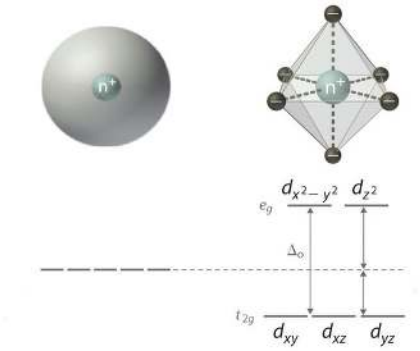


Figure 9.1.3: d-Orbitals Splitting in an octahedral ligand field. (CC BY-SA-NC; anonymous by request)

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 9.1.4*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 9.1.4*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.

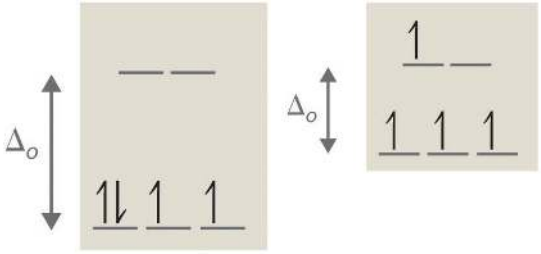


Figure 9.1.4: (a) Low Spin, Strong Field ($\Delta_o > P$). (b): High Spin, Weak Field ($\Delta_o < P$). (CC BY-SA-NC; anonymous)

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 9.1.1. 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 9.1.6). 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.

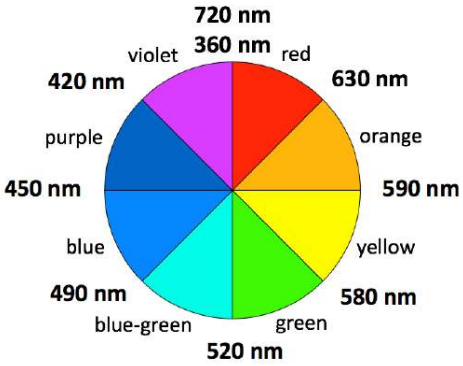


Figure 9.1.5: Color wheel with wavelengths marked (CC BY-SA 4.0 International; Tem5psu via source)

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 9.1.1

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 9.1.2

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 9.1.1 and 9.1.6 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 9.1.3

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)

9.1: Colors of Coordination Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Colors of Coordination Complexes** is licensed CC BY 4.0.

9.2: 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 field 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

The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$CFSE = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}} \tag{9.2.1}$$

The CSFE will depend on multiple factors including:

- Geometry (which changes the d-orbital splitting patterns)
- Number of d-electrons
- Spin Pairing Energy
- Ligand character (via Spectrochemical Series)

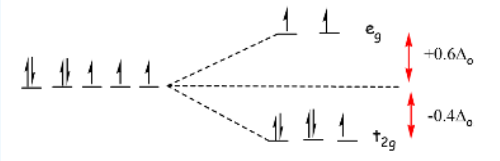
For an octahedral complex, an electron in the more stable t_{2g} subset is treated as contributing $-2/5\Delta_o$ whereas an electron in the higher energy e_g subset contributes to a destabilization of $+3/5\Delta_o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δ_o. If any electrons are paired within a single orbital, then the term P is used to represent the spin pairing energy.

Example 9.2.1: CFSE for a high Spin d^7 complex

What is the Crystal Field Stabilization Energy for a high spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field ($E_{\text{isotropic field}}$) is

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (5 \times -2/5\Delta_o) + (2 \times 3/5\Delta_o) + 2P = -4/5\Delta_o + 2P$$

So via Equation 9.2.1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-4/5\Delta_o + 2P) - 2P \\ &= -4/5\Delta_o \end{aligned}$$

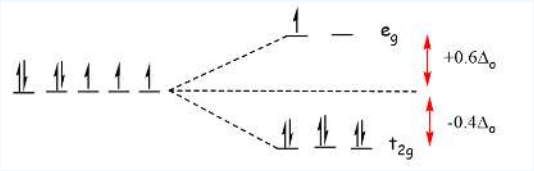
Notice that the Spin pairing Energy falls out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the ligand field is the same as that in isotropic field of the free metal ion.

Example 9.2.2: CFSE for a Low Spin d^7 complex

What is the Crystal Field Stabilization Energy for a low spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand\) field $E_{\text{ligand field}}$ is

$$\begin{aligned} E_{\text{ligand field}} &= (6 \times -2/5\Delta_o) + (1 \times 3/5\Delta_o) + 3P \\ &= -9/5\Delta_o + 3P \end{aligned}$$

So via Equation 9.2.1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-9/5\Delta_o + 3P) - 2P \\ &= -9/5\Delta_o + P \end{aligned}$$

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more a more stable configuration than the high spin d^7 configuration in Example 9.2.1, 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 9.2.1: Crystal Field Stabilization Energies (CFSE) for high and low spin octahedral complexes

Total d-electrons	Isotropic Field	Octahedral Complex				Crystal Field Stabilization Energy	
		High Spin		Low Spin			
	$E_{\text{isotropic field}}$	Configuration	$E_{\text{ligand field}}$	Configuration	$E_{\text{ligand field}}$	High Spin	Low Spin
d^0	0	$t_{2g}0e_g0$	0	${t_{2g}}^0{e_g}^0$	0	0	0
d^1	0	$t_{2g}1e_g0$	-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	$t_{2g}2e_g0$	-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	$t_{2g}3e_g0$	-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	$t_{2g}3e_g1$	-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	$t_{2g}3e_g2$	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	$t_{2g}4e_g2$	-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	$t_{2g}5e_g2$	-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	$t_{2g}6e_g2$	-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	$t_{2g}6e_g3$	-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	$t_{2g}6e_g4$	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

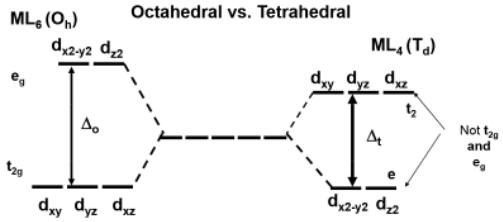
Similar CFSE values can be constructed for non-octahedral ligand field geometries once the knowledge of the d-orbital splitting is known and the electron configuration within those orbitals known, e.g., the tetrahedral complexes in Table 9.2.2. These energies geoemtries can then be contrasted to the octahedral CFSE to calculate a thermodynamic preference (Enthalpy-wise) for a metal-ligand combination to favor the octahedral geometry. This is quantified via a Octahedral Site Preference Energy defined below.

Definition: Octahedral Site Preference Energies

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:

$$OSPE = CFSE_{(oct)} - CFSE_{(tet)} \tag{9.2.2}$$

The OSPE quantifies the preference of a complex to exhibit an octahedral geometry vs. a tetrahedral geometry.



Note: the conversion between Δ_o and Δ_t used for these calculations is:

$$\Delta_t \approx \frac{4}{9}\Delta_o \tag{9.2.3}$$

which is applicable for comparing octahedral and tetrahedral complexes that involve same ligands only.

Table 9.2.2: Octahedral Site Preference Energies (OSPE)

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.

> Tetrahedral complexes are always high spin since the splitting is appreciably smaller than P (Equation 9.2.3).

After conversion with Equation 9.2.3. The data in Tables 9.2.1 and 9.2.2 are represented graphically by the curves in Figure 9.2.1 below for the high spin complexes only. The low spin complexes require knowledge of P to graph.

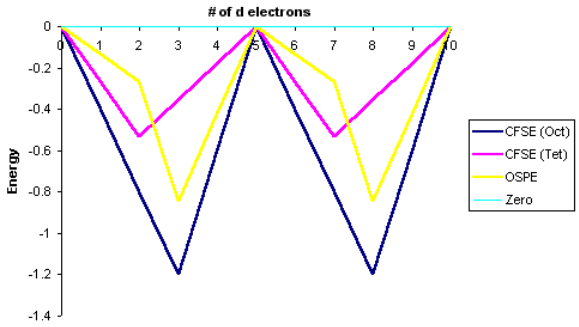


Figure* 9.2.1*: *Crystal Field Stabilization Energies for both octahedral fields ($CFSE_{oct}$) and tetrahedral fields ($CFSE_{tet}$). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes.*

From a simple inspection of Figure 9.2.1, the following observations can be made:

- The OSPE is *small* in d^1, d^2, d^5, d^6, d^7 complexes and other factors influence the stability of the complexes including steric factors
- The OSPE is *large* in d^3 and d^8 complexes which strongly favor octahedral geometries

Applications

The "double-humped" curve in Figure 9.2.1 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:

$$M^{2+}(g) + H_2O \rightarrow [M(OH_2)_6]^{2+}(aq)$$

Table 9.2.3 and Figure 9.2.1 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.

Table 9.2.3: 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:

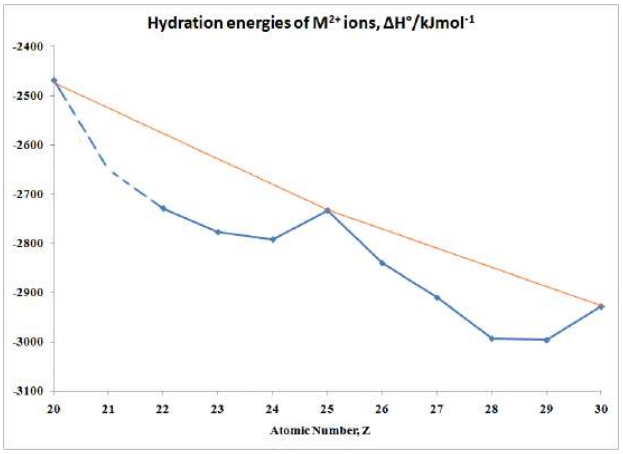


Figure* 9.2.2*: hydration energies of M^{2+} ions

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

9.2: Crystal Field Stabilization Energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Crystal Field Stabilization Energy** is licensed CC BY-NC-SA 4.0.

9.3: Crystal Field Theory

Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color. This theory was developed by Hans Bethe and John Hasbrouck van Vleck.

Basic Concept

In Crystal Field Theory, it is assumed that the ions are **simple point charges** (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

$$E \propto \frac{q_1 q_2}{r}$$

with

- E the bond energy between the charges and
- q_1 and q_2 are the charges of the interacting ions and
- r is the distance separating them.

This approach leads to the correct prediction that large cations of low charge, such as K^+ and Na^+, should form few coordination compounds. For transition metal cations that contain varying numbers of d electrons in orbitals that are NOT spherically symmetric, however, the situation is quite different. The shapes and occupations of these d-orbitals then become important in building an accurate description of the bond energy and properties of the transition metal compound.

When examining a single transition metal ion, the five *d*-orbitals have the same energy (Figure 9.3.1). When ligands approach the metal ion, some experience more opposition from the *d*-orbital electrons than others based on the geometric structure of the molecule. Since ligands approach from different directions, not all *d*-orbitals interact directly. These interactions, however, create a splitting due to the electrostatic environment.

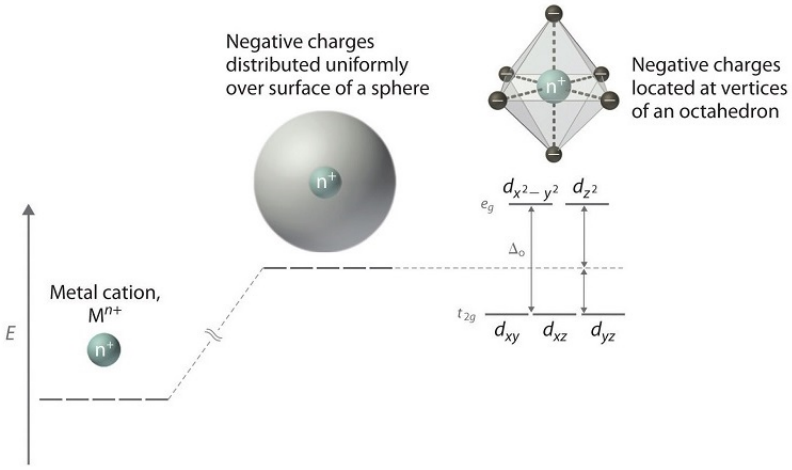


Figure 9.3.1: Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. The two e_g orbitals point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

For example, consider a molecule with octahedral geometry. Ligands approach the metal ion along the x, y, and z axes. Therefore, the electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals (which lie along these axes) experience greater repulsion. It requires more energy to have an electron in these orbitals than it would to put an electron in one of the other orbitals. This causes a splitting in the energy levels of the *d*-orbitals. This is known as **crystal field splitting**. For octahedral complexes, crystal field splitting is denoted by Δ_o (or Δ_{oct}). The energies of the d_{z^2} and $d_{x^2-y^2}$ orbitals increase due to greater interactions with the ligands. The d_{xy}, d_{xz}, and d_{yz} orbitals decrease with respect to this normal energy level and become more stable.

Electrons in Orbitals

According to the Aufbau principle, electrons are filled from lower to higher energy orbitals (Figure 9.3.1). For the octahedral case above, this corresponds to the d_{xy}, d_{xz}, and d_{yz} orbitals. Following Hund's rule, electrons are filled in order to have the highest number of unpaired electrons. For example, if one had a d^3 complex, there would be three unpaired electrons. If one were to add an electron, however, it has the ability to fill a higher energy orbital (d_{z^2} or $d_{x^2-y^2}$) or pair with an electron residing in the d_{xy}, d_{xz}, or d_{yz} orbitals. This pairing of the electrons requires energy (spin pairing

energy). If the pairing energy is less than the crystal field splitting energy, Δ_o, then the next electron will go into the d_{xy}, d_{xz}, or d_{yz} orbitals due to stability. This situation allows for the least amount of unpaired electrons, and is known as low spin. If the pairing energy is greater than Δ_o, then the next electron will go into the d_{z^2} or $d_{x^2-y^2}$ orbitals as an unpaired electron. This situation allows for the most number of unpaired electrons, and is known as high spin. Ligands that cause a transition metal to have a small crystal field splitting, which leads to high spin, are called weak-field ligands. Ligands that produce a large crystal field splitting, which leads to low spin, are called **strong field ligands**.

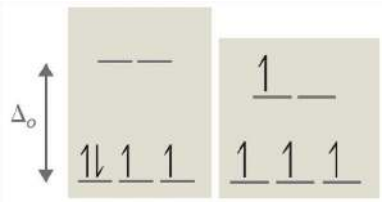


Figure 9.3.2: Low Spin, Strong Field (Δ_o>P) High Spin, Weak Field (Δ_o<P)Splitting for a d^4 complex under a strong field (left) and a weak field (right). The strong field is a low spin complex, while the weak field is a high spin complex.

As mentioned above, CFT is based primarily on symmetry of ligands around a central metal/ion and how this anisotropic (properties depending on direction) ligand field affects the metal's atomic orbitals; the energies of which may increase, decrease or not be affected at all. Once the ligands' electrons interact with the electrons of the *d*-orbitals, the electrostatic interactions cause the energy levels of the d-orbital to fluctuate depending on the orientation and the nature of the ligands. For example, the oxidation state and the strength of the ligands determine splitting; the higher the oxidation state or the stronger the ligand, the larger the splitting. Ligands are classified as strong or weak based on the spectrochemical series:

$$I^- < Br^- < Cl^- < \underline{S}CN^- < F^- < OH^- < ox^{2-} < \underline{O}NO^- < H_2O < SC\underline{N}^- < EDTA^{4-} < NH_3 < en < \underline{N}O_2^- < CN^-$$

Note that SCN^- and NO_2- ligands are represented twice in the above spectrochemical series since there are two different Lewis base sites (e.g., free electron pairs to share) on each ligand (e.g., for the SCN^- ligand, the electron pair on the sulfur or the nitrogen can form the coordinate covalent bond to a metal). The specific atom that binds in such ligands is underlined.

In addition to octahedral complexes, two common geometries observed are that of tetrahedral and square planar. These complexes differ from the octahedral complexes in that the orbital levels are raised in energy due to the interference with electrons from ligands. For the tetrahedral complex, the d_{xy}, d_{xz}, and d_{yz} orbitals are raised in energy while the d_{z^2}, $d_{x^2-y^2}$ orbitals are lowered. For the square planar complexes, there is greatest interaction with the $d_{x^2-y^2}$ orbital and therefore it has higher energy. The next orbital with the greatest interaction is d_{xy}, followed below by d_{z^2}. The orbitals with the lowest energy are the d_{xz} and d_{yz} orbitals. There is a large energy separation between the d_{z^2} orbital and the d_{xz} and d_{yz} orbitals, meaning that the crystal field splitting energy is large. We find that the square planar complexes have the greatest crystal field splitting energy compared to all the other complexes. This means that most square planar complexes are low spin, strong field ligands.

Description of *d*-Orbitals

To understand CFT, one must understand the description of the lobes:

- d_{xy}: lobes lie in-between the x and the y axes.
- d_{xz}: lobes lie in-between the x and the z axes.
- d_{yz}: lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z^2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

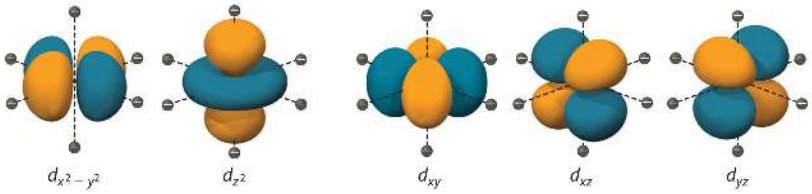


Figure 9.3.3: Spatial arrangement of ligands in the an octahedral ligand field with respect to the five d-orbitals.

Octahedral Complexes

In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels (Figure 9.3.4). The bottom three energy levels are named d_{xy}, d_{xz}, and d_{yz} (collectively referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (collectively referred to as e_g).

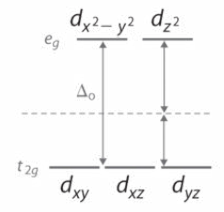


Figure 9.3.4.

The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} is lower ($0.4\Delta_o$). The distance that the electrons have to move from t_{2g} from e_g and it dictates the energy that the complex will absorb from white light, which will determine the color. Whether the complex is paramagnetic or diamagnetic will be determined by the spin state. If there are unpaired electrons, the complex is paramagnetic; if all electrons are paired, the complex is diamagnetic.

Tetrahedral Complexes

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the d_{xy}, d_{xz}, and d_{yz} orbitals. The bottom two consist of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not.

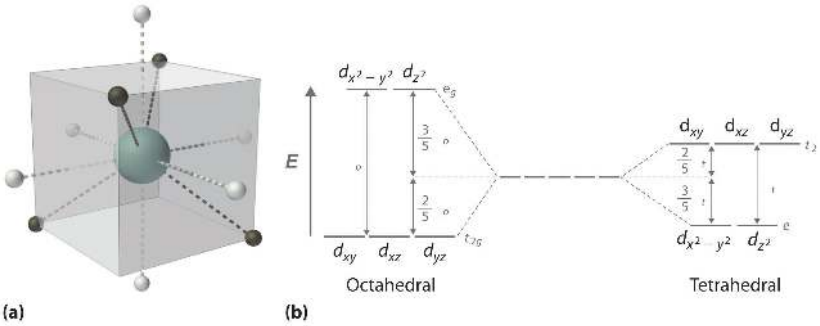


Figure 9.3.5: (a) Tetraheral ligand field surrounding a central transition metal (blue sphere). (b) Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field (left diagram) and the tetrahedral field (right diagram).

The difference in the splitting energy is tetrahedral splitting constant (Δ_t), which less than (Δ_o) for the same ligands:

$$\Delta_t = 0.44\,\Delta_o \tag{9.3.1}$$

Consequentially, Δ_t is typically smaller than the spin pairing energy, so tetrahedral complexes are usually **high spin**.

Square Planar Complexes

In a square planar, there are four ligands as well. However, the difference is that the electrons of the ligands are only attracted to the xy plane. Any orbital in the xy plane has a higher energy level (Figure 9.3.6). There are four different energy levels for the square planar (from the highest energy level to the lowest energy level): $d_{x^2-y^2}$, d_{xy}, d_{z^2}, and both d_{xz} and d_{yz}.

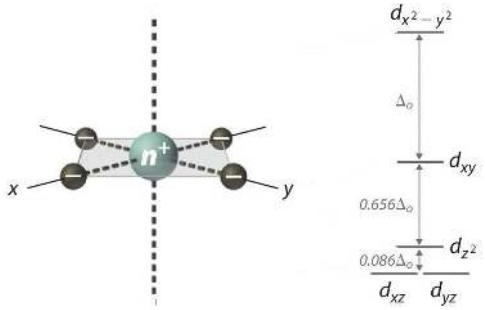


Figure 9.3.6: Splitting of the degenerate d-orbitals (without a ligand field) due to an square planar ligand field.

The splitting energy (from highest orbital to lowest orbital) is Δ_{sp} and tends to be larger then Δ_o

$$\Delta_{sp} = 1.74\,\Delta_o \tag{9.3.2}$$

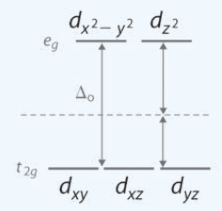
Moreover, Δ_{sp} is also larger than the pairing energy, so the square planar complexes are usually **low spin** complexes.

Example 9.3.1

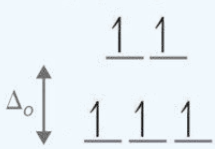
For the complex ion $[Fe(Cl)_6]^{3-}$ determine the number of d electrons for Fe, sketch the d-orbital energy levels and the distribution of d electrons among them, list the number of lone electrons, and label whether the complex is paramagnetic or diamagnetic.

Solution

- Step 1: Determine the oxidation state of Fe. Here it is Fe^{3+}. Based on its electron configuration, Fe^{3+} has **5 d-electrons**.
- Step 2: Determine the geometry of the ion. Here it is an octahedral which means the energy splitting should look like:



- Step 3: Determine whether the ligand induces is a strong or weak field spin by looking at the spectrochemical series. Cl^- is a weak field ligand (i.e., it induces high spin complexes). Therefore, electrons fill all orbitals before being paired.



- Step four: Count the number of lone electrons. Here, there are **5 electrons**.
- Step five: The five unpaired electrons means this complex ion is **paramagnetic** (and strongly so).

Example 9.3.2

A *tetrahedral* complex absorbs at 545 nm. What is the respective octahedral crystal field splitting (Δ_o)? What is the color of the complex?

Solution

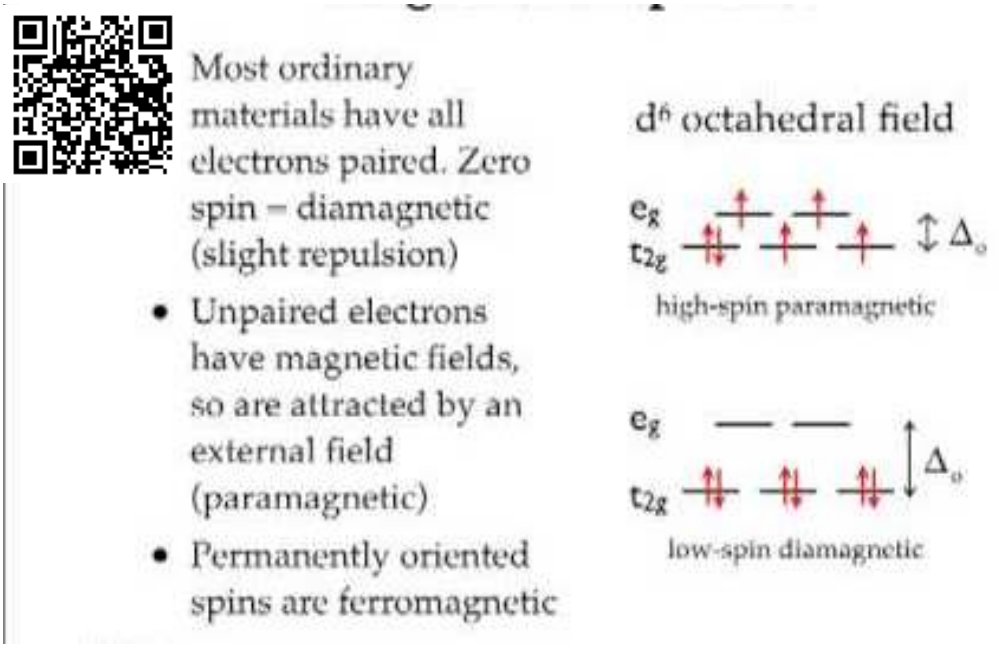
$$\begin{aligned}\Delta_t &= \frac{hc}{\lambda} \\ &= \frac{(6.626\times10^{-34}J\cdot s)(3\times10^{8}m/s)}{545\times10^{-9}m} \\ &= 3.65\times10^{-19}\ J\end{aligned}$$

However, the *tetrahedral* splitting (Δ_t) is ~4/9 that of the *octahedral* splitting (Δ_o).

$$\begin{aligned}\Delta_t &= 0.44\Delta_o \\ \Delta_o &= \frac{\Delta_t}{0.44} \\ &= \frac{3.65\times10^{-19}J}{0.44} \\ &= 8.30\times10^{-18}J\end{aligned}$$

This is the energy needed to promote *one* electron in *one* complex. Often the crystal field splitting is given per mole, which requires this number to be multiplied by Avogadro's Number (6.022×10^{23}).

This complex appears red, since it absorbs in the complementary green color (determined via the color wheel).



Video:

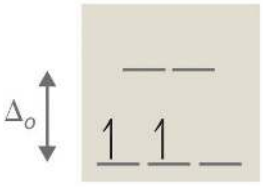
Problems

For each of the following, sketch the d-orbital energy levels and the distribution of d electrons among them, state the geometry, list the number of d-electrons, list the number of lone electrons, and label whether they are paramagnetic or dimagnetic:

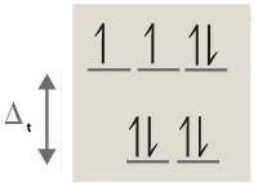
1. $[Ti(H_2O)_6]^{2+}$
2. $[NiCl_4]^{2-}$
3. $[CoF_6]^{3-}$ (also state whether this is low or high spin)
4. $[Co(NH_3)_6]^{3+}$ (also state whether this is low or high spin)
5. True or False: Square Planer complex compounds are usually low spin.

Answers

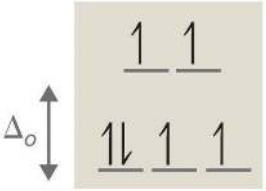
1. octahedral, 2, 2, paramagnetic



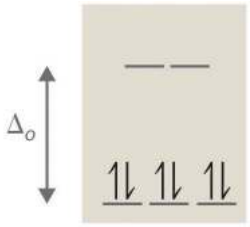
2. tetrahedral, 8, 2, paramagnetic (see Octahedral vs. Tetrahedral Geometries)



3. octahedral, 6, 4, paramagnetic, high spin



4. octahedral, 6, 0, diamagnetic, low spin



5. True

Contributors and Attributions

- Asadullah Awan (UCD), Hong Truong (UCD)
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

9.3: Crystal Field Theory is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Crystal Field Theory** is licensed CC BY-NC-SA 4.0.

9.4: High Spin and Low Spin Complexes

Learning Objectives

- Discuss the d-orbital degeneracy of square planar and tetrahedral metal complexes.

Tetrahedral Geometry

Tetrahedral geometry is a bit harder to visualize than square planar geometry. Tetrahedral geometry is analogous to a pyramid, where each of corners of the pyramid corresponds to a ligand, and the central molecule is in the middle of the pyramid. This geometry also has a coordination number of 4 because it has 4 ligands bound to it. Finally, the bond angle between the ligands is 109.5°. An example of the tetrahedral molecule CH_4, or methane.

In a tetrahedral complex, Δ_t is relatively small even with strong-field ligands as there are fewer ligands to bond with. It is rare for the Δ_t of tetrahedral complexes to exceed the pairing energy. Usually, electrons will move up to the higher energy orbitals rather than pair. Because of this, *most tetrahedral complexes are high spin.*

Square Planar Complexes

In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The geometry is prevalent for transition metal complexes with d^8 configuration. This includes Rh(I), Ir(I), Pd(II), Pt(II), and Au(III). Notable examples include the anticancer drugs cisplatin ($PtCl_2(NH_3)_2$).

A square planar complex also has a coordination number of 4. The structure of the complex differs from tetrahedral because the ligands form a simple square on the x and y axes. Because of this, the crystal field splitting is also different (Figure 9.4.1). Since there are no ligands along the z-axis in a square planar complex, the repulsion of electrons in the d_{xz}, d_{yz}, and the d_{z^2} orbitals are considerably lower than that of the octahedral complex (the d_{z^2} orbital is slightly higher in energy to the "doughnut" that lies on the x,y axis). The $d_{x^2-y^2}$ orbital has the most energy, followed by the d_{xy} orbital, which is followed by the remaining orbtails (although d_{z^2} has slightly more energy than the d_{xz} and d_{yz} orbital). This pattern of orbital splitting remains constant throughout all geometries. Whichever orbitals come in direct contact with the ligand fields will have higher energies than orbitals that slide past the ligand field and have more of indirect contact with the ligand fields. So when confused about which geometry leads to which splitting, think about the way the ligand fields interact with the electron orbitals of the central atom.

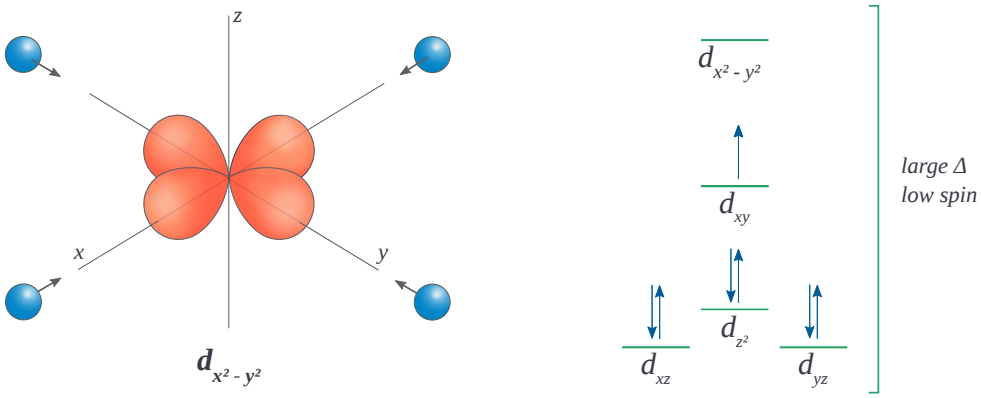


Figure 9.4.1: In square planar complexes Δ will almost always be large, even with a weak-field ligand. Electrons tend to be paired rather than unpaired because paring energy is usually much less than Δ. Therefore, square planar complexes are usually low spin. (CC BY-SA; Ümit Kaya)

In square planar complexes Δ will almost always be large (Figure 9.4.1), even with a weak-field ligand. Electrons tend to be paired rather than unpaired because paring energy is usually much less than Δ. Therefore, *square planar complexes are usually low spin.*

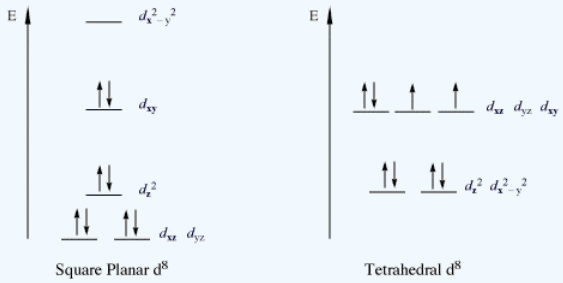
Advanced: $[PdCl_4]^{2-}$ is square planar and $[NiCl_4]^{2-}$ is tetrahedral

The molecule $[PdCl_4]^{2-}$ is diamagnetic, which indicates a square planar geometry as all eight d-electrons are paired in the lower-energy orbitals. However, $[NiCl_4]^{2-}$ is also d^8 but has two unpaired electrons, indicating a tetrahedral geometry. Why is $[PdCl_4]^{2-}$ square planar if Cl^- is not a strong-field ligand?

Solution

The geometry of the complex changes going from $[NiCl_4]^{2-}$ to $[PdCl_4]^{2-}$. Clearly this cannot be due to any change in the ligand since it is the same in both cases. It is the other factor, the metal, that leads to the difference.

Consider the splitting of the d-orbitals in a generic d^8 complex. If it were to adopt a square planar geometry, the electrons will be stabilized (with respect to a tetrahedral complex) as they are placed in orbitals of lower energy. However, this comes at a cost: two of the electrons, which were originally unpaired in the tetrahedral structure, are now paired in the square-planer structure:



We can label these two factors as ΔE (stabilization derived from occupation of lower-energy orbitals) and P (spin pairing energy) respectively. One can see that:

- If $\Delta E > P$, then the complex will be square planar
- If $\Delta E < P$, then the complex will be tetrahedral.

This is analogous to deciding whether an octahedral complex adopts a high- or low-spin configuration; where the crystal field splitting parameter Δ_o ΔE does above. Unfortunately, unlike Δ_o in octahedral complexes, there is no simple graphical way to represent ΔE on the diagram above since multiple orbitals are changed in energy between the two geometries.

Interpreting the origin of metal-dependent stabilization energies can be tricky. However, we know experimentally that Pd^{2+} has a larger splitting of the d-orbitals and hence a larger ΔE than Ni^{2+} (moreover P is also smaller).

Practically all 4d and 5d d^8 ML_4 complexes adopt a square planar geometry, irrespective if the ligands are strong-field ligand or not. Other examples of such square planar complexes are $[PtCl_4]^{2-}$ and $[AuCl_4]^-$.

Summary

- In tetrahedral molecular geometry, a central atom is located at the center of four substituents, which form the corners of a tetrahedron.
- Tetrahedral geometry is common for complexes where the metal has d^0 or d^{10}electron configuration.
- The CFT diagram for tetrahedral complexes has $d_{x^2-y^2}$ and d_{z^2} orbitals equally low in energy because they are between the ligand axis and experience little repulsion.
- In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane.
- The square planar geometry is prevalent for transition metal complexes with d^8 configuration.
- The CFT diagram for square planar complexes can be derived from octahedral complexes yet the dx2-y2 level is the most destabilized and is left unfilled.

Contributors and Attributions

- Angad Oberoi (UCD), Justin Nuckles (UCD)
- StackExchange (orthocresol)

9.4: High Spin and Low Spin Complexes is shared under a CC BY license and was authored, remixed, and/or curated by LibreTexts.

- **Tetrahedral vs. Square Planar Complexes** is licensed CC BY 4.0.

9.5: Introduction to Crystal Field Theory

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $9.5.1a$). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure $9.5.1b$, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

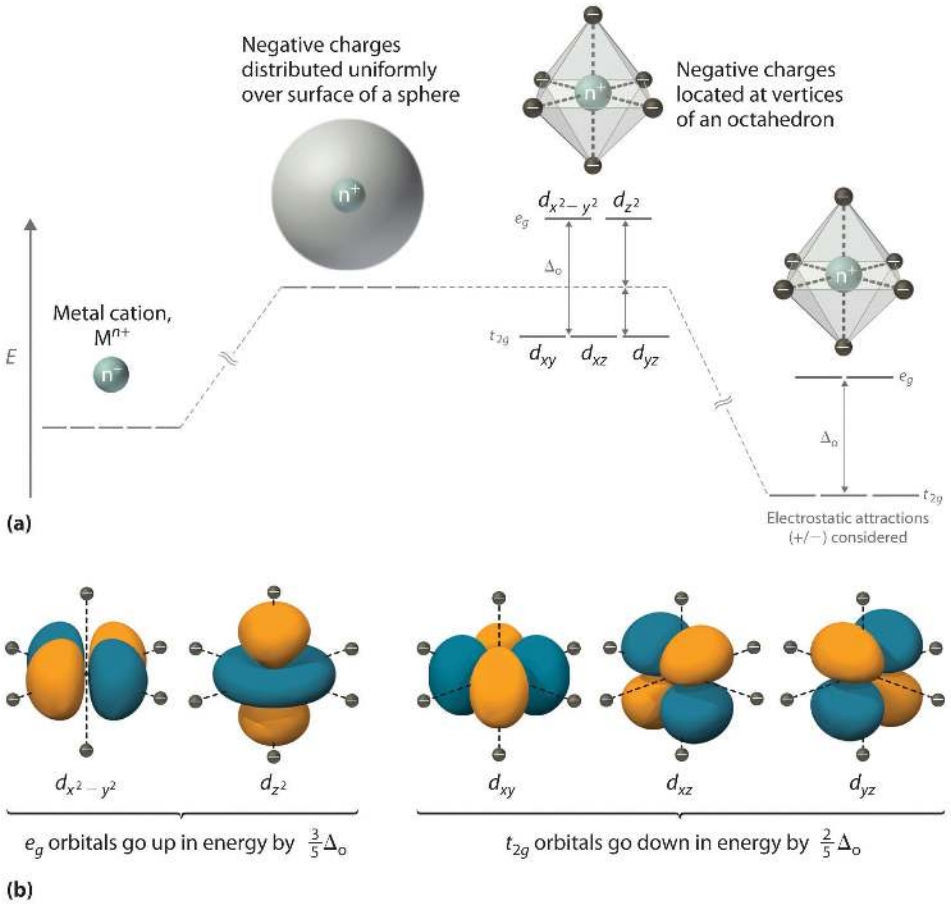


Figure 9.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase 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. (CC BY-SA-NC; anonymous by request)

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0. \tag{9.5.1}$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 9.5.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 9.5.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 9.5.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

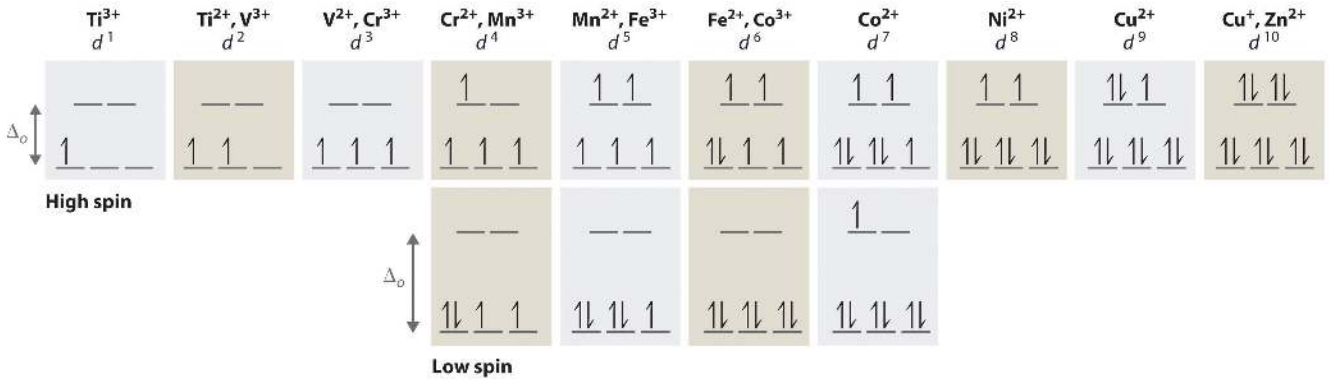


Figure 9.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 9.5.1.

Table 9.5.1: 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})

*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.

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).

Factor 1: Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion 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}.

Factor 2: 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_o (3d) < Δ_o (4d) < Δ_o (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_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. 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.

Factor 3: The Nature of the Ligands

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 ion. 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, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O} > oxalate^{2-} > OH^- > F > acetate^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table 9.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Example 9.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

   B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

   C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

   D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

   B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

   D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Exercise 9.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answer a

octahedral; high spin; five

Answer b

square planar; low spin; no unpaired electrons

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 9.5.2 gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 9.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
	t_{2g}	e_g		t_{2g}	e_g	
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

9.5: Introduction to Crystal Field Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **24.5: Bonding in Complex Ions: Crystal Field Theory** is licensed CC BY-NC-SA 4.0.

9.6: Magnetic Moments of Transition Metals

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

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Fe(II)	d^6 high spin ($t_{2g}^4\ e_g^2$)	$\sqrt{24} = 4.90$	5.1-5.7
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin ($t_{2g}^5\ e_g^2$)	$\sqrt{15} = 3.88$	4.3-5.2
Co(II)	d^7 low spin ($t_{2g}^6\ e_g^1$)	$\sqrt{3} = 1.73$	1.8
Ni(II)	d^8 ($t_{2g}^6\ e_g^2$)	$\sqrt{8} = 2.83$	2.9-3.3
Cu(II)	d^9 ($t_{2g}^6\ e_g^3$)	$\sqrt{3} = 1.73$	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)	$\sqrt{3} = 1.73$	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	$\sqrt{8} = 2.83$	2.6 - 2.8
Fe(V)	d^3 ($e^2\ t_2^1$)	$\sqrt{15} = 3.88$	3.6-3.7
-	d^4 ($e^2\ t_2^2$)	$\sqrt{24} = 4.90$	-
Mn(II)	d^5 ($e^2\ t_2^3$)	$\sqrt{35} = 5.92$	5.9-6.2
Fe(II)	d^6 ($e^3\ t_2^3$)	$\sqrt{24} = 4.90$	5.3-5.5
Co(II)	d^7 ($e^4\ t_2^3$)	$\sqrt{15} = 3.88$	4.2-4.8
Ni(II)	d^8 ($e^4\ t_2^4$)	$\sqrt{8} = 2.83$	3.7-4.0
Cu(II)	d^9 ($e^4\ t_2^5$)	$\sqrt{3} = 1.73$	-

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

9.6: Magnetic Moments of Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Magnetic Moments of Transition Metals** is licensed CC BY-NC-SA 4.0.

9.7: Magnetism

Movement of an electrical charge (which is the basis of electric currents) generates a magnetic field in a material. Magnetism is therefore a characteristic property of all materials that contain electrically charged particles and for most purposes can be considered to be entirely of electronic origin.

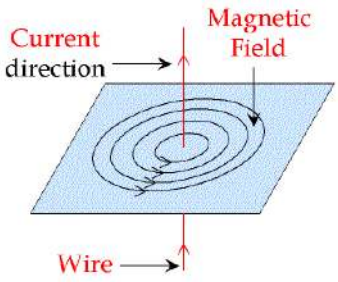


Figure 9.7.1: The Right Hand Rule for an induced magnetic field

In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes whereas the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties.

Historically, magnetism has been recognized for thousands of years. An account, that is probably apochryphal, tells of a shepherd called Magnes in Crete who around 900 B.C discovered the naturally occurring magnet lodestone (a form of the the spinel magnetite, Fe_3O_4) in a region later named Magnesia. Supposedly while he was walking over a deposit, the lodestone pulled the nails out of his sandals and the metal tip from his staff.

The Classical Theory of Magnetism

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law states that when a substance is placed within a magnetic field, H, the field within the substance, B, differs from H by the induced field, $4\pi I$, which is proportional to the intensity of magnetization, I. That is;

$$B = H + 4\pi I$$

where B is the magnetic field within the substance and H is the applied magnetic field and I is the intensity of magnetization

Lenz's Law (1834)

Lenz's Law can also be written as

$$\frac{B}{H} = 1 + \frac{4\pi I}{H}$$

or

$$\frac{B}{H} = 1 + 4\pi\kappa$$

where

- B/H is called the magnetic permeability of the material and
- κ is the magnetic susceptibility per unit volume, (I/H)

By definition, κ in a vacuum is zero, so under those conditions the equation would reduce to $B = H$. It is usually more convenient to measure mass than volume and the mass susceptibility, χ_g, is related to the volume susceptibility, κ, through the density.

$$\chi_g = \frac{\kappa}{\rho}$$

where ρ is the density.

Finally to get our measured quantity on a basis that can be related to atomic properties, we convert to molar susceptibility

$$\chi_m = \chi_g \times RMM$$

Since this value includes the underlying diamagnetism of paired electrons, it is necessary to correct for the diamagnetic portion of χ_m to get a corrected paramagnetic susceptibility.

$$\chi'_m = \chi_m + \chi_{dia}$$

Examples of these corrections are tabulated below.

Table 9.7.1: Table of Diamagnetic Corrections (Pascal's constants, 10^{-6} c.g.s. units)

Ion	DC	Ion	DC
Na^+	6.8	Co^{2+}	12.8
K^+	14.9	Co^{3+}	12.8
NH_4^+	13.3	Ni^{2+}	12.8
Hg^{2+}	40	VO^{2+}	12.5
Fe^{2+}	12.8	Mn^{3+}	12.5
Fe^{3+}	12.8	Cr^{3+}	12.5
Cu^{2+}	12.8	Cl^-	23.4
Br^-	34.6	SO_4^{2-}	40.1
I^-	50.6	OH^-	12
NO_3^-	18.9	$C_2O_4^{2-}$	34
ClO_4^-	32	OAc^-	31.5
IO_4^-	51.9	pyr	49.2
CN^-	13	Me-pyr	60
NCS^-	26.2	$Acac^-$	62.5
H_2O	13	en	46.3
$EDTA^{4-}$	~150	urea	33.4

these can be converted to S.I units of $m^3\ mol^{-1}$ by multiplying by $4\ \pi \times 10^{-7}$

There are numerous methods for measuring magnetic susceptibilities, including, the **Gouy, Evans and Faraday methods**. These all depend on measuring the force exerted upon a sample when it is placed in a magnetic field. The more paramagnetic the sample, the more strongly it will be drawn toward the more intense part of the field.

Determination of Magnetic Susceptibility

- **The Gouy Method:** The underlying theory of the Gouy method is described here and a form for calculating the magnetic moment from the collected data is available as well.
- **The Evans method:** The Evans balance measures the change in current required to keep a pair of suspended magnets in place or balanced after the interaction of the magnetic field with the sample. The Evans balance differs from that of the Gouy in that, in the former the permanent magnets are suspended and the position of the sample is kept constant while in the latter the position of the magnet is constant and the sample is suspended between the magnets.

Orbital contribution to magnetic moments

From a quantum mechanics viewpoint, the magnetic moment is dependent on both spin and orbital angular momentum contributions. The spin-only formula used last year was given as:

$$\mu_{s.o.} = \sqrt{4S(S+1)}$$

and this can be modified to include the orbital angular momentum

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$$

An orbital angular momentum contribution is expected when the ground term is triply degenerate (i.e. a triplet state). These show temperature dependence as well.

In order for an electron to contribute to the orbital angular momentum the orbital in which it resides must be able to transform into an exactly identical and degenerate orbital by a simple rotation (it is the rotation of the electrons that induces the orbital contribution). For example, in an octahedral complex the degenerate t_{2g} set of orbitals (d_{xz},d_{yx},d_{yz}) can be interconverted by a 90° rotation. However the orbitals in the e_g subset (d_{z2},d_{x2-y2}) cannot be interconverted by rotation about any axis as the orbital shapes are different; therefore an electron in the e_g set does not contribute to the orbital angular momentum and is said to be quenched. In the free ion case the electrons can be transformed between any of the orbitals as they are all degenerate, but there will still be partial orbital quenching as the orbitals are not identical.

Electrons in the t_{2g} set do not always contribute to the orbital angular moment. For example in the d^3, t_{2g}^3 case, an electron in the d_{xz} orbital cannot by rotation be placed in the d_{yz} orbital as the orbital already has an electron of the same spin. This process is also called quenching.

Tetrahedral complexes can be treated in a similar way with the exception that we fill the e orbitals first, and the electrons in these do not contribute to the orbital angular momentum. The tables in the links below give a list of all d^1 to d^9 configurations including high and low spin complexes and a statement of whether or not a direct orbital contribution is expected.

- Octahedral complexes
- Tetrahedral complexes

A and E ground terms

The configurations corresponding to the A_1 (free ion S term), E (free ion D term), or A_2 (from F term) do not have a direct contribute to the orbital angular momentum. For the A_2 and E terms there is always a higher T term of the same multiplicity as the ground term which can affect the magnetic moment (usually by a only small amount).

$$\mu_{eff} = \mu_{s.o.}(1 - \alpha\lambda/\Delta) \tag{9.7.1}$$

where α is a constant (2 for an E term, 4 for an A_2 term) and λ is the spin-orbit coupling constant which is generally only available for the free ion but this does give important information since the sign of the value varies depending on the orbital occupancy.

Table 9.7.1: Some spin-orbit coupling constants for 1st row TM ions

metal ion	Ti(III)	V(III)	Cr(III)	Mn(III)	Fe(II)	Co(II)	Ni(II)	Cu(II)
d configuration	1	2	3	4	6	7	8	9
λ / cm^{-1}	155	105	90	88	-102	-172	-315	-830

For d^1 to d^4 the value is positive hence μ_{eff} is less than μ_{so} and for d^6 to d^9 the value is negative hence μ_{eff} is greater than μ_{so}. Δ is the crystal field splitting factor which again is often not available for complexes.

For the tetrahedral Co(II) ion, $CoCl_4^{2-}$, the observed experimental magnetic moment, μ_{obs} = 4.59 Bohr Magneton (B.M.) The spin-only magnetic moment, $\mu_{s.o.}$ = 3.88 B.M. which is not in good agreement. How can we improve the analysis?

Since the ground term in the tetrahedral field is split from a ^4F to a $^4A_2$ term then we can apply the Equation 9.7.1. For an A term

the constant α = 4. The spin-orbit coupling constant, λ for the free ion is -172 cm^{-1} which we can use as an approximation and Δ= 3100 cm^{-1}. Hence

$$\mu_{eff} = 3.88 \times (1 - (4 * -172)/3100)$$

which comes out at μ_{eff} = 4.73 B.M.

This gives a much better fit than the spin-only formula. In the case of the series;

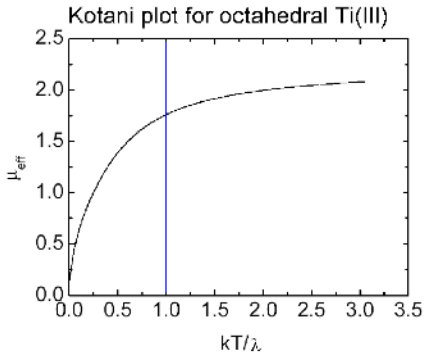
$$CoI_4^{2-}, CoBr_4^{2-}, CoCl_4^{2-}, Co(NCS)_4^{2-}$$

the magnetic moments have been recorded as 4.77, 4.65, 4.59, 4.40 BM assuming that λ is roughly a constant, then this variation shows the inverse effect of the spectrochemical series on the magnetic moment, since Δ is expected to increase from I- to NCS-.

T ground terms

The configurations corresponding to the T_2 term (from D) or a T_1 term (from an F term) are those where there is a direct contribution to orbital angular momentum expected. The magnetic moments of complexes with T terms are often found to show considerable temperature dependence. This is as a result of spin-orbit coupling that produces levels whose energy differences are frequently of the order *k*T, so as a result, temperature will have a direct effect on the population of the levels arising in the magnetic field.

In a Kotani plot μ_{eff} is plotted against kT/λ and when this corresponds to a value of 1 then μ equals the "spin-only" value. If this is extrapolated to infinity then the value corresponds to μ_{S+L}.



Measuring the magnetic moment at 80 K and 300 K often shows up this variation with temperature.

Example 9.7.1:

Account for the magnetic moments of the complex, $(Et_4N)_2[NiCl_4]$ recorded at 80, 99 and 300 K.

80 K	99 K	300 K
3.25 B.M.	3.43 B.M.	3.89 B.M.

Ni^{2+} is a d^8 metal ion.

The formula suggests a 4 coordinate complex and we can assume that the complex is tetrahedral with a d electron configuration of e^4 t_2^4 therefore the spin-only magnetic moment can be calculated as 2.83 BM.

Why did we ignore the possibility of it being square-planar?

The free ion Russell-Saunders ground term is ^3F (L=3 and S=1) which will give rise to a lowest energy T term in a tetrahedral field and hence the resultant magnetic moment is expected to be temperature dependent and have a direct orbital contribution. The observed values may be quite different then to the calculated spin only magnetic moment. The value of μ_{S+L} can be calculated as:

$$mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$$

or

$$\mu_{S+L} = \sqrt{8+12}$$

or

$$\mu_{S+L} = \sqrt{20} = 4.472\ B.M.$$

From the observed values it can be seen that the magnetic moment of the d^8 Ni^{2+} complex is intermediate between the μ_{so} and μ_{S+L} values (probably due to partial quenching of the orbital angular momentum contribution) and is dependent on temperature. Further worked examples and some selected magnetic data are available.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

9.7: Magnetism is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Magnetism** is licensed CC BY-NC-SA 4.0.

9.8: Metals, Tetrahedral and Octahedral

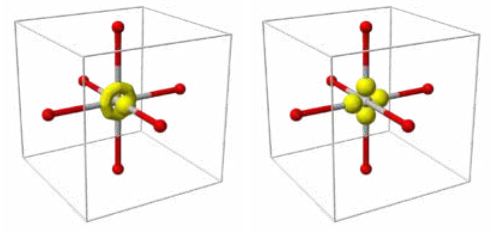
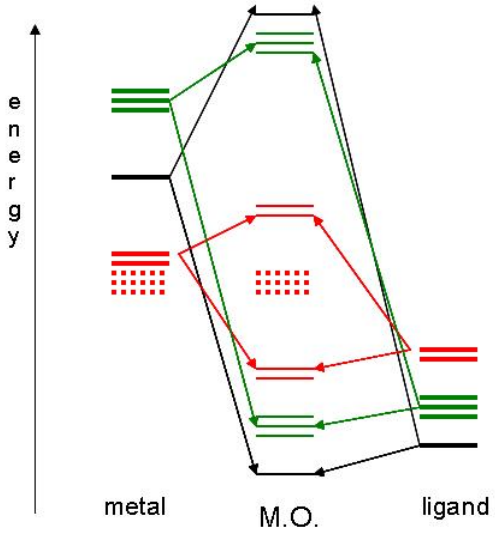


Figure 1: The d_{z^2} (left) and $d_{x^2-y^2}$ (right) orbitals. Images used with permission from Wikipedia.

Let us continue to consider an octahedral complex. The remaining d orbitals, d_{xy}, d_{xz} and d_{yz} see their energy increase to a lesser extent. We refer to the d_{xy}, d_{xz} and d_{yz} orbitals collectively as the t_{2g} d orbitals.

Hybrid orbital theory can be used to describe how metals bond to ligands. When metals bond to ligands, magnetic data shows that some electrons are paired when there is no obvious reason for them to be paired. Molecular orbitals begin to account for this phenomenon by allowing wave functions to interfere in a constructive, low energy (bonding) or destructive, or high energy (antibonding) manner. Thus, the electrons can fill the lowest energy molecular orbitals available to them. However, the electron pairing may be different if the electrons were allowed to fill the lowest energy atomic orbitals available to them.



This diagram shows the field splitting of a metal with ligands in an octahedral configuration. The thick horizontal lines represent atomic orbitals of the metal (left) and ligands (right). The colors correspond to s (black), p (green) and d (red) orbitals. The middle column of horizontal lines represents molecular orbitals made of bonding (lower energy) and antibonding (higher energy) components.

If the ligands are oriented on the cartesian coordinate axes, the metal will still own 3 d orbitals, xy, xz, and xz, which do not intersect (and therefore do not interact) with the ligands. These are considered "nonbonding" orbitals, and are represented by dotted lines in the diagram.

References

1. Jean, Yves; "molecular orbitals of transition metal complexes"; Oxford University Press, 2005

9.8: Metals, Tetrahedral and Octahedral is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Metals, Tetrahedral and Octahedral** is licensed CC BY-NC-SA 4.0.

9.9: Non-octahedral Complexes

Learning Objectives

- Understand the d-orbital degeneracies of square planar and tetrahedral metal complexes.

Tetragonal and Square Planar Complexes

If two *trans*- ligands in an octahedral complex are either chemically different from the other four (as in *trans*-$[Co(NH_3)_4Cl_2]^+$), or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as $[Co(NH_3)_6]^{3+}$: two *trans*- NH_3 molecules are slowly removed from the metal along the ±z axes, as shown in the top half of Figure 9.9.1. As the two axial Co–N distances increase simultaneously, the d-orbitals that interact most strongly with the two axial ligands decrease in energy due to a decrease in electrostatic repulsions between the electrons in these orbitals and the negative ends of the ligand dipoles. The affected d orbitals are those with a component along the ±z axes—d_{z^2}, d_{xz}, and d_{yz}. These orbitals are not affected equally, however: because the d_{z^2} orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the degenerate energies of the d_{xz} and d_{yz}, as shown in the bottom half of Figure 9.9.1. In addition, the effective positive charge on the metal increases somewhat as the axial ligands are removed, increasing the attraction between the four remaining ligands and the metal. This increases the extent of their interactions with the other two d orbitals and increases their energies. Again, the two d orbitals are not affected equally: because the $d_{x^2-y^2}$ orbital points directly at the four in-plane ligands, its energy increases to a greater extent than the energy of the d_{xy} orbital, which points between the in-plane ligands. If the two axial ligands are moved infinitely far away from the metal, a square planar complex is formed. The energy of the d_{xy} orbital actually surpasses that of the d_{z^2} orbital in the process. The largest orbital splitting in a square planar complex, between the $d_{x^2-y^2}$ and d_{xy} energy levels, is identical in magnitude to Δ_o.

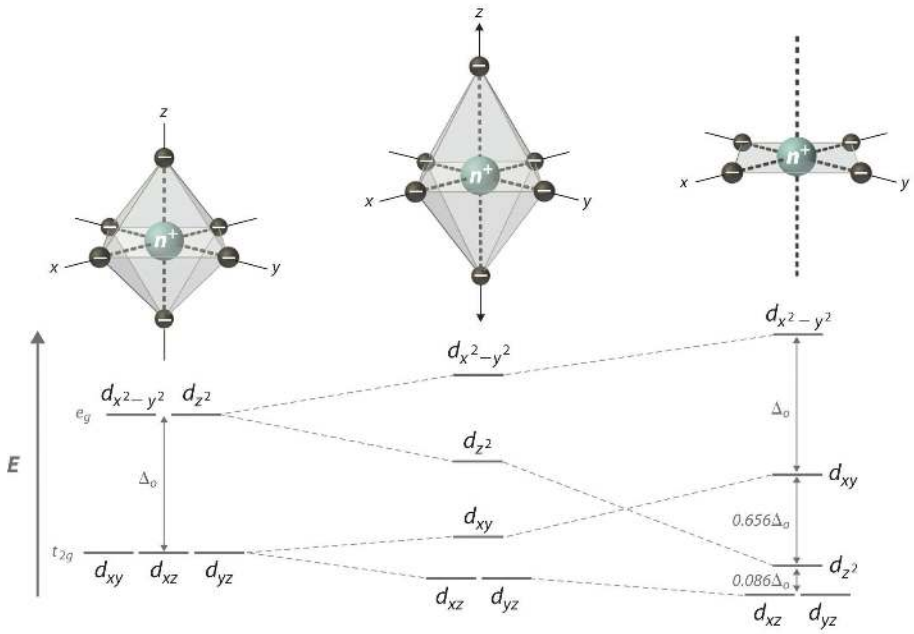


Figure 9.9.1 d-Orbital Splittings for Tetragonal and Square Planar Complexes. (CC BY-SA-NC; anonymous by request)

Moving the two axial ligands away from the metal ion along the z axis initially generates an elongated octahedral complex (the center compound of Figure 9.9.1) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes the d_{z^2} d_{xz} and d_{yz} orbitals to decrease in energy and the $d_{x^2-y^2}$ and d_{xy} orbitals to increase in energy. The change in energy is not the same for all five d orbitals. The d_{z^2} orbital has a smaller xy component than does the d_{xy} orbital, so it reaches a lower energy level; thus, the order of these orbitals is reversed.

Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (illustrated in part (a) in Figure 9.9.2); consequently, none of the five d orbitals points directly at the ligands. Nonetheless, the d_{xy}, d_{xz}, and d_{yz} orbitals interact more strongly with the ligands than do $d_{x^2-y^2}$ and d_{z^2}; this again results in a splitting of the five d orbitals into two groups. The splitting of the energies of the orbitals in a tetrahedral complex (Δ_t) is much smaller than that for an octahedral complex (Δ_o), however, for two reasons: first, the d orbitals interact less strongly with the ligands in a tetrahedral arrangement; second, there are only four negatively-charged regions rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that for complexes of the same metal ion with the same charge, the same ligands, and the same M–L distance, $\Delta_t = \frac{4}{9}\Delta_o$. The relationship between the splitting of the five d orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure 9.9.2.

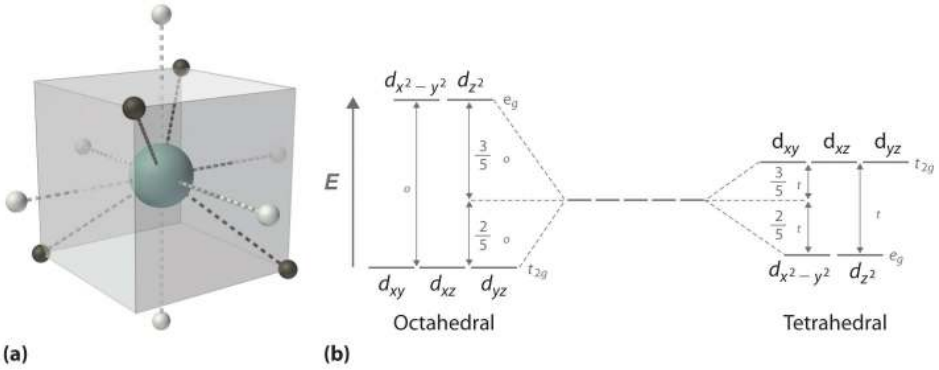


Figure 9.9.2: d-Orbital Splittings for a Tetrahedral Complex. (a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the d_{xy}, d_{xz}, and d_{yz}orbitals (the t_{2g} orbitals) interact more strongly with the ligands than do the $d_{x^2-y^2}$ and d_{z^2} orbitals (the e_g orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex. (CC BY-SA-NC; anonymous by request)

> *Δ_t < Δ_o because of weaker d-orbital–ligand interactions and decreased electrostatic interactions.*

Example 9.9.1: Predicting Structure

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

1. $[Cu(NH_3)_4]^{2+}$
2. $[Ni(CN)_4]^{2-}$

Solution

Because Δ_o is so large for the second- and third-row transition metals, all four-coordinate complexes of these metals are square planar due to the much higher crystal field stabilization energy (CFSE) for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+}, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral; the former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

1.

The copper in this complex is a d^9 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 9 electrons and ask which has a lower energy. Comparing the square planer (Figure 9.9.1) splitting diagram with tetrahedral (Figure 9.9.2), suggests that 9 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, neither high nor low spin states are possible (only one state) with a single unpaired electron.

2.

The nickle in this complex is a d^8 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 8 electrons and ask which has a

lower energy. Comparing the square planer (Figure 9.9.1) splitting diagram with tetrahedral (Figure 9.9.2), suggests that 8 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, it is a low spin complex since a high spin requires a lot of energy to promote to the $d_{x^2-y^2}$ orbital. Hence, there are no unpaired electrons

? Exercise 9.9.1

What are the geometries of the following two complexes?

1. $[AlCl_4]^-$
2. $[Ag(NH_3)_2]^+$

Answer 1

tetrahedral

Answer 2

linear

Summary

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. In tetrahedral molecular geometry, a central atom is located at the center of four substituents, which form the corners of a tetrahedron. Tetrahedral geometry is common for complexes where the metal has d^0 or d^{10} electron configuration. The CFT diagram for tetrahedral complexes has $d_{x^2-y^2}$ and d_{z^2} orbitals equally low in energy because they are between the ligand axis and experience little repulsion. In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The square planar geometry is prevalent for transition metal complexes with d^8 configuration. The CFT diagram for square planar complexes can be derived from octahedral complexes yet the $d_{x^2-y^2}$ level is the most destabilized and is left unfilled.

9.9: Non-octahedral Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Non-octahedral Complexes** by Anonymous is licensed CC BY-NC-SA 4.0.

9.10: Octahedral vs. Tetrahedral Geometries

How do we tell whether a particular complex is octahedral, tetrahedral, or square planar? Obviously if we know the formula, we can make an educated guess: something of the type ML_6 will almost always be octahedral (there is an alternative geometry for 6-coordinate complexes, called trigonal prismatic, but it's pretty rare), whereas something of formula ML_4 will usually be *tetrahedral* unless the metal atom has the d^8 electron configuration, in which case it will probably be *square planar*. But what if we take a particular metal ion and a particular ligand? Can we predict whether it will form an octahedral or a tetrahedral complex, for example? To an extent, the answer is yes... we can certainly say what factors will encourage the formation of tetrahedral complexes instead of the more usual octahedral.

The Crystal Field Stabilization Energy (CFSE) is the additional stabilization gained by the splitting of the orbitals according to the crystal field theory, against the energy of the original five degenerate d orbitals. So, for example, in a d^1situation such as $[Ti(OH_2)_6]^{3+}$, putting the electron into one of the orbitals of the t_{2g} level gains -0.4 Δ_o of CFSE. Generally speaking, octahedral complexes will be favored over tetrahedral ones because:

- It is more (energetically) favorable to form six bonds rather than four
- The CFSE is usually greater for octahedral than tetrahedral complexes. Remember that Δ_o is bigger than Δ_{tet} (in fact, Δ_{tet} is approximately 4/9 Δ_o).

If we make the assumption that Δ_{tet} = 4/9 Δ_o, we can calculate the difference in stabilization energy between octahedral and tetrahedral geometries by referencing everything in terms of Δ_o.

Example 9.10.1: d^3 Stabilized Structures

Which is the preferred configuration for a d^3 metal: tetrahedral or octahedral?

Solution

To answer this, the *Crystal Field Stabilization Energy* has to be calculated for a $(d^3$ metal in both configurations. The geometry with the greater stabilization will be the preferred geometry.

- For a d^3 *octahedral* configuration, the *Crystal Field Stabilization Energy* is

$$3 \times -0.4\Delta_o = -1.2\Delta_o$$

- For a d^3 *tetrahedral* configuration (assuming high spin), the *Crystal Field Stabilization Energy* is

$$-0.8\Delta_{tet}$$

Remember that because Δ_{tet} is less than half the size of Δ_o, tetrahedral complexes are often high spin. We can now put this in terms of Δ_o (we can make this comparison because we're considering the same metal ion and the same ligand: all that's changing is the geometry)

So for tetrahedral d^3, the Crystal Field Stabilization Energy is:

$$\text{CFSE} = -0.8 \text{ x } 4/9\ \Delta_o = -0.355\ \Delta_o.$$

And the difference in Crystal Field Stabilization Energy between the two geometries will be:

$$1.2 - 0.355 = 0.845\ \Delta_o.$$

If we do a similar calculation for the other configurations, we can construct a Table of Δ_o, Δ_{tet} and the difference between them (we'll ignore their signs since we're looking for the difference between them).

Table 9.10.1: Crystal Field Stabilization Energies (not splitting parameters). This table compares the values of the CFSE for octahedral and tetrahedral geometries, assuming high spin configurations. The units are Δ_o, and we're assuming that Δ_{tet} = 4/9 Δo.

	Octahedral	Tetrahedral	Difference
d^0, d^5, d^{10}	0	0	0
d^1, d^6	0.4	0.27	0.13
d^2, d^7	0.8	0.53	0.27

	Octahedral	Tetrahedral	Difference
d^3, d^8	1.2	0.36	0.84
d^4, d^9	0.6	0.18	0.42

These values can be plotted:.

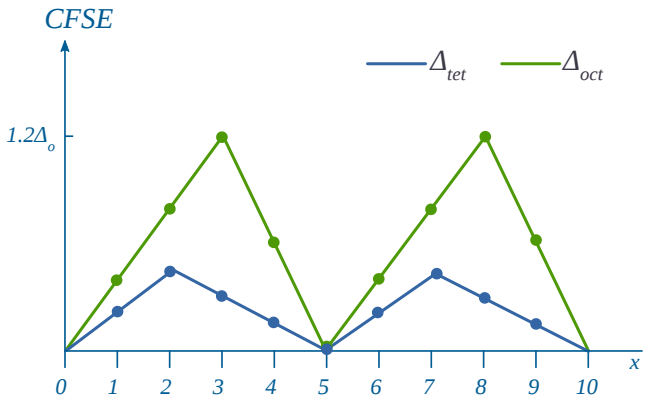


Figure 9.10.1: Crystal Field Stabilization Energy as a function of d-electrons for a hypothetical molecule in the octahedral (green curve) and tetrahedral (blue curve) geometries. (CC BY-NC; Ümit Kaya)

Notice that the Crystal Field Stabilization Energy almost always favors octahedral over tetrahedral in most cases, but the degree of favorability varies with the *electronic configuration*. In other words, for d^1 there's only a small gap between the oct and tet lines, whereas at d^3 and d^8 there's a big gap. However, for d^0, d^5 high spin and d^{10}, there is **no** CFSE difference between octahedral and tetrahedral. The ordering of favorability of octahedral over tetrahedral is:

$$d^3, d^8 > d^4, d^9 > d^2, d^7 > d^1, d^6 > d^0, d^5, d^{10}$$

The units of the graph are Δ_o. So if we have strong field ligands present, Δ_o will be bigger anyway (according to the spectrochemical series), and any energy difference between the oct and tet lines will be all the greater for it. A bigger Δ_o might also push the complexes over to low spin. Similarly, as we saw previously, high oxidation states and metals from the 2nd and 3rd rows of the transition series will also push up Δ_o.

On the other hand, if large or highly charged ligands are present, they may suffer large interligand repulsions and thus prefer a lower coordination number (4 instead of 6). Consequently if you set out to make something that would have a tetrahedral geometry, you would use large, negatively charged, weak field ligands, and use a metal atom with a d^0, d^5 or d^{10} configuration from the first row of the transition series (though of course having weak field ligands doesn't matter in these three configurations because the difference between oct and tet is 0 Δ_o). As Table 2 shows, you can find tetrahedral complexes for most configurations, but there are very few for d^3 and d^8.

Table 9.10.2: Tetrahedral complexes of different d electron counts

d^0	MnO_4^-	d^5	$MnCl_4^{2-}$
d^1	$TiCl_4^-$	d^6	$FeCl_4^{2-}$
d^2	$Cr(OR)_4$	d^7	$CoCl_4^{2-}$

Contributors and Attributions

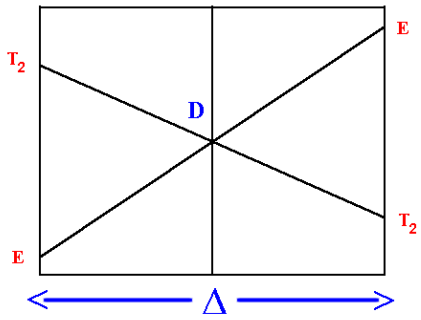
- Dr Mike Morris, March 2001

9.10: Octahedral vs. Tetrahedral Geometries is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Octahedral vs. Tetrahedral Geometries** is licensed CC BY-NC-SA 4.0.

9.11: Orgel Diagrams

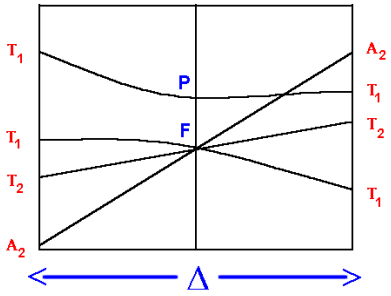
Orgel diagrams are useful for showing the energy levels of both high spin octahedral and tetrahedral transition metal ions. They **ONLY** show the spin-allowed transitions. For complexes with D ground terms only one electronic transition is expected and the transition energy corresponds directly to D. Hence, the following high spin configurations are dealt with: d^1, d^4, d^6 and d^9.



D Orgel diagram

On the left hand side d^1, d^6 tetrahedral and d^4, d^9 octahedral complexes are covered and on the right hand side d^4, d^9 tetrahedral and d^1, d^6 octahedral. For simplicity, the g subscripts required for the octahedral complexes are not shown.

For complexes with F ground terms, three electronic transitions are expected and D may not correspond directly to a transition energy. The following configurations are dealt with: d^2, d^3, high spin d^7 and d^8.



F Orgel diagram

On the left hand side, d^2, d^7 tetrahedral and d^3, d^8 octahedral complexes are covered and on the right hand side d^3, d^8 tetrahedral and d^2 and high spin d^7 octahedral. Again for simplicity, the g subscripts required for the octahedral complexes are not shown.

On the left hand side, the first transition corresponds to D, the equation to calculate the second contains expressions with both D and C.I. (the configuration interaction from repulsion of like terms) and the third has expressions which contain D, C.I. and the Racah parameter B.

- $^4T_{2g}$ <--- $^4A_{2g}$ transition energy = D
- $^4T_{1g}(F)$ <--- $^4A_{2g}$ transition energy = 9/5 *D - C.I.
- $^4T_{1g}(P)$ <--- $^4A_{2g}$ transition energy = 6/5 *D + 15B' + C.I.

On the right hand side, the first transition can be unambiguously assigned as:

$$^3T_{2g} \text{ <--- } ^3T_{1g} \text{ transition energy} = 4/5 \text{ *D} + \text{C.I.}$$

But, depending on the size of the ligand field (D) the second transition may be due to:

$$^3A_{2g} \text{ <--- } ^3T_{1g} \text{ transition energy} = 9/5 \text{ *D} + \text{C.I.}$$

for a weak field or

$$^3T_{1g}(P) \text{ <--- } ^3T_{1g} \text{ transition energy} = 3/5 \text{ *D} + 15B' + 2 * \text{C.I.}$$

for a strong field.

Tanabe-Sugano Diagrams

An alternative method is to use Tanabe Sugano diagrams, which are able to predict the transition energies for both spin-allowed and spin-forbidden transitions, as well as for both strong field (low spin), and weak field (high spin) complexes. In this method the energy of the electronic states are given on the vertical axis and the ligand field strength increases on the horizontal axis from left to right. Linear lines are found when there are no other terms of the same type and curved lines are found when 2 or more terms are repeated. This is as a result of the "non-crossing rule". The baseline in the Tanabe-Sugano diagram represents the lowest energy or ground term state.

✔ case (not many examples documented)

The electronic spectrum of the V^{3+} ion, where V(III) is doped into alumina (Al_2O_3), shows three major peaks with frequencies of: ν_1=17400 cm^{-1}, ν_2=25400 cm^{-1} and ν_3=34500 cm^{-1}.

These have been assigned to the following *spin-allowed* transitions.

- $^3T_{2g}$<---$^3T_{1g}$
- $^3T_{1g}(P)$<---$^3T_{1g}$
- $^3A_{2g}$<---$^3T_{1g}$

The ratio between the first two transitions is calculated as $\frac{\nu_1}{\nu_2}$ which is equal to 25400 / 17400 = 1.448.

To calculate the Racah parameter, **B**, the position on the horizontal axis where the ratio between the lines representing ν_2 and ν_1 is equal to 1.448, has to be determined. On the diagram below, this occurs at D/B=30.9. Having found this value, a vertical line is drawn at this position.

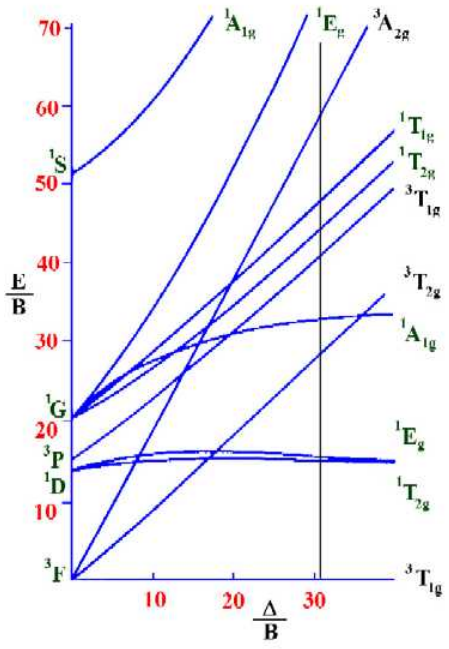


***Figure* 9.11.1:** *Tanabe-Sugano diagram for d^2 octahedral complexes*

On moving up the line from the ground term to where lines from the other terms cross it, we are able to identify both the spin-forbidden and spin-allowed transition and hence the total number of transitions that are possible in the electronic spectrum.

Next, find the values on the vertical axis that correspond to the spin-allowed transitions so as to determine the values of n1/B, n2/B and n3/B. From the diagram above these are 28.78, 41.67 and 59.68 respectively.

Knowing the values of n1, n2 and n3, we can now calculate the value of B. Since n1/B=28.78 and n1 is equal to 17,400 cm^{-1}, then

$$B = \frac{n_1}{28.78} = \frac{17400}{28.78}$$

or

$$B = 604.5\ cm^{-1}$$

Then it is possible to calculate the value of D. Since D/B=30.9, then: D=B*30.9 and hence: D = 604.5 * 30.9 = 18680 cm^{-1}

case

Calculate the value of B and D for the Cr^{3+} ion in $[Cr(H_2O)_6]^{3+}$ if n1=17000 cm^{-1}, n2=24000 cm^{-1} and n3=37000 cm^{-1}.

Solution

These values have been assigned to the following spin-allowed transitions.

$$^4T_{2g} \leftarrow ^4A_{2g}$$

$$^4T_{1g} \leftarrow ^4A_{2g}$$

$$^4T_{1g}(P) \leftarrow ^4A_{2g}$$

From the information given, the ratio \(n_2 / n_1 = 24000 / 17000 = 1.412\). Using a Tanabe-Sugano diagram for a d^3 system this ratio is found at D/B=24.00

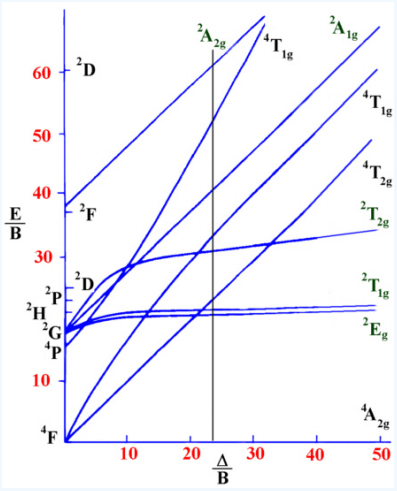


***Figure* 9.11.2:** *Tanabe-Sugano diagram for d^3 octahedral complexes*

Interpolation of the graph to find the Y-axis values for the spin-allowed transitions gives:

- \(\dfrac{n_1}{B}=24.00\)
- \(\dfrac{n_2}{B}=33.90\)
- \(\dfrac{n_3}{B}=53.11\)

Recall that $n_1 = 17000\ cm^{-1}$. Therefore for the first spin-allowed transition,

17000 /B =24.00 from which B can be obtained, B=17000 / 24.00 or B=708.3 cm^{-1}.

This information is then used to calculate D.

Since D / B=24.00 then D = B*24.00 = 708.3 * 24.00 = 17000 cm^{-1}.

It is observed that the value of **Racah parameter** B in the complex is 708.3 cm^{-1}, while the value of B in the free Cr^{3+} ion is 1030 cm^{-1}. This shows a 31% reduction in the Racah parameter indicating a strong Nephelauxetic effect.

The Nephelauxetic Series is as follows:

F^->H_2O>urea>NH_3 >en~$C_2O_4^{2-}$ >NCS^- >Cl^-~CN^->Br^- >S^{2-} ~I^-.

Ionic ligands such as F^-give small reduction in B, while covalently bonded ligands such as I^- give a large reduction in B.

The original paper by Tanabe and Sugano[10] had the d^5 and d^6 diagrams each missing a T term from excited I states. These diagrams were reproduced in the often quoted text by Figgis[12(a)] and so the errors have been perpetuated. An exception is the text by Purcell and Kotz[15] where the missing T terms have been included, however in their case they have ignored lower lying terms from excited D, F, G and H states which for d^5 are the main transitions seen in the spin forbidden spectra of Mn(II) complexes.

A set of qualitative diagrams have been drawn for each configuration (which include the missing T terms) and along with the newest release of "Ligand Field Theory and its applications" by Figgis and Hitchman [12(b)] represent the only examples of Tanabe-Sugano diagrams that provide a comprehensive set of terms for spectral interpretation

References

1. Basic Inorganic Chemistry, F.A.Cotton, G.Wilkinson and P.L.Gaus, 3rd edition, John Wiley and Sons, Inc. New York, 1995.
2. Physical Inorganic Chemistry, S.F.A.Kettle, Oxford University Press, New York, 1998.
3. Complexes and First-Row Transition Elements, D.Nicholls, Macmillan Press Ltd, London 1971.
4. The Chemistry of the Elements, N.N.Greenwood and A.Earnshaw, Pergamon Press, Oxford, 1984.
5. Concepts and Models of Inorganic Chemistry, B.E.Douglas, D.H.McDaniel and J.J.Alexander 2nd edition, John Wiley & Sons, New York, 1983.
6. Inorganic Chemistry, J.A.Huheey, 3rd edition, Harper & Row, New York, 1983.
7. Inorganic Chemistry, G.L.Meissler and D.A.Tarr, 2nd edition, Prentice Hall, New Jersey, 1998.
8. Inorganic Chemistry, D.F.Shriver and P.W.Atkins, 3rd edition, W.H.Freeman, New York, 1999.
9. Basic Principles of Ligand Field Theory, H.L.Schlafer and G.Gliemann, Wiley-Interscience, New York, 1969.
10. Y.Tanabe and S.Sugano, J. Phys. Soc. Japan, 9, 1954, 753 and 766.
11. a). Inorganic Electronic Spectroscopy, A.B.P.Lever, 2nd Edition, Elsevier Publishing Co., Amsterdam, 1984.
12. (b). A.B.P.Lever in Werner Centennial, Adv. in Chem Series, 62, 1967, Chapter 29, 430.
13. (a). Introduction to Ligand Fields, B.N.Figgis, Wiley, New York, 1966.
14. (b). Ligand Field Theory and its applications, B.N. Figgis and M.A. Hitchman, Wiley-VCH, New York, 2000.
15. E.Konig, Structure and Bonding, 9, 1971, 175.
16. Y. Dou, J. Chem. Educ, 67, 1990, 134.
17. Inorganic Chemistry, K.F. Purcell and J.C. Kotz, W.B. Saunders Company, Philadelphia, USA, 1977.

Contributors and Attributions

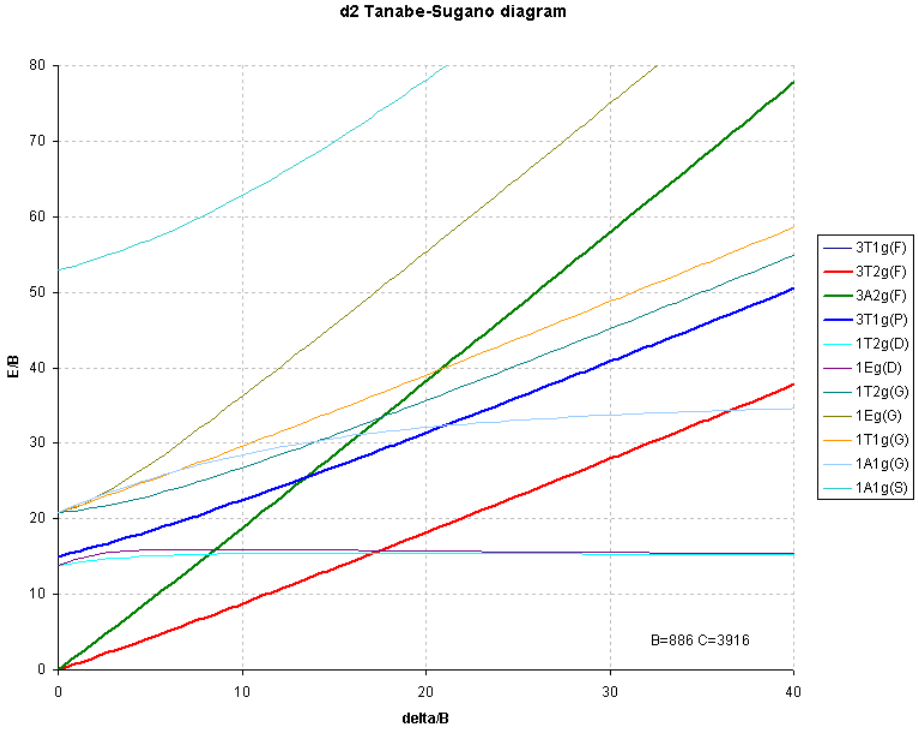
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

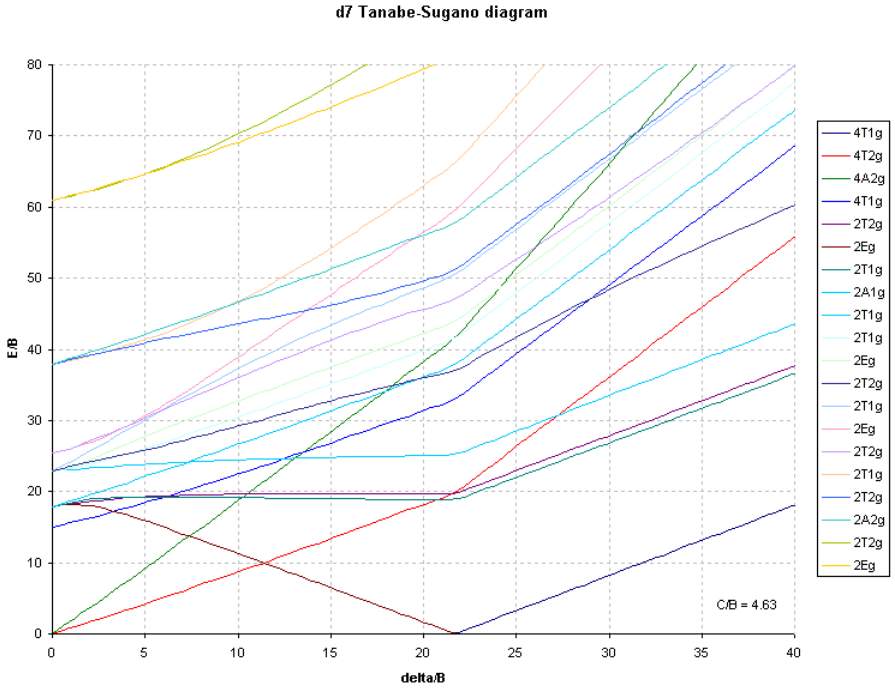
This page titled 9.11: Orgel Diagrams is shared under a not declared license and was authored, remixed, and/or curated by Robert J. Lancashire.

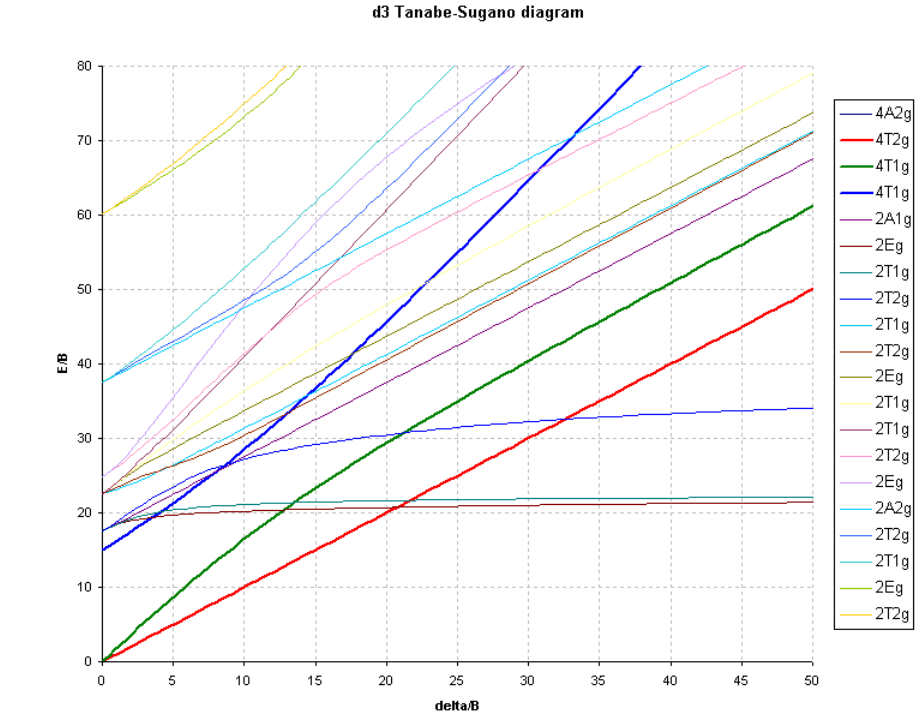
- **Orgel Diagrams** by Robert J. Lancashire is licensed CC BY-NC-SA 4.0.

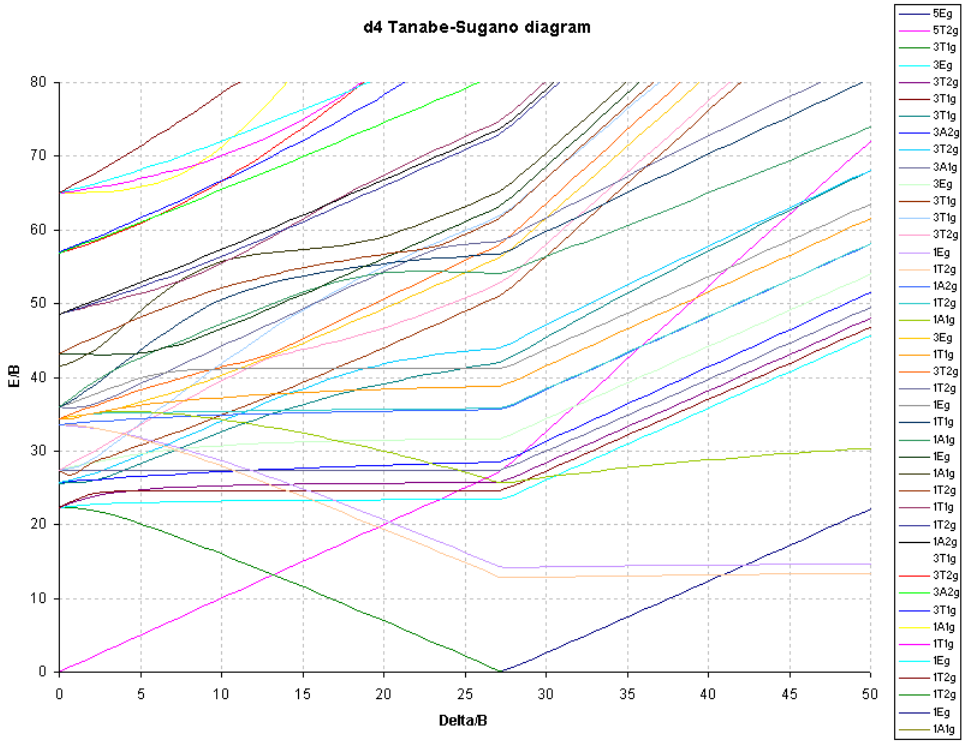
9.11.1: Qualitative Orgel Diagrams

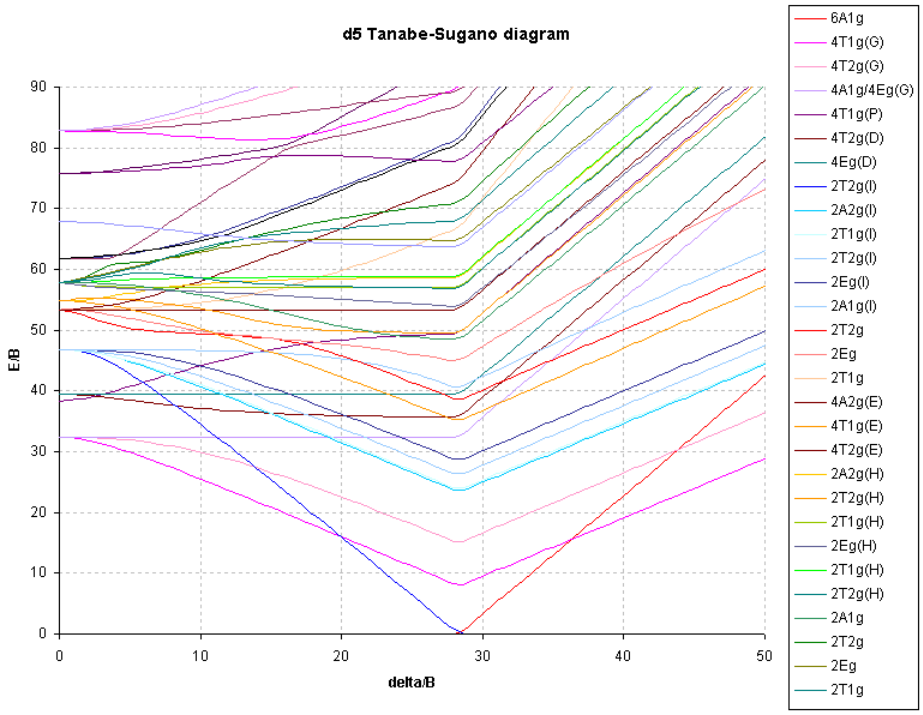
A set of qualitative diagrams have been drawn for each configuration (which include the missing T terms) and along with the newest release of "Ligand Field Theory and its applications" by Figgis and Hitchman [12(b)] represent the only examples of Tanabe-Sugano diagrams that provide a comprehensive set of terms for spectral interpretation.

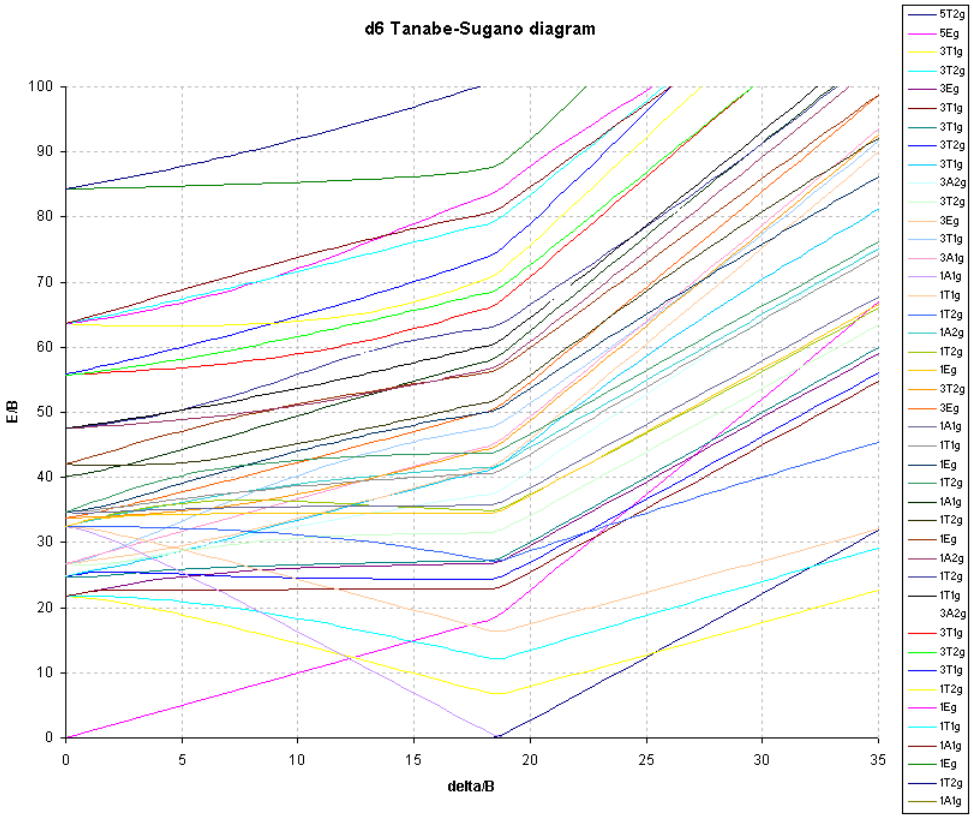


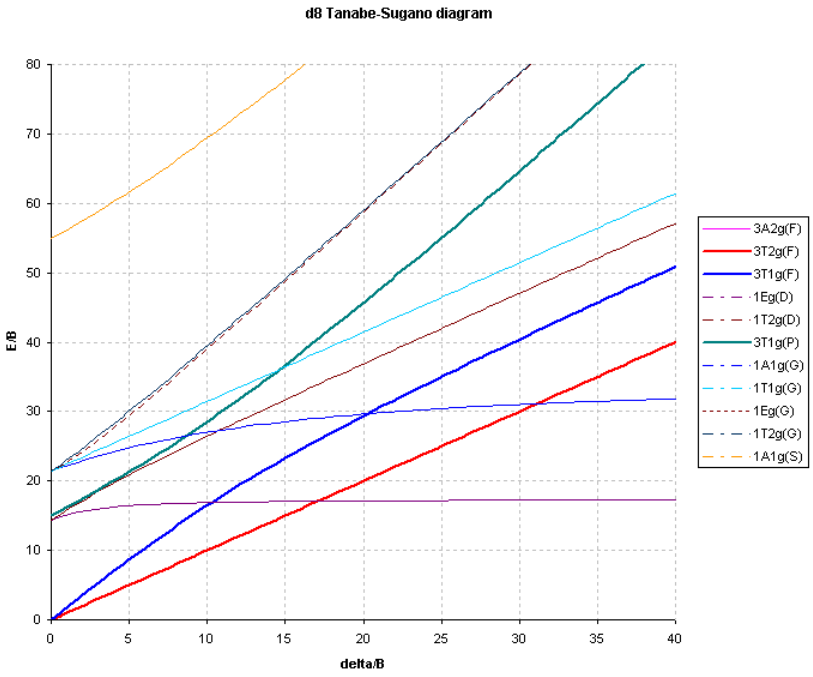



d3 Tanabe-Sugano diagram
E/B
delta/B
0
10
20
30
40
50
60
70
80
0
5
10
15
20
25
30
35
40
45
50
4A2g
4T2g
4T1g
4T1g
2A1g
2Eg
2T1g
2T2g
2T1g
2T2g
2Eg
2T1g
2T1g
2T2g
2Eg
2A2g
2T2g
2T1g
2Eg
2T2g


d4 Tanabe-Sugano diagram
E/B
Delta/B
0
10
20
30
40
50
60
70
80
0
5
10
15
20
25
30
35
40
45
50
5Eg
5T2g
3T1g
3Eg
3T2g
3T1g
3T1g
3A2g
3T2g
3A1g
3Eg
3T1g
3T1g
3T2g
1Eg
1T2g
1A2g
1T2g
1A1g
3Eg
1T1g
3T2g
1T2g
1Eg
1T1g
1A1g
1Eg
1A1g
1T2g
1T1g
1T2g
1A2g
3T1g
3T2g
3A2g
3T1g
1A1g
1T1g
1Eg
1T2g
1T2g
1Eg
1A1g


d5 Tanabe-Sugano diagram
E/B
delta/B
0
10
20
30
40
50
60
70
80
90
6A1g
4T1g(G)
4T2g(G)
4A1g/4Eg(G)
4T1g(P)
4T2g(D)
4Eg(D)
2T2g(I)
2A2g(I)
2T1g(I)
2T2g(I)
2Eg(I)
2A1g(I)
2T2g
2Eg
2T1g
4A2g(E)
4T1g(E)
4T2g(E)
2A2g(H)
2T2g(H)
2T1g(H)
2Eg(H)
2T1g(H)
2T2g(H)
2A1g
2T2g
2Eg
2T1g


d6 Tanabe-Sugano diagram
E/B
delta/B
0
5
10
15
20
25
30
35
40
50
60
70
80
90
100
5T2g
5Eg
3T1g
3T2g
3Eg
3T1g
3T1g
3T2g
3T1g
3A2g
3T2g
3Eg
3T1g
3A1g
1A1g
1T1g
1T2g
1A2g
1T2g
1Eg
3T2g
3Eg
1A1g
1T1g
1Eg
1T2g
1A1g
1T2g
1Eg
1A2g
1T2g
1T1g
3A2g
3T1g
3T2g
3T1g
1T2g
1Eg
1T1g
1A1g
1Eg
1T2g
1A1g



9.11.1: Qualitative Orgel Diagrams is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Qualitative Orgel Diagrams** is licensed CC BY-NC-SA 4.0.

9.12: Tanabe-Sugano Diagrams

Tanabe-Sugano diagrams are used in coordination chemistry to predict electromagnetic absorptions of metal coordination compounds of tetrahedral and octahedral complexes. The analysis derived from the diagrams can also be compared to experimental spectroscopic data. Armed with spectroscopic data, an approximation to the crystal field splitting energy (10Dq), generated by ligands attached to a metal center, can be found.

Crystal Field Splitting Energy

Within Crystal Field Theory, the interaction of the metal and ligand arise from the positive charge of the metal and negative charge on the ligands. The theory is developed by looking at the five degenerate d-orbitals and how the energies are changed on being surrounded by the negative point charges of the ligands. As the ligands are moved closer to the metal the repulsion between the electrons of the metal and ligands break the degeneracy of the d-orbitals. In the case of an octahedral complex 6 ligands surround a metal center with a single pair on each axis. This raises the energies of $d_{x\hat{}2-y\hat{}2}$, $d_{z\hat{}2}$ relative to those of d_{xy} d_{xz} d_{yz}. This energy split is called Δ_{oct}. The tetrahedral energy split is about $4/9\Delta_{oct}$.[1]

Racah Parameters

Racah parameters were generated as a means to describe the effects of electron-electron repulsion within the metal complexes. The Racah parameters are *A*, *B* and *C*. In the case of Tanabe-Sugano diagrams each electron configuration split has an energy that can be related by the *B* value. *A* is ignored because it is roughly the same for any metal center and *C* generally approximated as being 1/4*B*. What *B* represents is an approximation of the bond strength between the ligand and metal.[1] Comparisons between tabulated free ion *B* and *B* of a coordination complex is called the nephelauxetic ratio (the effect of reducing electron-electron repulsion via ligands). This effect is what gives rise to the spectrochemical series of ligands described later.

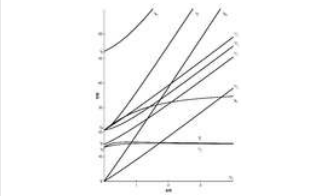
$$\beta = \frac{\beta_{complex}}{\beta_{freeion}} \tag{1}$$

Parameters

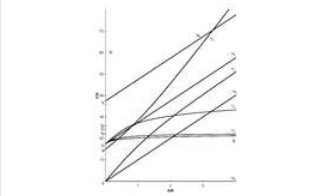
The x-axis in a Tanabe-Sugano diagram is in terms of the crystal field splitting parameter, 10Dq, or Δ_{oct}, scaled by the *B* Racah Parameter. The y-axis is in terms of energy of a electronic transition, E, scaled by *B*. Each line represents the energy of an electronic state while varying the strength of octahedral ligand field. And while only a few electronic states are spin allowed the spin forbidden electron transitions are included since spin forbidden transitions can appear in spectrum. Each term symbol is created from the splitting of term symbols from spherical to octahedral symmetry. With the relative energy ordering of the states are determined via Hund's rules.

Diagrams for d^4, d^5, d^6, and d^7 metal ions have a discontinuity in energies as the ligand field is varied. The discontinuity, shown with the vertical line, represents complexes changing from high-spin to low-spin complexes. At the line, the spin pairing energy is equal to the crystal field splitting energy. To the left of the line metal complexes are high-spin as the spin pairing energy is greater than that of the ligand field splitting. To the right of the line metal complexes are low-spin as the spin pairing energy is less than that of the ligand field splitting energy.

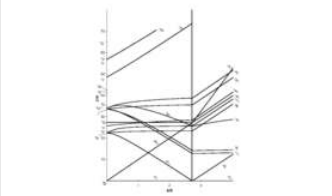
Diagrams



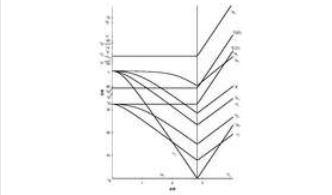
d^2 Tanabe-Sugano diagram



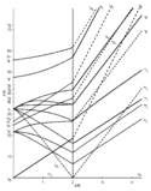
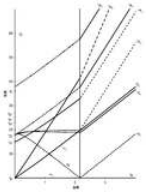
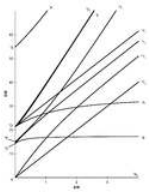
d^3 Tanabe-Sugano diagram



d^4 Tanabe-Sugano diagram



d^5 Tanabe-Sugano diagram

			Note: Each of the images is a thumbnail clicking on one will expand the image.
d^6 Tanabe-Sugano diagram	d^7 Tanabe-Sugano diagram	d^8 Tanabe-Sugano diagram	

How to use the Diagrams

1. Before looking at the diagrams the d-configuration of the metal ion must be determined.
2. Choose the appropriate Tanabe-Sugano diagram matching the d-configuration (http://chemistry.bd.psu.edu/jircitano/TSdiagram.pdf has full page diagrams necessary for measurements).
3. Take a spectrum of the complex and identify λ_{max} for spin-allowed (strong intensity) and spin forbidden (weak intensity) transitions.
4. Convert λ_{max} to wavenumbers and generate energy ratios relative to the lowest allowed transition. (i.e. $E_2/E_1$and E_3/E_1)
5. Using a ruler, slide it across the printed diagram until the E/*B* ratios between lines is equivalent to the ratios found in step 4.
6. Solve for *B* using the E/*B* values (y-axis, step 4) and Δ_{oct}/B (x-axis, step 5) to yield the ligand field splitting energy 10Dq.

Example 9.12.1: Chromium Splitting

A Cr^{3+} metal complex has strong transitions and λ_{max} at

- 431.03 nm,
- 781.25 nm, and
- 1,250 nm.

Determine the Δ_{oct} for this complex.

Solution

1. Cr has 6 electrons. Cr^{3+} has three electrons so its has a d-configuration of d^3
2. Locate the d^3 Tanabe-Sugano diagram
3. Convert to wavenumbers:

$$\frac{10^7 (nm/cm)}{1250\ nm} = 8,000\ cm^{-1}$$

$$\frac{10^7 (nm/cm)}{781.25\ nm} = 13,600\ cm^{-1}$$

$$\frac{10^7 (nm/cm)}{431.03\ nm} = 23,200\ cm^{-1}$$

4. Allowed transitions are $^4T_{1g} \leftarrow {}^4A_{2g}$, $^4T_{1g} \leftarrow {}^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$.

Transition	Energy cm^{-1}	Ratios to lowest
$^4T_{1g} \leftarrow {}^4A_{2g}$	23,200	2.9
$^4T_{1g} \leftarrow {}^4A_{2g}$	13,600	1.7
$^4T_{2g} \leftarrow {}^4A_{2g}$	8,000	1

5. Sliding the ruler perpendicular to the x-axis of the d^3 diagram yields the following values:

Δ_{oct}/B	10	20	30	40
Height E(ν_3)/B	29	45	64	84

Δ_{oct}/B	10	20	30	40
Height E(ν_2)/B	17	30	40	51
Height E(ν_1)/B	10	20	30	40
Ratio E(ν_3)/E(ν_1)	2.9	2.25	2.13	2.1
Ratio E(ν_2)/E(ν_1)	1.7	1.5	1.33	1.275

6. Based on the two tables above it should be assessed that the Δ_{oct}/B value is 10. B is found by finding the dividing E by the height.

Energy cm^{-1}	Height	B
23,200	29	800
13,600	17	800
8,000	10	800

7. Next multiply Δ_{oct}/B by B to yield the Δ_{oct} energy.

$$10 \times 800 = 8000\ cm^{-1} = \Delta_{oct}$$

Each problem is of varying complexity as several steps may be needed to find the correct Δ_{oct}/B values that yield the proper energy ratios.

Nephelauxetic Effect

Imagine you had an abundance of $V(H_2O)_6^{3+}$ (d^2) which has two absorptions. If you had no other available metal centers, but an abundance of ligands, the complex's absorption spectrum (therefore its color) could be changed via application of the spectrochemical series:

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN <$ py (pyridine) $< NH_3 <$ en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- \approx CO$

If you wanted higher energy absorptions (shift toward purple colors) you use ligands to the right of H_2O and if you wanted redder colors attach ligands to the left of H_2O. Here you could measure the nephelauxetic ratio of the ligands to compare how each ligand modifies the B Racah parameter. The series of complexes would also serve as a very good demonstration for a classroom. The reason behind modifying metal ligands has implications for commercial products. Unique colors in ceramics and glass products can be traced back to many metal compounds.

References

1. H.A.O. Hill, P. Day. Physical Methods in Advanced Inorganic Chemistry. John Wiley & Sons, Inc. 1968.
2. Tanabe, Yukito; Sugano, Satoru (1954). "On the absorption spectra of complex ions I". Journal of the Physical Society of Japan 9 (5): 753–766.
3. Tanabe, Yukito; Sugano, Satoru (1954). "On the absorption spectra of complex ions II". Journal of the Physical Society of Japan 9 (5): 766–779
4. Tanabe, Yukito; Sugano, Satoru (1956). "On the absorption spectra of complex ions III". Journal of the Physical Society of Japan 11 (8): 864–877.

Problems

1. For a d^7 metal ion determine the energy ratios for allowed transitions at Δ_{oct}/B of 20.
2. For a d^6metal ion of Δ_{oct}/B = 30 and B=530 cm^{-1} what would the energies of the 5 allowed transitions be? How many are in the UV-Vis range? How many are in the IR range?
3. Write out the allowed transitions for a d^5 metal ion in a E/B> 28 ligand field.

4. A d^4 complex exhibits absorptions at 5500 cm^{-1} (strong) and 31350 cm^{-1} (weak). What are the transitions that are being exhibited in the complex? What is the corresponding Δ_{oct} for the complex?
5. A spectrum of d^7 metal complex seemingly exhibits only two intense transitions. What is the Δ_{oct}/B that this situation occurs? Please use reference to specific transitions and energy splitting.

Answers

1. Δ_{oct}/B of 20 yields E/*B* values of 38, 32, 18. Ratios then are 2.11 and 1.78
2. Δ_{oct}/B = 30 yields E/*B* heights of 27, 40, 57, 65, 85. Energies are then 14310, 21200, 30210, 34450 and 45050 cm^{-1}. All are in the UV-Vis range. *note you need to infer the E/*B* value for the last transition as the diagram does not extend that far up.
3. $^2A_{2g}$<-$^2T_{2g}$, $^2T_{1g}$<-$^2T_{2g}$, ^2E_g<-$^2T_{2g}$, and $^2A_{1g}$<-$^2T_{2g}$.
4. 31,350/5,500 gives a ratio of 5.7/1. The only Δ_{oct}/B value that matches is at 10. *B* value is then 550 cm^{-1}. Δ_{oct}equals 5500 cm^{-1}.
5. Three transitions are generated at low Δ_{oct}/B. However, at about a value of Δ_{oct}/B = 13 the transitions $^4A_{2g}$<-$^4T_{1g}$, and $^4T_{1g}$<-$^4T_{1g}$ have the same energies which results in the appearance of only two absorptions.

Contributors and Attributions

- Evan Sarina, UC Davis

9.12: Tanabe-Sugano Diagrams is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Tanabe-Sugano Diagrams** is licensed CC BY-NC-SA 4.0.

9.13: Thermodynamics and Structural Consequences of d-Orbital Splitting

The energy level splitting of the d-orbitals due to their interaction with the ligands in a complex has important structural and thermodynamic effects on the chemistry of transition-metal complexes. Although these two types of effects are interrelated, they are considered separately here.

Structural Effects

There are two major kinds of structural effects: effects on the ionic radii of metal ions with regular octahedral or tetrahedral geometries, and structural distortions observed for specific electron configurations.

Ionic Radii

Figure 9.13.1 is a plot of the ionic radii of the divalent fourth-period metal ions versus atomic number. The dashed line represents the behavior predicted based on the effects of screening and variation in effective nuclear charge (Z_{eff}), assuming a spherical distribution of the 3d electrons. Because these radii are based on the structures of octahedral complexes and Cr^{2+} and Cu^{2+} do not form truly octahedral complexes, the points for these ions are shown as open circles.

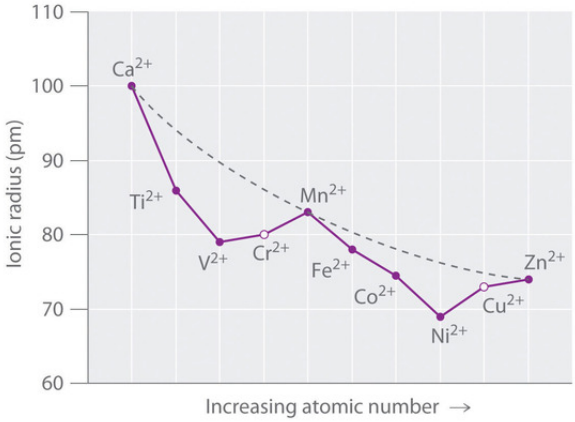


Figure 9.13.1: The Effect of d-Orbital Splittings on the Radii of the Divalent Ions of the Fourth-Period Metals. Only Ca^{2+}(d^0), Mn^{2+} (high-spin d^5), and Zn^{2+} (d^{10}) lie on the smooth dashed curve. All other divalent ions fall below this curve because they have asymmetrical distributions of d electrons. To explain why an asymmetrical distribution of d electrons makes a metal ion smaller than expected, consider the Ti^{2+} ion, which has a d^2 configuration with both electrons in the t_{2g} orbitals. Because the t_{2g} orbitals are directed between the ligands, the two d-electrons are unable to shield the ligands from the nuclear charge. Consequently, the ligands experience a higher effective nuclear charge than predicted, the metal–ligand distance is unusually short, and the ionic radius is smaller than expected. If instead the two electrons were distributed uniformly over all five d orbitals, they would be much more effective at screening the ligands from the nuclear charge, making the metal–ligand distances longer and giving the metal a larger ionic radius.

A similar effect is observed for the V^{2+} ion, which has a d^3 configuration. Because the three electrons in the t_{2g} orbitals provide essentially no shielding of the ligands from the metal, the ligands experience the full increase of +1 in nuclear charge that occurs from Ti^{2+} to V^{2+}. Consequently, the observed ionic radius of the V^{2+} ion is significantly smaller than that of the Ti^{2+} ion.

Skipping the Cr^{2+} ion for the moment, consider the d^5 Mn^{2+} ion. Because the nuclear charge increases by +2 from V^{2+} to Mn^{2+}, Mn^{2+} might be expected to be smaller than V^{2+}. The two electrons added from V^{2+} to Mn^{2+} occupy the e_g orbitals, however, which are oriented directly toward the six ligands. Because these electrons are localized directly between the metal ion and the ligands, they are effective at screening the ligands from the increased nuclear charge. As a result, the ionic radius actually increases significantly from V^{2+} to Mn^{2+}, despite the higher nuclear charge of the latter.

The same effects are observed in the second half of the first-row transition metals. In the Fe^{2+}, Co^{2+}, and Ni^{2+} ions, the extra electrons are added successively to the t_{2g} orbitals, resulting in increasingly poor shielding of the ligands from the nuclei and in abnormally small ionic radii. Skipping over Cu^{2+}, adding the last two electrons causes a significant increase in the ionic radius of Zn^{2+}, despite its greater nuclear charge.

The Jahn–Teller Effect

Because simple octahedral complexes are not observed for the Cr^{2+} and Cu^{2+} ions, only estimated values for their radii are shown in Figure 9.13.1. Since both Cr^{2+} and Cu^{2+} ions have electron configurations with an odd number of electrons in the e_g orbitals.

Because the single electron (in the case of Cr^{2+}) or the third electron (in the case of Cu^{2+}) can occupy either one of two degenerate e_g orbitals, both systems have degenerate ground states. The Jahn–Teller theorem states that such non-linear systems are not stable; they undergo a distortion that makes the complex less symmetrical and splits the degenerate states, which decreases the energy of the system. The distortion and resulting decrease in energy are collectively referred to as the Jahn–Teller effect. Neither the nature of the distortion nor its magnitude is specified, and in fact, they are difficult to predict. In principle, Jahn–Teller distortions are possible for many transition-metal ions; in practice, however, they are observed only for systems with an odd number of electrons in the e_g orbitals, such as the Cr^{2+} and Cu^{2+} ions.

Consider an octahedral Cu^{2+} complex, $[Cu(H_2O)_6]^{2+}$, which is elongated along the z axis. As indicated in Figure 9.13.2, this kind of distortion splits both the e_g and t_{2g} sets of orbitals. Because the axial ligands interact most strongly with the d_{z^2} orbital, the splitting of the e_g set (δ_1) is significantly larger than the splitting of the t_{2g} set (δ_2), but both δ_1 and δ_2 are much, much smaller than the Δ_o. This splitting does not change the centerpoint of the energy within each set, so a Jahn–Teller distortion results in no net change in energy for a filled or half-filled set of orbitals. If, however, the e_g set contains one electron (as in the d^4 ions, Cr^{2+} and Mn^{3+}) or three electrons (as in the d^9 ion, Cu^{2+}), the distortion decreases the energy of the system. For Cu^{2+}, for example, the change in energy after distortion is $2(-\delta_1/2) + 1(\delta_1/2) = -\delta_1/2$. For Cu^{2+} complexes, the observed distortion is always an elongation along the z axis by as much as 50 pm; in fact, many Cu^{2+} complexes are distorted to the extent that they are effectively square planar. In contrast, the distortion observed for most Cr^{2+} complexes is a compression along the z axis. In both cases, however, the net effect is the same: the distorted system is more stable than the undistorted system.

Jahn–Teller distortions are most important for d^9 and high-spin d^4 complexes; the distorted system is more stable than the undistorted one.

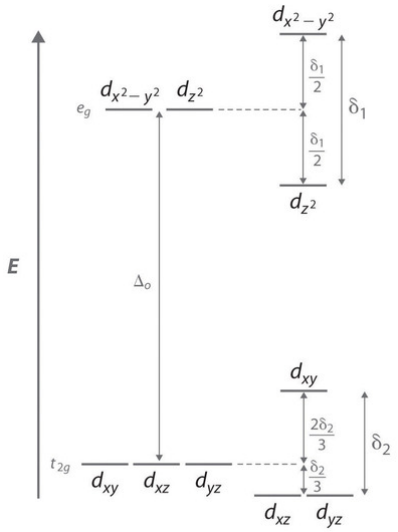


Figure 9.13.2: The Jahn–Teller Effect

Increasing the axial metal–ligand distances in an octahedral d^9 complex is an example of a Jahn–Teller distortion, which causes the degenerate pair of e_g orbitals to split in energy by an amount δ_1; δ_1 and δ_2 are much smaller than Δ_o. As a result, the distorted system is more stable (lower in energy) than the undistorted complex by $\delta_1/2$.

Thermodynamic Effects

As previously noted, crystal field splitting energies (CFSEs) can be as large as several hundred kilojoules per mole, which is the same magnitude as the strength of many chemical bonds or the energy change in most chemical reactions. Consequently, CFSEs are important factors in determining the magnitude of hydration energies, lattice energies, and other thermodynamic properties of the transition metals.

Hydration Energies

The hydration energy of a metal ion is defined as the change in enthalpy for the following reaction:

$$M^{2+}_{(g)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} \tag{9.13.1}$$

Although hydration energies cannot be measured directly, they can be calculated from experimentally measured quantities using thermochemical cycles. In Figure 9.13.3*a*, a plot of the hydration energies of the fourth-period metal dications versus atomic number forms a curve with two valleys. Note the relationship between the plot in Figure 9.13.3*a* and the plot of ionic radii in Figure 9.13.1 the overall shapes are essentially identical, and only the three cations with spherically symmetrical distributions of d electrons (Ca^{2+}, Mn^{2+}, and Zn^{2+}) lie on the dashed lines. In Figure 9.13.3*a*, the dashed line corresponds to hydration energies calculated based solely on electrostatic interactions. Subtracting the CFSE values for the $[M(H_2O)_6]^{2+}$ ions from the experimentally determined hydration energies gives the points shown as open circles, which lie very near the calculated curve. Therefore, CFSEs are primarily responsible for the differences between the measured and calculated values of hydration energies.

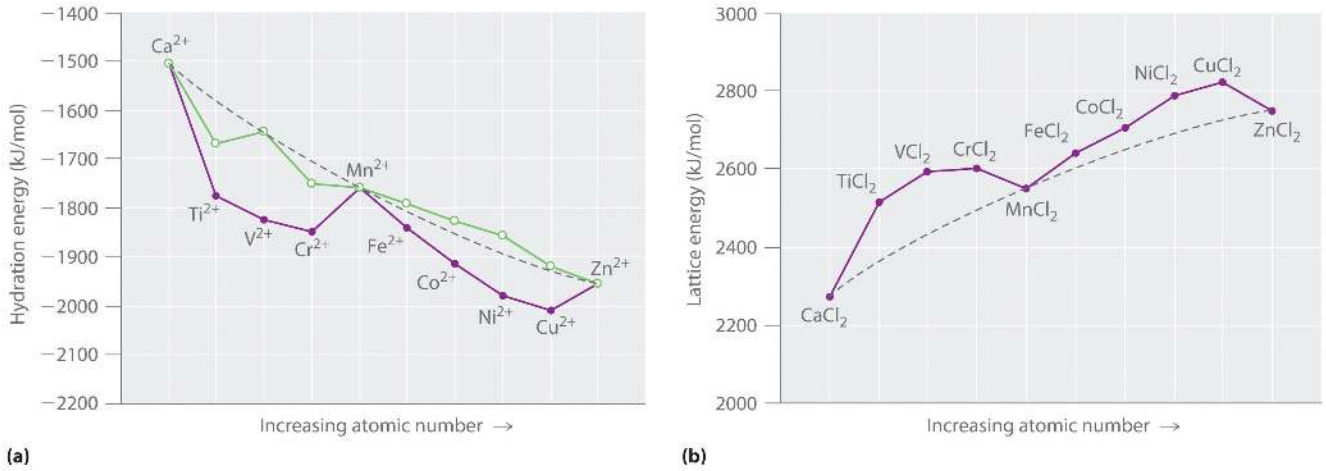


Figure 9.13.3: Thermochemical Effects of d-Orbital Splittings. (a) A plot of the hydration energies of the divalent fourth-period metal ions versus atomic number (solid circles) shows large deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed line). Correcting for CFSE gives the points shown as open circles, which, except for Ti^{2+} and Cr^{2+}, are close to the calculated values. The apparent deviations for these ions are caused by the fact that solutions of the Ti^{2+} ion in water are not stable, and Cr^{2+} does not form truly octahedral complexes. (b) A plot of the lattice energies for the fourth-period metal dichlorides versus atomic number shows similar deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed lines), again illustrating the importance of CFSEs.

Lattice Energies

Values of the lattice energies for the fourth-period metal dichlorides are plotted against atomic number in part (b) of Figure 9.13.3. Recall that the lattice energy is defined as the negative of the enthalpy change for the reaction below. Like hydration energies, lattice energies are determined indirectly from a thermochemical cycle.

$$M^{2+}(g) + 2Cl^{-}(g) \rightarrow MCl_2(s) \tag{9.13.2}$$

The shape of the lattice-energy curve is essentially the mirror image of the hydration-energy curve in part (a) of Figure 9.13.3, with only Ca^{2+}, Mn^{2+}, and Zn^{2+} lying on the smooth curve. It is not surprising that the explanation for the deviations from the curve is exactly the same as for the hydration energy data: all the transition-metal dichlorides, except $MnCl_2$ and $ZnCl_2$, are more stable than expected due to CFSE.

Summary

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. The crystal field stabilization energy (CFSE) is the additional stabilization of a complex due to placing electrons in the lower-energy set of d orbitals. CFSE explains the unusual curves seen in plots of ionic radii, hydration energies, and lattice energies versus atomic number. The Jahn–Teller theorem states that a non-linear molecule with a spatially degenerate electronic ground state undergoes a geometrical distortion to remove the degeneracy and lower the overall energy of the system.

9.13: Thermodynamics and Structural Consequences of d-Orbital Splitting is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Thermodynamics and Structural Consequences of d-Orbital Splitting** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

10: Ligand Field Theory

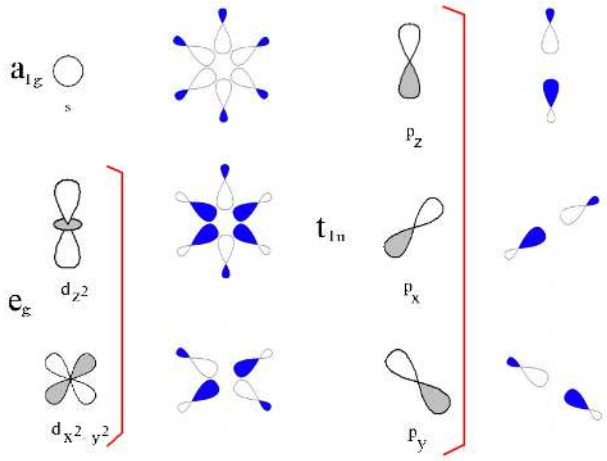
Ligand field theory (LFT) describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has *nine* valence atomic orbitals: five *n*d, one (*n*+1)s, and three (*n*+1)p orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex, but most explanations begin by describing octahedral complexes, where six ligands coordinate to the metal.

10.1: Ligand Field Theory Fundamentals

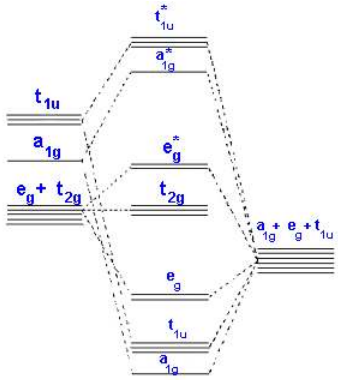
10: Ligand Field Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.1: Ligand Field Theory Fundamentals

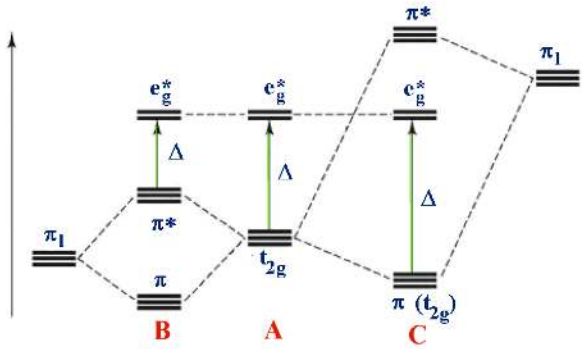
Ligand Field Theory can be considered an extension of Crystal Field Theory such that all levels of covalent interactions can be incorporated into the model. Treatment of the bonding in LFT is generally done using Molecular Orbital Theory. A qualitative approach that can be used for octahedral metal complexes is given in the following 3 diagrams.



In the first diagram, the 3d, 4s and 4p metal ion atomic orbitals are shown together with the ligand group orbitals that would have the correct symmetry to be able to overlap with them. The symmetry adapted linear comination of ligand orbitals are generated by taking 6 sigma orbitals from the ligands, designated as σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z, σ_{-z} and then combining them to make 6 ligand group orbitals. (labelled e_g, a_{1g}, t_{1u})



In the second diagram only sigma bonding is considered and it shows the combination of the metal 3d, 4s and 4p orbitals with OCCUPIED ligand group orbitals (using 1 orbital from each ligand). The result is that that the metal electrons would be fed into t2g and eg* molecular orbitals which is similar to the CFT model except that the eg orbital is now eg*.



For example: B - $[M(II)I_6]^{4-}$ A - $[M(II)(H_2O)_6]^{2+}$ C - $[M(II)(CN)_6]^{4-}$

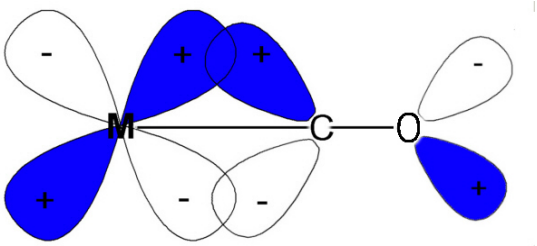
In the third diagram, π (pi) bonding is considered. In general π bonds are weaker than σ (sigma) bonds and so the effect is to modify rather than dramatically alter the description. 2 orbitals from each ligand are combined to give a total of 12 which are subdivided into four sets with three ligand group orbitals in each set. These are labelled t_{1g}, t_{1u}, t_{2g} and t_{2u}. The metal t_{2g} orbital is the most suitable for interaction and this is shown in the 2 cases above.
Case A is the same as above, ignoring π interactions.

- For case B, the ligand π orbitals are full and at lower energy than the metal t_{2g}. This causes a decrease in the size of Δ.
- For case C, the ligand π orbitals are empty and at higher energy than the metal t_{2g}. This causes an increase in the size of Δ.

Returning to the problem of correctly placing ligands in the Spectrochemical series, the halides are examples of case A and groups like CN- and CO are examples of case B. It is possible then to explain the Spectrochemical series once covalent effects are considered.

Some convincing arguments for covalency and effects on Δ come from a study of the IR spectra recorded for simple carbonyl compounds e.g. $M(CO)_6$.

- The CO molecule has a strong triple bond which in the IR gives rise to a strong absorption at ~2140 cm^{-1}. For the series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which are isoelectronic, the IR bands for the CO have shifted to 2090, 2000 and 1860 cm^{-1} respectively. Despite the fact that the metals have the same number of electrons (isoelectronic) the frequency of force constant of the CO bond is seen to vary $Mn^+ > Cr > V^-$.
- This can not be explained on an ionic basis but is consistent with the π bonding scheme since the greater the positive charge on the metal, the less readily the metal can delocalize electrons back into the π^* orbitals of the CO group.



Note that the IR values we are dealing with relate to the CO bond and not the M-C so when the CO frequency gets less then it is losing triple bond character and becoming more like a double bond. This is expected if electrons are pushed back from the metal into what were empty π^* antibonding orbitals.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

10.1: Ligand Field Theory Fundamentals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Ligand Field Theory Fundamentals** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

11: Spectroscopic Techniques

- 11.1: Fundamentals of Electron Absorption Spectroscopy
- 11.2: Basics of Spectroscopy
  - 11.2.1: Breakdown of EM Radiation
- 11.3: Electronic Spectroscopy
- 11.4: Vibrational Spectroscopy
- 11.5: X-ray Spectroscopy
  - 11.5.1: Extended X-ray Absorption Fine Structure (EXAFS)
  - 11.5.2: X-ray Absorption Near Edge Structure (XANES)
  - 11.5.3: X-ray Absorption Spectroscopy (XAS)
- 11.6: Magnetic Resonance Spectroscopies
  - 11.6.1: NMR Animations
    - 11.6.1.1: Basic Concepts
      - 11.6.1.1.1: Magnetic Resonance Imaging
    - 11.6.1.2: pi Pulses
    - 11.6.1.3: Pulsed NMR Introduction
    - 11.6.1.4: Spin Echo

11: Spectroscopic Techniques is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.1: Fundamentals of Electron Absorption Spectroscopy

UV-Vis Spectroscopy

UV-Vis spectroscopy is an analytical chemistry technique used to determine the presence of various compounds, such as transition metals/transition metal ions, highly conjugated organic molecules, and more. However, due to the nature of this course, only transition metal complexes will be discussed. UV-Vis spectroscopy works by exciting a metal's d-electron from the ground state configuration to an excited state using light. In short, when energy in the form of light is directed at a transition metal complex, a d-electron will gain energy and a UV-Vis spectrophotometer measures the abundance of transition metal atoms with excited electrons at a specific wavelength of light, from the visible light region to the UV region.

When using a UV-Vis Spectrophotometer, the solution to be analyzed is prepared by placing the sample in a cuvette then placing the cuvette inside the spectrophotometer. The machine then shines light waves from the visible and ultraviolet wavelengths and measures how much light of each wavelength the sample absorbs and then emits.

Absorbance of the sample can be calculated via Beer's Law: $A=\varepsilon lc$ where A is the absorbance, ε is the molar absorptivity of the sample, l is the length of the cuvette used, and c is the concentration of the sample.[1] When the spectrophotometer produces the absorption graph, the molar absorptivity can then be calculated.

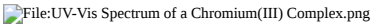


Figure 11.1.1. UV-Vis Spectrum of a Chromium(III) complex

To illustrate what this looks like, you will find a sample absorbance spectrum to the right.[2] 404-5</ref> </ref> As can be seen, the y-axis represents absorbance and the x-axis represents the wavelengths of light being scanned. This specific transition metal complex, $[CrCl(NH_3)_5]^{2+}$, has the highest absorbance in the UV region of light, right around 250-275 nm, and two slight absorbance peaks near 400 nm and 575 nm respectively. The two latter peaks are much less pronounced than the former peak due to the electron's transition being partially forbidden—a concept that will be discussed later in this chapter. If a transition is forbidden, not many transition metal electrons will undergo the excitation.

Theory Behind UV-Vis Spectroscopy

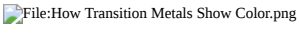
Splitting of the D-Orbitals

Figure 11.1.2 D orbitals

As is widely known, the d-orbitals contain five types of sub-orbitals: d_{xy}, d_{yz}, d_{xz}, d_x^2-$_y^2$, and d_z^2 which are all shown to the right[3]. When in the absence of a magnetic field—such as when there are no electrons present—all the sub-orbitals combine together to form a degenerate spherical orbital. This singular orbital promptly differentiates back into its sub-orbitals when electrons are introduced or the transition metal is bonded to a set of ligands.

Figure 11.1.3 This differentiation gives rise to the origin of color in metallic complexes.

The Origination of Color in Transition Metal Complexes

When looking at color in transition metal complexes, it is necessary to pay attention to the differentiated d-orbitals. Color in this sense originates from the excitation of d-orbital electrons from one energy level to the next. For instance, an electron in the t_{2g} bonding orbital can be excited by light to the e_g^* bonding orbital and upon its descent back to the ground state, energy is released in the form of light: 

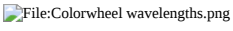


Figure 11.1.4. Colorwheel wavelengths

The specific wavelength of light required to excite an electron to the e_g^* orbital directly correlates to the color given off when the electron moves back down to the ground state. The figure on the right helps visualize the properties of transition metal color. Whichever color is absorbed, the complimentary color (directly opposite from the color in the figure) is emitted. For instance, if a metal complex emits green light we can figure out that the complex absorbed red light with a wavelength between 630 nm-750 nm in length.

Rules of Color Intensity and Forbidden Transitions

The intensity of the emitted color is based on two rules:[4]

1. Spin multiplicity: the spin multiplicity of a complex cannot change when an electron is excited. Multiplicity can be calculated via the equation 2S+1 where S is calculated by (1/2)(number of unpaired d-electrons).
2. If there is a center of symmetry in the molecule (i.e. center of inversion) then a g to g or u to u electron excitation is not allowed.

If a complex breaks one of these rules, we say it is a forbidden transition. If one rule is broken, it is singly forbidden. If two rules are broken, we call it double forbidden and so on. Even though the convention is to call it forbidden, this does not mean it will not happen; rather, the more rules the complex breaks, the more faded its color will be because the more unlikely the chances the transition will happen. Let's again look at the previous example: How Transition Metals Show Color

If we apply the intensity rules to it:

1. Multiplicity before transition=2(0.5[1 unpaired electron])+1=3, Multiplicity after transition=2(0.5[1 unpaired electron])+1=3. Both multiplicities are the same, so this transition is allowed under rule 1.
2. If we assume this molecule is octahedral in symmetry, this means it has an inversion center and thus the transition of e_g^* to t_{2g} is forbidden under rule 2 due to both orbitals being gerade (g).
3. We are only exciting one electron and thus it is allowed under rule 3.

Based on these rules, we can see that this transition is only singly forbidden, and thus it will appear only slightly faded and light rather than a deep, rich green.

Ligand Field Theory: How Ligands Affect Color

As it turns out, the atoms bonded to a transition metal affect the wavelength that the complex needs to absorb in order to give off light; we refer to this as Ligand Field Theory. While certain transition metals like to absorb different wavelengths than other transition metals, the ligand(s) plays the most important role in determining the wavelength of light needed for electron excitation.[5]

The terms low spin and high spin are used to describe the difference in energy levels of the t_{2g} and e_g^* orbitals, which correlates to the wavelength of light needed to excite an electron from t_{2g} to e_g^*. When a complex is characterized as low spin, the ligands attached to the metal raise the energy of the e_g^* orbital so much that the ground state configuration of the complex fills the first six electrons in the t_{2g} orbital before the e_g^* orbital is filled. As a result, high energy wavelengths of light—violet, blue, and green—are needed to successful excite an electron to the e_g^* bonding orbital. This means that the transition metal complex will emit yellow, orange, and red light, respectively. Conversely, high spin complexes have ligands which lower the energy level of the e_g^* orbital so that low energy light—red, orange, and yellow—or even high energy light can successfully excite an electron. Thus, a high spin complex can emit any color. High spin complexes can be thought of as all-inclusive while low spin complexes are half-exclusive in terms of the wavelengths needed to excite an electron.

To determine whether a complex is high spin or low spin:

1. Look at the transition metal. First row metals will want to be high spin unless the ligand(s) forces it to be low spin. Second row metals want to be low spin unless the ligand(s) forces it high spin. Third row metals will low spin.
2. Look at the ligand(s) as they will be the ultimate determining factor. If the ligand matches the transition metal in terms of high spin/low spin, then the complex's spin will be whatever is "agreed" upon. If they differ, follow the ligand's spin type. If the ligand is classified neither as high nor low spin, follow the transition metal's spin type. Ligand spin types are enumerated below.
3. If there are multiple ligands with differing spin types, go with whichever spin type is most abundant in the complex.

The ligands below are ranked from low spin (greatest energy difference between t_{2g} and e_g^*) to high spin (lowest energy difference):[6] File:Spectrochemical Series.png

To illustrate this concept, let's take the following complexes:

$[Ni(NH_3)_6]^{2+}$, $[Ni(CN)_4]^{2-}$

The nickel complexes all have the same oxidation state on the metal (2+), and thus the same d-electron count. In the first complex, nickel wants to be high spin, while ammonia prefers neither high nor low spin. Therefore the complex will be high spin and emit blue light, which is an absorbance of orange—weak energy—light. For the second complex, nickel again wants to be high spin, but cyanide prefers low spin. As a result, the complex becomes low spin and will emit yellow light, which is an absorbance of violet—strong energy—light.

References

1. Inorganic Chemistry, Miessler, Fischer, and Tarr, 2013, Pages 404 and 405
2. ↑ Chemistry LibreTexts, Electronic Spectroscopy: Interpretation, https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Electronic_Spectroscopy/Electronic_Spectroscopy%3A_Interpretation
3. ↑ Principles of Inorganic Chemistry, Brian William Pfennig, 2015, Page 88
4. ↑ Inorganic Chemistry, Miessler, Fischer, and Tarr, 2013, Page 414
5. ↑ Principles of Inorganic Chemistry, Brian William Pfennig, 2015, Page 526
6. ↑ Principles of Inorganic Chemistry, Brian William Pfennig, 2015, Page 523

11.1: Fundamentals of Electron Absorption Spectroscopy is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

11.2: Basics of Spectroscopy

Bra/Ket Notation

Basics

- Beers-Lambert Law
- Spectrophotometry
- Fermi's Golden Rule
- Transition Integrals

Group Theory and Symmetry

- Theory
- Application
- Interpretation

11.2: Basics of Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.2.1: Breakdown of EM Radiation

Spectroscopy is the study of the interaction of **radiation** with **matter**. Electromagnetic radiation is a form of energy that is produce by oscillating electric and magnetic disturbance. It travels at the speed of light as a quantized harmonic wave. The electric and magnetic waves travel perpendicular to each other. Characteristics of waves include amplitude, wavelength, and frequency.

The electromagnetic spectrum consists of Radio/TV, Microwaves, Infrared, Visible, Ultraviolet, X-rays, and Gamma-rays (Figure 11.2.1.1). The longest waves, radio waves, are approximately 10^3 m in wavelength. As the name implies, radio waves are transmitted by radio broadcasts, TV broadcasts, and even cell phones. The shortest waves, Gamma rays, are approximately 10^{-12} m in wavelength. Out this huge spectrum, the human eyes can only detect waves from 390 nm to 780 nm.

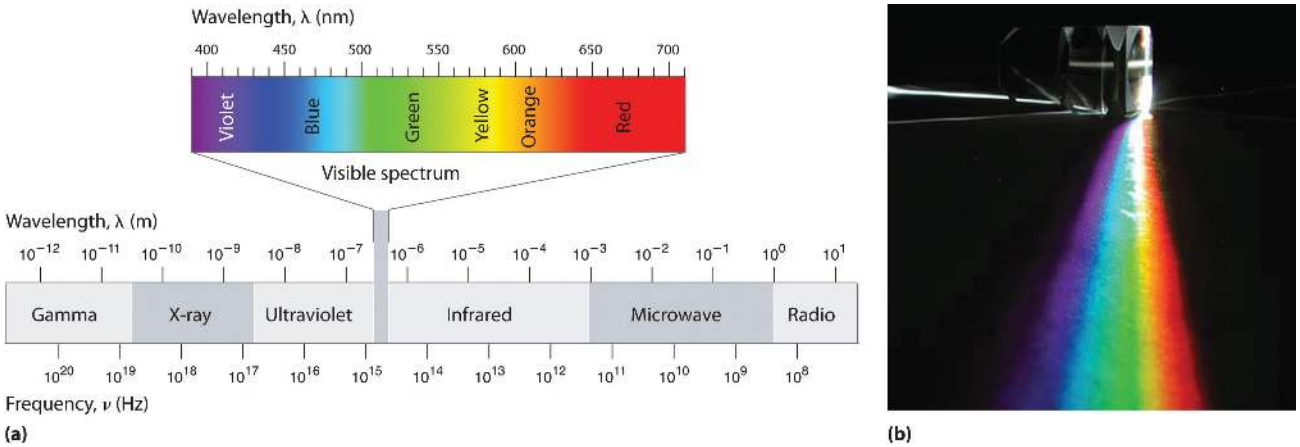


Figure 11.2.1.1: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum. (CC BY-NC-SA; anonymous)

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism (Figure 11.2.1.1b). A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 11.2.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	x-ray
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

We know that EM radiation of photons whose energy each with energies given by **Planck's law**:

$$E = h\nu \tag{11.2.1.1}$$

where h is Planck's constant = $6.626068 \times 10^{-34}\ m^2 kg/s$ and ν is the frequency ($1/s$ or Hz).

The speed of the electromagnetic radiation in vacuum is c, which is equal to 299,792,458 m/s. Since

$$c = \lambda\nu$$

EEquation 11.2.1.1 can be written in the following two alternate forms:

$$E = \frac{hc}{\lambda} = hc\tilde{\nu}$$

or

$$\tilde{\nu} = \frac{1}{\lambda}.$$

where $1/\lambda$ is the inverse wavelength or wavenumber (cm^{-1}).

The effect that a photon will have on matter or molecule will depend on E, and thus on v.

- For $\tilde{\nu} < 10^{-2}$ cm^{-1} ($\lambda \sim 1$ m), we have **radio frequencies**. These are too low an energy photons for anything except to affect the magnetic energy of a nucleus in an external magnetic field (NMR Spectroscopy)
- For 10^{-2} $cm^{-1} < \tilde{\nu} < 10$ cm^{-1} ($\lambda \sim 1$ cm), we have **microwave frequencies**. Photons have enough energy to be absorbed by unpaired electrons spins in an externally magnetic field (ESR) or to change the rotational energy of a molecule (microwave rotational spectroscopy)
- For 10 $cm^{-1} < \tilde{\nu} < 10^{4}$ cm^{-1} ($\lambda \sim 5$ μm), we have **infrared frequencies**. Photons have sufficient energy to be absorbed in the rotational motion of the molecules. This is called vibrational spectroscopy.
- For 10^{-2} $cm^{-1} < \tilde{\nu} < 10^{5}$ cm^{-1} ($\lambda < 1$ μm), we have **visible and UV spectroscopy** which involves excitations of electrons (valence) from stable orbits to higher energy orbits in the molecule. Electronic spectroscopy (UV-VIS)
- For 10^{5} $cm^{-1} < \tilde{\nu} < 10^{6}$ cm^{-1}, we have **vacuum UV**, where the photons have enough energy that if absorbed by a valence electron, the electron can be “knocked” out of the molecule. This is called photoelectron spectroscopy
- For 10^{6} $cm^{-1} < \tilde{\nu} < 10^{8}$ cm^{-1}, these are **X-rays** and have enough energy to ionize not only valence electrons, but also core electrons. This spectroscopy is call X-ray Photo-electron spectroscopy (XPS) and also Extended X-ray absorption fine structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES).
- For $\tilde{\nu} < 10^{8}$ cm^{-1}. These are very energetic **gamma rays** and are not used extensively for spectroscopy with chemists. One key exception is Mössbauer spectroscopy which is enough energy to promote changes in the nuclei of the atoms.

That is a quick run-down of the spectroscopies we will be address in this course. We will not be discussing mass spectroscopy or diffraction techniques although used quite constructively for many scientific endeavors.

11.2.1: Breakdown of EM Radiation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **1.1: Electromagnetic Radiation (Component 1)** is licensed CC BY-NC-SA 4.0.

11.3: Electronic Spectroscopy

- Theory
- Application
- Interpretation
- Atomic & Molecular Term Symbols
- Selection rules and transition moment integral
- SALCs
- Jablonski diagram
- Tanabe-Sugano Diagrams

11.3: Electronic Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.4: Vibrational Spectroscopy

Normal Modes

Raman

- Theory
- Application
- Interpretation
- Resonant vs. Nonresonant Raman Spectroscopy

Infrared

- Theory
- Application
- Interpretation
- Combination Bands, Overtones and Fermi Resonance
- The Power of the Fourier Transform for Spectroscopists
- How an FTIR Spectrometer Operates

11.4: Vibrational Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

11.5: X-ray Spectroscopy

XAS, or X-ray Absorption Spectroscopy, is a broadly used method to investigate atomic local structure as well as electronic states. Very generally, an X-ray strikes an atom and excites a core electron that can either be promoted to an unoccupied level, or ejected from the atom. Both of these processes will create a core hole. If the electron dissociates, this produces an excited ion as well as photoelectron and is studied by X-ray Photoelectron Spectroscopy (XPS).

Topic hierarchy

11.5.1: Extended X-ray Absorption Fine Structure (EXAFS)

11.5.2: X-ray Absorption Near Edge Structure (XANES)

11.5.3: X-ray Absorption Spectroscopy (XAS)

11.5: X-ray Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.5.1: Extended X-ray Absorption Fine Structure (EXAFS)

Extended X-ray Absorption Fine Structure (EXAFS)

11.5.1: Extended X-ray Absorption Fine Structure (EXAFS) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.5.2: X-ray Absorption Near Edge Structure (XANES)

X-ray Absorption Near Edge Structure (XANES)

11.5.2: X-ray Absorption Near Edge Structure (XANES) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.5.3: X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy (XAS)

11.5.3: X-ray Absorption Spectroscopy (XAS) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6: Magnetic Resonance Spectroscopies

Nuclear Magenetic Resonance

- Theory
- Application
- Interpretation

Electron Paramagenetic Resonance

- Theory
- Application
- Interpretation
- ENDOR: Theory
- Parallel Mode EPR: Theory

11.6: Magnetic Resonance Spectroscopies is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6.1: NMR Animations

NMR Animations

11.6.1: NMR Animations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6.1.1: Basic Concepts

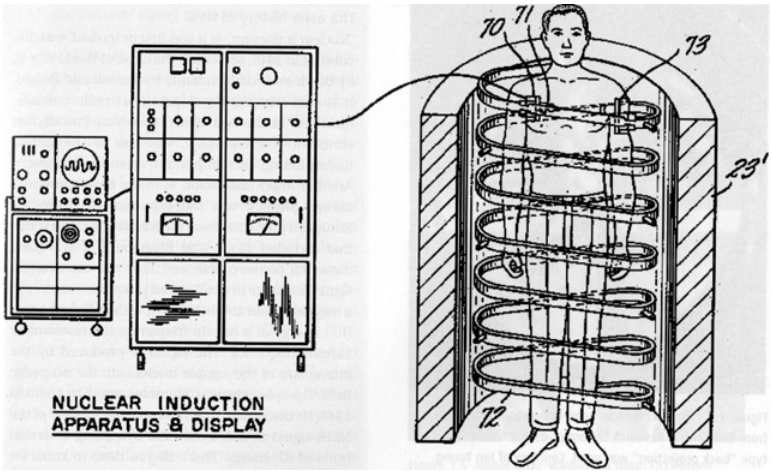
Basic Concepts

11.6.1.1: Basic Concepts is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6.1.1.1: Magnetic Resonance Imaging

Magnetic Resonance Imaging (MRI), nuclear magnetic resonance imaging (NMRI), or magnetic resonance tomography (MRT) is a medical imaging technique used in radiology to visualize internal structures of the body in detail. MRI makes use of the property of nuclear magnetic resonance (NMR) to image nuclei of atoms inside the body.

An MRI scanner is a device in which the patient lies within a large, powerful magnet where the magnetic field is used to align the magnetization of some atomic nuclei in the body, and radio frequency magnetic fields are applied to systematically alter the alignment of this magnetization.[1] This causes the nuclei to produce a rotating magnetic field detectable by the scanner—and this information is recorded to construct an image of the scanned area of the body.[2]:36 Magnetic field gradients cause nuclei at different locations to precess at different speeds, which allows spatial information to be recovered using Fourier analysis of the measured signal. By using gradients in different directions, 2D images or 3D volumes can be obtained in any arbitrary orientatation.



11.6.1.1.1: Magnetic Resonance Imaging is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6.1.2: pi Pulses

pi Pulses

11.6.1.2: pi Pulses is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6.1.3: Pulsed NMR Introduction

Pulsed NMR Introduction

11.6.1.3: Pulsed NMR Introduction is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.6.1.4: Spin Echo

Spin Echo

11.6.1.4: Spin Echo is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

Index

A

achiral
8.2.4.1: Optical Isomers in Inorganic Complexes
acidity
8.3.1: Acidity of the Hexaaqua Ions
alloys
7.2.5: Bonding and Properties of Solids
ambidentate ligands
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
ammine
8.3.5: Nomenclature of Complex Ions
ammine ligands
8.3.4: Ligand Exchange Reactions (Thermodynamics)
ammonia
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
ammonia ligands
8.4.5: Stability of Metal Complexes and Chelation
amorphous solid
7.2.1: Crystalline and Amorphous Solids
Amphoteric hydroxides
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
analogous complexes
8.4.5: Stability of Metal Complexes and Chelation
aqua
8.3.5: Nomenclature of Complex Ions
aqua ligands
8.3.4: Ligand Exchange Reactions (Thermodynamics)
association constant
8.4.2: Complex-Ion Equilibria
atomization enthalpy
7.1.6.3: Lattice Enthalpies and Born Haber Cycles
Aufbau principle
2.2.3: Aufbau Principle

B

band theory
7.2.6: Metals and Semiconductors
bent
3.2: Valence Shell Electron-Pair Repulsion
Bicapped square antiprism geometry
8.2.2: Coordination Numbers and Geometry
Bidentate ligands
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
8.2.5: Ligands
8.2.6: What is a Complex Ion?
Binary crystals
7.2.3: Stucture of Simple Binary Compounds
block diagonal
4.3.3: Representations of Point Groups
body centered cubic
7.2.2: Arrangement of Atoms in Crystals
bond angle
3.2: Valence Shell Electron-Pair Repulsion
bonding
8.2.6: What is a Complex Ion?

C

Capped octahedron
8.2.2: Coordination Numbers and Geometry
Capped trigonal prism
8.2.2: Coordination Numbers and Geometry
carbonate ions
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
ceramics
7.2.9: Modern Materials
character (matrix)
4.3.3: Representations of Point Groups
character table
4.3.5: Character Tables
Chelate complexes
8.4.5: Stability of Metal Complexes and Chelation
chelate effect
8.3.4: Ligand Exchange Reactions (Thermodynamics)
8.4.5: Stability of Metal Complexes and Chelation
chelating agent
8.4.1: Chelation
Chelation
8.2.5: Ligands
8.4.1: Chelation
8.4.5: Stability of Metal Complexes and Chelation
Chelation Effect
8.4.2: Complex-Ion Equilibria
chemical equilibria
8.4.2: Complex-Ion Equilibria
chiral
8.2.4.1: Optical Isomers in Inorganic Complexes
chiral center
8.2.4.1: Optical Isomers in Inorganic Complexes
chloro
8.3.5: Nomenclature of Complex Ions
Cis isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
cis isomes
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
Colors
8.3.6: Origin of Color in Complex Ions
complex compounds
8.2.3: Introduction to Coordination Chemistry
Complex Equilibrium
8.4.3: Complex Equilibrium
complex ion
8.2.6: What is a Complex Ion?
8.3.1: Acidity of the Hexaaqua Ions
8.4.2: Complex-Ion Equilibria
Complex Ion Equilibria
8.4: Complex Ion Equilibria
complex ions
8.3.2: Geometry of Complex Ions
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.5: Nomenclature of Complex Ions
8.3.6: Origin of Color in Complex Ions
8.3.10: Stereoisomerism in complex ions
Complex Metal Complexes
8.2.4.5: Stereoisomers of Complex Metal Complexes
complex metal ions
8.3.5: Nomenclature of Complex Ions
Complexes
8.2.3: Introduction to Coordination Chemistry
compression
8.2.2.1: Jahn-Teller Distortions
conductors
7.2.6: Metals and Semiconductors
coordinate bond
8.2.6: What is a Complex Ion?
coordinate compound
8.2.4.1: Optical Isomers in Inorganic Complexes
coordinate covalent bonds
8.4.2: Complex-Ion Equilibria
coordination
8.3.6: Origin of Color in Complex Ions
Coordination Chemistry
8: Coordination Chemistry
8.2: Structure and Nomenclature of Coordination Compounds
coordination complex
9.1: Colors of Coordination Complexes
Coordination Complexes
9.1: Colors of Coordination Complexes
coordination compounds
8.1.1: History of Coordination Compounds
8.2: Structure and Nomenclature of Coordination Compounds
8.2.1: Intro to Coordination Chemistry
8.2.3: Introduction to Coordination Chemistry
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
Coordination Isomerism
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
coordination number
8.2.2: Coordination Numbers and Geometry
covalent solid
7.2.5: Bonding and Properties of Solids
Crystal Defects
7.2.4: Crystal Defects
crystal field splitting
9.2: Crystal Field Stabilization Energy
crystal field stabilization energy
9.2: Crystal Field Stabilization Energy
crystal field theory
8.2.5.2: The Irving-Williams Series
9: Crystal Field Theory
9.1: Colors of Coordination Complexes
9.2: Crystal Field Stabilization Energy
crystals
7.2.1: Crystalline and Amorphous Solids
Cube
8.2.2: Coordination Numbers and Geometry
Cube geometry
8.2.2: Coordination Numbers and Geometry
cubic
7.2.2: Arrangement of Atoms in Crystals
cuboctahedron geometry
8.2.2: Coordination Numbers and Geometry
Cupric Complexes
8.4.3: Complex Equilibrium

cyano
8.3.5: Nomenclature of Complex Ions

D
dative bond
8.2.6: What is a Complex Ion?
dipole moment
3.2: Valence Shell Electron-Pair Repulsion
Dodecahedron
8.2.2: Coordination Numbers and Geometry
Dodecahedron Geometry
8.2.2: Coordination Numbers and Geometry

E
EDTA
8.2.5.1: EDTA
electromagnetic spectrum
9.1: Colors of Coordination Complexes
Electronic Configurations
8.2.2.1: Jahn-Teller Distortions
Elongation
8.2.2.1: Jahn-Teller Distortions
enantiomers
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
equilibrium
8.4.3: Complex Equilibrium
ethylenediamine ligands
8.4.5: Stability of Metal Complexes and Chelation
ethylenediaminetetraacetic acid
8.2.5.1: EDTA

F
Face Centered Cubic
7.2.2: Arrangement of Atoms in Crystals
first sphere
8.2.3: Introduction to Coordination Chemistry
fluoro
8.3.5: Nomenclature of Complex Ions
formal charge
3.1.3: Formal Charge
formation constant
8.4.2: Complex-Ion Equilibria
formation constants
8.3.4: Ligand Exchange Reactions (Thermodynamics)

G
Geometric Isomerism
8.3.10: Stereoisomerism in complex ions
geometric isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.5: Stereoisomers of Complex Metal Complexes
geometric isomers (complex ions)
8.3.10: Stereoisomerism in complex ions
geometry
8.3.2: Geometry of Complex Ions
grain boundary
7.2.4: Crystal Defects

H
hard acids
8.4.4: Hard and Soft Acids and Bases
hard base
8.4.4: Hard and Soft Acids and Bases
hexaaqua ion
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
Hexaaqua Ions
8.3.1: Acidity of the Hexaaqua Ions
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
hexaaquachromium
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
hexaaquacobalt
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
hexaaquairon
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
Hexadentate Ligand
8.2.6: What is a Complex Ion?
Hexagonal bipyramid
8.2.2: Coordination Numbers and Geometry
Hexagonal bipyramid geometry
8.2.2: Coordination Numbers and Geometry
hexagonal closest packing
7.2.2: Arrangement of Atoms in Crystals
Hexagonal planar Geometry
8.2.2: Coordination Numbers and Geometry
high spin
8.2.2.1: Jahn-Teller Distortions
9.2: Crystal Field Stabilization Energy
HSA
8.4.4: Hard and Soft Acids and Bases
hydrate isomer
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
hydration
9.2: Crystal Field Stabilization Energy
hydroxide ions
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
hydroxo
8.3.5: Nomenclature of Complex Ions

I
impurities
7.2.4: Crystal Defects
inner coordination sphere
8.2.3: Introduction to Coordination Chemistry
insulators
7.2.6: Metals and Semiconductors
ionic radius
8.3.1: Acidity of the Hexaaqua Ions
ionic solid
7.2.5: Bonding and Properties of Solids
ionization isomerism
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
isomerism
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
8.3.10: Stereoisomerism in complex ions
isomers
8.2.4: Isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.5: Stereoisomers of Complex Metal Complexes

J
jmol
8.2.2.2: Molecular Examples

L
Lancashire
8.2.2: Coordination Numbers and Geometry
8.2.2.1: Jahn-Teller Distortions
8.2.2.2: Molecular Examples
8.2.4.5: Stereoisomers of Complex Metal Complexes
8.4.1: Chelation
Lanthanide Contraction
8.2.5.2: The Irving-Williams Series
Lattice Energy
7.1.6.1: Lattice Energy
lattice enthalpy
7.1.6.3: Lattice Enthalpies and Born Haber Cycles
Le Chatelier's principle
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
Lenz's Law
9.7: Magnetism
Lewis base
8.4.2: Complex-Ion Equilibria
ligand
8.2.5: Ligands
8.2.6: What is a Complex Ion?
8.4.3: Complex Equilibrium
Ligand Close Packing (LCP)
3.2.4: Ligand Close Packing
ligand exchange
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
Ligand Exchange Reaction
8.3.3: Ligand Exchange Reactions (Introduction)
Ligand Exchange Reactions
8.3.4: Ligand Exchange Reactions (Thermodynamics)
Ligands
8.2.3: Introduction to Coordination Chemistry
8.2.6: What is a Complex Ion?
8.3.5: Nomenclature of Complex Ions
linear
3.2: Valence Shell Electron-Pair Repulsion
8.2.4.5: Stereoisomers of Complex Metal Complexes
low spin
8.2.2.1: Jahn-Teller Distortions
9.2: Crystal Field Stabilization Energy

M
Magnetic resonance imaging
11.6.1.1.1: Magnetic Resonance Imaging

magnetism
9.7: Magnetism
Metal Complexes
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.4.5: Stability of Metal Complexes and Chelation
metal ion
8.4.2: Complex-Ion Equilibria
metals
7.2.6: Metals and Semiconductors
Mirror Image Method
8.2.4.1: Optical Isomers in Inorganic Complexes
molecular geometry
8.2.4.5: Stereoisomers of Complex Metal Complexes
molecular solid
7.2.5: Bonding and Properties of Solids
monodentate
8.4.5: Stability of Metal Complexes and Chelation
monodentate ligands
8.3.2: Geometry of Complex Ions
8.4.5: Stability of Metal Complexes and Chelation
multidentate ligands
8.3.6: Origin of Color in Complex Ions

N

nephelauxetic ratio
9.12: Tanabe-Sugano Diagrams
Nephelauxetic Series
9.11: Orgel Diagrams
9.12: Tanabe-Sugano Diagrams
nylon
7.2.8: Polymers

O

octahedral
3.2: Valence Shell Electron-Pair Repulsion
8.2.2: Coordination Numbers and Geometry
8.2.4.5: Stereoisomers of Complex Metal Complexes
Octahedral Complexes
8.3.6: Origin of Color in Complex Ions
Octahedral Isomers
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
octahedral metal complexes
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
Octahedral Preference
9.2: Crystal Field Stabilization Energy
Octahedral Site Preference Energy
9.2: Crystal Field Stabilization Energy
Optical isomerism
8.3.10: Stereoisomerism in complex ions
Optical Isomers
8.2.4.1: Optical Isomers in Inorganic Complexes
8.2.4.5: Stereoisomers of Complex Metal Complexes
optical isomers (complex ions)
8.2.4.1: Optical Isomers in Inorganic Complexes
8.3.10: Stereoisomerism in complex ions
Orgel Diagrams
9.11: Orgel Diagrams
outer coordination sphere
8.2.3: Introduction to Coordination Chemistry
Oxidation State
8.3.6: Origin of Color in Complex Ions

P

Pentagonal Bipyramid
8.2.2: Coordination Numbers and Geometry
Planar Isomers
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
Plane of Symmetry Method
8.2.4.1: Optical Isomers in Inorganic Complexes
polarimeter
8.2.4.1: Optical Isomers in Inorganic Complexes
Polarimetry
8.2.4.1: Optical Isomers in Inorganic Complexes
8.2.4.1.3: Polarimetry
Polydentate ligands
8.2.3: Introduction to Coordination Chemistry
8.2.5: Ligands
polyethylene
7.2.8: Polymers
polymerization
7.2.8: Polymers
polymers
7.2.8: Polymers

Q

Quadridentate Ligand
8.2.6: What is a Complex Ion?

R

Racah parameter
9.11: Orgel Diagrams
9.12: Tanabe-Sugano Diagrams
radius
8.3.1: Acidity of the Hexaaqua Ions
rotation axis
4.3.3: Representations of Point Groups

S

SALC
6.2: CO_2
second sphere
8.2.3: Introduction to Coordination Chemistry
seesaw
3.2: Valence Shell Electron-Pair Repulsion
semiconductor
7.2.6: Metals and Semiconductors
Shottky defect
7.2.4: Crystal Defects
soft acid
8.4.4: Hard and Soft Acids and Bases
Soft Acids
8.4.4: Hard and Soft Acids and Bases
soft bases
8.4.4: Hard and Soft Acids and Bases
solids
7.2: Solids
Solubility Effects
8.4.2: Complex-Ion Equilibria
spectrochemical series
9.1: Colors of Coordination Complexes
spin pairing energy
9.2: Crystal Field Stabilization Energy
Square antiprism
8.2.2: Coordination Numbers and Geometry
Square antiprism geometry
8.2.2: Coordination Numbers and Geometry
square planar
8.2.4.5: Stereoisomers of Complex Metal Complexes
8.3.2: Geometry of Complex Ions
square planar complex
8.3.2: Geometry of Complex Ions
Square Planar Geometry
8.2.2: Coordination Numbers and Geometry
Square pyramid Geometry
8.2.2: Coordination Numbers and Geometry
square pyramidal
3.2: Valence Shell Electron-Pair Repulsion
stability constant
8.4.2: Complex-Ion Equilibria
stability constants
8.3.4: Ligand Exchange Reactions (Thermodynamics)
stepwise equilibrium constants
8.4.3: Complex Equilibrium
stereoisomerism
8.3.10: Stereoisomerism in complex ions
stereoisomers
8.2.4: Isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.5: Stereoisomers of Complex Metal Complexes
structural isomers
8.2.4: Isomers
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
superalloys
7.2.9: Modern Materials
symmetry
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes
symmetry elements
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes
symmetry operation
4.3.3: Representations of Point Groups
symmetry operations
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes

T

Tetrahedral
3.2: Valence Shell Electron-Pair Repulsion
8.2.4.5: Stereoisomers of Complex Metal Complexes
Tetrahedral Complexes
8.3.6: Origin of Color in Complex Ions
Tetrahedral Geometry
8.2.2: Coordination Numbers and Geometry
Tetrahedral ions
8.3.2: Geometry of Complex Ions
thermodynamically
8.4.5: Stability of Metal Complexes and Chelation
thermodynamically stable
8.4.5: Stability of Metal Complexes and Chelation
thermodynamics
8.3.4: Ligand Exchange Reactions (Thermodynamics)

Trans Isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
transition metals
8.3.6: Origin of Color in Complex Ions
Trigonal Bipyramid Geometry
8.2.2: Coordination Numbers and Geometry
trigonal bipyramidal
3.2: Valence Shell Electron-Pair Repulsion
Trigonal Planar
3.2: Valence Shell Electron-Pair Repulsion
Trigonal planar Geometry
8.2.2: Coordination Numbers and Geometry
Trigonal prism Geometry
8.2.2: Coordination Numbers and Geometry
Trigonal pyramid Geometry
8.2.2: Coordination Numbers and Geometry
trigonal pyramidal
3.2: Valence Shell Electron-Pair Repulsion
trimethylenediamine
8.4.5: Stability of Metal Complexes and Chelation

U

unit cell
7.2.2: Arrangement of Atoms in Crystals

V

valence shell electron pair repulsion theory
3.2: Valence Shell Electron-Pair Repulsion
VSEPR
3.2: Valence Shell Electron-Pair Repulsion

Index

A

achiral
8.2.4.1: Optical Isomers in Inorganic Complexes
acidity
8.3.1: Acidity of the Hexaaqua Ions
alloys
7.2.5: Bonding and Properties of Solids
ambidentate ligands
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
ammine
8.3.5: Nomenclature of Complex Ions
ammine ligands
8.3.4: Ligand Exchange Reactions (Thermodynamics)
ammonia
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
ammonia ligands
8.4.5: Stability of Metal Complexes and Chelation
amorphous solid
7.2.1: Crystalline and Amorphous Solids
Amphoteric hydroxides
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
analogous complexes
8.4.5: Stability of Metal Complexes and Chelation
aqua
8.3.5: Nomenclature of Complex Ions
aqua ligands
8.3.4: Ligand Exchange Reactions (Thermodynamics)
association constant
8.4.2: Complex-Ion Equilibria
atomization enthalpy
7.1.6.3: Lattice Enthalpies and Born Haber Cycles
Aufbau principle
2.2.3: Aufbau Principle

B

band theory
7.2.6: Metals and Semiconductors
bent
3.2: Valence Shell Electron-Pair Repulsion
Bicapped square antiprism geometry
8.2.2: Coordination Numbers and Geometry
Bidentate ligands
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
8.2.5: Ligands
8.2.6: What is a Complex Ion?
Binary crystals
7.2.3: Stucture of Simple Binary Compounds
block diagonal
4.3.3: Representations of Point Groups
body centered cubic
7.2.2: Arrangement of Atoms in Crystals
bond angle
3.2: Valence Shell Electron-Pair Repulsion
bonding
8.2.6: What is a Complex Ion?

C

Capped octahedron
8.2.2: Coordination Numbers and Geometry
Capped trigonal prism
8.2.2: Coordination Numbers and Geometry
carbonate ions
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
ceramics
7.2.9: Modern Materials
character (matrix)
4.3.3: Representations of Point Groups
character table
4.3.5: Character Tables
Chelate complexes
8.4.5: Stability of Metal Complexes and Chelation
chelate effect
8.3.4: Ligand Exchange Reactions (Thermodynamics)
8.4.5: Stability of Metal Complexes and Chelation
chelating agent
8.4.1: Chelation
Chelation
8.2.5: Ligands
8.4.1: Chelation
8.4.5: Stability of Metal Complexes and Chelation
Chelation Effect
8.4.2: Complex-Ion Equilibria
chemical equilibria
8.4.2: Complex-Ion Equilibria
chiral
8.2.4.1: Optical Isomers in Inorganic Complexes
chiral center
8.2.4.1: Optical Isomers in Inorganic Complexes
chloro
8.3.5: Nomenclature of Complex Ions
Cis isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
cis isomes
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
Colors
8.3.6: Origin of Color in Complex Ions
complex compounds
8.2.3: Introduction to Coordination Chemistry
Complex Equilibrium
8.4.3: Complex Equilibrium
complex ion
8.2.6: What is a Complex Ion?
8.3.1: Acidity of the Hexaaqua Ions
8.4.2: Complex-Ion Equilibria
Complex Ion Equilibria
8.4: Complex Ion Equilibria
complex ions
8.3.2: Geometry of Complex Ions
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.5: Nomenclature of Complex Ions
8.3.6: Origin of Color in Complex Ions
8.3.10: Stereoisomerism in complex ions
Complex Metal Complexes
8.2.4.5: Stereoisomers of Complex Metal Complexes
complex metal ions
8.3.5: Nomenclature of Complex Ions
Complexes
8.2.3: Introduction to Coordination Chemistry
compression
8.2.2.1: Jahn-Teller Distortions
conductors
7.2.6: Metals and Semiconductors
coordinate bond
8.2.6: What is a Complex Ion?
coordinate compound
8.2.4.1: Optical Isomers in Inorganic Complexes
coordinate covalent bonds
8.4.2: Complex-Ion Equilibria
coordination
8.3.6: Origin of Color in Complex Ions
Coordination Chemistry
8: Coordination Chemistry
8.2: Structure and Nomenclature of Coordination Compounds
coordination complex
9.1: Colors of Coordination Complexes
Coordination Complexes
9.1: Colors of Coordination Complexes
coordination compounds
8.1.1: History of Coordination Compounds
8.2: Structure and Nomenclature of Coordination Compounds
8.2.1: Intro to Coordination Chemistry
8.2.3: Introduction to Coordination Chemistry
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
Coordination Isomerism
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
coordination number
8.2.2: Coordination Numbers and Geometry
covalent solid
7.2.5: Bonding and Properties of Solids
Crystal Defects
7.2.4: Crystal Defects
crystal field splitting
9.2: Crystal Field Stabilization Energy
crystal field stabilization energy
9.2: Crystal Field Stabilization Energy
crystal field theory
8.2.5.2: The Irving-Williams Series
9: Crystal Field Theory
9.1: Colors of Coordination Complexes
9.2: Crystal Field Stabilization Energy
crystals
7.2.1: Crystalline and Amorphous Solids
Cube
8.2.2: Coordination Numbers and Geometry
Cube geometry
8.2.2: Coordination Numbers and Geometry
cubic
7.2.2: Arrangement of Atoms in Crystals
cuboctahedron geometry
8.2.2: Coordination Numbers and Geometry
Cupric Complexes
8.4.3: Complex Equilibrium

cyano
8.3.5: Nomenclature of Complex Ions

D
dative bond
8.2.6: What is a Complex Ion?
dipole moment
3.2: Valence Shell Electron-Pair Repulsion
Dodecahedron
8.2.2: Coordination Numbers and Geometry
Dodecahedron Geometry
8.2.2: Coordination Numbers and Geometry

E
EDTA
8.2.5.1: EDTA
electromagnetic spectrum
9.1: Colors of Coordination Complexes
Electronic Configurations
8.2.2.1: Jahn-Teller Distortions
Elongation
8.2.2.1: Jahn-Teller Distortions
enantiomers
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
equilibrium
8.4.3: Complex Equilibrium
ethylenediamine ligands
8.4.5: Stability of Metal Complexes and Chelation
ethylenediaminetetraacetic acid
8.2.5.1: EDTA

F
Face Centered Cubic
7.2.2: Arrangement of Atoms in Crystals
first sphere
8.2.3: Introduction to Coordination Chemistry
fluoro
8.3.5: Nomenclature of Complex Ions
formal charge
3.1.3: Formal Charge
formation constant
8.4.2: Complex-Ion Equilibria
formation constants
8.3.4: Ligand Exchange Reactions (Thermodynamics)

G
Geometric Isomerism
8.3.10: Stereoisomerism in complex ions
geometric isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.5: Stereoisomers of Complex Metal Complexes
geometric isomers (complex ions)
8.3.10: Stereoisomerism in complex ions
geometry
8.3.2: Geometry of Complex Ions
grain boundary
7.2.4: Crystal Defects

H
hard acids
8.4.4: Hard and Soft Acids and Bases
hard base
8.4.4: Hard and Soft Acids and Bases
hexaaqua ion
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
Hexaaqua Ions
8.3.1: Acidity of the Hexaaqua Ions
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
hexaaquachromium
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
hexaaquacobalt
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
hexaaquairon
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
Hexadentate Ligand
8.2.6: What is a Complex Ion?
Hexagonal bipyramid
8.2.2: Coordination Numbers and Geometry
Hexagonal bipyramid geometry
8.2.2: Coordination Numbers and Geometry
hexagonal closest packing
7.2.2: Arrangement of Atoms in Crystals
Hexagonal planar Geometry
8.2.2: Coordination Numbers and Geometry
high spin
8.2.2.1: Jahn-Teller Distortions
9.2: Crystal Field Stabilization Energy
HSA
8.4.4: Hard and Soft Acids and Bases
hydrate isomer
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
hydration
9.2: Crystal Field Stabilization Energy
hydroxide ions
8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions
hydroxo
8.3.5: Nomenclature of Complex Ions

I
impurities
7.2.4: Crystal Defects
inner coordination sphere
8.2.3: Introduction to Coordination Chemistry
insulators
7.2.6: Metals and Semiconductors
ionic radius
8.3.1: Acidity of the Hexaaqua Ions
ionic solid
7.2.5: Bonding and Properties of Solids
ionization isomerism
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
isomerism
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
8.3.10: Stereoisomerism in complex ions
isomers
8.2.4: Isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.5: Stereoisomers of Complex Metal Complexes

J
jmol
8.2.2.2: Molecular Examples

L
Lancashire
8.2.2: Coordination Numbers and Geometry
8.2.2.1: Jahn-Teller Distortions
8.2.2.2: Molecular Examples
8.2.4.5: Stereoisomers of Complex Metal Complexes
8.4.1: Chelation
Lanthanide Contraction
8.2.5.2: The Irving-Williams Series
Lattice Energy
7.1.6.1: Lattice Energy
lattice enthalpy
7.1.6.3: Lattice Enthalpies and Born Haber Cycles
Le Chatelier's principle
8.3.3: Ligand Exchange Reactions (Introduction)
8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions
Lenz's Law
9.7: Magnetism
Lewis base
8.4.2: Complex-Ion Equilibria
ligand
8.2.5: Ligands
8.2.6: What is a Complex Ion?
8.4.3: Complex Equilibrium
Ligand Close Packing (LCP)
3.2.4: Ligand Close Packing
ligand exchange
8.3.7: Reactions of the Hexaaqua Ions with Ammonia
Ligand Exchange Reaction
8.3.3: Ligand Exchange Reactions (Introduction)
Ligand Exchange Reactions
8.3.4: Ligand Exchange Reactions (Thermodynamics)
Ligands
8.2.3: Introduction to Coordination Chemistry
8.2.6: What is a Complex Ion?
8.3.5: Nomenclature of Complex Ions
linear
3.2: Valence Shell Electron-Pair Repulsion
8.2.4.5: Stereoisomers of Complex Metal Complexes
low spin
8.2.2.1: Jahn-Teller Distortions
9.2: Crystal Field Stabilization Energy

M
Magnetic resonance imaging
11.6.1.1.1: Magnetic Resonance Imaging

magnetism
9.7: Magnetism
Metal Complexes
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
8.4.5: Stability of Metal Complexes and Chelation
metal ion
8.4.2: Complex-Ion Equilibria
metals
7.2.6: Metals and Semiconductors
Mirror Image Method
8.2.4.1: Optical Isomers in Inorganic Complexes
molecular geometry
8.2.4.5: Stereoisomers of Complex Metal Complexes
molecular solid
7.2.5: Bonding and Properties of Solids
monodentate
8.4.5: Stability of Metal Complexes and Chelation
monodentate ligands
8.3.2: Geometry of Complex Ions
8.4.5: Stability of Metal Complexes and Chelation
multidentate ligands
8.3.6: Origin of Color in Complex Ions

N

nephelauxetic ratio
9.12: Tanabe-Sugano Diagrams
Nephelauxetic Series
9.11: Orgel Diagrams
9.12: Tanabe-Sugano Diagrams
nylon
7.2.8: Polymers

O

octahedral
3.2: Valence Shell Electron-Pair Repulsion
8.2.2: Coordination Numbers and Geometry
8.2.4.5: Stereoisomers of Complex Metal Complexes
Octahedral Complexes
8.3.6: Origin of Color in Complex Ions
Octahedral Isomers
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
octahedral metal complexes
8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands
Octahedral Preference
9.2: Crystal Field Stabilization Energy
Octahedral Site Preference Energy
9.2: Crystal Field Stabilization Energy
Optical isomerism
8.3.10: Stereoisomerism in complex ions
Optical Isomers
8.2.4.1: Optical Isomers in Inorganic Complexes
8.2.4.5: Stereoisomers of Complex Metal Complexes
optical isomers (complex ions)
8.2.4.1: Optical Isomers in Inorganic Complexes
8.3.10: Stereoisomerism in complex ions
Orgel Diagrams
9.11: Orgel Diagrams
outer coordination sphere
8.2.3: Introduction to Coordination Chemistry
Oxidation State
8.3.6: Origin of Color in Complex Ions

P

Pentagonal Bipyramid
8.2.2: Coordination Numbers and Geometry
Planar Isomers
8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes
Plane of Symmetry Method
8.2.4.1: Optical Isomers in Inorganic Complexes
polarimeter
8.2.4.1: Optical Isomers in Inorganic Complexes
Polarimetry
8.2.4.1: Optical Isomers in Inorganic Complexes
8.2.4.1.3: Polarimetry
Polydentate ligands
8.2.3: Introduction to Coordination Chemistry
8.2.5: Ligands
polyethylene
7.2.8: Polymers
polymerization
7.2.8: Polymers
polymers
7.2.8: Polymers

Q

Quadridentate Ligand
8.2.6: What is a Complex Ion?

R

Racah parameter
9.11: Orgel Diagrams
9.12: Tanabe-Sugano Diagrams
radius
8.3.1: Acidity of the Hexaaqua Ions
rotation axis
4.3.3: Representations of Point Groups

S

SALC
6.2: CO_2
second sphere
8.2.3: Introduction to Coordination Chemistry
seesaw
3.2: Valence Shell Electron-Pair Repulsion
semiconductor
7.2.6: Metals and Semiconductors
Shottky defect
7.2.4: Crystal Defects
soft acid
8.4.4: Hard and Soft Acids and Bases
Soft Acids
8.4.4: Hard and Soft Acids and Bases
soft bases
8.4.4: Hard and Soft Acids and Bases
solids
7.2: Solids
Solubility Effects
8.4.2: Complex-Ion Equilibria
spectrochemical series
9.1: Colors of Coordination Complexes
spin pairing energy
9.2: Crystal Field Stabilization Energy
Square antiprism
8.2.2: Coordination Numbers and Geometry
Square antiprism geometry
8.2.2: Coordination Numbers and Geometry
square planar
8.2.4.5: Stereoisomers of Complex Metal Complexes
8.3.2: Geometry of Complex Ions
square planar complex
8.3.2: Geometry of Complex Ions
Square Planar Geometry
8.2.2: Coordination Numbers and Geometry
Square pyramid Geometry
8.2.2: Coordination Numbers and Geometry
square pyramidal
3.2: Valence Shell Electron-Pair Repulsion
stability constant
8.4.2: Complex-Ion Equilibria
stability constants
8.3.4: Ligand Exchange Reactions (Thermodynamics)
stepwise equilibrium constants
8.4.3: Complex Equilibrium
stereoisomerism
8.3.10: Stereoisomerism in complex ions
stereoisomers
8.2.4: Isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.5: Stereoisomers of Complex Metal Complexes
structural isomers
8.2.4: Isomers
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
superalloys
7.2.9: Modern Materials
symmetry
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes
symmetry elements
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes
symmetry operation
4.3.3: Representations of Point Groups
symmetry operations
8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes

T

Tetrahedral
3.2: Valence Shell Electron-Pair Repulsion
8.2.4.5: Stereoisomers of Complex Metal Complexes
Tetrahedral Complexes
8.3.6: Origin of Color in Complex Ions
Tetrahedral Geometry
8.2.2: Coordination Numbers and Geometry
Tetrahedral ions
8.3.2: Geometry of Complex Ions
thermodynamically
8.4.5: Stability of Metal Complexes and Chelation
thermodynamically stable
8.4.5: Stability of Metal Complexes and Chelation
thermodynamics
8.3.4: Ligand Exchange Reactions (Thermodynamics)

Trans Isomers
8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
Transition Metal Complexes
8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II
8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
transition metals
8.3.6: Origin of Color in Complex Ions
Trigonal Bipyramid Geometry
8.2.2: Coordination Numbers and Geometry
trigonal bipyramidal
3.2: Valence Shell Electron-Pair Repulsion
Trigonal Planar
3.2: Valence Shell Electron-Pair Repulsion
Trigonal planar Geometry
8.2.2: Coordination Numbers and Geometry
Trigonal prism Geometry
8.2.2: Coordination Numbers and Geometry
Trigonal pyramid Geometry
8.2.2: Coordination Numbers and Geometry
trigonal pyramidal
3.2: Valence Shell Electron-Pair Repulsion
trimethylenediamine
8.4.5: Stability of Metal Complexes and Chelation

U

unit cell
7.2.2: Arrangement of Atoms in Crystals

V

valence shell electron pair repulsion theory
3.2: Valence Shell Electron-Pair Repulsion
VSEPR
3.2: Valence Shell Electron-Pair Repulsion

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: Chem 124A: Fundamentals of Inorganic Chemistry

Webpages: 214

Applicable Restrictions: Noncommercial

All licenses found:

- Undeclared: 65.4% (140 pages)
- CC BY-NC-SA 4.0: 12.6% (27 pages)
- CC BY-NC 4.0: 8.9% (19 pages)
- CC BY-SA 4.0: 7% (15 pages)
- CC BY-NC 3.0: 5.1% (11 pages)
- Public Domain: 0.5% (1 page)
- CC BY 4.0: 0.5% (1 page)

By Page

- Chem 124A: Fundamentals of Inorganic Chemistry - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Introduction to Inorganic Chemistry - *Undeclared*
    - 1.1: What is inorganic chemistry? - *Undeclared*
    - 1.2: Inorganic vs Organic Chemistry - *Undeclared*
    - 1.3: History of Inorganic Chemistry - *Undeclared*
    - 1.4: Perspectives - *Undeclared*
    - 1.5: Practice problems - *Undeclared*
  - 2: Atomic Structure - *Undeclared*
    - 2.1: Historical Development of Atomic Theory - *Undeclared*
      - 2.1.1: The Periodic Table - *Undeclared*
      - 2.1.2: Discovery of Subatomic Particles and the Bohr Atom - *Undeclared*
    - 2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions - *CC BY-NC-SA 4.0*
      - 2.2.1: Particle in a Box - *CC BY-NC-SA 4.0*
      - 2.2.2: Quantum Numbers and Atomic Wave Functions - *CC BY-NC-SA 4.0*
      - 2.2.3: Aufbau Principle - *Public Domain*
      - 2.2.4: Shielding - *CC BY-NC-SA 4.0*
    - 2.3: Periodic Properties of Atoms - *Undeclared*
      - 2.3.1: Ionization energy - *Undeclared*
      - 2.3.2: Electron Affinity - *Undeclared*
      - 2.3.3: Covalent and Ionic Radii - *Undeclared*
    - 2.4: Problems (do we want this here?) - *Undeclared*
  - 3: Simple Bonding Theory - *Undeclared*
    - 3.1: Lewis Electron-Dot Diagrams - *Undeclared*
      - 3.1.1: Resonance - *Undeclared*
      - 3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms) - *Undeclared*
      - 3.1.3: Formal Charge - *Undeclared*
      - 3.1.4: Lewis fails to predict unusual cases- Boron and Beryllium - *Undeclared*
    - 3.2: Valence Shell Electron-Pair Repulsion - *CC BY-NC-SA 4.0*
      - 3.2.1: Lone Pair Repulsion - *Undeclared*
      - 3.2.2: Multiple Bonds - *Undeclared*
      - 3.2.3: Electronegativity and Atomic Size Effects - *Undeclared*
      - 3.2.4: Ligand Close Packing - *Undeclared*
    - 3.3: Molecular Polarity - *Undeclared*
    - 3.4: Hydrogen Bonding - *Undeclared*
  - 4: Symmetry and Group Theory - *Undeclared*
    - 4.1: Symmetry Elements and Operations - *Undeclared*
      - 4.1.1: Symmetry Elements - *CC BY-SA 4.0*
    - 4.2: Molecular Point Groups - *CC BY-SA 4.0*
      - 4.2.1: Point Groups - *Undeclared*
        - 4.2.1.1: Groups of Low and High Symmetry - *Undeclared*
        - 4.2.1.2: Other Groups - *Undeclared*
    - 4.3: Properties and Representations of Groups - *Undeclared*
      - 4.3.1: Matrices - *Undeclared*
      - 4.3.2: Matrix - *CC BY-SA 4.0*

- 4.3.3: Representations of Point Groups - *Undeclared*
- 4.3.4: Representations - *CC BY-SA 4.0*
- 4.3.5: Character Tables - *Undeclared*
- 4.4: Character Tables - *CC BY-SA 4.0*
- 4.5: Examples and Applications of Symmetry - *Undeclared*
  - 4.5.1: Chirality - *CC BY-NC 4.0*
  - 4.5.2: Molecular Vibrations - *Undeclared*
  - 4.5.3: Normal Modes of Vibration - *CC BY-SA 4.0*
  - 4.5.4: Selection Rules for IR and Raman Spectroscopy - *CC BY-SA 4.0*
  - 4.5.5: Stretching Frequencies and Structure Determination - *CC BY-SA 4.0*
- 4.6: Problems (do we want this here?) - *Undeclared*

5: Molecular Orbitals - *CC BY-NC-SA 4.0*

- 5.1: Formation of Molecular Orbitals from Atomic Orbitals - *CC BY-NC-SA 4.0*
  - 5.1.1: Molecular Orbitals from s Orbitals - *CC BY-NC 3.0*
  - 5.1.2: Molecular Orbitals from p Orbitals - *CC BY-NC 3.0*
  - 5.1.3: Molecular orbitals from d orbitals - *CC BY-NC-SA 4.0*
  - 5.1.4: Nonbonding Orbitals and Other Factors - *CC BY-NC-SA 4.0*
- 5.2: Homonuclear Diatomic Molecules - *CC BY-NC-SA 4.0*
  - 5.2.1: Molecular Orbitals - *CC BY-NC-SA 4.0*
  - 5.2.2: Orbital Mixing - *CC BY-NC-SA 4.0*
  - 5.2.3: Diatomic Molecules of the First and Second Periods - *CC BY-NC-SA 4.0*
  - 5.2.4: Photoelectron Spectroscopy - *CC BY-NC-SA 4.0*
- 5.3: Heteronuclear Diatomic Molecules - *CC BY-NC-SA 4.0*
  - 5.3.1: Polar bonds - *CC BY-NC-SA 4.0*
  - 5.3.2: Ionic Compounds and Molecular Orbitals - *CC BY-NC-SA 4.0*
- 5.4: Diatomic Molecular Orbitals - *CC BY-SA 4.0*
  - 5.4.1: Molecular Orbital Theory - *Undeclared*
- 5.P: Problems - *CC BY-NC-SA 4.0*

6: Larger (Polyatomic) Molecules - *CC BY-NC-SA 4.0*

- 6.1: Bifluoride anion - *CC BY-NC-SA 4.0*
- 6.2: CO_2 - *CC BY-NC-SA 4.0*
- 6.3: H_2O - *CC BY-NC-SA 4.0*
- 6.4: NH_3 - *CC BY-NC-SA 4.0*
- 6.5: CO_2 revisted with Projection Operators - *CC BY-NC-SA 4.0*
- 6.6: BF_3 - *CC BY-NC-SA 4.0*
- 6.7: SALCs and the projection operator technique - *CC BY-SA 4.0*
  - 6.7.1: NH3 Molecular Orbitals - *CC BY-SA 4.0*
  - 6.7.2: Td Molecular Orbitals - *CC BY-SA 4.0*
  - 6.7.3: D4h Molecular Orbitals - *CC BY-SA 4.0*
  - 6.7.4: Pi Donor and Acceptor Ligands - *CC BY-SA 4.0*

7: Solids - *Undeclared*

- 7.1: Crystal Lattices - *Undeclared*
  - 7.1.1: Inorganic Solids - *Undeclared*
  - 7.1.2: Lattice Basics - *Undeclared*
    - 7.1.2.1: Covalent Network Solids - *CC BY-NC 4.0*
    - 7.1.2.2: How to Decide What Type of Structure - *CC BY-NC 4.0*
    - 7.1.2.3: Ionic Structures - *CC BY-NC 4.0*
    - 7.1.2.4: Metallic Structures - *CC BY-NC 4.0*
    - 7.1.2.5: Molecular Structures - *CC BY-NC 4.0*
  - 7.1.3: Lattice Defects - *Undeclared*
    - 7.1.3.1: Frenkel Defect - *Undeclared*
    - 7.1.3.2: Metal Oxides - *Undeclared*
    - 7.1.3.3: Schottky Defects - *Undeclared*
    - 7.1.3.4: Solid Defects - *Undeclared*
  - 7.1.4: Metal Lattices - *CC BY-NC 3.0*
    - 7.1.4.1: Structure and Properties of Metals - *CC BY-NC 3.0*
    - 7.1.4.2: Metal Packing- Layers - *CC BY-NC 3.0*
    - 7.1.4.3: Metal Packing- Three Dimensions - *CC BY-NC 3.0*
    - 7.1.4.4: Problems - *CC BY-NC 3.0*
    - 7.1.4.5: Solutions to Selected Problems - *CC BY-NC 3.0*
  - 7.1.5: Solids - *Undeclared*
    - 7.1.5.1: Body Centered Packing - *Undeclared*
    - 7.1.5.2: Metal Structures - *Undeclared*
    - 7.1.5.3: Simple Cubic - *Undeclared*
    - 7.1.5.4: Solids - *Undeclared*
    - 7.1.5.5: Sphere Packing - *Undeclared*
    - 7.1.5.6: Tetrahedral and Octahedral Sites - *Undeclared*
  - 7.1.6: Thermodynamics of Lattices - *Undeclared*
    - 7.1.6.1: Lattice Energy - *Undeclared*
    - 7.1.6.2: Lattice Energy- The Born-Haber cycle - *Undeclared*
    - 7.1.6.3: Lattice Enthalpies and Born Haber Cycles - *CC BY-NC 4.0*
    - 7.1.6.4: The Born-Lande' equation - *Undeclared*
- 7.2: Solids - *Undeclared*

- 7.2.1: Crystalline and Amorphous Solids - *Undeclared*
- 7.2.2: Arrangement of Atoms in Crystals - *Undeclared*
- 7.2.3: Stucture of Simple Binary Compounds - *Undeclared*
- 7.2.4: Crystal Defects - *Undeclared*
- 7.2.5: Bonding and Properties of Solids - *Undeclared*
- 7.2.6: Metals and Semiconductors - *Undeclared*
- 7.2.7: Superconductors - *Undeclared*
- 7.2.8: Polymers - *Undeclared*
- 7.2.9: Modern Materials - *Undeclared*
- 7.2.10: End of Chapter Material - *Undeclared*

8: Coordination Chemistry - *Undeclared*

- 8.1: Introduction and History of Coordination Compounds - *Undeclared*
  - 8.1.1: History of Coordination Compounds - *CC BY-NC-SA 4.0*
- 8.2: Structure and Nomenclature of Coordination Compounds - *Undeclared*
  - 8.2.1: Intro to Coordination Chemistry - *Undeclared*
  - 8.2.2: Coordination Numbers and Geometry - *Undeclared*
    - 8.2.2.1: Jahn-Teller Distortions - *Undeclared*
    - 8.2.2.2: Molecular Examples - *Undeclared*
  - 8.2.3: Introduction to Coordination Chemistry - *Undeclared*
  - 8.2.4: Isomers - *Undeclared*
    - 8.2.4.1: Optical Isomers in Inorganic Complexes - *Undeclared*
      - 8.2.4.1.1: Enantiomers in Octahedral Complexes with Bidentate Ligands - *CC BY-NC 3.0*
      - 8.2.4.1.2: Identifying Planes of Symmetry in Octahedral Complexes - *Undeclared*
      - 8.2.4.1.3: Polarimetry - *CC BY-NC 3.0*
    - 8.2.4.2: Stereoisomers- Geometric Isomers in cis-platin - *CC BY-NC 3.0*
    - 8.2.4.3: Stereoisomers- Geometric Isomers in Transition Metal Complexes - *Undeclared*
    - 8.2.4.4: Stereoisomers- Geometric Isomers in Transition Metal Complexes II - *Undeclared*
    - 8.2.4.5: Stereoisomers of Complex Metal Complexes - *Undeclared*
    - 8.2.4.6: Structural Isomers- Coordination Isomerism in Transition Metal Complexes - *Undeclared*
    - 8.2.4.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes - *Undeclared*
    - 8.2.4.8: Structural Isomers- Linkage Isomerism in Transition Metal Complexes - *Undeclared*
  - 8.2.5: Ligands - *Undeclared*
    - 8.2.5.1: EDTA - *Undeclared*
    - 8.2.5.2: The Irving-Williams Series - *Undeclared*
  - 8.2.6: What is a Complex Ion? - *CC BY-NC 4.0*
  - 8.2.7: Nomenclature of Coordination Complexes - *Undeclared*
- 8.3: Complex Ion Chemistry - *CC BY-NC 4.0*
  - 8.3.1: Acidity of the Hexaaqua Ions - *CC BY-NC 4.0*
  - 8.3.2: Geometry of Complex Ions - *CC BY-NC 4.0*
  - 8.3.3: Ligand Exchange Reactions (Introduction) - *CC BY-NC 4.0*
  - 8.3.4: Ligand Exchange Reactions (Thermodynamics) - *CC BY-NC 4.0*
  - 8.3.5: Nomenclature of Complex Ions - *CC BY-NC 4.0*
  - 8.3.6: Origin of Color in Complex Ions - *CC BY-NC 4.0*
  - 8.3.7: Reactions of the Hexaaqua Ions with Ammonia - *CC BY-NC 4.0*
  - 8.3.8: Reactions of the Hexaaqua Ions with Carbonate Ions - *CC BY-NC 4.0*
  - 8.3.9: Reactions of the Hexaaqua Ions with Hydroxide Ions - *CC BY-NC 4.0*
  - 8.3.10: Stereoisomerism in complex ions - *CC BY-NC 4.0*
- 8.4: Complex Ion Equilibria - *Undeclared*
  - 8.4.1: Chelation - *Undeclared*
  - 8.4.2: Complex-Ion Equilibria - *Undeclared*
  - 8.4.3: Complex Equilibrium - *Undeclared*
  - 8.4.4: Hard and Soft Acids and Bases - *Undeclared*
  - 8.4.5: Stability of Metal Complexes and Chelation - *Undeclared*

9: Crystal Field Theory - *Undeclared*

- 9.1: Colors of Coordination Complexes - *Undeclared*
- 9.2: Crystal Field Stabilization Energy - *Undeclared*
- 9.3: Crystal Field Theory - *CC BY-NC-SA 4.0*
- 9.4: High Spin and Low Spin Complexes - *CC BY 4.0*
- 9.5: Introduction to Crystal Field Theory - *Undeclared*
- 9.6: Magnetic Moments of Transition Metals - *Undeclared*
- 9.7: Magnetism - *Undeclared*

- 9.8: Metals, Tetrahedral and Octahedral - *Undeclared*
- 9.9: Non-octahedral Complexes - *Undeclared*
- 9.10: Octahedral vs. Tetrahedral Geometries - *Undeclared*
- 9.11: Orgel Diagrams - *Undeclared*
  - 9.11.1: Qualitative Orgel Diagrams - *Undeclared*
- 9.12: Tanabe-Sugano Diagrams - *Undeclared*
- 9.13: Thermodynamics and Structural Consequences of d-Orbital Splitting - *Undeclared*

10: Ligand Field Theory - *Undeclared*
- 10.1: Ligand Field Theory Fundamentals - *Undeclared*

11: Spectroscopic Techniques - *Undeclared*
- 11.1: Fundamentals of Electron Absorption Spectroscopy - *CC BY-SA 4.0*
- 11.2: Basics of Spectroscopy - *Undeclared*
  - 11.2.1: Breakdown of EM Radiation - *Undeclared*
- 11.3: Electronic Spectroscopy - *Undeclared*
- 11.4: Vibrational Spectroscopy - *Undeclared*
- 11.5: X-ray Spectroscopy - *Undeclared*
  - 11.5.1: Extended X-ray Absorption Fine Structure (EXAFS) - *Undeclared*
  - 11.5.2: X-ray Absorption Near Edge Structure (XANES) - *Undeclared*
  - 11.5.3: X-ray Absorption Spectroscopy (XAS) - *Undeclared*
- 11.6: Magnetic Resonance Spectroscopies - *Undeclared*
  - 11.6.1: NMR Animations - *Undeclared*
    - 11.6.1.1: Basic Concepts - *Undeclared*
      - 11.6.1.1.1: Magnetic Resonance Imaging - *Undeclared*
    - 11.6.1.2: pi Pulses - *Undeclared*
    - 11.6.1.3: Pulsed NMR Introduction - *Undeclared*
    - 11.6.1.4: Spin Echo - *Undeclared*

Back Matter - *Undeclared*
- Index - *Undeclared*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*