CHEM 4210: INORGANIC CHEM II



Tasneem Siddiquee
Tennessee State University

LibreTexts™

Inorganic Chemistry II (CHEM4210)

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 06/08/2025

TABLE OF CONTENTS

Licensing

1: Basic Inorganic Concepts

- 1.1: Introduction to Inorganic Chemistry
  - 1.1.1: What is Inorganic Chemistry?
  - 1.1.2: Inorganic vs Organic Chemistry
  - 1.1.3: History of Inorganic Chemistry
  - 1.1.4: Perspectives
  - 1.1.5: Practice problems
- 1.2: Atomic Structure
  - 1.2.1: Historical Development of Atomic Theory
    - 1.2.1.1: The Periodic Table
    - 1.2.1.2: Discovery of Subatomic Particles and the Bohr Atom
  - 1.2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions
    - 1.2.2.1: Particle in a Box
    - 1.2.2.2: Quantum Numbers and Atomic Wave Functions
    - 1.2.2.3: Aufbau Principle
    - 1.2.2.4: Shielding
  - 1.2.3: Periodic Properties of Atoms
    - 1.2.3.1: Ionization energy
    - 1.2.3.2: Electron Affinity
    - 1.2.3.3: Covalent and Ionic Radii
  - 1.2.4: Problems
- 1.3: Simple Bonding Theory
  - 1.3.1: Lewis Electron-Dot Diagrams
    - 1.3.1.1: Resonance
    - 1.3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)
    - 1.3.1.3: Formal Charge
    - 1.3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium
  - 1.3.2: Valence Shell Electron-Pair Repulsion
    - 1.3.2.1: Lone Pair Repulsion
    - 1.3.2.2: Multiple Bonds
    - 1.3.2.3: Electronegativity and Atomic Size Effects
    - 1.3.2.4: Ligand Close Packing
  - 1.3.3: Molecular Polarity
  - 1.3.4: Hydrogen Bonding
  - 1.3.5: Problems
- 1.4: Symmetry and Group Theory
  - 1.4.1: Symmetry Elements and Operations
  - 1.4.2: Point Groups
    - 1.4.2.1: Groups of Low and High Symmetry
    - 1.4.2.2: Other Groups
  - 1.4.3: Properties and Representations of Groups
    - 1.4.3.1: Matrices

- 1.4.3.2: Representations of Point Groups
- 1.4.3.3: Character Tables
- 1.4.4: Examples and Applications of Symmetry
  - 1.4.4.1: Chirality
  - 1.4.4.2: Molecular Vibrations
- 1.4.P: Problems (under construction)

2: d-Block Metal Chemistry- General Considerations

- 2.1: Prelude to Coordination Chemistry I - Structure and Isomers
- 2.2: History
- 2.3: Nomenclature and Ligands
- 2.4: Isomerism
- 2.5: Coordination Numbers and Structures
- 2.6: Coordination Frameworks
- 2.P: Problems

3: d-Block Metal Chemistry- Coordination Complexes

- 3.1: Evidence for Electronic Structures
  - 3.1.1: Thermodynamic Data
  - 3.1.2: Magnetic Susceptibility
  - 3.1.3: Electronic Spectra
  - 3.1.4: Coordination Number and Molecular Shapes
- 3.2: Bonding Theories
  - 3.2.1: Crystal Field Theory
- 3.3: Ligand Field Theory
  - 3.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex
  - 3.3.2: Orbital Splitting and Electron Spin
  - 3.3.3: Ligand Field Stabilization Energy
  - 3.3.4: Tetrahedral Complexes
  - 3.3.5: Square-Planar Complexes
- 3.4: Angular Overlap
  - 3.4.1: Sigma Bonding in the Angular Overlap Model
  - 3.4.2: Pi Acceptors in the Angular Overlap Model
  - 3.4.3: Pi Donors in the Angular Overlap Model
  - 3.4.4: The Spectrochemical Series
  - 3.4.5: The Magnitude of Parameters $e\sigma$, $e\pi$ and Δ
  - 3.4.6: The Magnetochemical Series
- 3.5: The Jahn-Teller Effect
- 3.6: Four- and Six-Coordinate Preferences
- 3.7: Other Shapes
- 3.P: Problems

4: d-Block Metal Chemistry

- 4.1: Properties of Transition Metals
  - 4.1.1: A Brief Survey of Transition-Metal Chemistry
  - 4.1.2: Electron Configuration of Transition Metals
  - 4.1.3: General Trends among the Transition Metals
  - 4.1.4: Introduction to Transition Metals I

- 4.1.5: Introduction to Transition Metals II
- 4.1.6: Metallurgy
  - 4.1.6.1: An Introduction to the Chemistry of Metal Extraction
  - 4.1.6.2: The Extraction of Copper
  - 4.1.6.3: The Extraction of Iron
    - 4.1.6.3.1: Iron Production
  - 4.1.6.4: The Extraction of Silver
    - 4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate
- 4.1.7: Oxidation States of Transition Metals
- 4.1.8: Transition Metals in Biology

- 4.2: Transition Metals
  - 4.2.1: Chemistry of Actinium
  - 4.2.2: Chemistry of Lanthanum
  - 4.2.3: Chemistry of Scandium
  - 4.2.4: Chemistry of Yttrium
  - 4.2.5: Group 3 Elemental Properties
- 4.3: Transition Metals
  - 4.3.1: Group 4 Elemental Properties
  - 4.3.2: Chemistry of Hafnium
  - 4.3.3: Chemistry of Rutherfordium
  - 4.3.4: Chemistry of Titanium
  - 4.3.5: Chemistry of Zirconium
- 4.4: Transition Metals
  - 4.4.1: Chemistry of Dubnium
  - 4.4.2: Chemistry of Niobium
  - 4.4.3: Chemistry of Tantalum
  - 4.4.4: Chemistry of Vanadium
  - 4.4.5: Group 5 Elemental Properties
- 4.5: Transition Metals
  - 4.5.1: Chemistry of Chromium
    - 4.5.1.1: Chemistry of Chromium
    - 4.5.1.2: Potassium Chromium Sulfate
  - 4.5.2: Chemistry of Molybdenum
    - 4.5.2.1: Molybdenum Disulfide
  - 4.5.3: Chemistry of Seaborgium
  - 4.5.4: Chemistry of Tungsten
- 4.6: Transition Metals
  - 4.6.1: Chemistry of Bohrium
  - 4.6.2: Chemistry of Manganese
    - 4.6.2.1: Chemistry of Manganese
  - 4.6.3: Chemistry of Rhenium
  - 4.6.4: Chemistry of Technetium
- 4.7: Transition Metals
  - 4.7.1: Chemistry of Hassium
  - 4.7.2: Chemistry of Iron
    - 4.7.2.1: Iron in Humans
  - 4.7.3: Chemistry of Osmium
  - 4.7.4: Chemistry of Ruthenium

- 4.8: Transition Metals
  - 4.8.1: Chemistry of Cobalt
  - 4.8.2: Chemistry of Iridium
  - 4.8.3: Chemistry of Meitnerium
  - 4.8.4: Chemistry of Rhodium
- 4.9: Transition Metals
  - 4.9.1: Chemistry of Darmstadtium
  - 4.9.2: Chemistry of Nickel
  - 4.9.3: Chemistry of Palladium
  - 4.9.4: Chemistry of Platinum
- 4.10: Transition Metals
  - 4.10.1: Chemistry of Copper
  - 4.10.2: Chemistry of Gold
  - 4.10.3: Chemistry of Roentgenium
  - 4.10.4: Chemistry of Silver
    - 4.10.4.1: Silver Chloride
    - 4.10.4.2: Silver Nitrate
- 4.11: Transition Metals
  - 4.11.1: Chemistry of Cadmium
    - 4.11.1.1: Cadmium Sulfide
  - 4.11.2: Chemistry of Copernicium
  - 4.11.3: Chemistry of Mercury
  - 4.11.4: Chemistry of Zinc

5: Reactions of Complexes

- 5.1: Introduction to Reactions of Metal Complexes
- 5.2: Substitutions Reactions
  - 5.2.1: Introduction to Substitution Reactions
  - 5.2.2: Inert and Labile Complexes
  - 5.2.3: Mechanistic Possibilities
- 5.3: Kinetics Hint at the Reaction Mechanism
  - 5.3.1: Rate Law for Dissociative Mechanisms
  - 5.3.2: Rate Laws for Interchange Mechanisms
  - 5.3.3: Rate Law for Associative Mechanisms
  - 5.3.4: Preassociation Complexes
  - 5.3.5: Activation Parameters
  - 5.3.6: Some Reasons for Differing Mechanisms
- 5.4: Experimental Evidence in Octahedral Substitutions
  - 5.4.1: Dissociation
  - 5.4.2: Linear Free Energy Relationships
  - 5.4.3: Associative Mechanisms
  - 5.4.4: The conjugate base mechanism
  - 5.4.5: The Kinetic Chelate Effect
- 5.5: Stereochemistry of Octahedral Reactions
  - 5.5.1: Substitution in trans-en octahedral complexes
  - 5.5.2: Substitution in cis-en octahedral complexes
  - 5.5.3: Isomerization of Chelate Rings
- 5.6: Substitutions in Square Planar Complexes

- 5.6.1: Kinetics and Stereochemistry of Square Planar Reactions
- 5.6.2: Evidence for Associative Reactions
- 5.7: The Trans Effect
- 5.8: Redox Mechanisms
  - 5.8.1: Outer Sphere Electron Transfer
  - 5.8.2: Inner Sphere Electron Transfer
- 5.9: Reactions of Coordinated Ligands
  - 5.9.1: Metal-catalyzed Hydrolysis
  - 5.9.2: Template Reactions
  - 5.9.3: Electrophilic Substitutions

6: Catalysis

- 6.1: Introduction to Organometallic Chemistry
- 6.2: Nomenclature, Ligands, and Classification
- 6.3: Electron Counting in Organometallic Complexes
  - 6.3.1: The 18 Electron Rule
  - 6.3.2: Simplifying the Organometallic Complex by Deconstruction
- 6.4: Survey of Organometallic Ligands
  - 6.4.1: Carbon Monoxide (Carbonyl Complexes)
  - 6.4.2: Ligands similar to CO
  - 6.4.3: Hydrides and Dihydrogen Complexes
- 6.5: Bonding between Metal Atoms and Organic Pi Systems
  - 6.5.1: Linear π Systems
  - 6.5.2: Cyclic π systems
  - 6.5.3: Odd-numbered π Systems
  - 6.5.4: Fullerene Complexes
- 6.6: Metal-Carbon Bonds
  - 6.6.1: Metal Alkyls
  - 6.6.2: Carbenes
  - 6.6.3: Carbyne (Alkylidyne) Complexes
  - 6.6.4: Carbido and Cumulene Complexes
  - 6.6.5: Carbon Wires- Polyyne and Polyene Bridges
- 6.7: Characterization of Organometallic Complexes

7: Organometallic Reactions and Catalysis

- 7.1: Reactions Involving Gain or Loss of Ligands
  - 7.1.1: Ligand Dissociation and Substitution
  - 7.1.2: Oxidative Addition
  - 7.1.3: Reductive Elimination
  - 7.1.4: Sigma Bond Metathasis
  - 7.1.5: Application of Pincer Ligands
- 7.2: Reactions Invloving Modification of Unsaturated Ligands
  - 7.2.1: Introduction to Insertion
  - 7.2.2: CO Insertions (Alkyl Migration)
  - 7.2.3: Migratory Insertion-1,2-Insertions
  - 7.2.4: β-Elimination Reactions
  - 7.2.5: Abstraction and Addition
- 7.3: Organometallic Catalysts

- 7.3.1: Catalytic Deuteration
- 7.3.2: Hydroformylation
- 7.3.3: Monsanto Acetic Acid Process
- 7.3.4: Wacker (Smidt) Process
- 7.3.5: Hydrogenation by Wilkinson's Catalyst
- 7.3.6: Olefin Metathesis
- 7.4: Heterogeneous Catalysts
  - 7.4.1: Ziegler-Natta Polymerizations
  - 7.4.2: Water-Gas Shift Reaction
- 7.5: Problems
  - 7.5.1: Concept Review Questions Chapter 12
  - 7.5.2: Homework Problems Chapter 12

8: Lanthanides and Actinides

- 8.1: The Lanthanides
  - 8.1.1: Lanthanides- Properties and Reactions
    - 8.1.1.1: Lanthanide Contraction
  - 8.1.2: Chemistry of Cerium
  - 8.1.3: Chemistry of Dysprosium
  - 8.1.4: Chemistry of Europium
  - 8.1.5: Chemistry of Gadolinium
    - 8.1.5.1: Gadolinium(III) Chloride
  - 8.1.6: Chemistry of Holmium
  - 8.1.7: Chemistry of Lutetium
  - 8.1.8: Chemistry of Neodymium
  - 8.1.9: Chemistry of Praseodymium
  - 8.1.10: Chemistry of Promethium
  - 8.1.11: Chemistry of Samarium
  - 8.1.12: Chemistry of Terbium
  - 8.1.13: Chemistry of Thulium
  - 8.1.14: Chemistry of Ytterbium
  - 8.1.15: Chemistry of Yttrium
- 8.2: The Actinides
  - 8.2.1: General Properties and Reactions of The Actinides
  - 8.2.2: Chemistry of Americium
  - 8.2.3: Chemistry of Berkelium
  - 8.2.4: Chemistry of Californium
  - 8.2.5: Chemistry of Curium
  - 8.2.6: Chemistry of Einsteinium
  - 8.2.7: Chemistry of Fermium
  - 8.2.8: Chemistry of Lawrencium
  - 8.2.9: Chemistry of Mendelevium
  - 8.2.10: Chemistry of Neptunium
  - 8.2.11: Chemistry of Nobelium
  - 8.2.12: Chemistry of Plutonium
  - 8.2.13: Chemistry of Protoactinium
  - 8.2.14: Chemistry of Thorium
  - 8.2.15: Chemistry of Uranium

9: Inorganic Materials and Nanotechnology

- 9.1: Electronic Properties of Materials - Superconductors and Semiconductors
  - 9.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors
  - 9.1.2: Metal-Insulator Transitions
  - 9.1.3: Superconductors
  - 9.1.4: Periodic Trends- Metals, Semiconductors, and Insulators
  - 9.1.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping
  - 9.1.6: Semiconductor p-n Junctions
  - 9.1.7: Diodes, LEDs and Solar Cells
  - 9.1.8: Amorphous Semiconductors
  - 9.1.9: Discussion Questions
  - 9.1.10: Problems
  - 9.1.11: References
- 9.2: Basic Science of Nanomaterials
  - 9.2.1: Prelude to Basic Science of Nanomaterials
  - 9.2.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets
  - 9.2.3: Semiconductor Quantum Dots
  - 9.2.4: Synthesis of Semiconductor Nanocrystals
  - 9.2.5: Surface Energy
  - 9.2.6: Nanoscale Metal Particles
  - 9.2.7: Applications of Nanomaterials
  - 9.2.8: Discussion Questions
  - 9.2.9: Problems
  - 9.2.10: References

Index

Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Basic Inorganic Concepts

1.1: Introduction to Inorganic Chemistry
1.1.1: What is Inorganic Chemistry?
1.1.2: Inorganic vs Organic Chemistry
1.1.3: History of Inorganic Chemistry
1.1.4: Perspectives
1.1.5: Practice problems
1.2: Atomic Structure
1.2.1: Historical Development of Atomic Theory
1.2.1.1: The Periodic Table
1.2.1.2: Discovery of Subatomic Particles and the Bohr Atom
1.2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions
1.2.2.1: Particle in a Box
1.2.2.2: Quantum Numbers and Atomic Wave Functions
1.2.2.3: Aufbau Principle
1.2.2.4: Shielding
1.2.3: Periodic Properties of Atoms
1.2.3.1: Ionization energy
1.2.3.2: Electron Affinity
1.2.3.3: Covalent and Ionic Radii
1.2.4: Problems
1.3: Simple Bonding Theory
1.3.1: Lewis Electron-Dot Diagrams
1.3.1.1: Resonance
1.3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)
1.3.1.3: Formal Charge
1.3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium
1.3.2: Valence Shell Electron-Pair Repulsion
1.3.2.1: Lone Pair Repulsion
1.3.2.2: Multiple Bonds
1.3.2.3: Electronegativity and Atomic Size Effects
1.3.2.4: Ligand Close Packing
1.3.3: Molecular Polarity
1.3.4: Hydrogen Bonding
1.3.5: Problems
1.4: Symmetry and Group Theory
1.4.1: Symmetry Elements and Operations
1.4.2: Point Groups
1.4.2.1: Groups of Low and High Symmetry
1.4.2.2: Other Groups
1.4.3: Properties and Representations of Groups
1.4.3.1: Matrices

1.4.3.2: Representations of Point Groups
1.4.3.3: Character Tables
1.4.4: Examples and Applications of Symmetry
1.4.4.1: Chirality
1.4.4.2: Molecular Vibrations
1.4.P: Problems (under construction)

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

SECTION OVERVIEW

1.1: Introduction to Inorganic Chemistry

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

1.1.1: What is Inorganic Chemistry?

1.1.2: Inorganic vs Organic Chemistry

1.1.3: History of Inorganic Chemistry

1.1.4: Perspectives

1.1.5: Practice problems

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

1.1.1: 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 1.1.1.1. 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.

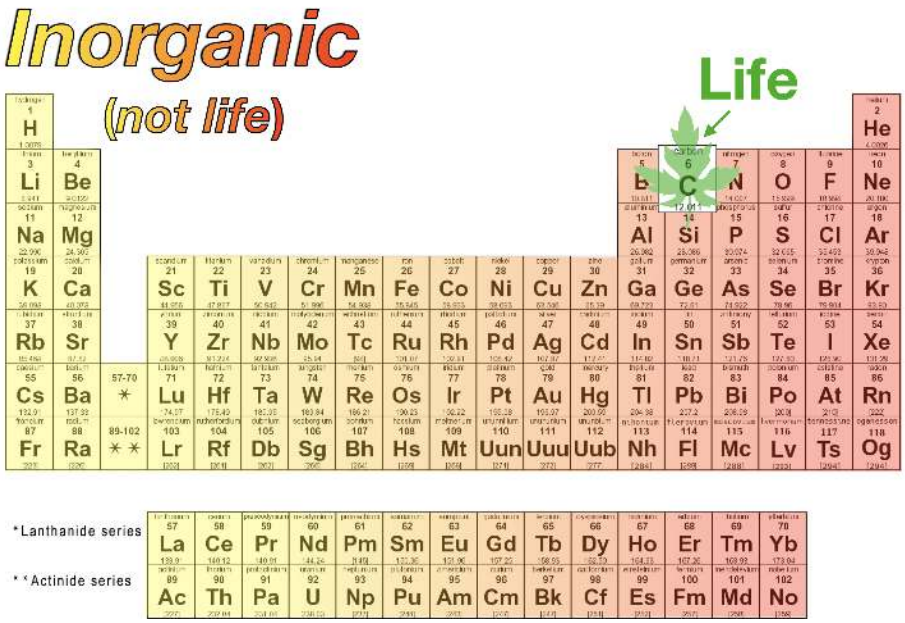


Figure 1.1.1.1. An illustration of the historic meaning of "organic" and "inorganic". The modern understanding of organic and inorganic chemistry is not consistent with these historical meanings. (Kathryn Haas; CC-NC-BY-SA)

External links:

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

Practice

? What are the Sub-Fields of Inorganic Chemistry?

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

Answer

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

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

1.1.1: What is Inorganic Chemistry? is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **1.1: What is Inorganic Chemistry?** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

1.1.2: Inorganic vs Organic Chemistry

The division between the fields of Inorganic and Organic chemistry has become blurred. For example, let's look at one of the major classes of catalysts used for organic synthesis reactions: organometalic catalysts (Figure 1.1.2.1). 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 1.1.2.1, right) and a cobalt-carbon bond.

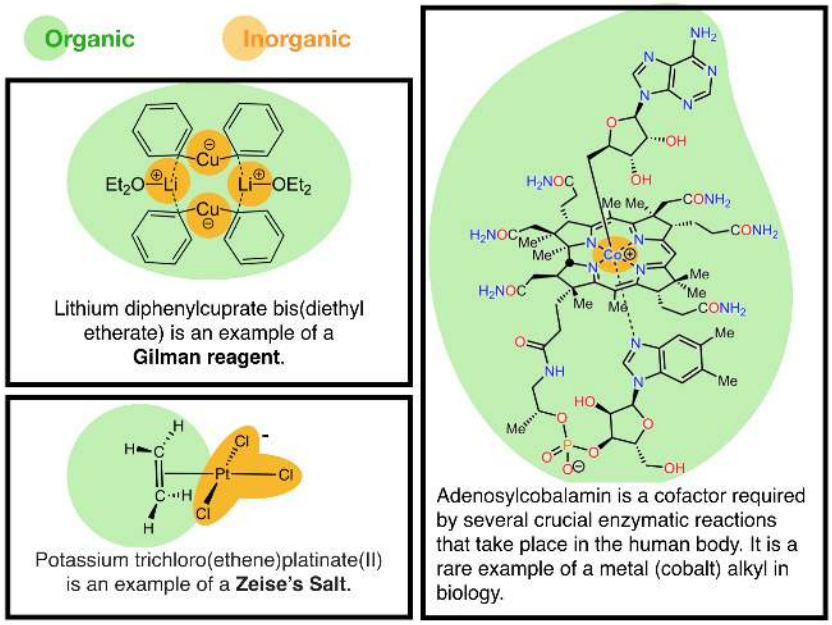


Figure 1.1.2.1: Some examples of organometallic catalysts. These compounds catalyze organic reactions or biochemical reactions and they are compounds that contain both carbon and metals. These compounds are examples of molecules that cannot be defined only as organic molecules or only as inorganic molecules. Adenosylcobalbumin is an example of an organometallic catalyst that is present in biology, further illustrating that "inorganic" metals are important cofactors in biology. This image is based on information on the Wikipedia article on Organometallic Chemistry and is created from images found there; attribution to images created by Alsosaid1987, AdoCbl-ColorCoded, CC BY-SA 4.0 and Smokefoot, Zeise'sSalt, CC BY-SA 3.0. (Kathryn Haas; CC-BY-SA)

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

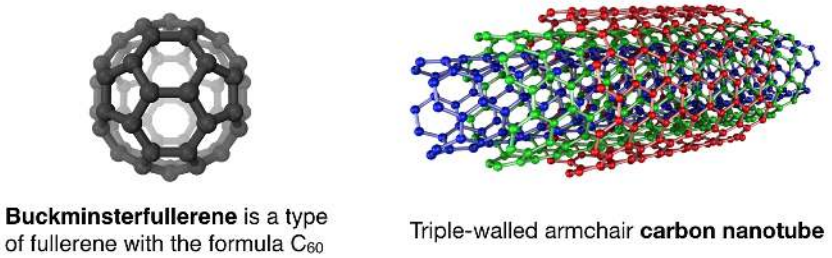


Figure 1.1.2.2: This figure is created from information found on the Wikipedia articles for Buckmisterfullerene and carbon nanotubes. Attribution Eric Wieser, Multi-walled Carbon Nanotube, CC BY-SA 3.0. (Kathryn Haas; CC-BY-SA)

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

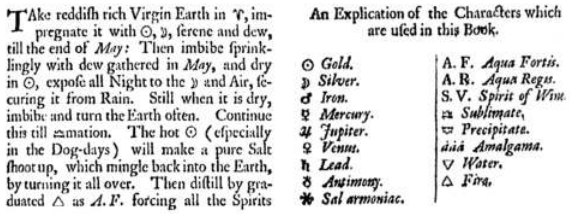
This page titled 1.1.2: Inorganic vs Organic Chemistry is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **1.2: Inorganic vs Organic Chemistry** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

1.1.3: History of Inorganic Chemistry

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

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


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

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

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

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

Figure 1.1.3.1. 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.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{1.1.3.1}$$

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

1.1.3: History of Inorganic Chemistry is shared under a CC BY-NC-SA 4.0 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.

1.1.4: 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

1.1.4: 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.

1.1.5: 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?

1.1.5: 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.

SECTION OVERVIEW

1.2: Atomic Structure

1.2.1: Historical Development of Atomic Theory

1.2.1.1: The Periodic Table
1.2.1.2: Discovery of Subatomic Particles and the Bohr Atom

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

1.2.2.1: Particle in a Box
1.2.2.2: Quantum Numbers and Atomic Wave Functions
1.2.2.3: Aufbau Principle
1.2.2.4: Shielding

1.2.3: Periodic Properties of Atoms

1.2.3.1: Ionization energy
1.2.3.2: Electron Affinity
1.2.3.3: Covalent and Ionic Radii

1.2.4: Problems

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

1.2.1: 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* 1.2.1.1*:* 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 1.2.1.1). 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 1.2.1.2).
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 1.2.1.3).

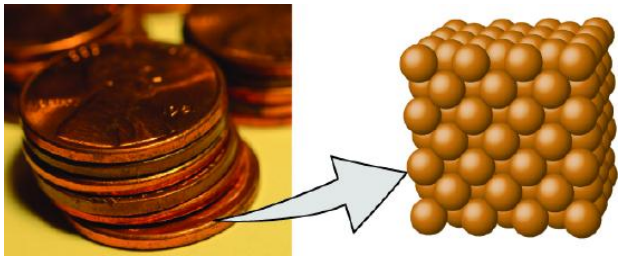


Figure 1.2.1.1: *A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)*

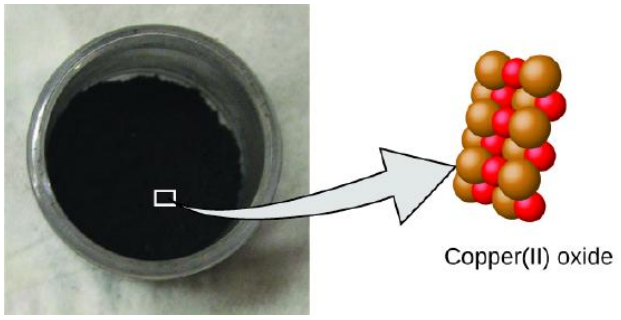


Figure 1.2.1.2: *Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)*

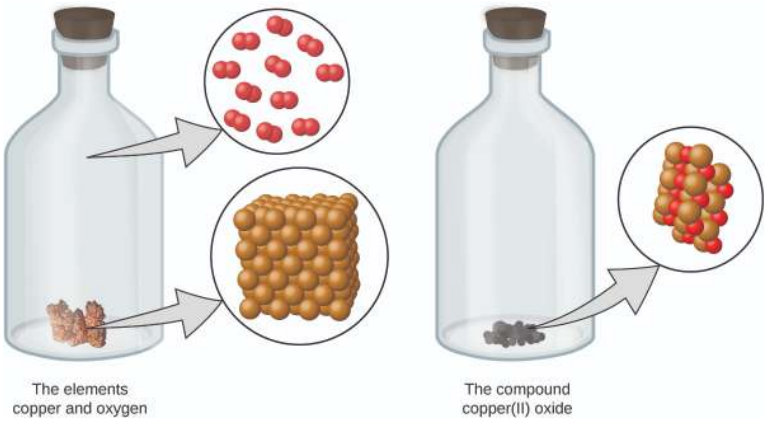


Figure 1.2.1.3*: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work 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* 1.2.1.2*: "We are made of star stuff" - Carl Sagan.

Example 1.2.1.1: 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?

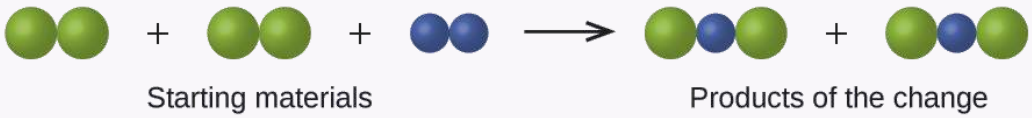


Solution

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 1.2.1.1

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 1.2.1.1.

Table* 1.2.1.1*: 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.

$$\frac{\frac{1.116\text{ g Cl}}{1\text{ g Cu}}}{\frac{0.558\text{ g Cl}}{1\text{ g Cu}}} = \frac{2}{1} \tag{1.2.1.1}$$

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 1.2.1.4).

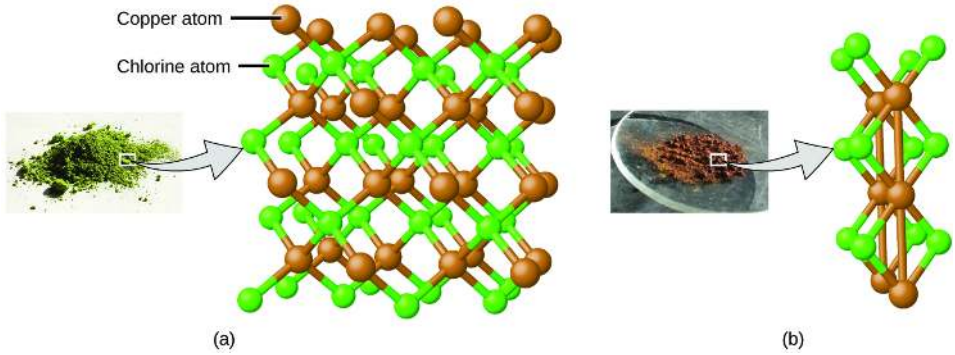


***Figure* 1.2.1.4**: *Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)*

Example 1.2.1.2: 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 1.2.1.2

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 1.2.1.1).

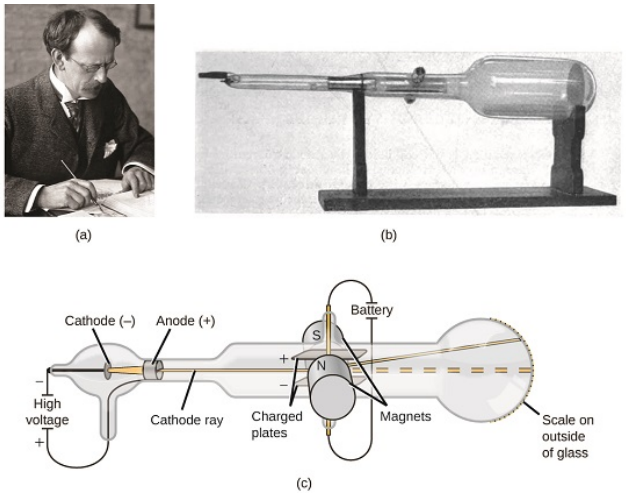
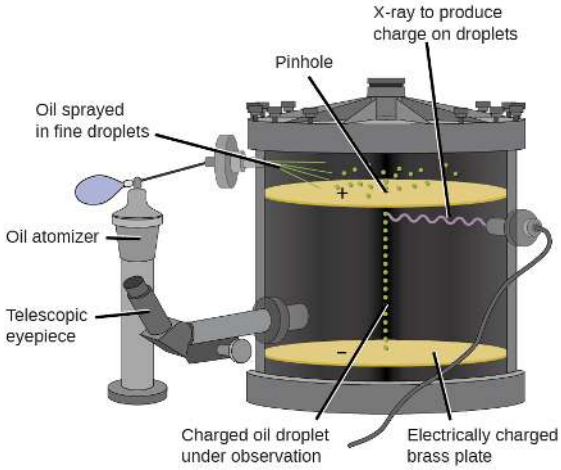


***Figure* 1.2.1.5** *: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at 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 1.2.1.2).



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* 1.2.1.6*: *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 1.2.1.3).

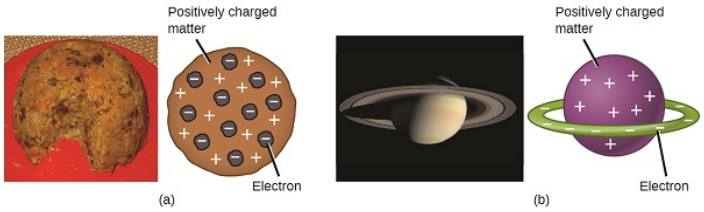


***Figure* 1.2.1.7** *: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification 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 1.2.1.4). 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).

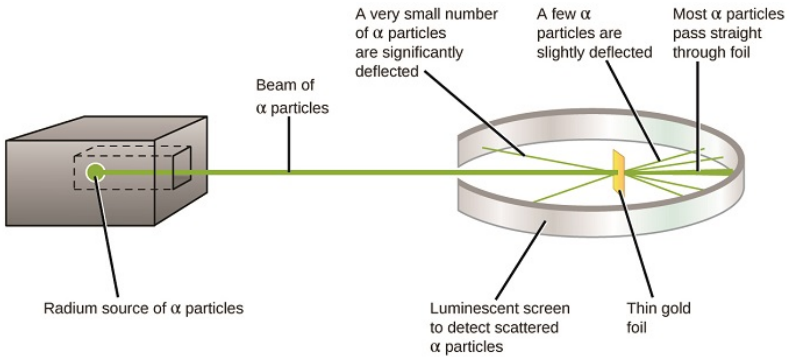


Figure* 1.2.1.8*: *Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly 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 1.2.1.5).

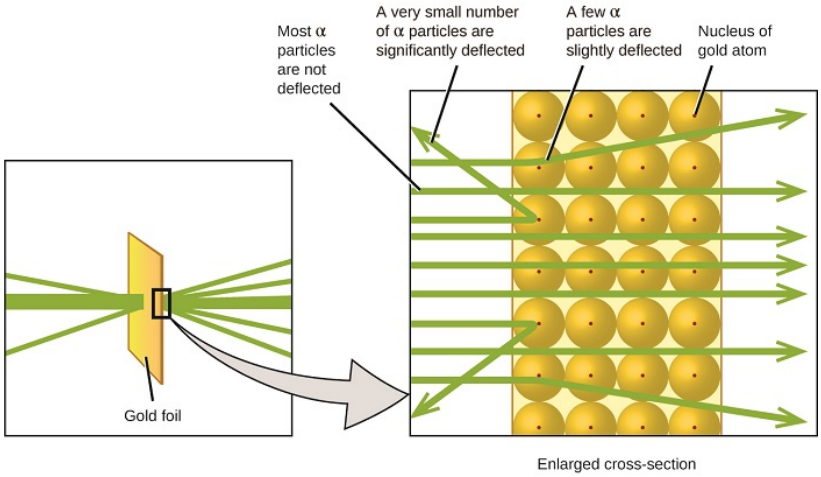
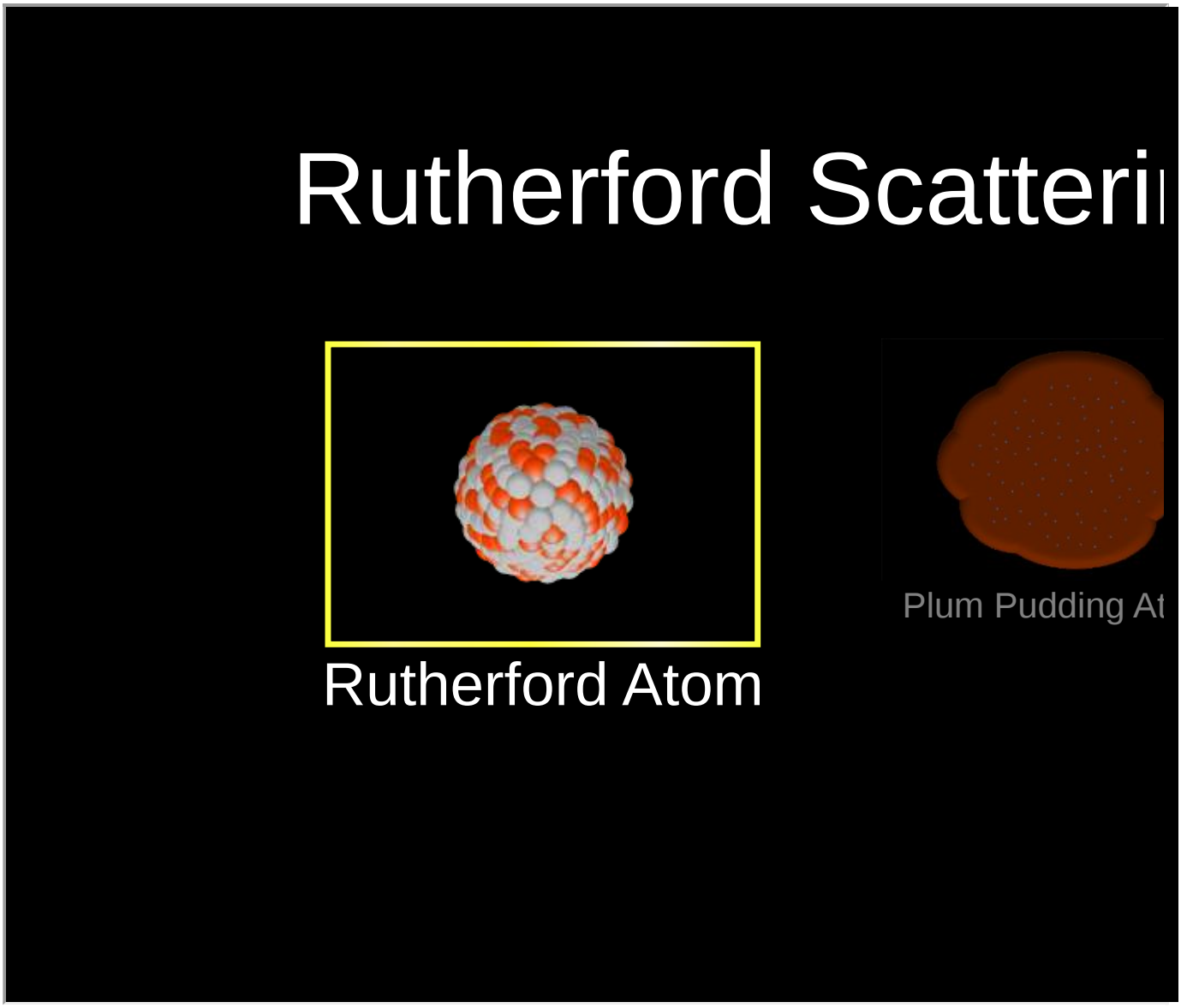


***Figure* 1.2.1.9** *: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied 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* 1.2.1.2*: An Introduction to Subatomic Particles

Summary



***Video* 1.2.1.3*:** A summary of discoveries in atomic theory.*



***Video* 1.2.1.4*:** 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.

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

- **2.1: Historical Development of Atomic Theory** has no license indicated.

1.2.1.1: 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.

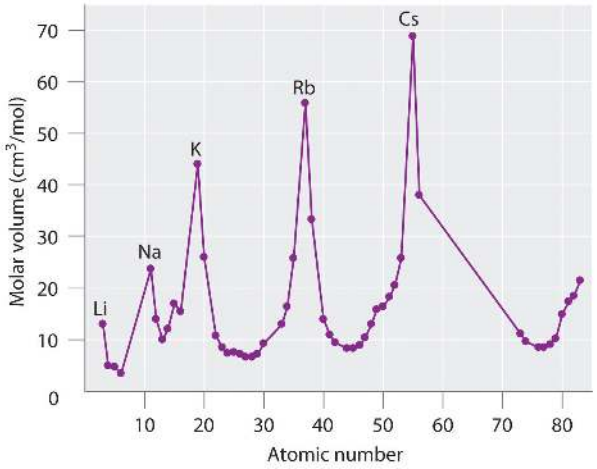


Figure 3.4.2 Variation of atomic volume with atomic number, adapted from Meyer's plot of **1870:** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

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.



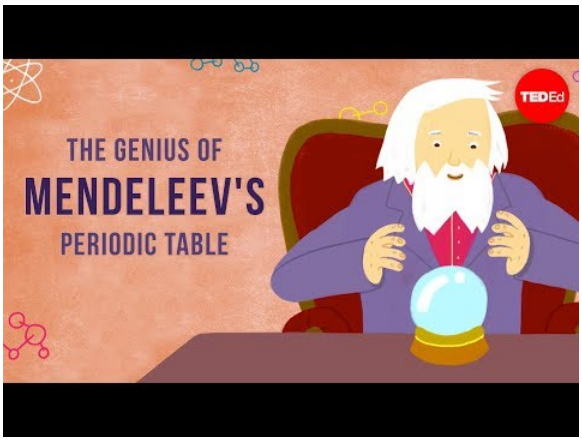


Table 3.4.1 Comparison of the properties predicted by Mendeleev in 1869 for *eka*-aluminum and *eka*-silicon with the properties of gallium (discovered in 1875) and germanium (discovered in 1886)

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.

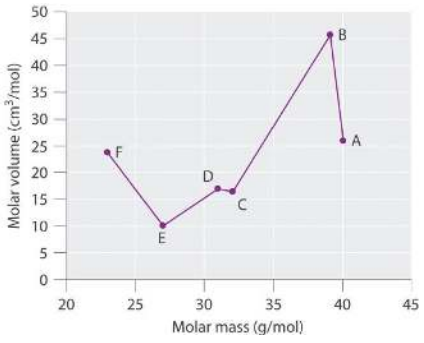
Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

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

1.2.1.1: 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.

1.2.1.2: 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 1.2.1.2.1). 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.

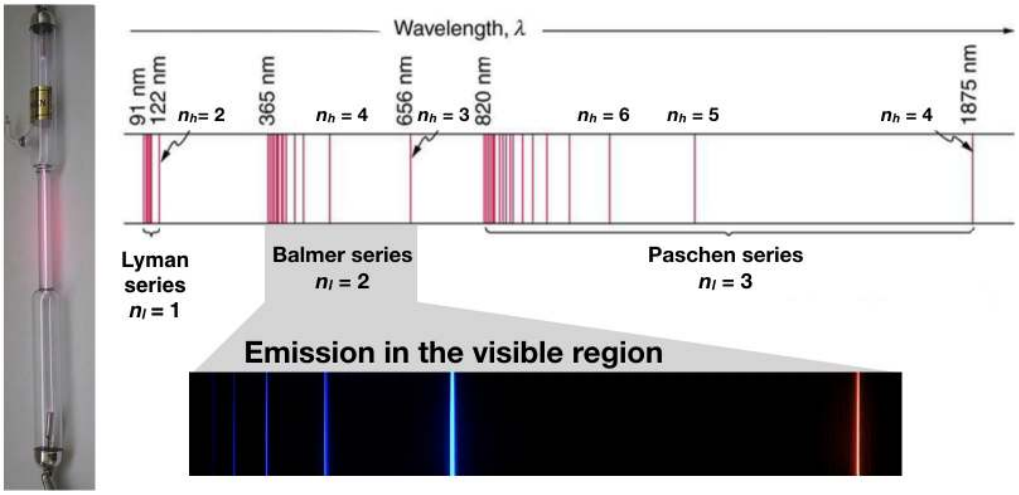


Figure 1.2.1.2.1: The emission of light by hydrogen atoms. (left) A sample of excited hydrogen atoms emits a characteristic red light. (bottom) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and 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:

$$u = constant\ \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{1.2.1.2.1}$$

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*:

$$\frac{1}{\lambda} = R_H\ \left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right) \tag{1.2.1.2.2}$$

,

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., $n_l = 1$)?

$$\frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.2.1.2.3}$$

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

Table 1.2.1.2.1: The Lyman Series of Hydrogen Emission Lines ($n_l = 1$)

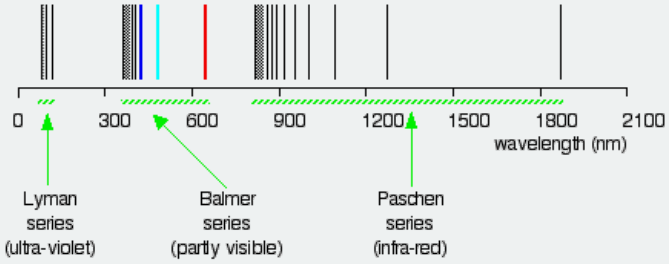
n_h	2	3	4	5
λ (nm)	121	102	97	94
$\tilde{u}$ (cm^{-1})	82,2291	97,530	102,864	105,332

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 1.2.1.2.1: 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 1.2.1.2.1: 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

$$E_n = \frac{-R_H hc}{n^2} \tag{1.2.1.2.4}$$

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.

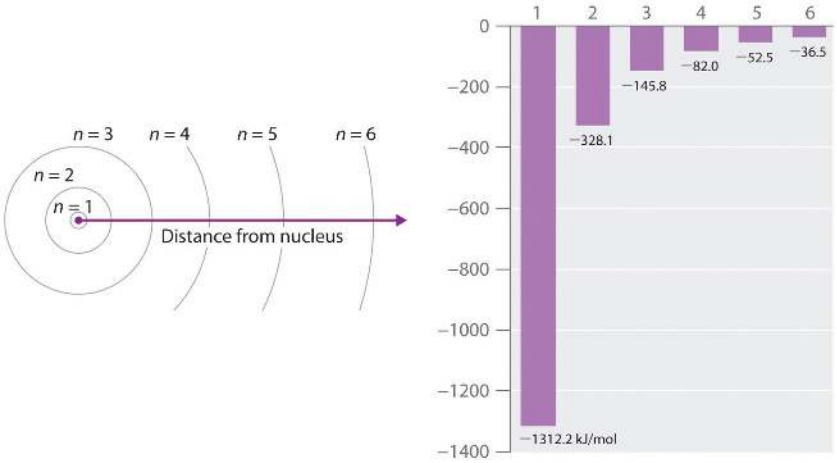
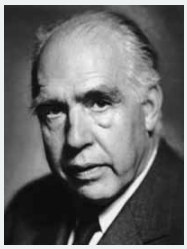


Figure 1.2.1.2.2*: The Bohr Model of the hydrogen atom (a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.*

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 1.2.1.2.2*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 1.2.1.2.1).

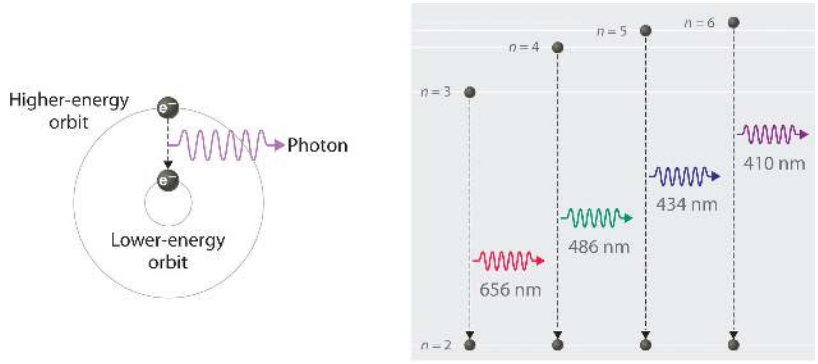


Figure 1.2.1.2.3: *The emission of light by a hydrogen atom in an excited state. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is 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

$$\Delta E = E_{final} - E_{initial} = -\frac{R_H hc}{n_h^2} - \left(-\frac{R_H hc}{n_l^2}\right) = -R_H hc\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{1.2.1.2.5}$$

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 1.2.1.2.3 Substituting *hc*/λ for Δ*E* gives

$$\Delta E = \frac{hc}{\lambda} = -R_H hc\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{1.2.1.2.6}$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -R_H\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{1.2.1.2.7}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 1.2.1.2.6 and 1.2.1.2.7 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 (1.2.1.2.3*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 1.2.1.2.3*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 1.2.1.2.1*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 1.2.1.2.4:

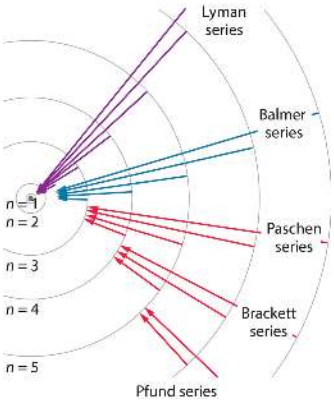


Figure 1.2.1.2.4: Electron transitions responsible for the various series of lines observed in the emission spectrum of hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding 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 1.2.1.2.1: 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 1.2.1.2.1: 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 1.2.1.2.5). 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.

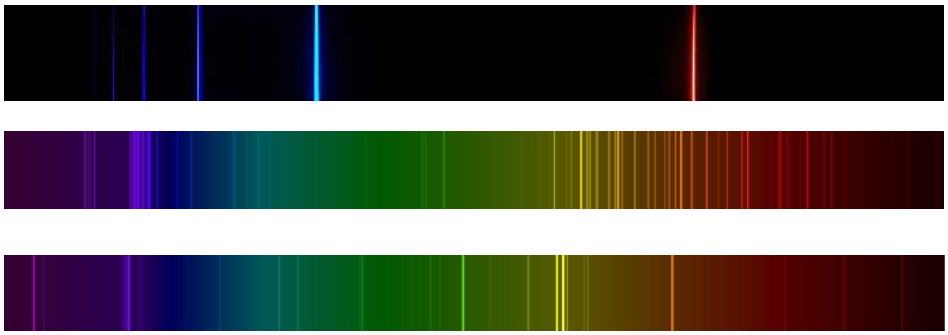


Figure 1.2.1.2.5 : The emission spectra of elements compared to hydrogen. **Top:** hydrogen gas (atomized to hydrogen atoms in the discharge tube). **Middle:** neon. **Bottom:** mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest 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.

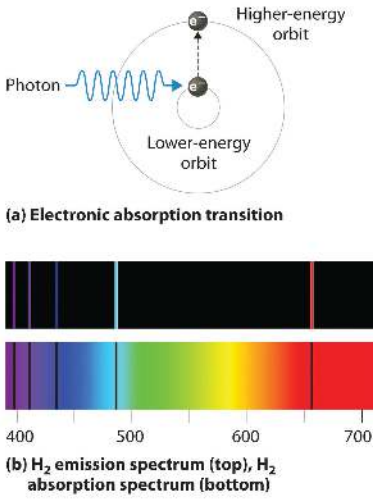


Figure 1.2.1.2.6 : Absorption and emission spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

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 1.2.1.2.7. 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.

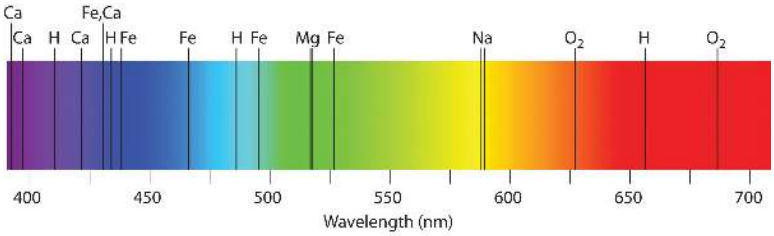


Figure 1.2.1.2.7: *The visible spectrum of sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the 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 1.2.1.2.5 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 1.2.1.2.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

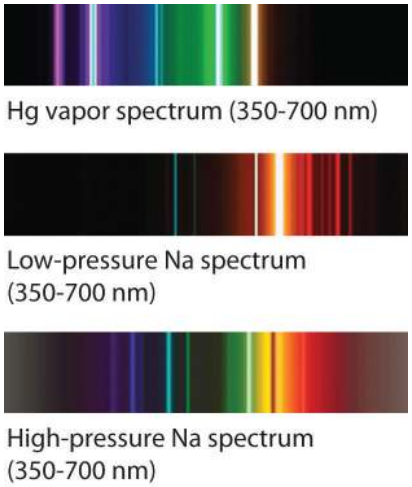


Figure 1.2.1.2.8: *The emission spectra of sodium and mercury. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line 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)

This page titled 1.2.1.2: Discovery of Subatomic Particles and the Bohr Atom is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Anonymous.

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

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

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

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

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

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

The Hamiltonian, $\hat{H}$

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

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

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

Kinetic Energy

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

Potential energy

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

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

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

The Wavefunction, ψ

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

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

Quantum Numbers define ψ

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

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

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

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

Some important considerations and limitations

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

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

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

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

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

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

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

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

Awesome Sources for further reading

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

This page titled 1.2.2: 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: The Schrödinger equation, particle in a box, and atomic wavefunctions** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

1.2.2.1: 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.

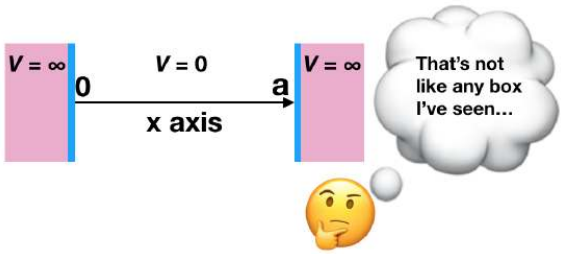


Figure 1.2.2.1.1 . An illustration of the particle in the box model (particle not shown). The box is actually just a one-dimensional space, often assigned to the x-dimension (the x-axis). The particle has wave properties and is trapped in the box. Since no forces act on the particle inside the box, the 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:

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi(x)}{\partial x^2}\right) = E\psi \qquad (1.2.2.1.1)$$

? Exercise 1.2.2.1.1

Follow the steps that were described in the last paragraph to find Equation 1.2.2.1.1 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 1.2.2.1.1

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

The wavefunction of a one-dimensional wave

Although we've simplified the Schrödinger Equation by considering the particle in the box, Equation 1.2.2.1.1 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 1.2.2.1.1. 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:

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-8\pi^2 m_e E}{h^2}\psi = -C\psi \qquad (1.2.2.1.2)$$

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 1.2.2.1.1 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 1.2.2.1.2 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 1.2.2.1.3 (that was the hand-wavy part...see, not so bad):

$$\psi = A\sin(rx) + B\cos(sx) \qquad (1.2.2.1.3)$$

A, B, r, and s are constants in Equation 1.2.2.1.3. 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 1.2.2.1.3 into Equation 1.2.2.1.1 and solve for r and s, we find the expressions below.

$$r = s = \sqrt{2m_e E}\left(\frac{2\pi}{h}\right) \qquad (1.2.2.1.4)$$

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 1.2.2.1.2: Prove that Equation 1.2.2.1.3 is true

Show that Equation 1.2.2.1.3 is true in the case that Equation 1.2.2.1.2 ($\frac{\partial^2\psi(x)}{\partial x^2} = -C\psi$) is true. Also consider Equation 1.2.2.1.4 (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 1.2.2.1.3 is true by substituting 1.2.2.1.3 back into Equation 1.2.2.1.2 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 1.2.2.1.4 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 1.2.2.1.4

*Complete Exercise 1.2.2.1.2before attempting this one.

Derive the expression for r below (from Equation 1.2.2.1.4) using the 1-D wavefunction (1.2.2.1.3 $\psi = A\sin(rx) + B\cos(sx)$) and the 1-D Schrödinger equation (1.2.2.1.1: $\left(\frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi(x)}{\partial x^2}\right) = E\psi\right)$).

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

Answer

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

(1) Rearrange

Let's move **all constants** to the right side of 1.2.2.1.1so that we arrive at the expression that is shown in part of Equation 1.2.2.1.2

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

(2) Take the second derivative of ψ, which we found in Exercise 1.2.2.1.2

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

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 1.2.2.1.2.

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

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 1.2.2.1.1, 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:

$$\psi = A\sin(rx) \tag{1.2.2.1.5}$$

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:

$$r = \frac{n\pi}{a} \tag{1.2.2.1.6}$$

and substitute the value $r = \frac{n\pi}{a}$ into Equation 1.2.2.1.5to get:

$$\psi = A\sin\left(\frac{n\pi x}{a}\right) \tag{1.2.2.1.7}$$

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 1.2.2.1.7, and we have a wavefunction that can be visualized using any graphing program/calculator!

$$\psi = \sqrt{\frac{2}{a}}\left(\sin\left(\frac{n\pi x}{a}\right)\right) \tag{1.2.2.1.8}$$

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 1.2.2.1.4and 1.2.2.1.6) equal to one another and then solve for E:

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

$$E = \frac{n^2h^2}{8ma^2} \tag{1.2.2.1.9}$$

Expression 1.2.2.1.9can 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 1.2.2.1.2 You could create plots similar to these simply by plotting the function shown in Equation 1.2.2.1.8 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.

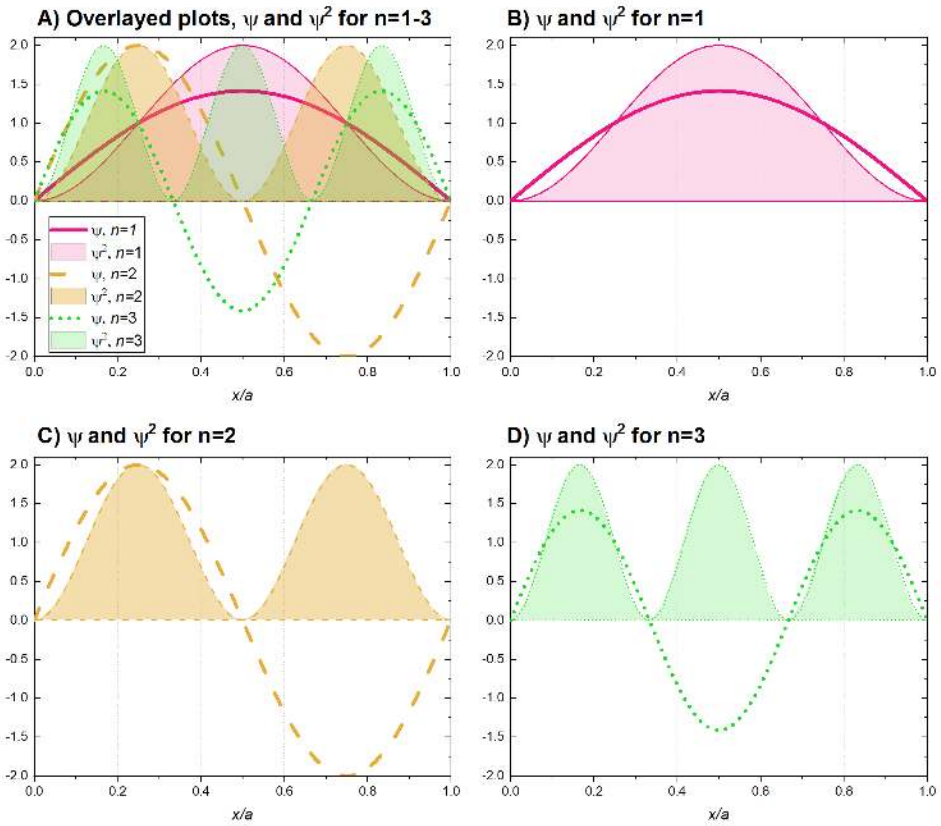


Figure 1.2.2.1.2. Plots of the 1-D ψ and ψ^2 for $n = 1$, $n = 2$, and $n = 3$ of a box of length a. The wavefunction (ψ) is plotted as a thick solid, dashed, or dotted line. The square of the wavefunction (ψ), which represents the probability of finding the particle at position x, is plotted as the 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 1.2.2.1.2 B. The solution of $n = 2$ is plotted in Figure 1.2.2.1.2 C, and so on. These values for n are some of the possible solutions to the 1-dimensional ψ, and they yield descriptions of the wave behavior and probability of finding a particle in 1-dimensional space.

How does this apply to atoms?

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

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

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

https://chem.libretexts.org/@go/page/429116

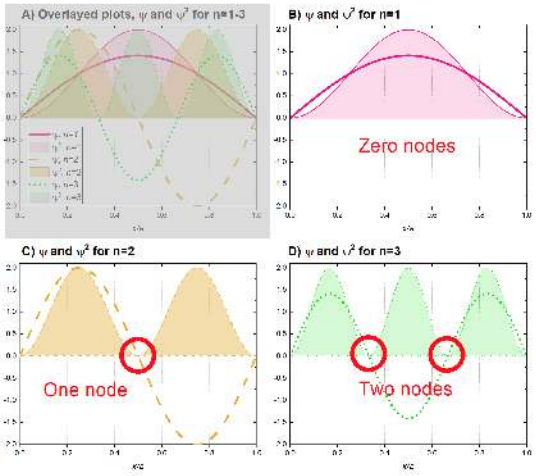
A change in sign of the ψ (and where both $psi = 0$ and $\psi^2 = 0$) is a node. In both the 1-dimensional particle in a box model and in the more realistic 3-dimensional case, a node is found where the ψ changes sign. At this point, $\psi = \psi^2 = 0$; in other words there is zero probability of finding 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 1.2.2.1.4

Identify the points on plots B, C, and D in Figure 1.2.2.1.2that 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 1.2.2.1.5

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 1.2.2.1.8):

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

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

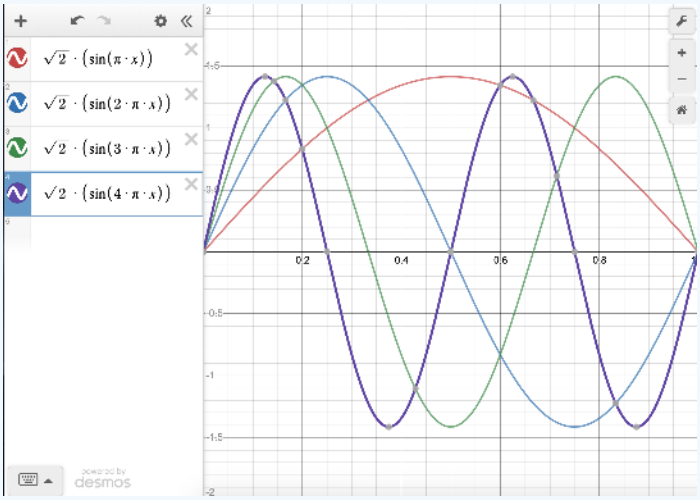
For n=2,3,4 you would repeat the process above. You will get the following functions:

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

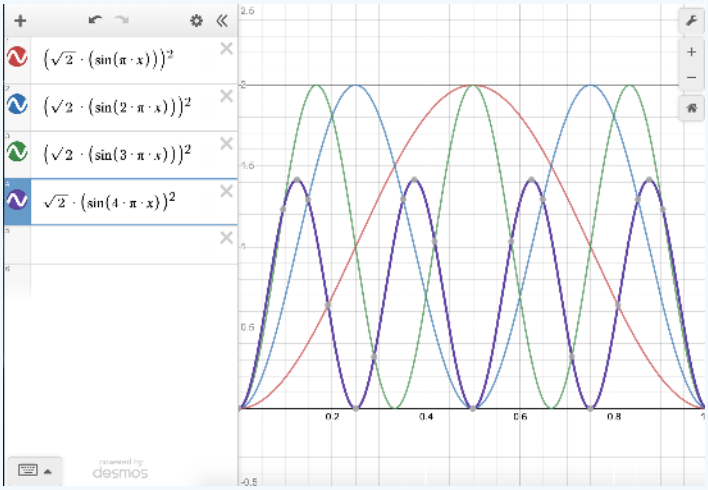
For n=3: $\psi = \sqrt{2}\left(\sin(3\pi x)\right)$

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 1.2.2.1: 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.

1.2.2.2: 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 1.2.2.2.1 . 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** ($Y_{l,m_l}(\theta, \phi)$).

$$\psi_{(n,l,m_l)} = R_{n,l}(r) \times Y_{l,m_l}(\theta, \phi) \tag{1.2.2.2.1}$$

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 1.2.2.2.2from 1.2.2.2.1because 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 1.2.2.2.2

$$E_n = -\frac{hcRZ^2}{n^2} = -(13.607\,eV)\left(\frac{Z}{n}\right)^2 \qquad (1.2.2.2.2)$$

,

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 1.2.2.2.1

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 1.2.2.2.2 and the Rydberg equation.

a. Using Equation 1.2.2.2.2for 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 1.2.2.2.2. 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 1.2.2.2.2

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 1.2.2.2.2 and they are plotted in Figure 1.2.2.2.1 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.

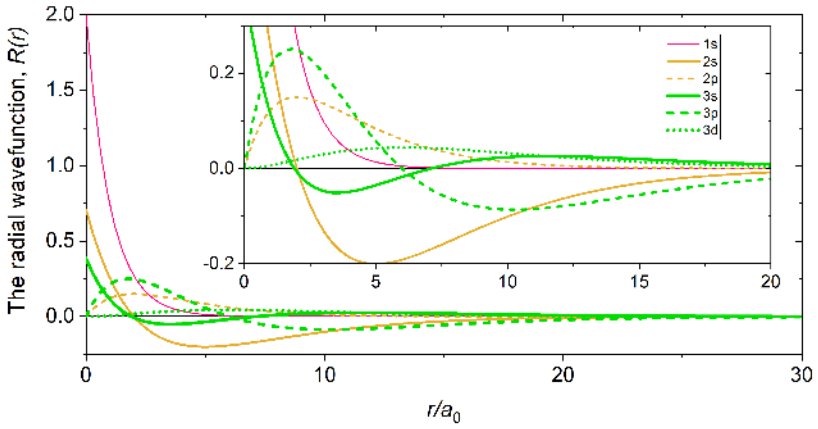


Figure 1.2.2.2.1. Plots of the radial wavefunction, $R_{n,l}(r)$, for the first three shells. The wavefunctions are plotted relative to $\frac{r}{a_0}$, where $a_0 = 52.9pm = 0.529$Å is the Bohr Radius (the radius of a hydrogen 1s orbital). The expressions for these radial wavefunctions ($R_{n,l}(r)$) are shown in Table 1.2.2.2.2. (Kathryn Haas; CC-NC-BY-SA)

Table 1.2.2.2.2. 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 1.2.2.2.1.

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 1.2.2.2.2 The normalized probability functions are compared to the original radial part of the wavefunctions in Figure 1.2.2.2.3 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 $\frac{r}{a_0}$.

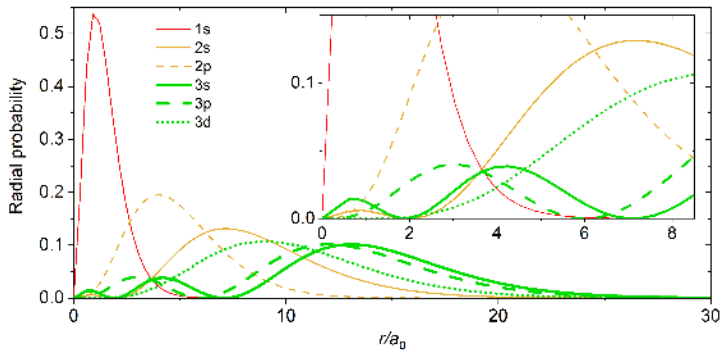


Figure 1.2.2.2.2: Plots of the normalized radial probability functions for the first three shells. The radial wavefunctions ($R_{n,l}(r)$) are shown in Table 1.2.2.2.2. (Kathryn Haas; CC-NC-BY-SA)

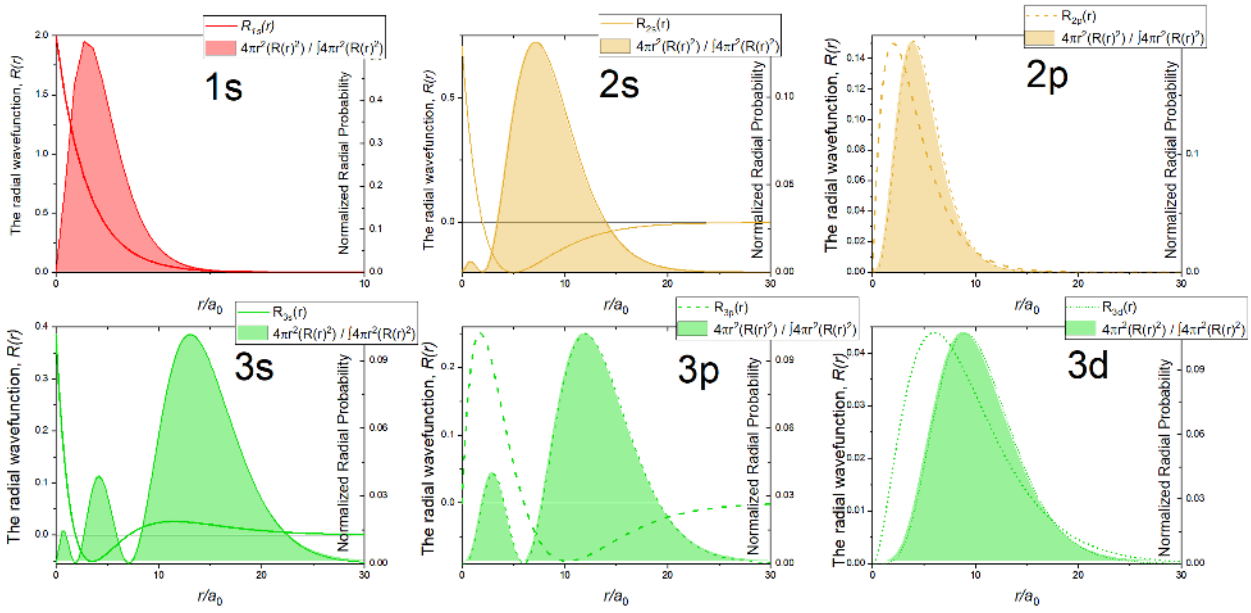


Figure 1.2.2.2.2. Plots of the normalized radial probability function for each orbital in the first three shells (shaded curves). The radial wavefunctions are also shown (Table 1.2.2.2.2). The y-axis on the left of each plot corresponds to the radial wavefunction (line); the y-axis on the right of each 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.

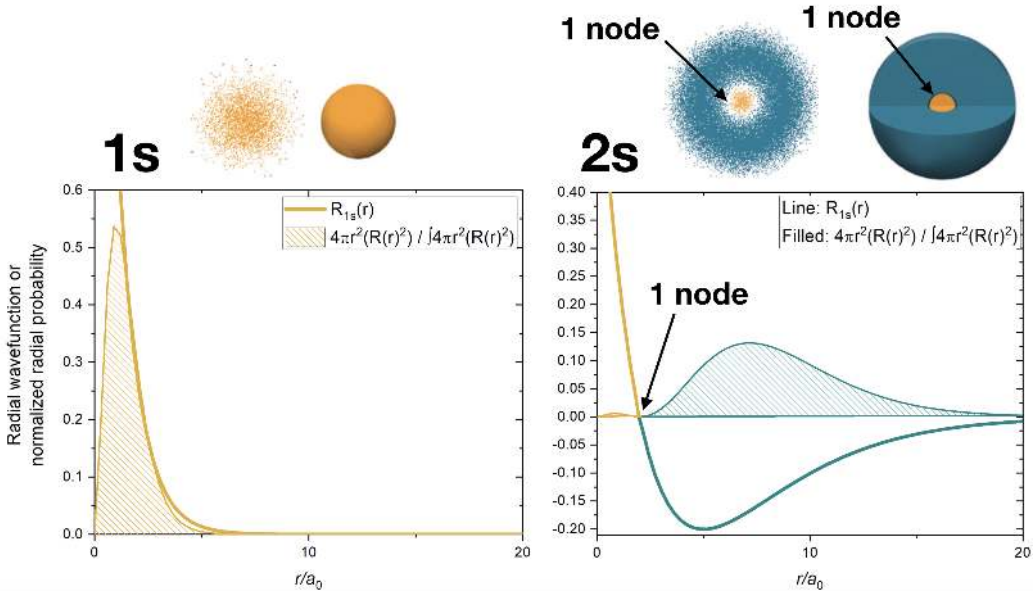


Figure 1.2.2.2.3: Visualization of the 1s and 2s atomic orbitals. Each orbital is shown as both an electron probability density plot and a contour plot above its wavefunction and probability density function. The 1s orbital has zero radial nodes. The 2s orbital has one radial node where its wavefunction 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 1.2.2.2.1

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

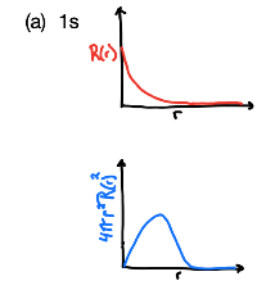
? Exercise 1.2.2.2.1

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.

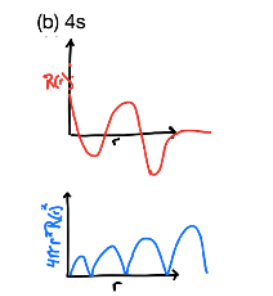
Answer, 1s

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).



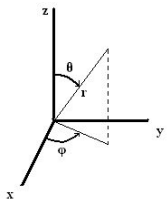
Answer, 4s

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.

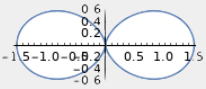
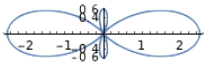
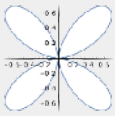
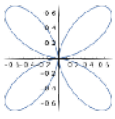


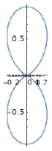
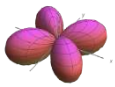
$$Y_{l,m_l}(\theta,\phi)=\left(\frac{1}{4\pi}\right)^{1/2} y\,(\theta,\phi)$$

$Y_{l,m_l}(\theta,\phi)$, 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 $1.2.2.2.3$ 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 $1.2.2.2.3$. 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 1.2.2.2.4

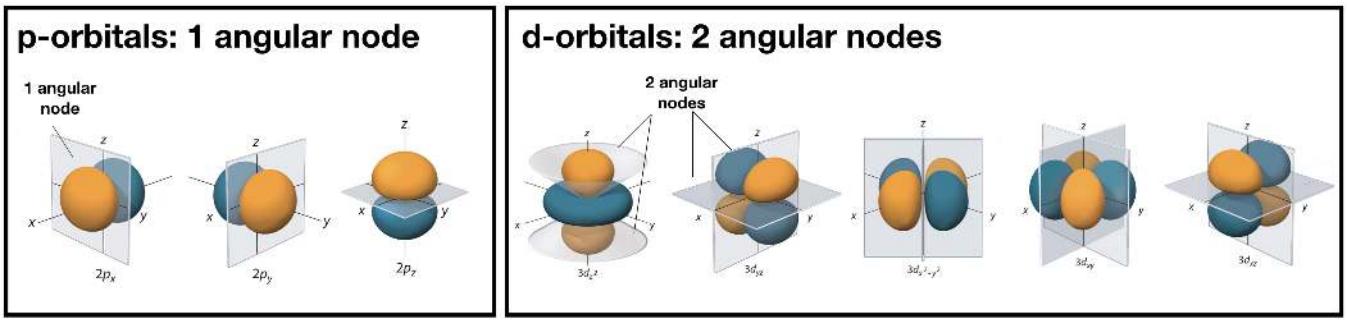
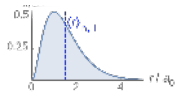
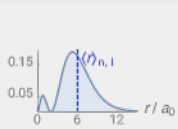
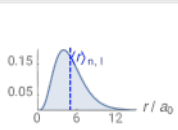
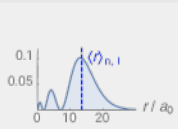
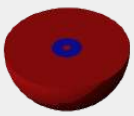


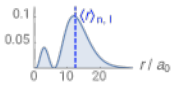
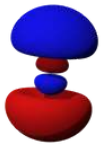
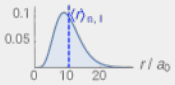
Figure 1.2.2.2.4: The angular nodes in p-orbitals and d-orbitals are shown. Every p orbital has one angular node, and every d orbital has two angular nodes. The number of angular nodes in any orbital is equal to the value of the quantum number, l. (CC BY-NC-SA; anonymous by request)

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 1.2.2.2: 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.

1.2.2.3: 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.

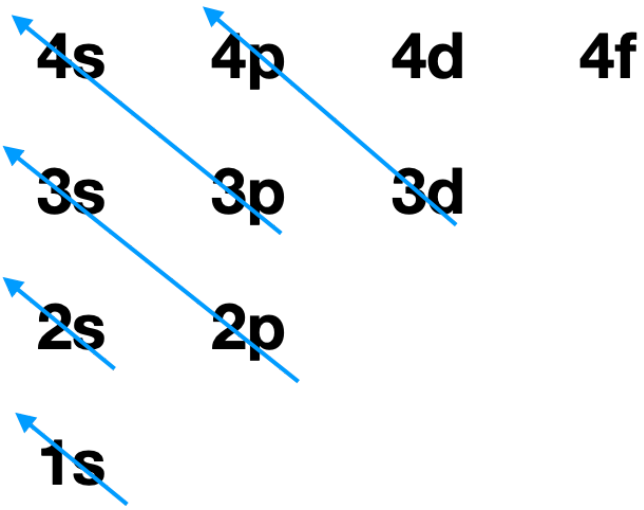


Figure 1.2.2.3.1. The order of filling of ground state electron orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc... (CC-BY-NC-SA; Kathryn Haas)

(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.

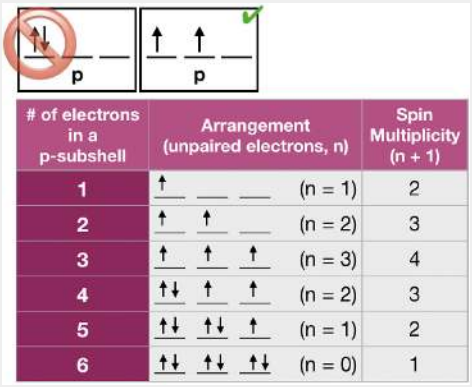


Figure 1.2.2.3.2 . Hund's rule is that spin multiplicity must be maximized in the ground state. (Kathryn Haas; CC-NC-BY-SA)

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

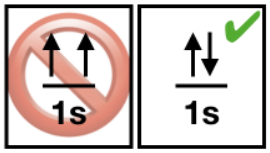


Figure 1.2.2.3.3 . Pauli's principle tells us that paired electrons must have opposite spin. (Kathryn Haas; CC-NC-BY-SA)

(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.

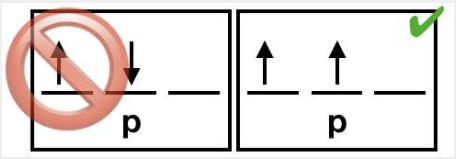


Figure 1.2.2.3.4 . Unpaired electrons should have identical spins due to the exchange interaction. (Kathryn Haas; CC-NC-BY-SA)

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.

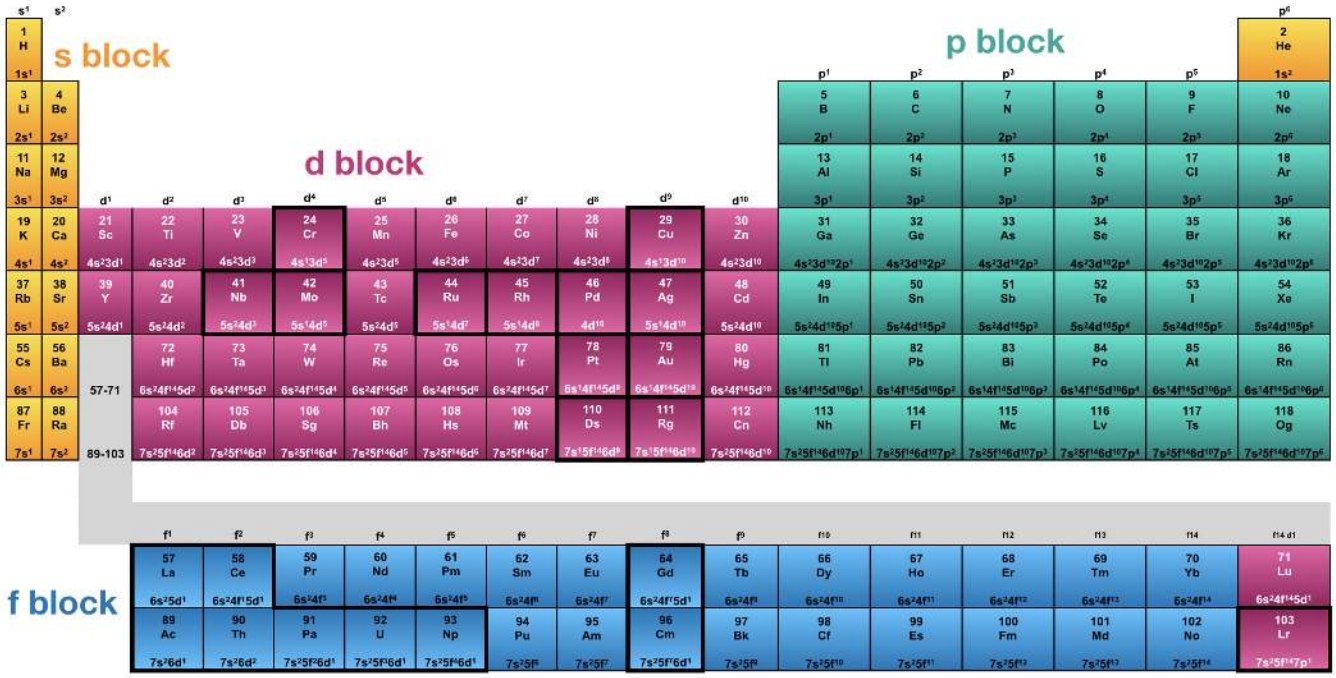


Figure 1.2.2.3.5 . This is a depiction of the periodic table that highlights the s-, p-, d-, and f- blocks in different colors. Violations of the expected trend in electron configurations are outlined in a heavy black line. Several elements of the d block and f block violate the general trends in electron 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 1.2.2.3.5 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 1.2.2.3: Aufbau Principle is shared under a CC BY-NC-SA 4.0 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.

1.2.2.4: 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*)

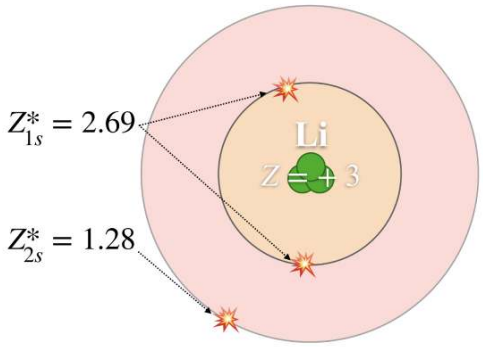


Figure 1.2.2.4.1. In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

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 1.2.2.4.1). 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 1.2.2.4.2below shows plots of the radial probability function of the 1s, 2s, and 2p orbitals. From these plots, we can see that the 1s orbital is able to approach the closest to the nucleus; thus it is the most penetrating. While the 2s and 2p have most of their probability at a farther distance from the nucleus (compared to 1s), the 2s orbital and the 2p orbital have different extents of penetration. Notice that the 2s orbital is able to penetrate the 1s orbital because of the central 2s lobe. The 2p orbital penetrates somewhat into the 1s, but it cannot approach the nucleus as closely as the 2s orbital can. While the 2s orbital penetrates more than 2p (the 2s orbital can approach closer to the nucleus), the 2p is slightly *closer on average* than 2s. The order of Z* in 2s and 2p subshells depends on which factor (average distance or penetration) is more important. In the first two rows of the periodic table, penetration is the dominant factor that results in 2s having a lower energy than 2p (see Figure 1.2.2.4.4for values).

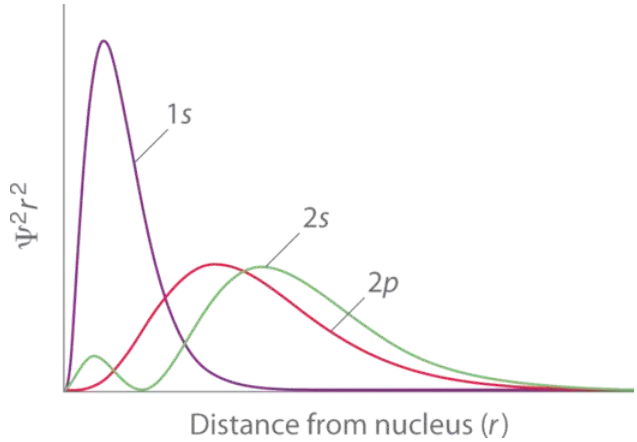


Figure 1.2.2.4.2 . Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner 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.

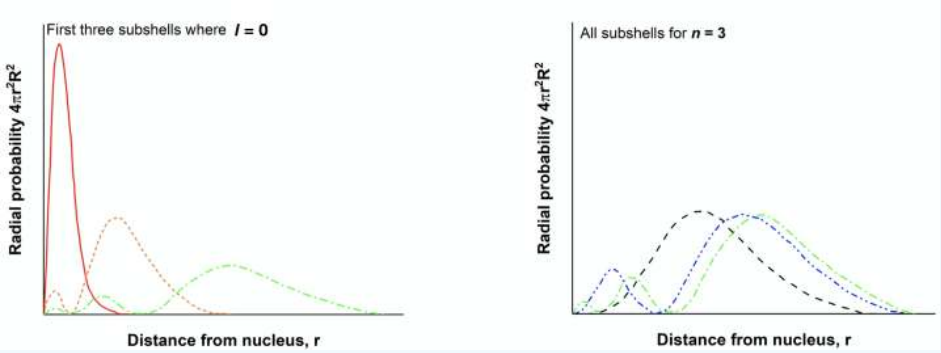
Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

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.

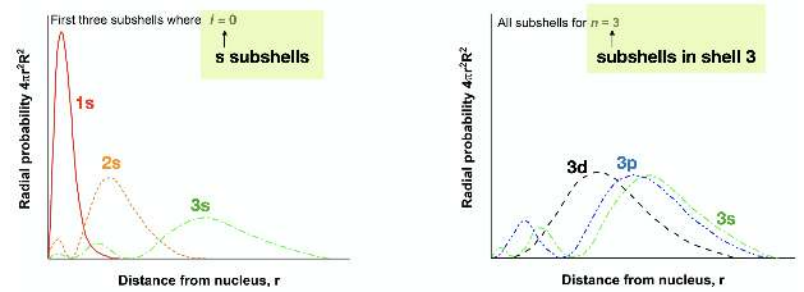
Answer 5

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*

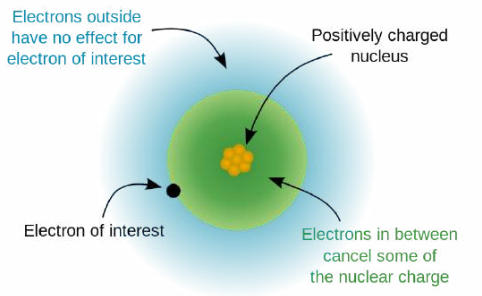


Figure 1.2.2.4.3. Diagram illustrating effective nuclear charge according to Slater's rules.

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:

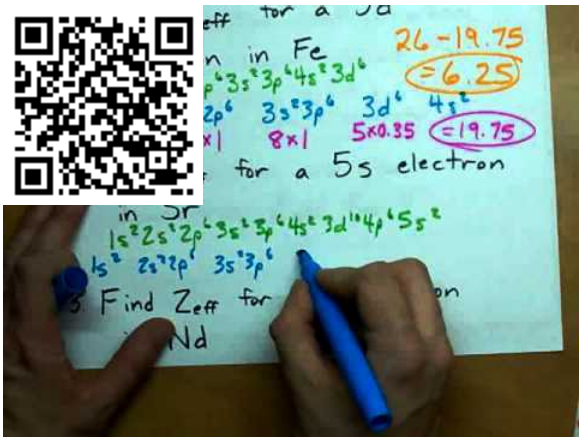
(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.

**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 1.2.2.4.1: 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 1.2.2.4.1

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 1.2.2.4.3for 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 1.2.2.4.4. 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 1.2.2.4.3and analysis of Slater's rules indicate that there are some predictable trends in Z*. The data from Figure 1.2.2.4.3is plotted below in Figure 1.2.2.4.4to provide a visual aid to the discussion below.

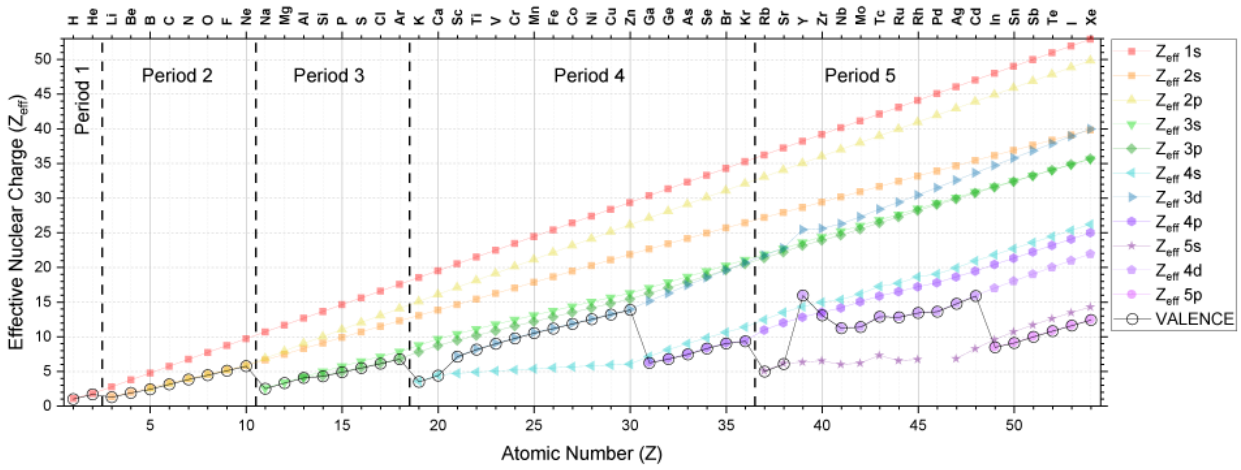


Figure 1.2.2.4.5: The Z* values for electrons in each subshell of the first 54 elements (H to Xe). Each subshell is plotted as a different series (see legend) and the valence shell is highlighted by a solid black line with open circles. (Kathryn Haas; CC-NC-BY-SA)

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

Do you notice any exceptions to this general trend?

Inspection of Figure 1.2.2.4.4should 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 1.2.2.4.4as 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 1.2.2.4.3

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 1.2.2.4.4 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 1.2.2.4.2

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

1.2.2.4: 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

1.2.3: Periodic Properties of Atoms

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

1.2.3.1: Ionization energy

1.2.3.2: Electron Affinity

1.2.3.3: 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.

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

1.2.3.1: 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 1.2.3.1.1and 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.

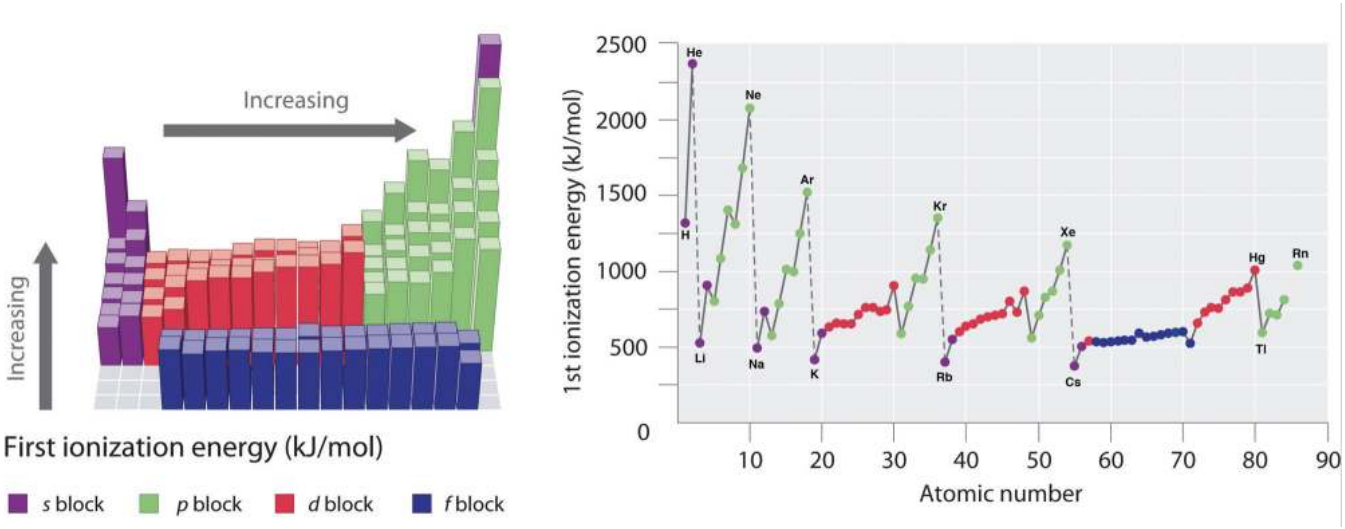


Figure 1.2.3.1.1: Graph showing the First Ionization Energy of the Elements. Left: ionization energies are mapped onto the periodic table, where the magnitude of ionization energy is depicted as a bar graph. Right: the first ionization energy is plotted against atomic number. In both panels the elements 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 1.2.3.1.2 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!

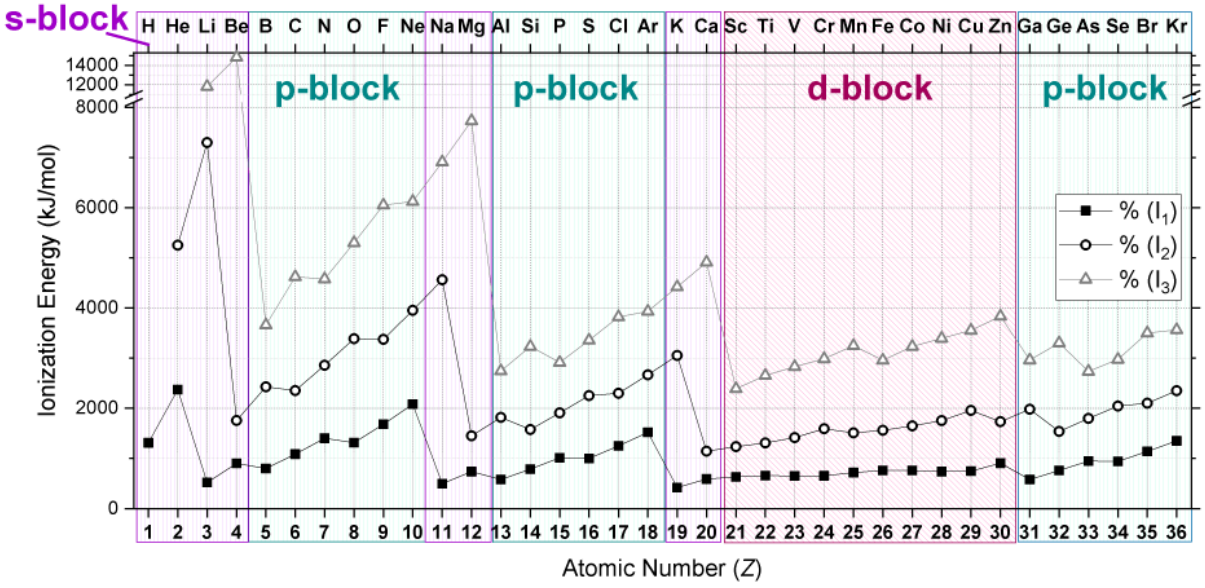


Figure 1.2.3.1.2. The first (I_1), second (I_2), and third (I_3) ionization energies plotted for elements with Z = 1 to 36 (H to Kr). The position of each element in its atomic form is indicated as s- p- or d-block. (CC-BY-NC-SA; Kathryn Haas)

1.2.3.1: Ionization energy is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Kathryn Haas, Swetha Ramireddy, Bingyao Zheng, Emily Nguyen, & Emily Nguyen.

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

1.2.3.2: 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 1.2.3.2.1is *endothermic* (positive ΔU) for elements except noble gases and alkaline earth metals. Under this definition, the more positive the EA value, the higher an atom's affinity for electrons.

$$A^-_{(g)} \longrightarrow A_{(g)} + e^- \qquad EA = \Delta U \tag{1.2.3.2.1}$$

The reaction shown in Equation 1.2.3.2.1is similar those that define ionization energy. For this reason, the EA is also described as the *zeroth ionization energy*.

Definition: Electron Affinity defined as addition of an electron

An alternate and more common definition is the microscopic reverse of Equation 1.2.3.2.1. 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 1.2.3.2.2 The reaction as shown in equation 1.2.3.2.2is *exothermic* (negative ΔU) for elements except noble gases and alkaline earth metals. The more negative this EA value, the higher an atom's affinity for electrons.

$$A_{(g)} + e^- \longrightarrow A^-_{(g)} \qquad EA = \Delta U \tag{1.2.3.2.2}$$

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

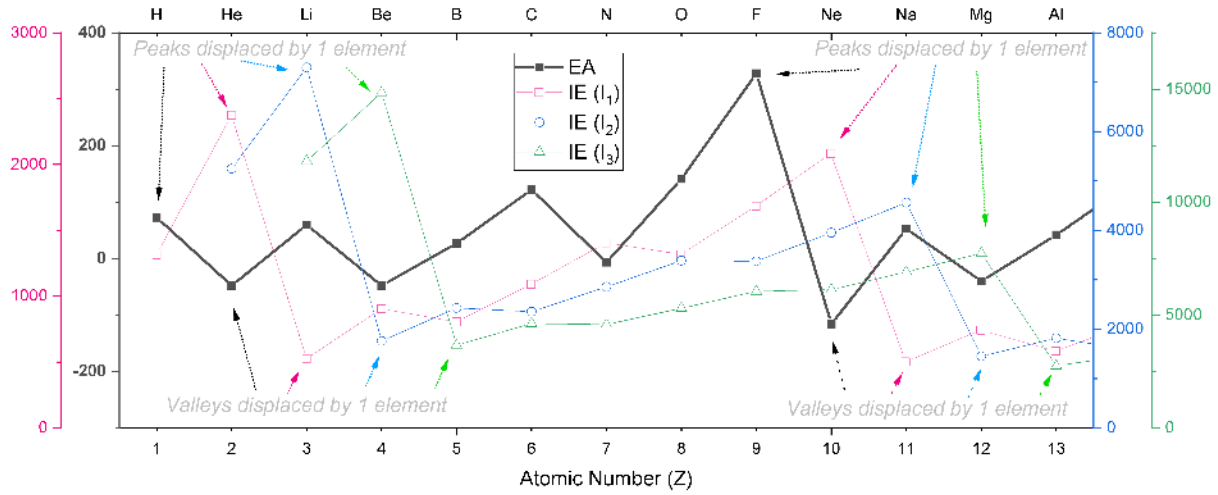


Figure 1.2.3.2.1. A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (I_1), second (I_2), and third (I_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys 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.

1.2.3.2: Electron Affinity is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

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

1.2.3.3: 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 1.2.3.3.1were 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.

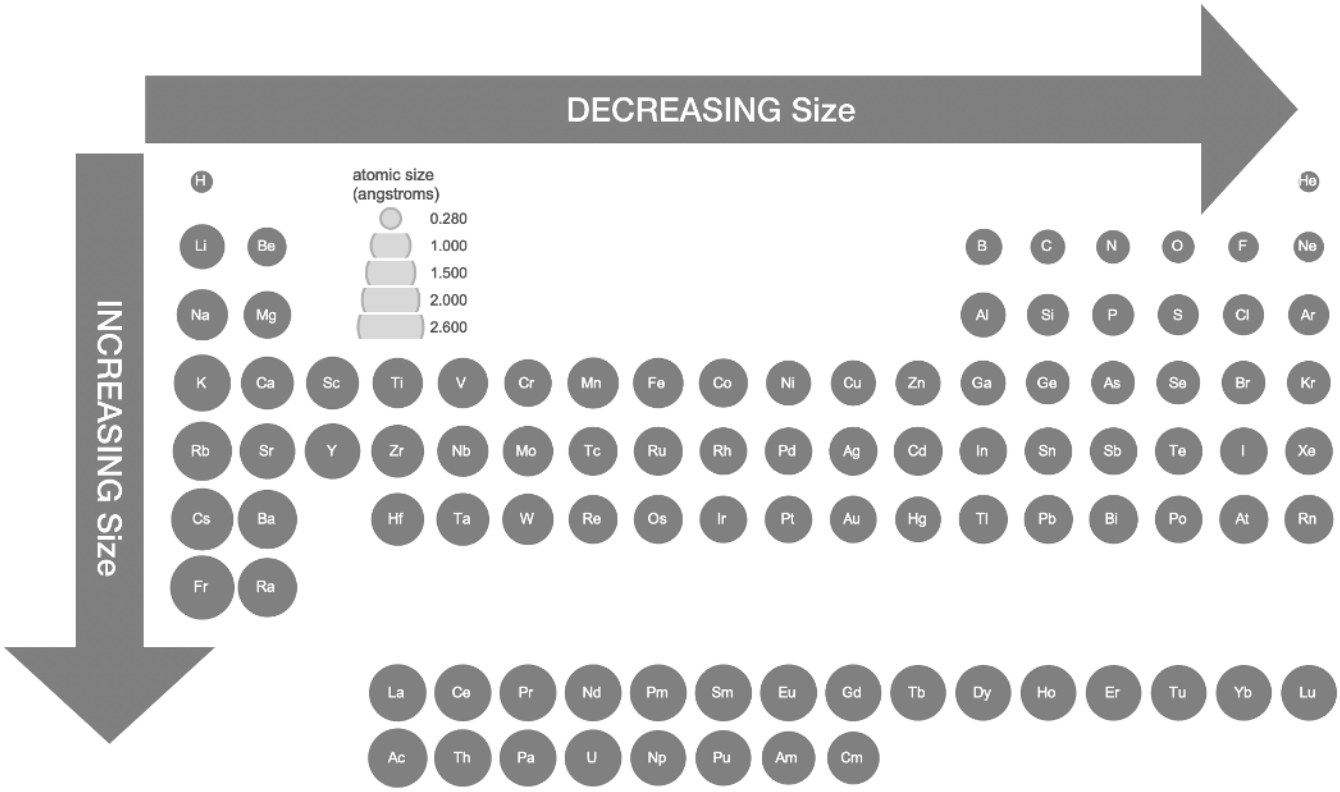


Figure 1.2.3.3.1. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.* (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 1.2.3.3.2 visually illustrates the relative size of atoms and some cations of the first four periods; the data is available in tabular format in Figure 1.2.3.3.3

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 1.2.3.3.2 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 1.2.3.3.3

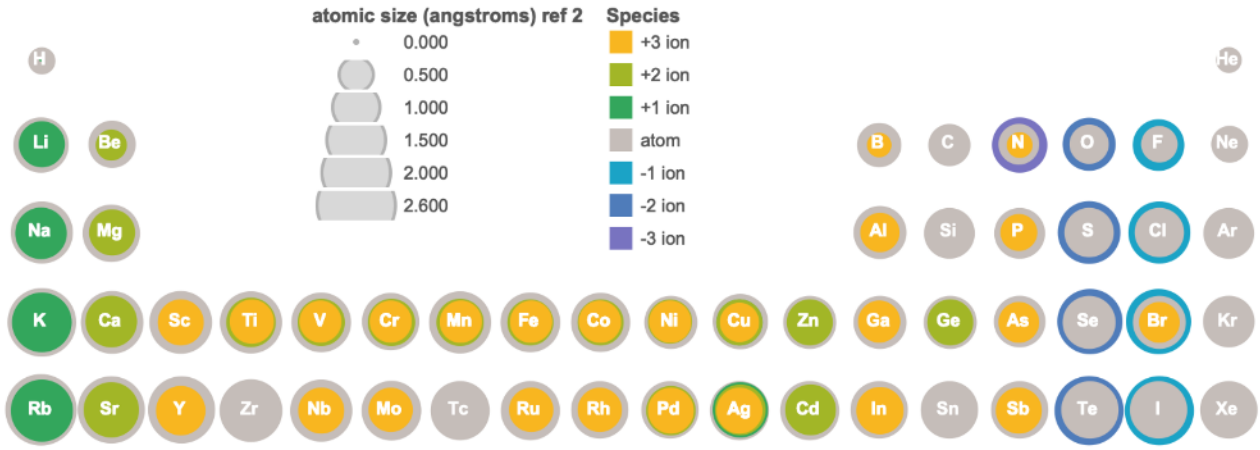


Figure 1.2.3.3.2 . This figure illustrates relative size of atoms and ions of the first four periods of the periodic table. Atomic radius is indicated by grey circles. Radius of cations is shown in green (+1), lime (+2), and yellow (+3) circles. Radius of anions are shown as aqua (-1), blue (-2), and 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 1.2.3.3.3 .

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.

1.2.3.3: Covalent and Ionic Radii is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Kathryn Haas, Swetha Ramireddy, Bingyao Zheng, Emily Nguyen, & Emily Nguyen.

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

1.2.4: Problems

Example Exercises

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

? Exercises

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

Answer 1

Helium (He).

Answer 2

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

Answer 3

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

Answer 4

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

Answer 5

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

Answer 6

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

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

- **2.4: Problems** by Kathryn Haas has no license indicated.

SECTION OVERVIEW

1.3: Simple Bonding Theory

1.3.1: Lewis Electron-Dot Diagrams

- 1.3.1.1: Resonance
- 1.3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)
- 1.3.1.3: Formal Charge
- 1.3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium

1.3.2: Valence Shell Electron-Pair Repulsion

- 1.3.2.1: Lone Pair Repulsion
- 1.3.2.2: Multiple Bonds
- 1.3.2.3: Electronegativity and Atomic Size Effects
- 1.3.2.4: Ligand Close Packing

1.3.3: Molecular Polarity

1.3.4: Hydrogen Bonding

1.3.5: Problems

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

1.3.1: 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.

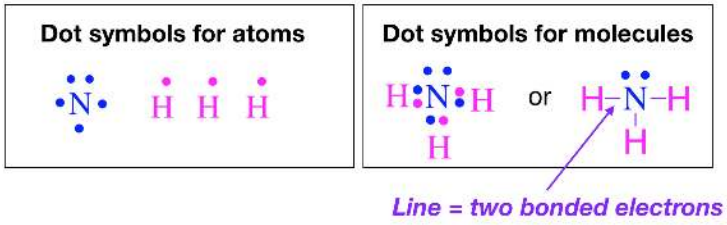


Figure 1.3.1.1: Lewis dot structure of atoms comprising ammonia and the dot structure of the molecule. (Kathryn Haas; CC-NC-BY-SA)

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.

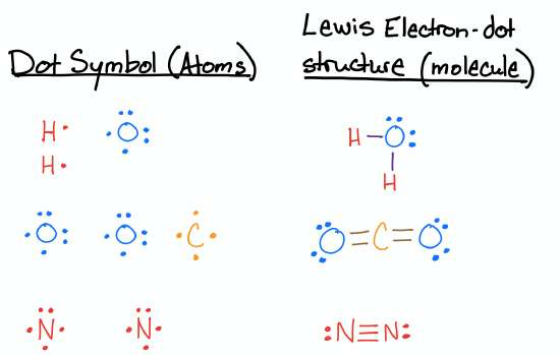
Electrons in valence (octet) = total unbonded electrons on the atom + total bonded electrons (2 electrons per bond)

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 1.3.1.1

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

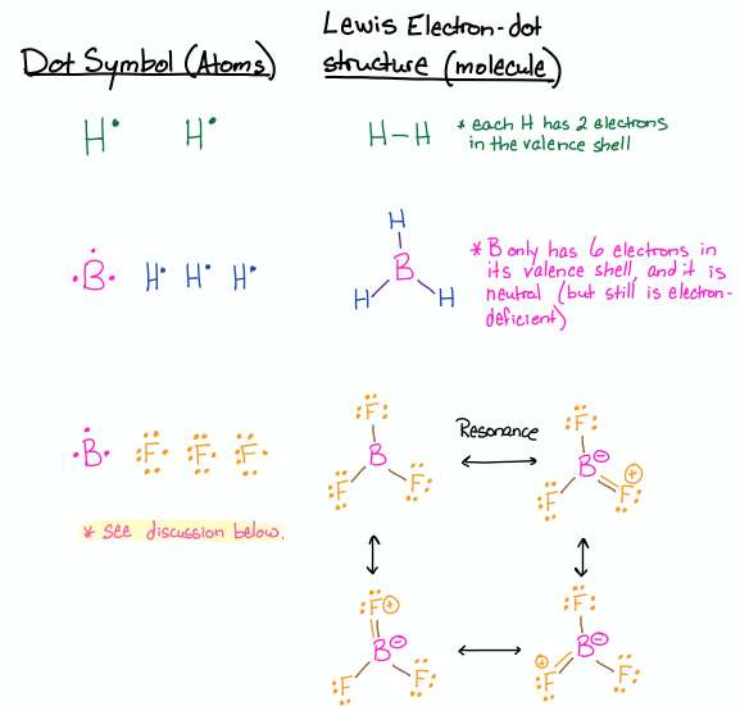
Answer



Exercise 1.3.1.2

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 1.3.1: Lewis Electron-Dot Diagrams is shared under a CC BY-NC 4.0 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.

1.3.1.1: 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°.

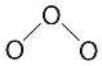
Ozone (O_3)

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



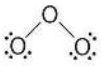
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

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



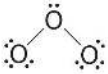
with 14 electrons left over.

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

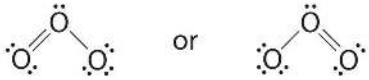


and have 2 electrons left over.

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



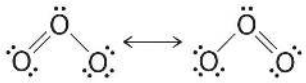
6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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:



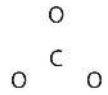
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *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:



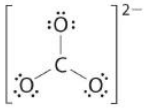
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

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:



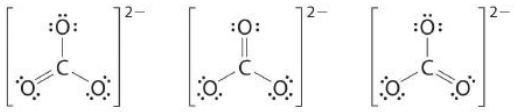
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



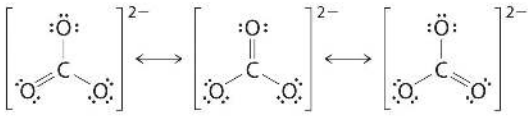
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

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:



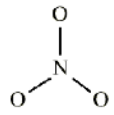
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

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

The Nitrate (NO_3^-) ion

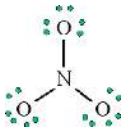
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

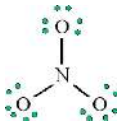


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

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

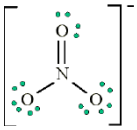


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

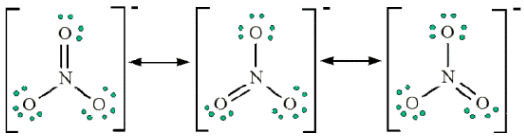
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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 1.3.1.1.1: 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

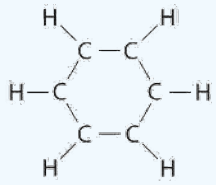
Asked for: resonance structures

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.

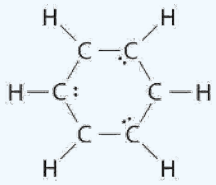
Solution:

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:



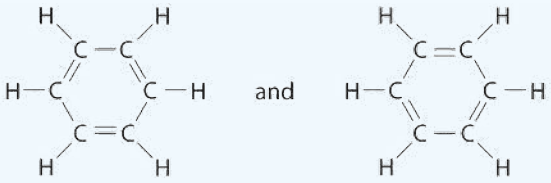
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

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

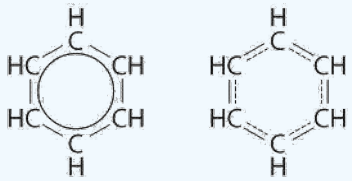


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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 1.3.1.1.1: 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 1.3.1.1.1 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.

1.3.1.1: Resonance is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by LibreTexts.

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

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

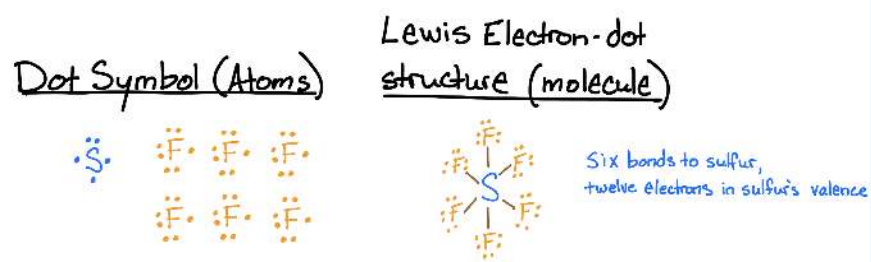
The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6. Even elements in the third and fourth row are known to follow this rule *sometimes*, but not always. In larger atoms, where $n \geq 3$ 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 1.3.1.2.1

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.

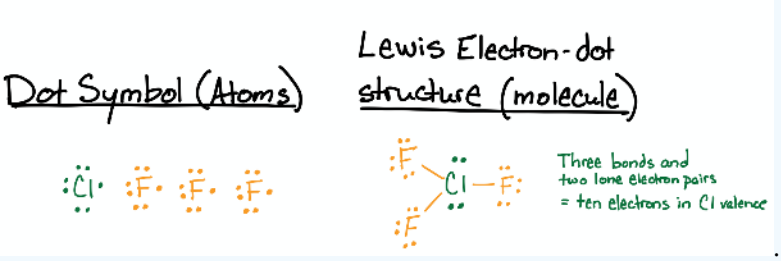


? Exercise 1.3.1.2.1

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 1.3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms) is shared under a CC BY-NC 4.0 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.

1.3.1.3: 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.

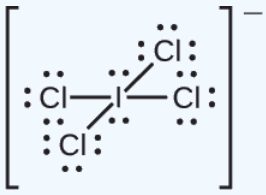
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

✔ 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 1.3.1.3.1

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



Answer

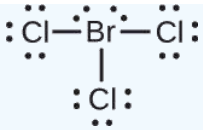
C −1, O +1

✔ 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

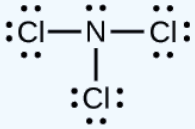
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 1.3.1.3.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



This page titled 1.3.1.3: Formal Charge is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by OpenStax.

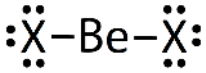
- **7.5: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.3.1.4: 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 1.3.1.4.1). 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 1.3.1.4.1

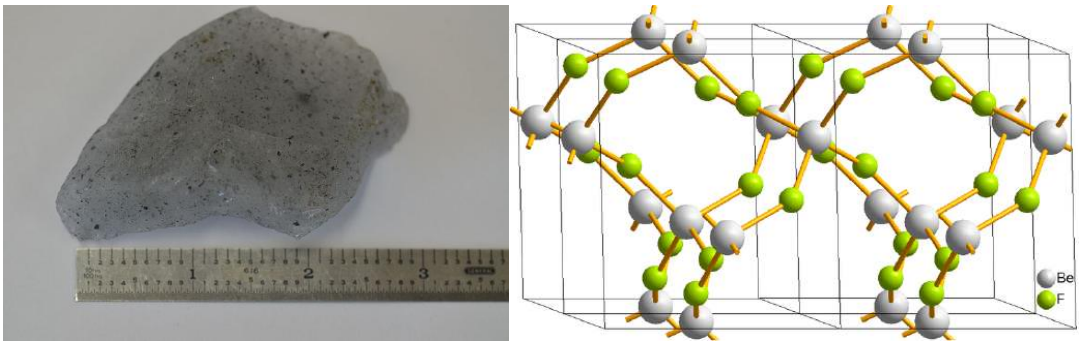


Figure 1.3.1.4.1: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

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.

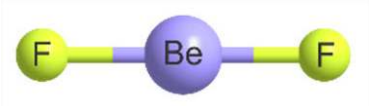


Figure 1.3.1.4.2: Geometries of BeF_2. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$BeCl_2$

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.

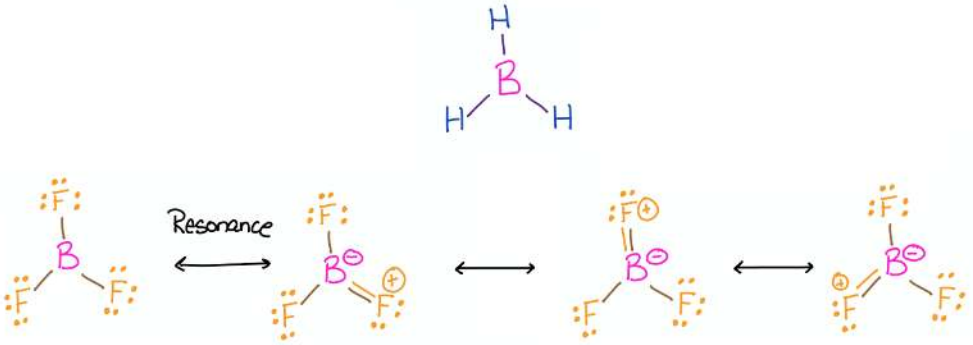


Figure 1.3.1.4.2 : Lewis structures of BH_3 and BF_3. (Kathryn Haas; CC-NC-BY-SA)

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 1.3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium is shared under a CC BY-NC 4.0 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.

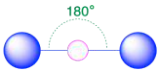
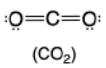
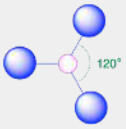
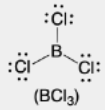
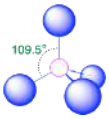
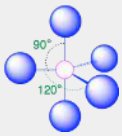
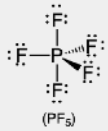
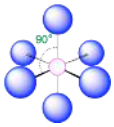
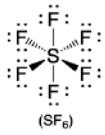
1.3.2: Valence Shell Electron-Pair Repulsion

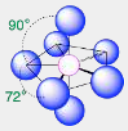
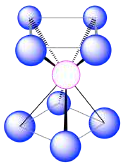
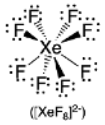
Introduction to VSEPR

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 1.3.2.1. The cases where lone pairs contribute to the total groups ($n \geq 1$) are discussed in the next section about lone pair repulsion.

Table 1.3.2.1. 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.

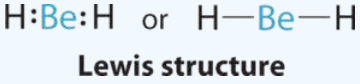
Use the procedure above to complete the exercises below

Exercise 1.3.2.1

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

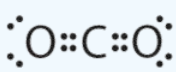
2. There are two groups around the central atom, and both groups are single bonds. Thus BeH_2 is designated as AX_2.

3. We see from Table 1.3.2.1that the arrangement that minimizes repulsions places the groups 180° apart.

4. From Table 1.3.2.1we 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.

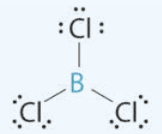
4. VSEPR only recognizes groups around the *central* atom (the carbon). Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonded groups on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Table 1.3.2.1). The structure of CO_2 is shown in Table 1.3.2.1.

? Exercise 1.3.2.2

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

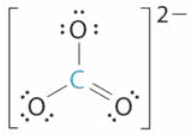
2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

3. To minimize repulsions, the groups are placed 120° apart (Table 1.3.2.1).

4. From Table 1.3.2.1 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

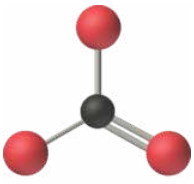


Lewis structure

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 1.3.2.1).

4. We see from Table 1.3.2.1 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.


Molecular geometry
(trigonal planar)

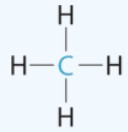
In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

? Exercise 1.3.2.3

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

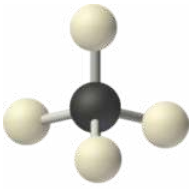


Lewis structure

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 1.3.2.1, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

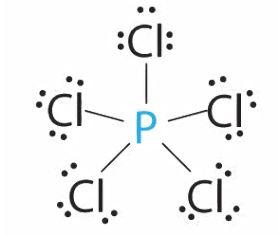
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table 1.3.2.1).



Molecular geometry (tetrahedral)

Answer PCl_5

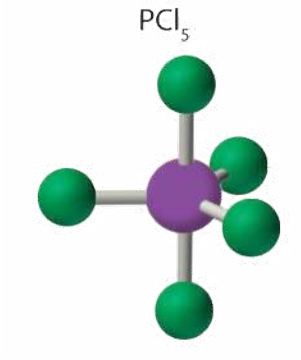
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



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

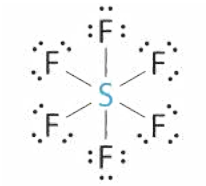
3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table 1.3.2.1).

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



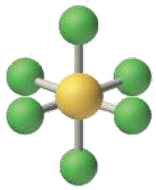
Lewis structure

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 1.3.2.2that 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 1.3.2: 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.

1.3.2.1: 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.

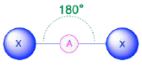
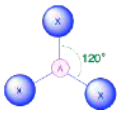
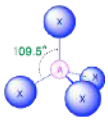
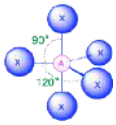
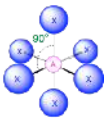
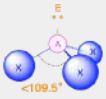
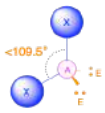
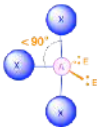
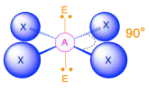
When one or more of the groups is a lone pair of electrons (non-bonded electrons), the experimentally-observed geometry around an atom is slightly different than in the case where all groups are bonds. The actual bond angles are similar, but not exactly the same, as those predicted based on the *total 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 1.3.2.1.1

Table 1.3.2.1.1 : 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°

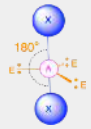
	Electron Groups (*m* + *n*)				
	2 (steric number = 2)	**3** (steric number = 3)	**4** (steric number = 4)	**5** (steric number = 5)	**6** (steric number = 6)
3 lone pairs AX_mE_3				 AX_2E_3, linear 180°	

Table 1.3.2.1.1 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.

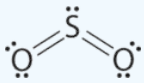
Three Electron Groups (m + n = 3)

(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 1.3.2.1.1).

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:

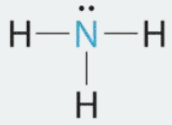
- When all electron groups are bonds (m=4 or AX_4), the molecular geometry is a ***tetrahedron*** with bond angles of **109.5°**.

- 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.

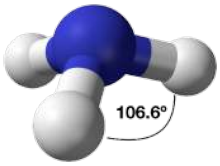
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



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

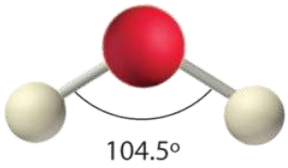
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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)

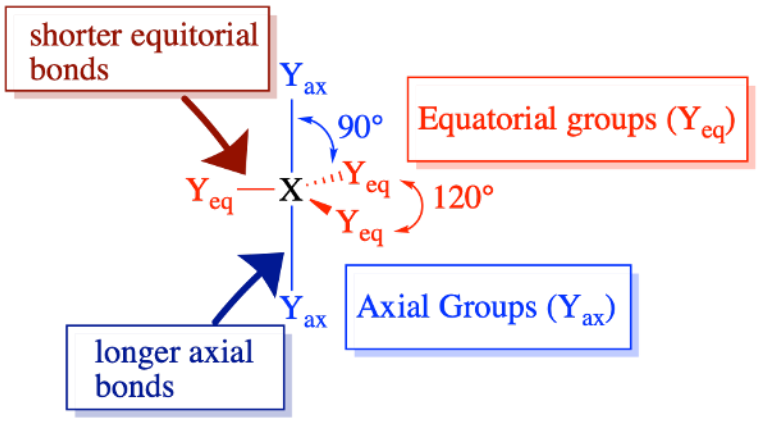


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

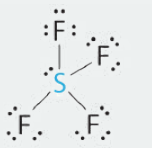
(Steric number = 5) In the case that there are five electron groups around a central atom, there are two different types of positions around the central atom: equatorial positions and axial positions. The three equatorial ligands are 120° from one another and are 90° from each of the two axial ligands. 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.

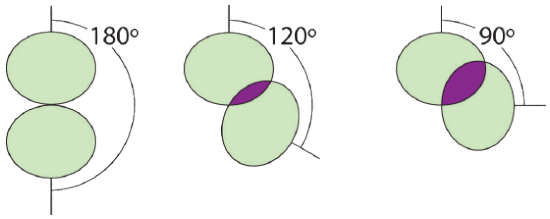
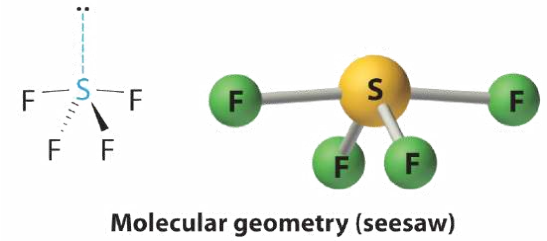


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

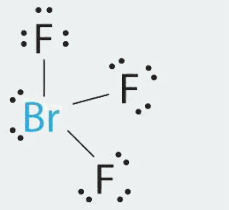
At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

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.

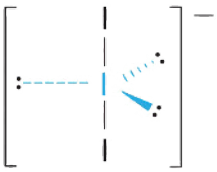
AX_2E_3 Molecules: I_3^-

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



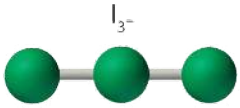
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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.



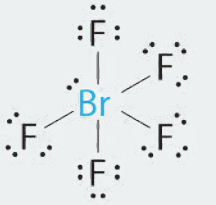
Six Electron Groups (m + n = 6)

(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

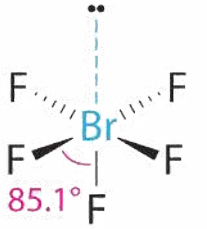
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

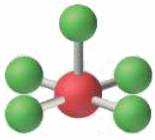
With its expanded valence, this species is an exception to the octet rule.

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.

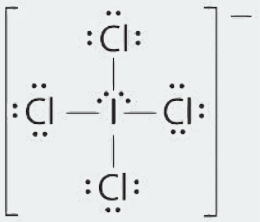
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



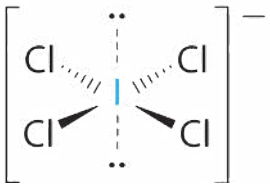
Molecular geometry
(square pyramidal)

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

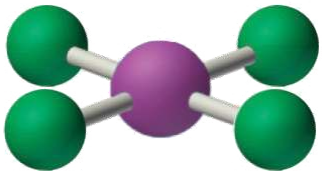


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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 1.3.2.1.1

Example Excercises

✔ Example 1.3.2.1.1

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

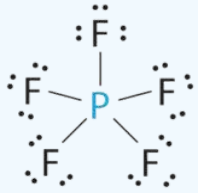
Asked for: molecular geometry

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



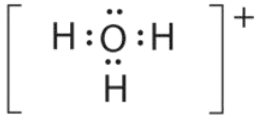
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

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.



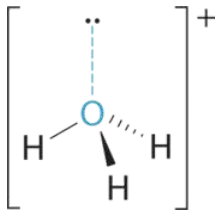
- **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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 1.3.2.1.1

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 1.3.2.1.2

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 Example1.3.2.1.1

Solution:

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



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

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



(a) (b) (c)

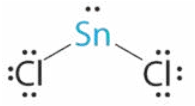
Interactions			
90 LP–LP	0	2	2

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 1.3.2.1.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

This page titled 1.3.2.1: 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.

1.3.2.2: 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.

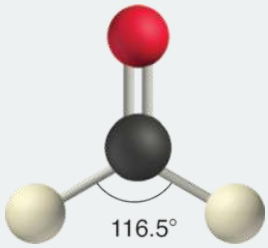
Double and triple bonds are more repulsive than single bonds

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 1.3.2.2.1

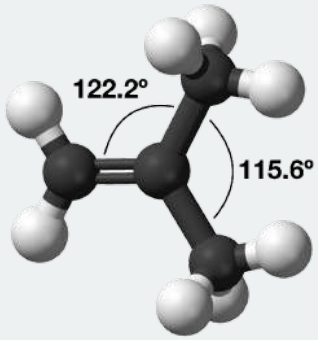
CH_2O

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

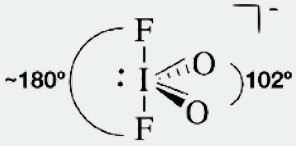
In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

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

Examples1.3.2.2.1

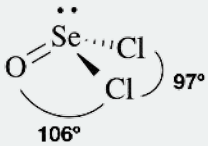
$IO_2F_2^-$

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

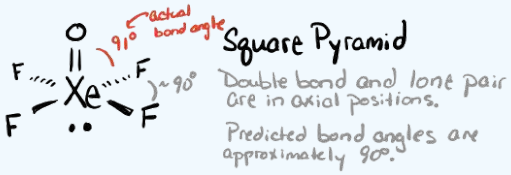
Exercise 1.3.2.2.1

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).



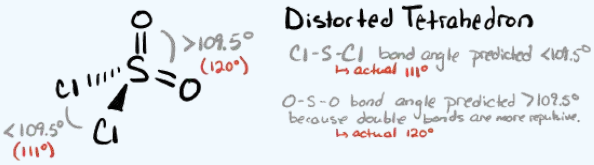
Answer b

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°.*



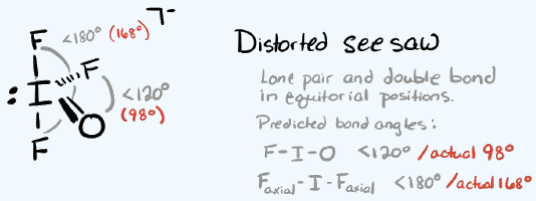
Answer c

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 1.3.2.2: 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.

1.3.2.3: Electronegativity and Atomic Size Effects

Introduction

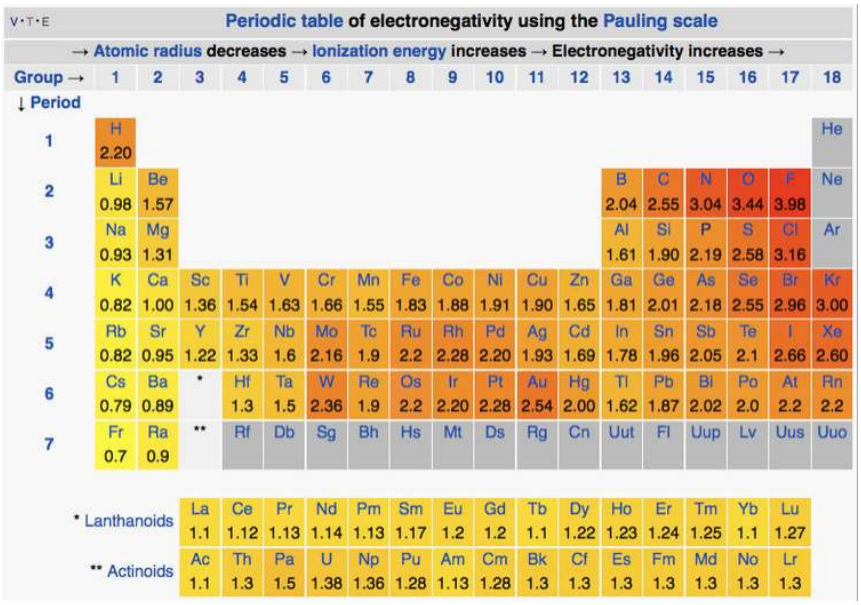
We saw in previous sections how lone pairs of electrons and multiple bonds distort bond angles between non-central atoms (ligands) around a central atom. This section describes how ligand **electronegativity and size also influence bond angles and molecular geometry**. Electronegativity is generally 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 1.3.2.3.1 : 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 1.3.2.3.2each have three identical "pendant groups" on the central atom (Figure 1.3.2.3.2). *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?

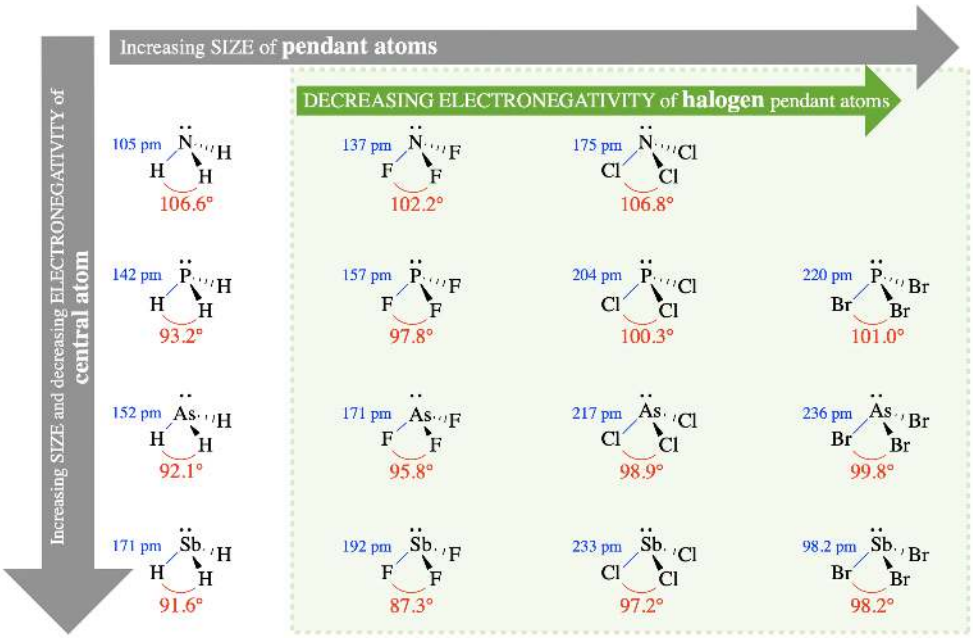


Figure 1.3.2.3.2: Several molecules with trigonal pyramidal electronic geometry are shown arranged according to size of the central atom (increasing size of central atom from top to bottom) and pendant atom (increasing size of pendant atoms from left to right). Bond angles and bond lengths are indicated. (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 1.3.2.3.2 (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 1.3.2.3.2 (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 1.3.2.3.3).

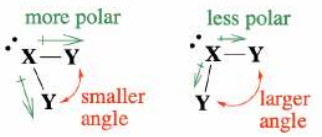


Figure 1.3.2.3.3. When electron pairs are distributed away from the central atom, repulsions are decreased, allowing smaller bond angles. (Kathryn Haas; CC-NC-BY-SA)

Electronegativity is an alternative explanation to the trends we already examined above in Figure 1.3.2.3.2. For example, when we compare the halogen pendant atoms (shaded region in Figure 1.3.2.3.2) , 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 1.3.2.3.2.

Exercise 1.3.2.3.1

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 1.3.2.3.2

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)

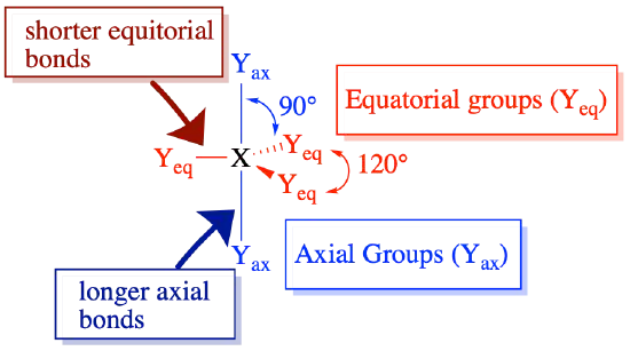
Add texts here. Do not delete this text first.

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

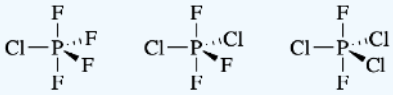
? Exercise 1.3.2.3.3

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 $PF_2(CH_3)_3$

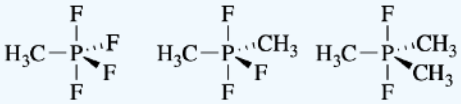
Answer (a)

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

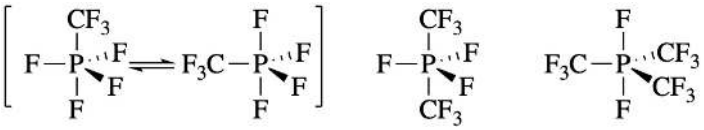


Answer (b)

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 1.3.2.3: 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.

1.3.2.4: 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.

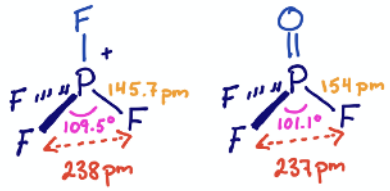


Figure 1.3.2.4.1: The molecular structures of PF_4^+ and PF_3O. The distances between neighboring F atoms are similar in the two molecules, while bond lengths and angles differ. The PF_4^+ ion has a $P-F$ bond length of 145.7 pm, an $F-P-F$ bond angle of 109.5°, and a distance of 238 pm between neighboring F atoms. The PF_3O molecule has a $P-F$ bond length of 154 pm, an $F-P-F$ bond angle of 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 1.3.2.4.2.



Figure 1.3.2.4.2: 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 1.3.2.4.2 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.

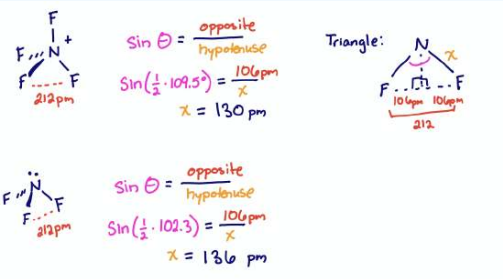


Figure 1.3.2.4.1 : Illustration of how right angle trigonometry can be applied to determine bond angle, bond length, or distance between neighboring atoms: any bond angle can be divided into two right angles where the bond length is the hypotenuse, the distance between neighbors is twice the opposite side, and the bond angle is twice θ. (CC-BY-NC-SA; Kathryn Haas)

Exercise 1.3.2.4.1

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

This page titled 1.3.2.4: Ligand Close Packing is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.2.4: Ligand Close Packing** by Kathryn Haas has no license indicated.

1.3.3: 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 1.3.3.1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{1.3.3.1}$$

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.

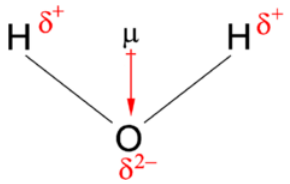


Figure 1.3.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

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 1.3.3.2); 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 1.3.3.2).

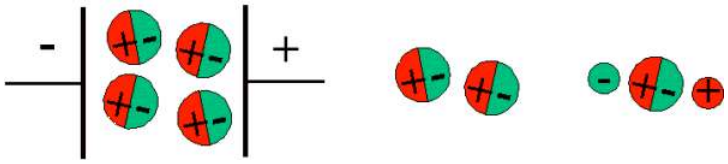


Figure 1.3.3.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 1.3.3.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{1.3.3.2}$$

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 1.3.3.2):

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

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:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D \tag{1.3.3.3}$$

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

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D \tag{1.3.3.4}$$

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

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D \tag{1.3.3.5}$$

Example 1.3.3.1: Water

The water molecule in Figure 1.3.3.1 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.

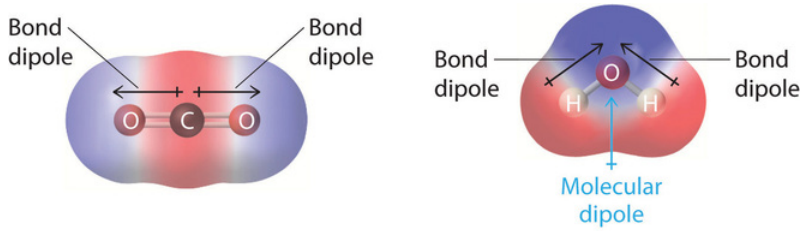


Figure 1.3.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 1.3.3.3*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.

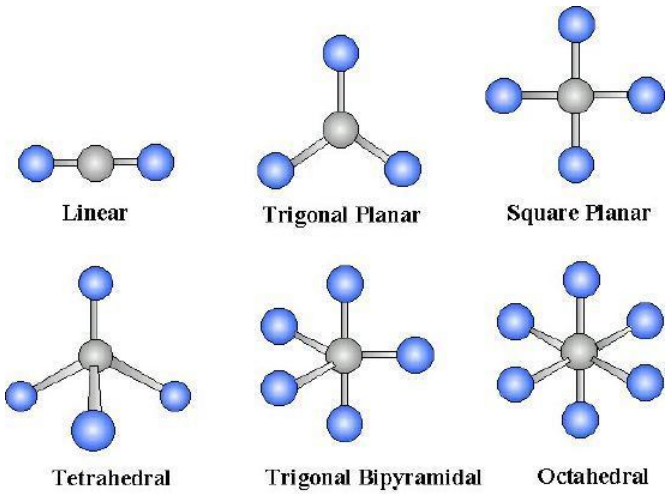
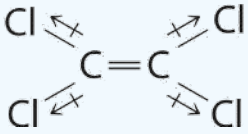


Figure 1.3.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 1.3.3.3: C_2Cl_4

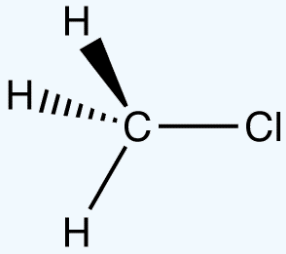
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 1.3.3.3: 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 1.3.3.1: 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)*

This page titled 1.3.3: Molecular Polarity is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **Dipole Moments** by Delmar Larsen, Mike Blaber is licensed CC BY 4.0.

1.3.4: 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.

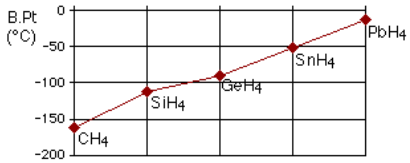


Figure 1: Boiling points of group 14 elemental halides.

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.

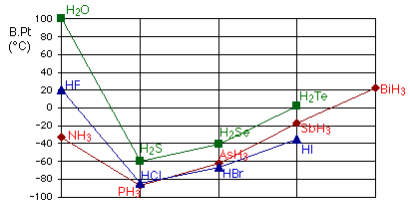


Figure 2: Boiling points of group 15-17 elemental halides.

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:

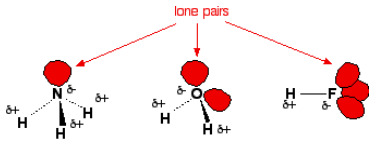


Figure 3: The lone pairs responsible for hydrogen bonding in NH_3, H_2O, and HF. The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you.

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.

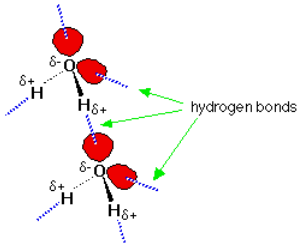


Figure 4: Hydrogen bonding in water

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.

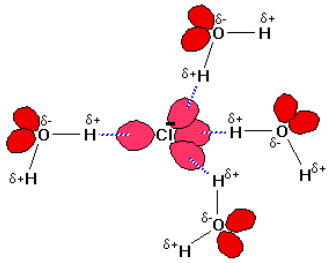


Figure 5: Hydrogen bonding between chloride ions and water.

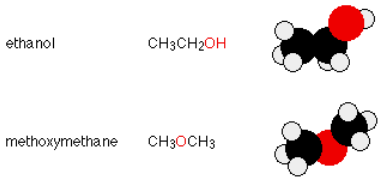
However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

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.

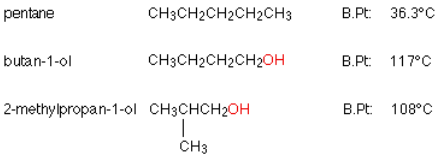


They have the same number of electrons, and a similar length. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be similar. However, ethanol has a hydrogen atom attached directly to an oxygen; here the oxygen still has two lone pairs like a water molecule. 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.

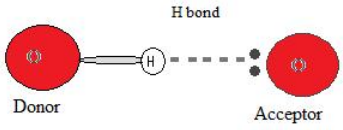
Hydrogen bonding in organic molecules containing nitrogen

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

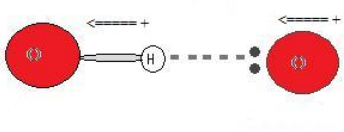
In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is usually a strongly electronegative atom such as N, O, or F that is covalently bonded to a hydrogen bond.

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)

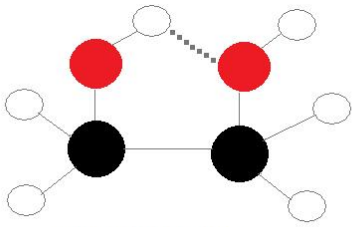


Types of hydrogen bonds

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

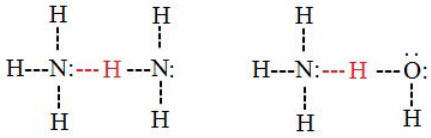
Intramolecular hydrogen bonds are those which occur *within* one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor a hydrogen acceptor must be present within one molecule, and they must be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

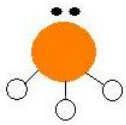
On Viscosity

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

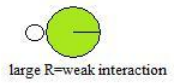
Electronegativity

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.

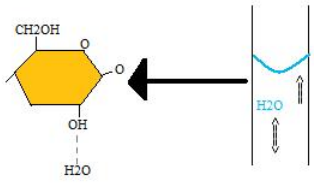


Hydrogen Bonding in Nature

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.

1.3.4: 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.

1.3.5: Problems

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

SECTION OVERVIEW

1.4: Symmetry and Group Theory

1.4.1: Symmetry Elements and Operations

1.4.2: Point Groups

1.4.2.1: Groups of Low and High Symmetry

1.4.2.2: Other Groups

1.4.3: Properties and Representations of Groups

1.4.3.1: Matrices

1.4.3.2: Representations of Point Groups

1.4.3.3: Character Tables

1.4.4: Examples and Applications of Symmetry

1.4.4.1: Chirality

1.4.4.2: Molecular Vibrations

1.4.P: Problems (under construction)

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

1.4.1: 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 1.4.1.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

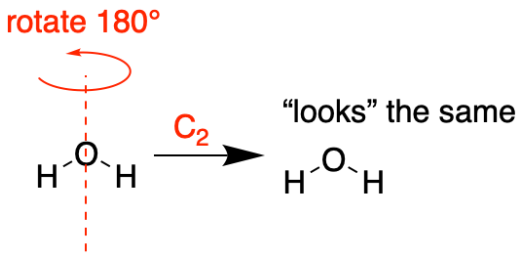


Figure 1.4.1.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

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 1.4.1.1.

Table 1.4.1.1: 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.

1.4.1: 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.

1.4.2: 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.

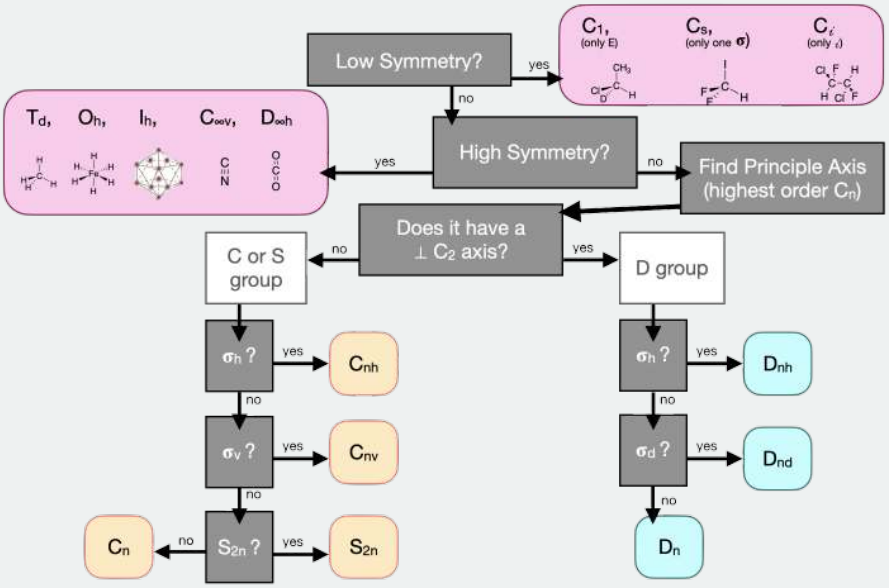


Figure 1.4.2.1: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

Example 1.4.2.1

Find the point group of benzene (C_6H_6).

Answer

Solution

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

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

See Also

Symmetry Gallery

1.4.2: 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.

1.4.2.1: 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

1.4.2.1: 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.

1.4.2.2: 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

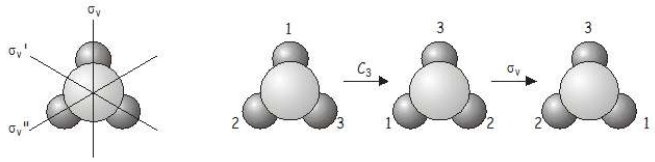
1.4.2.2: Other Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **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.

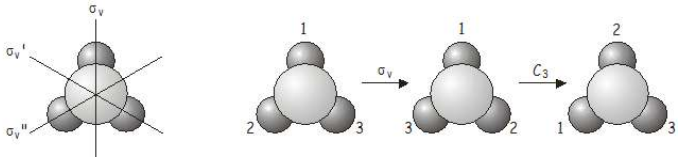
1.4.3: Properties and Representations of Groups

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

1.4.3: 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.

1.4.3.1: 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}.

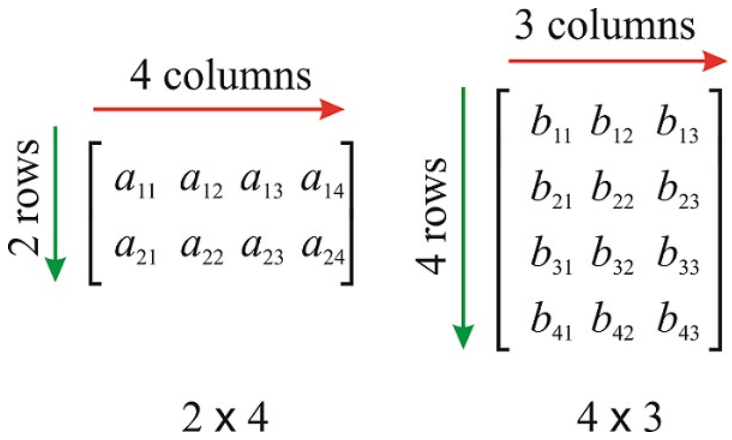


Figure 1.4.3.1.1 : Matrices of different dimensions

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:

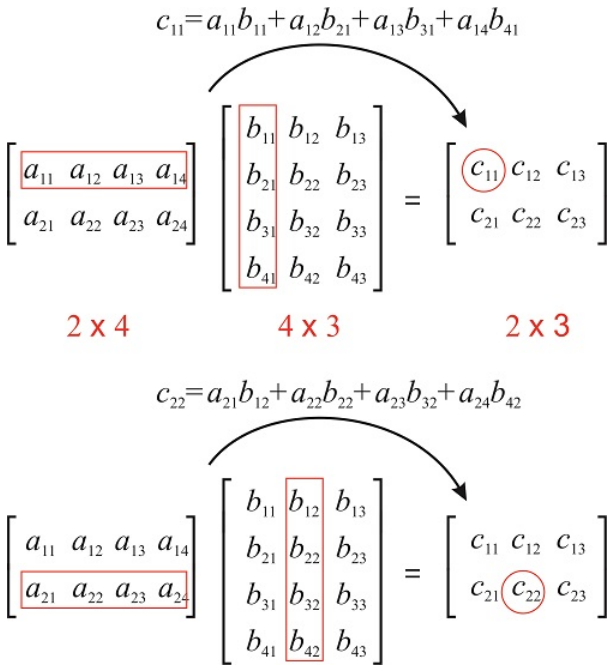


Figure 1.4.3.1.1 : Matrix multiplication

Example 1.4.3.1.1

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 1.4.3.1.2

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 1.4.3.1.3

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]).

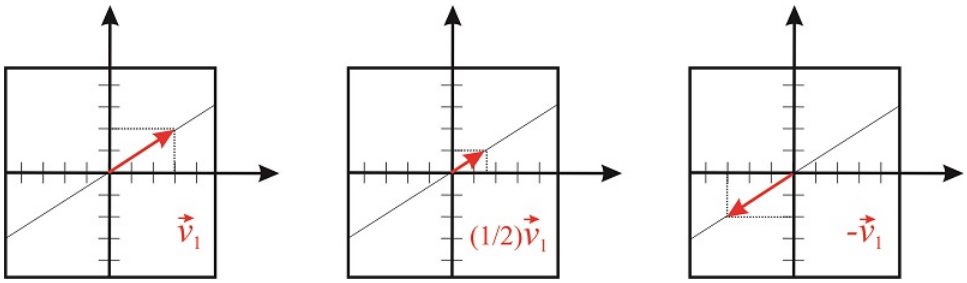


Figure 1.4.3.1.2 : Multiplication of a vector by a scalar

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 1.4.3.1.3).

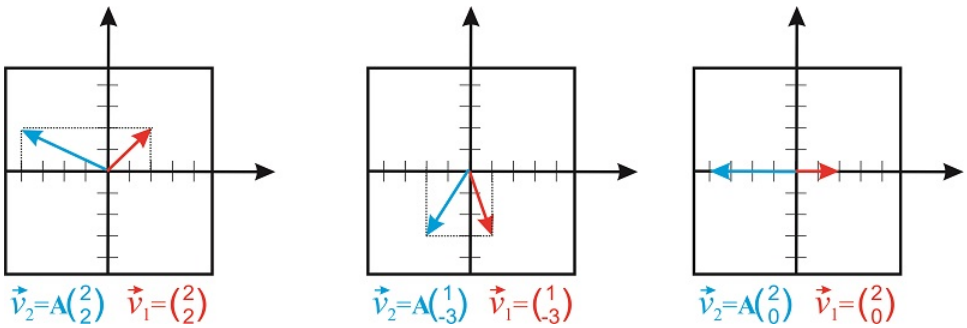


Figure 1.4.3.1.3 : Multiplication of a vector by a square matrix

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

1.4.3.1: 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.

1.4.3.2: Representations of Point Groups

Symmetry Operations: Matrix Representations

A **symmetry operation**, such as a rotation around a symmetry axis or a reflection through a plane, is an operation that, when performed on an object, results in a new orientation of the object that is indistinguishable from the original. For example, if we rotate a square in the plane by $\pi/2$ or π, the new orientation of the square is superimposable on the original one (Figure 1.4.3.2.1).

If rotation by an angle θ of a molecule (or object) about some axis results in an orientation of the molecule (or object) that is superimposable on the original, the axis is called a rotation axis. The molecule (or object) is said to have an n-fold rotational axis, where n is $2\pi/\theta$. The axis is denoted as C_n. The square of Figure 1.4.3.2.1has 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:

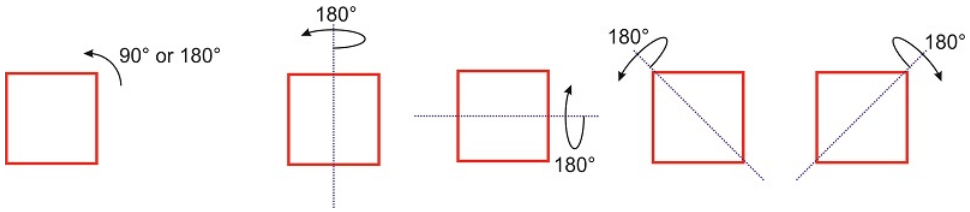


Figure 1.4.3.2.1: Symmetry operations performed on a square

A symmetry operation moves all the points of the object from one initial position to a final position, and that means that symmetry operators are 3×3 square matrices (or 2×2 in two dimensions). Each symmetry operation can be expressed as a **transformation matrix** where the vector (x', y', z') represents the new coordinates of the point (x, y, z) after the symmetry operation.

$$[\text{New Coordinates}(x', y', z')] = [\text{Transformation Matrix}] \times [\text{Old Coordinates}(x, y, z)]$$

We will use the example of water, which is in the C_{2v} point group, to illustrate how transformation matrices can be used to represent the symmetry of a group.

Figure 1.4.3.2.2shows 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.

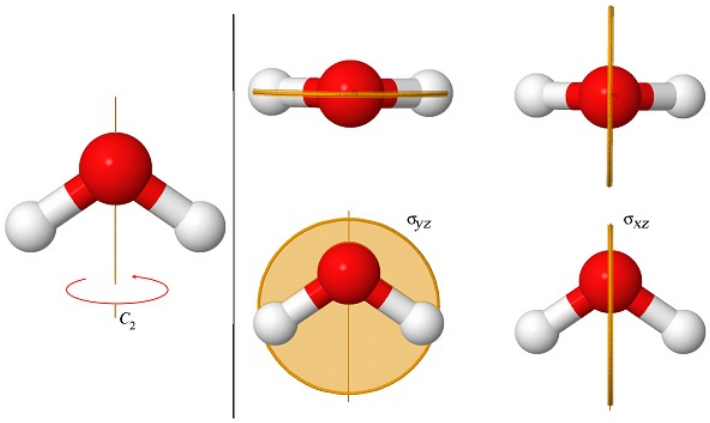


Figure 1.4.3.2.2: The symmetry elements of the molecule of water

Transformation Matrix of C_2 rotation

A 2-fold rotation around the $z-$axis changes the location of a point (x, y, z) to $(-x, -y, z)$ (see Figure 1.4.3.2.3). By convention, rotations are always taken in the counterclockwise direction.

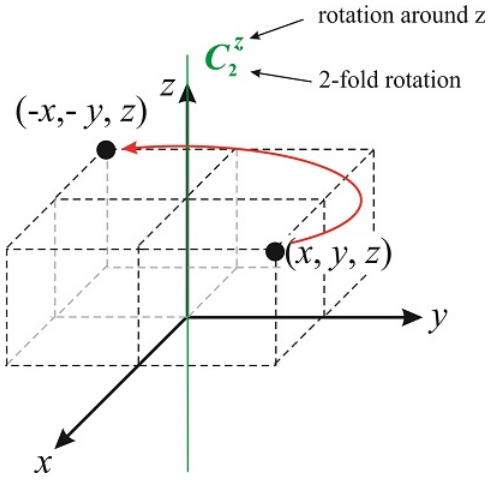


Figure 1.4.3.2.3 : A 2-fold rotation around the z-axis

What is the matrix that represents the C_2 rotation? The matrix transforms the vector (x, y, z) into $(-x, -y, z)$, so

$$C_2(x, y, z) = (-x, -y, z)$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

We know the matrix is a 3×3 square matrix because it needs to multiply a 3-dimensional vector. In addition, we write the vector as a vertical column to satisfy the requirements of matrix multiplication.

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$a_{11}x + a_{12}y + a_{13}z = -x$$

$$a_{21}x + a_{22}y + a_{23}z = -y$$

$$a_{31}x + a_{32}y + a_{33}z = z$$

and we conclude that $a_{11} = -1$, $a_{12} = a_{13} = 0$, $a_{22} = -1$, $a_{21} = a_{23} = 0$ and $a_{33} = 1$, $a_{31} = a_{32} = 0$. The transformation matrix of the C_2 operation of the C_{2v} point group is:

$$\boldsymbol{C_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{1.4.3.2.1}$$

Transformation Matrix of σ_{xz} reflection

Rotations are not the only symmetry operations we can perform on a molecule. Figure 1.4.3.2.4illustrates 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 $\hat{\sigma}_{xz}$:

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

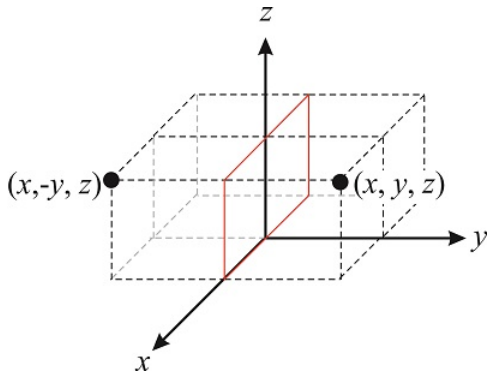


Figure 1.4.3.2.3: A reflection through the xz plane

Following the same logic we used for the rotation matrix, we can write the σ_{xz} transformation matrix as:

$$\boldsymbol{\sigma_{x,z}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{1.4.3.2.2}$$

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 1.4.3.2.1

Find the transformation matrix of the identity (E) and the $\sigma_{y,z}$ operations under the C_{2v} point group.

Answer

The transformation matrix for E is $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

The transformation matrix for $\sigma_{v(yz)}$" is $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Characters

For a square matrix, the ***character*** is the trace of the matrix. For the C_2 operation, with the transformation matrix

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

the trace is $(-1)+(-1)+1=-1$.

The set of characters for a point group is called a **reducible representation (Γ)**. The reducible representation for the C_{2v} point group is:

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

? Exercise 1.4.3.2.1

Prove that the characters in the reducible representation for C_{2v} are correct:

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Answer

For the E operation, with the transformation matrix $\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$, the trace is $1+1+1=3$.

For the C_2^z operation, with the transformation matrix $\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}$, the trace is $(-1)+(-1)+1=-1$.

For the $\sigma_{v(xz)'}$ operation, with the transformation matrix $\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}$, the trace is $1+(-1)+1=1$.

For the $\sigma_{v(yz)"}$ operation, with the transformation matrix $\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$, the trace is $-1+1+1=1$.

This gives the reducible representation

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Reducible and Irreducible Representations

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

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

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

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

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

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

1.4.3.2: 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.

1.4.3.3: Character Tables

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

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

Properties of Characters of Irreducible Representations in Point Groups

1. There is always a totally symmetric representation in which all the characters are 1.
   e.g. In C_{2v}, A_1 is totally symmetric.
2. The order of the group (h) is the total number of symmetry operations in the group.
   e.g. In C_{2v}, $h = 4$
3. Similar operations are listed as classes (R) and appear as columns in the table.
   e.g. In C_{2v}, there are four classes of operations, E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$
4. The number of irreducible representations (rows) must equal the number of classes (columns). This results in all character tables being square.
   e.g. In C_{2v}, there are four classes and four irreducible representations.
5. The sum of squares of all characters under E is equal to the order of the group: $h = \sum[\chi_i]^2$
   e.g. In C_{2v}, $h = 1^2 + 1^2 + 1^2 + 1^2 = 4$
6. For any irreducible representation (i), the sum of squares of its characters multiplied by the number of operations in the class is the order of the group: $h = \sum[\chi_i(R)]^2$
   e.g. For A_2 in C_{2v}, $h = (1\times1)^2 + (1\times1)^2 + (-1\times1)^2 + (-1\times1)^2 = 4$
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:

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

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

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

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

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

The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix (Figure 1.4.3.3.1):

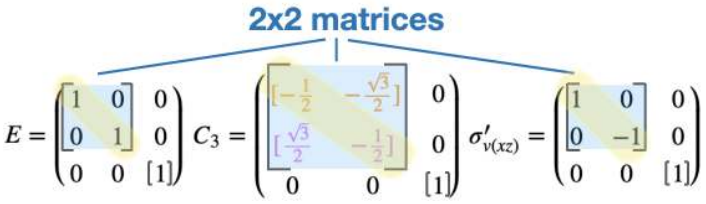


Figure 1.4.3.3.1 : The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

The character from a 2x2 matrix is the sum of the trace of that matrix. So, for the C_3 operation, the 2x2 matrix gives the character -1 (from $-\frac{1}{2} + -\frac{1}{2}$).

The character table for C_{3v} is shown below.

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	z, z^2, x^2+y^2
A_2	1	1	−1	R_z
E	2	−1	0	$(x, y), (xy, x^2+y^2), (xz, yz), (R_x, R_y)$

Additional features of character tables

Additional Features of Character Tables

1. Symmetry operations of the same class are grouped into the same column (class) in the character table and not listed separately.
   e.g. In the C_{3v} point group, there are four operations: E, C_3, C_3^2, and σ_v. The C_3 and C_3^2 operations are listed together in the character table as $2C_3$.
2. IF there are multiple C_2 axes (in a D group), the C_2 axes that are perpendicular to the principle axis are labeled with primes (e.g. C_2' and C_2''); when there are multiple types of perpendicular C_2 axes, one prime (C_2') means that it passes through more atoms, while a double prime (C_2'') means it goes between atoms.
3. Mirror planes that are perpendicular to the principle axis are "horizontal" mirror planes and are designated with an h subscript (σ_h). Mirror planes that are in-plane with the principle axis are "vertical" mirror planes, σ_v. When there are two types of vertical mirror planes, those that run through more atoms are σ_v while those that run between atoms are "dihedral", σ_d.
4. Matching the symmetry operations listed in the character table to the symmetry operations of a molecule can confirm its point group.

5. Irreducible representations are each assigned a Mulliken label, listed in the left-hand column, that indicates the symmetry of that representation as follows:

Mulliken Labels	**meaning**
A	singly degenerate (1x1), symmetric to principle axis
B	singly degenerate (1x1), antisymmetric to principle axis
E	doubly degenerate (2x2)
T	triply degenerate (3x3)
Subscripts and superscripts	**meaning**
1	symmetric to $\sigma_v$or perpendicular to C_2
2	anti-symmetric to $\sigma_v$or perpendicular to C_2
g	symmetric to inversion center
u	anti-symmetric to inversion center
$'$	symmetric to σ_h
$''$	anti-symmetric to σ_h

6. The right-hand columns of the character table list a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products (z^2, x^2+y^2, xy, xz, yz), and the rotations (R_x, R_y, R_z). These expressions indicate the properties of orbitals within the symmetry group. The s-orbital, which is totally symmetric, corresponds to the irreducible representation that possesses symmetry of x^2, y^2 and z^2 combined. The p-orbitals each possess the symmetry of the corresponding axis (e.g. p_x corresponds to the x axis). Each of the d-orbitals possess the symmetry of the corresponding binary product (e.g. d_{xy} corresponds to the binary product, xy, in the character table).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. The transformation properties of x, y, and z can be used to determine whether or not a molecule is IR-active or whether or not it can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A visual summary of the sections and their significance is given in Figure 1.4.3.3.2 Character tables for common point groups are given in the References section of LibreTexts Bookshelves.

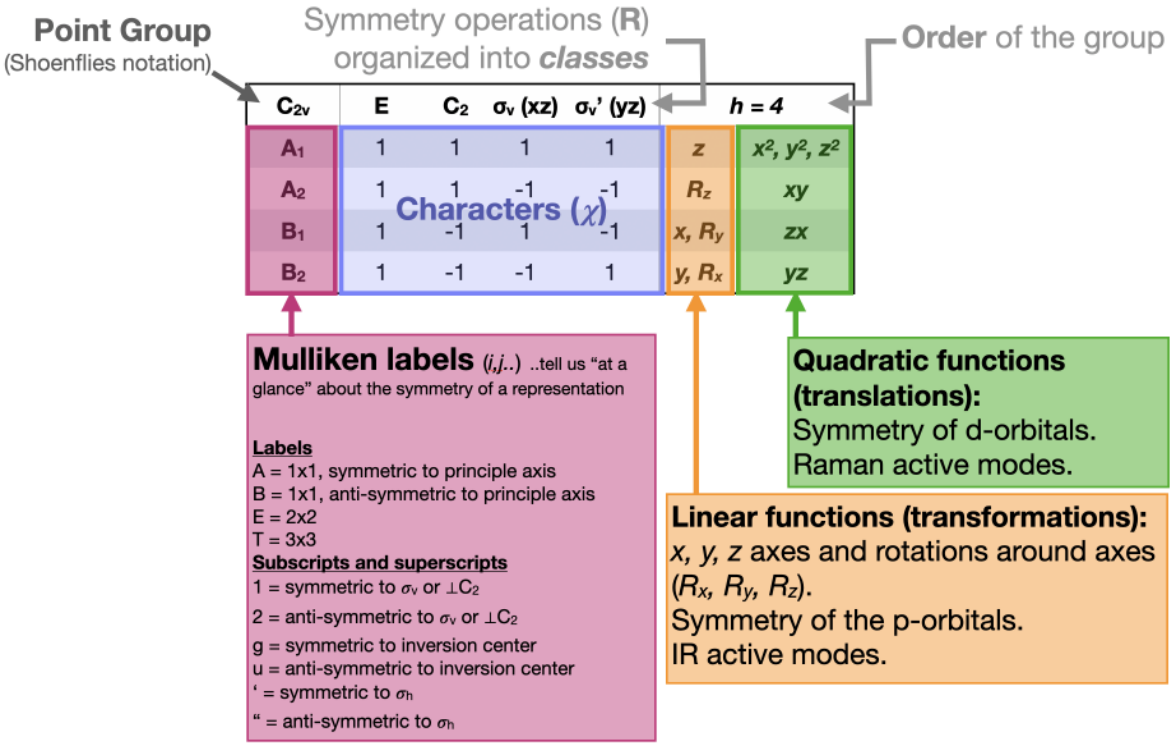


Figure 1.4.3.3.2 : Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

Contributors and Attributions

- Curated or created by Kathryn Haas
- Claire Vallance (University of Oxford)

  adapted from Character Tables (click here)

This page titled 1.4.3.3: 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.

SECTION OVERVIEW

1.4.4: Examples and Applications of Symmetry

The purpose of learning group theory is that molecular symmetry can be applied to understand the properties of molecules. This chapter introduces two applications of symmetry: chirality and molecular vibrations (in the context of analyzing IR and Raman spectra). An additional application of symmetry, to understand molecular bonding, deserves its own chapter and will be explored in Chapter 5.

1.4.4.1: Chirality

1.4.4.2: Molecular Vibrations

1.4.4: Examples and Applications of Symmetry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.4.4.1: Chirality

Introduction

Around the year 1847, the French scientist Louis Pasteur provided an explanation for the optical activity of tartaric acid salts. When he carried out a particular reaction, Pasteur observed that two types of crystals precipitated. Patiently and carefully using tweezers, Pasteur was able to separate the two types of crystals. Pasteur noticed that the types rotated plane-polarized light by the same amount but in different directions. These two compounds are called enantiomers.

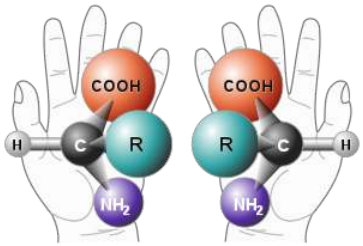


Figure 1.4.4.1.1 : Two enantiomers of an amino acid (with side chain R).

What is chirality?

A molecule is **chiral** (or **dissymetric**) if it is non-superimposable on its mirror image. The two mirror images of a chiral molecule are called enantiomers. Enantiomers have the same physical properties (e.g., melting point, etc.). They differ in their ability to rotate plane polarized light and in their reactivity with other chiral molecules. Due to their ability to rotate plane polarized light, they are referred to as being *optically active*.

Using Symmetry to Determine Chirality

There are some general rules of thumb that help determine whether a molecule is chiral or achiral. The point group of the molecule, and the symmetry operations within that point group, can give clues as to whether the molecule is chiral.

Symmetry operations of chiral molecules

A chiral molecule cannot possess a plane of symmetry (σ), a center of inversion (i), or an improper rotation (S_n). Due to the fact that all groups that lack both σ and i also lack S_n, **a molecule that belongs to any group that lacks S_n is chiral**.

An example of an inorganic coordination complex is tris(ethylenediamine)cobalt(III) (Figure 1.4.4.1.1). Figure 1.4.4.1.1shows the two enantiomers of tris(ethylenediamine)cobalt(III): the Δ and Λ isomers.

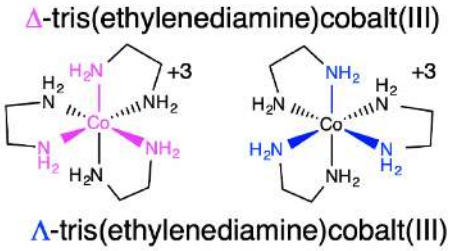


Figure 1.4.4.1.2 : Two chiral enantiomers of tris(ethylenediamine)coalt(III).

You can visualize the Λ and Δ isomers by imagining that the ligands around the metal centers are blades of a fan. To push the air toward you, you would need to rotate the Δ isomer clockwise, and the Λ isomer counter-clockwise.

Exercise 1.4.4.1.1

Which point groups are possible for chiral molecules?

Answer

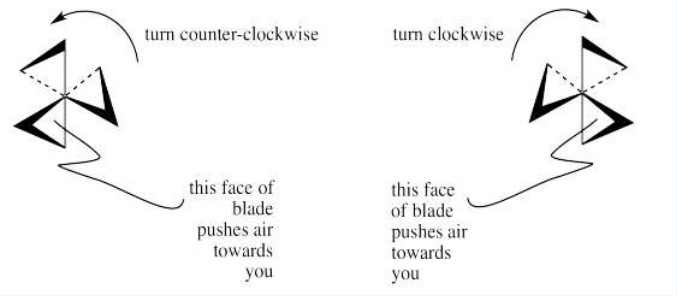


Figure 1.4.4.1.3: Another way of thinking about the chirality of the two chiral enantiomers of tris(ethylenediamine)coalt(III) shown in Figure 1.4.4.1.2. This figure was taken from Structure and Reactivity in Organic, Biological, and Inorganic Chemistry.

As a result of the previous discussion, there are a few classes of point groups that lack an improper axis. Those classes are C_1, C_n, and D_n.

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

- **4.4.1: Chirality** by Kathryn Haas is licensed CC BY-NC 4.0.

1.4.4.2: Molecular Vibrations

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

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

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

To answer this question with group theory, a pre-requisite is that you **assign the molecule's point group and assign an axis system** to the entire molecule. By convention, the z axis is collinear with the principle axis, the x axis is in-plane with the molecule or the most number of atoms. It is a good idea to stick with this convention (see Figure 1.4.4.2.1).

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

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

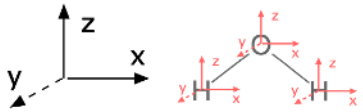


Figure 1.4.4.2.1: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom. (CC-BY-SA; Kathryn Haas)

Now that we know the molecule's point group, we can use group theory to determine the symmetry of all motions in the molecule, or the symmetry of each of its degrees of freedom. Then we will subtract rotational and translational degrees of freedom to find the vibrational degrees of freedom. The number of degrees of freedom depends on the number of atoms (N) in a molecule. Each atom in the molecule can move in three dimensions (x, y, z), and so the number of degrees of freedom is three dimensions times N number of atoms, or $3N$. The total degrees of freedom include a number of vibrations, three translations (in x, y, and z), and either two or three rotations. Linear molecules have two rotational degrees of freedom, while non-linear molecules have three. The vibrational modes are represented by the following expressions:

$$\begin{aligned} \text{Linear Molecule Degrees of Freedom} &= 3N-5 \\ \text{Non-Linear Molecule Degrees of Freedom} &= 3N-6 \end{aligned}$$

Our goal is to find the symmetry of all degrees of freedom, and then determine which are vibrations that are IR- and Raman-active.

STEP 1: Find the reducible representation for all normal modes Γ_{modes}.

The first major step is to **find a reducible representation (Γ)** for the movement of all atoms in the molecule (including rotational, translational, and vibrational degrees of freedom). We'll refer to this as Γ_{modes}. To find normal modes using group theory, **assign an axis system** to each individual atom to represent the three dimensions in which each atom can move. Each axis on each atom should be consistent with the conventional axis system you previously assigned to the entire molecule (see Figure 1.4.4.2.1).

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

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

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

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

Let's walk through the steps to assign characters of $\boldsymbol{\Gamma_{modes}}$ 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

(1.4.4.2.1)

STEP 2: Break $\boldsymbol{\Gamma_{modes}}$ into its component irreducible representations.

Now that we've found the Γ_{modes} (1.4.4.2.1), 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:

$$\#\text{ of } i = \frac{1}{h}\sum(\#\text{ of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \qquad (1.4.4.2.2)$$

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

Using equation 1.4.4.2.2, we find that for all normal modes of H_2O:

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2 \tag{1.4.4.2.3}$$

.

Notice there are 9 irreducible representations in Equation 1.4.4.2.3. These irreducible representations represent the symmetries of all 9 motions of the molecule: vibrations, rotations, and translations.

? Exercise 1.4.4.2.1: Derive the irreducible representation in equation 1.4.4.2.3.

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 1.4.4.2.3

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 (1.4.4.2.1), the C_{2v} character table (below), and equation 1.4.4.2.2

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

In the C_{2v} point group, each class has only one operation, so the number of operations in each class (from equation 1.4.4.2.2) 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 1.4.4.2.3, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{1.4.4.2.4}$$

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

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

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

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

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

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

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

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

IR and Raman Selection Rules

Infrared selection rules:

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

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

Raman selection rules:

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

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

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

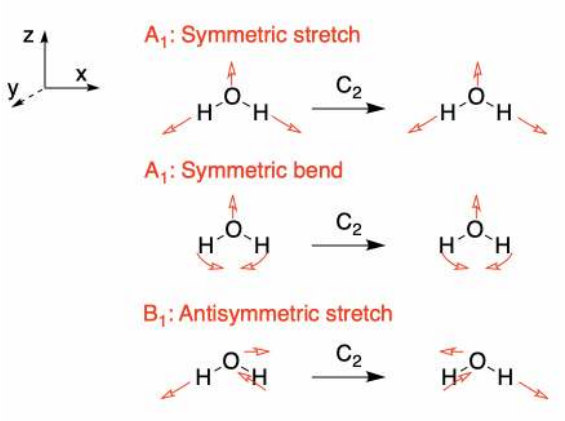


Figure 1.4.4.2.2 : Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

Table 1.4.4.2.1 : Summary of the Symmetry of Molecular Motions for Water

All Motions (step 2 above)	Translations (x,y,z)	Rotations (R_x, R_y, R_z)	**Remaining Vibrations**	Description of Vibration
$3A_1$	$1A_1$		$\mathbf{2A_1}$	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 1.4.4.2.2

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

Answer

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

(1.4.4.2.5)

.

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 1.4.4.2.1 The isomers in each case can be distinguished using vibrational spectroscopy.

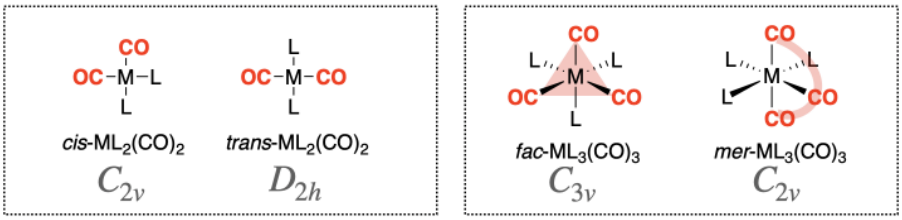


Figure 1.4.4.2.3: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box. *Mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$) are shown in the right box. The point group for each of the general structures is also shown. (CC-BY-NC-SA; Kathryn Haas)

EXAMPLE 1: Distinguishing *cis*- and *trans*- isomers of square planar metal dicarbonyl complexes

General structures of the *cis*- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box in Figure 1.4.4.2.1 We can use symmetry and group theory to predict how many carbonyl stretches we should expect for each isomer following the steps below.

Step 1: Assign the point group and Cartesian coordinates for each isomer.

The *cis*-isomer has C_{2v} symmetry and the *trans*-isomer has D_{2h} symmetry. We assign the Cartesian coordinates so that z is colinear with the principle axis in each case. For the D_2h isomer, there are several orientations of the z axis possible. The axes shown in Figure 1.4.4.2.2will be used here.



Figure 1.4.4.2.4: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown and oriented with respect to the Cartesian coordinates shown at the left so that the highest-order rotation axis is colinear with z and the molecule is co-planar with the xz plane. The vector along each C—O bond is shown using a red arrow (→). These vectors represent the direction of C—O stretching motions. (CC-BY-NC-SA; Kathryn Haas)

Step 2: Produce a reducible representation (Γ) for CO stretches in each isomer

First, assign a vector along each C—O bond in the molecule to represent the direction of C—O stretching motions, as shown in Figure 1.4.4.2.2(red arrows →). These vectors are used to produce a reducible representation (Γ) for the C—O stretching motions in each molecule. Using the symmetry operations under the appropriate character table, assign a value of 1 to each vector that remains in place during the operation, and a value of 0 if the vector moves out of place. There will be no occasion where a vector remains in place but is inverted, so a value of -1 will not occur.

cis- $ML_2(CO)_2$:

For *cis*- $ML_2(CO)_2$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{cis-CO}.

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0

trans- $ML_2(CO)_2$:

For trans- $ML_2(CO)_2$, the point group is D_{2h} and so we use the operations under the D_{2h} character table to create the $\Gamma_{trans-CO}$.

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0

Step 3: Break each Γ into its component irreducible representations

Each Γ can be reduced using inspection or by the systematic method described previously.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

(1.4.4.2.6)

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 1.4.4.2.6(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 1.4.4.2.6(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 1.4.4.2.3

Repeat the steps outlined above to determine how many CO vibrations are possible for *mer*-$ML_3(CO)_3$ and *fac*-$ML_3(CO)_3$ isomers (see Figure 1.4.4.2.1) in both IR and Raman spectra. Could either of these vibrational spectroscopies be used to distinguish the two isomers?

Answer

Step 1: Assign the point group and Cartesian coordinates for each isomer.
The *fac*-isomer is C_{3v}. The *mer*-isomer is C_{2v}.

Step 2: Produce a reducible representation for CO stretches in each isomer.

Step 3: Break each into its component irreducible representations.

Step 4: Determine which vibrational modes are IR-active and/or Raman-active.

***For fac*-$ML_3(CO)_3$**, the point group is C_{3v} and so we use the operations under the C_{3v} character table to create the Γ_{fac-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

$\mathbf{C_{3v}}$	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 1.4.4.2: Molecular Vibrations is shared under a CC BY-NC 4.0 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.

1.4.P: Problems (under construction)

Problems

1. Chlorophyll *a* is a green pigment that is found in plants. Its molecular formula is $C_{55}H_{77}O_5N_4Mg$. How many degrees of freedom does this molecule possess? How many vibrational degrees of freedom does it have?
2. CCl_4 was commonly used as an organic solvent until its severe carcinogenic properties were discovered. How many vibrational modes does CCl_4 have? Are they IR and/or Raman active?
3. The same vibrational modes in H_2O are IR and Raman active. WF_6^- has IR active modes that are not Raman active and vice versa. Explain why this is the case.
4. How many IR peaks do you expect from SO_3? Estimate where these peaks are positioned in an IR spectrum.
5. Calculate the symmetries of the normal coordinates of planar BF_3.

Answers to Problems

1. Chlorophyll *a* has 426 degrees of freedom and 420 vibrational modes.
2. The point group is T_d, $T_{vib} = a_1 + e + 2t_2$; a_1 and e are Raman active, t_2 is both IR and Raman active.
3. For molecules that possess a center of inversion i, modes cannot be simultaneously IR and Raman active.
4. Point group is D_{3h}; one would expect three IR active peaks. Asymmetric stretch highest (1391 cm^{-1}), two bending modes (both around 500 cm^{-1}). The symmetric stretch is IR inactive.
5. $T_{3N} = A_1' + A_2' + 3E' + 2\ A_2'' + E''$ and $T_{vib} = A_1' + 2E' + A_2''$

Contributors and Attributions

- Kristin Kowolik, University of California, Davis

Problems

1. The water molecule H_2O was used as an example; it was mentioned that when water was rotated 180 degrees around an axis bisecting the oxygen, the molecule was superimposable on the original water molecule. How about CO_2? Will it be like the water molecule since CO_2 also has 2 atoms of oxygen?

Of course not, because every molecule has a different molecular shape. To recognize the symmetry of any molecule, the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degrees around the axis bisecting the C atom, then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to? Why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry, since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates whether we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bonding for that molecule.

1.4.P: Problems (under construction) 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

2: d-Block Metal Chemistry- General Considerations

Coordination compounds are important to all areas of chemistry, engineering, the life and environmental sciences, and beyond. In the synthetic laboratory catalytic amounts of coordination compounds enable organic chemists to synthesize new compounds selectively and in high yield under mild conditions. Applied industrially, coordination compound catalysts serve as vital catalysts that facilitate the conversion of raw petrochemical or bio-derived feedstocks into useful industrial and consumer products. Without them life as we know it would be impossible, as many biochemical systems are coordination complexes. Examples include the hemoglobin that transports oxygen around our bodies and the myoglobin that stores it, the photosystems that harvest light and use light energy in photosynthesis, the constituents of the respiratory chain, and many of the enzymes involved in the expression and transmission of genetic information. In studying coordination chemistry you are about to take your first steps into a vast and exciting world.

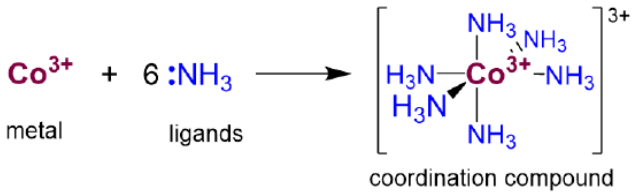
2.1: Prelude to Coordination Chemistry I - Structure and Isomers
2.2: History
2.3: Nomenclature and Ligands
2.4: Isomerism
2.5: Coordination Numbers and Structures
2.6: Coordination Frameworks
2.P: Problems

2: d-Block Metal Chemistry- General Considerations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

2.1: Prelude to Coordination Chemistry I - Structure and Isomers

What is a coordination compound?

Coordination compounds consist of one or more **metals** bound to one or more Lewis base **ligands**. For example, hexammineruthenium (3+) ion is a coordination complex in which six ammonia ligands coordinate a Co^{3+} ion, as shown in Scheme 2.1.1.



Scheme 2.1.1: Formation of hexammineruthenium(3+) ion from Co^{3+} and NH_3. (CC BY 4.0; Stephen Contakes)

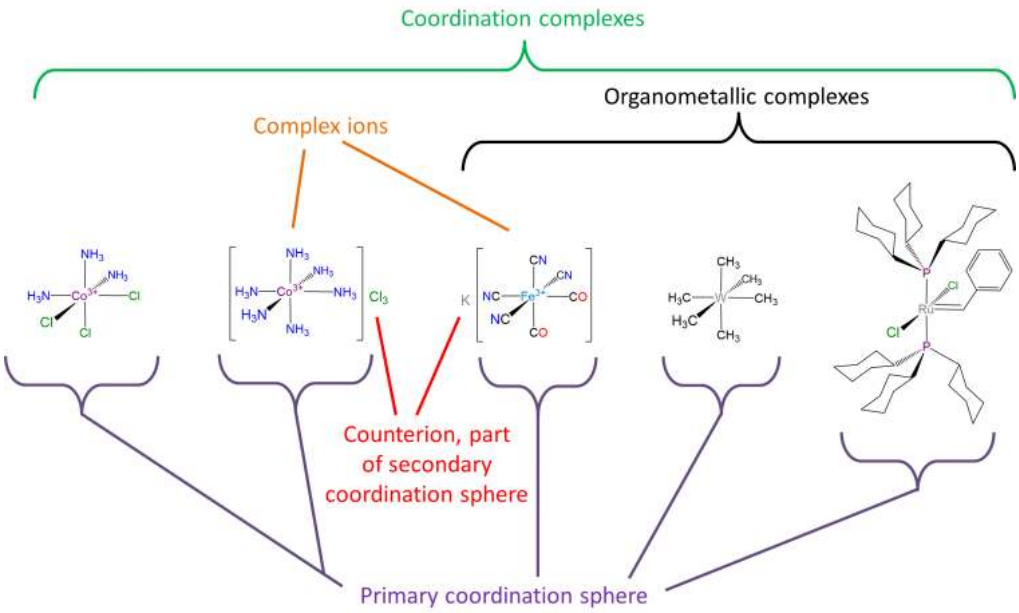
Such complexes are called coordination complexes because the ligand-metal bond may be thought of as a **coordinate covalent bond** in which both of the bonding electrons come from the ligand, which is then said to **coordinate** the metal. This coordinate covalent model is a very useful formalism for understanding the basic features of coordination chemistry, although it does not always accurately reflect the actual details of the bonding in every coordination complex. Nevertheless, even in those cases where the simple coordinate covalent bond model breaks down, the coordinate covalent bond concept supplies the language sophisticated models employ to describe the more complex bonding involved.

Additional important terms

Some of the common widely used terms that follow from the coordinate covalent model of bonding in coordination complexes include:

- Coordination compounds are also called **coordination complexes**, **metal complexes**, or just **complexes**. The term **complex** refers to coordination compounds' composite nature, in that they may be thought of as comprising multiple ligand and metal ion parts that can be restored by breaking the coordinate covalent bonds holding the complex together. This is in contrast to inorganic or organic molecules which are more commonly thought about as whole molecules held together by the sharing of electrons contributed by all the atoms.
- Coordination complexes that are ions are called **complex ions.**
- Ligands bound to the coordination complex are said to reside in the **primary** or **inner coordination sphere**. These bound ligands are not readily exchangeable, in contrast to nearby counterions and solvent molecules, which are said to reside in the **secondary** or **outer coordination sphere**.
- The portion of the complex contributing the electron pairs is said to be the **donor** and the portion which receives them the **acceptor**. In conventional coordination compounds the ligand is the donor and the metal the acceptor. In these cases it would be equally convenient to refer to the ligand donor as the Lewis base and the metal acceptor as the Lewis acid. However, in more complex bonding scenarios there may be multiple electron pair donation and acceptance interactions taking place between each pair of atoms and donor-acceptor language will be more convenient.
- The number of ligand sites donating lone pairs to the central atom is referred to as the **coordination number**. For most complexes this will just be equal to the number of ligand atoms bound to the metal. In simple complexes it is just equal to the number of ligands. For instance, the cobalt in Scheme 2.1.1 has a coordination number of six.
- Although technically compounds with metal-carbon bonds are coordination complexes, the term coordination complex is sometimes used to refer to complexes which do not possess metal-carbon bonds in their primary coordination sphere. Complexes which possess metal-carbon bonds are called **organometallic compounds** instead. The use of the terms organometallic and coordination to distinguish organometallic compounds from other types of coordination compounds is often convenient since many organometallic ligands engage in more than simple σ donor-acceptor coordinate covalent bond formation with the metal center. However, this is true of some wholly inorganic ligands too, so it should always be kept in mind that organometallic compounds are just a type of coordination compound and that inorganic ligands can in principle be tuned to interact with a metal center in much the same way an organic ligand does.

A summary of some of the concepts and terms used to describe coordination compounds is given in Scheme 2.1.2.



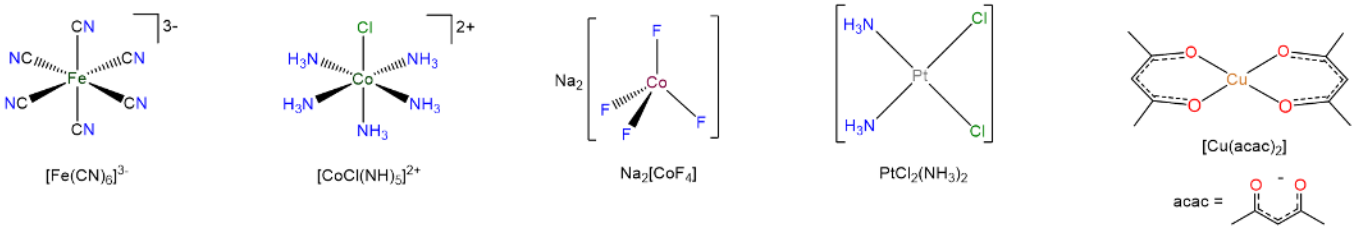
Scheme 2.1.2: Some terms used to describe coordination compounds. (CC BY 4.0; Stephen Contakes)

The formulae of coordination complexes

The way the formulae of coordination complexes are written reflects the fact that it is often convenient to think of coordination compounds as a composite of metals and ligands. When writing the formula of a complex

- the atoms of a ligand are not added to those of the rest of the compound. Instead, the ligand atoms are kept together, if necessary by enclosing the ligand formula in parentheses or giving an abbreviation for the ligand.
- For complex ions the metal and ligands are enclosed in square brackets. Sometimes this is also done for neutral coordination compounds as well. In either case the brackets enclose those parts of the compound which comprise the primary coordination sphere; anything else is in the secondary coordination sphere outside.

A careful perusal of the examples in Scheme 2.1.3 should make the important features of this system clear.



Scheme 2.1.3: Formulae of coordination compounds and complex ions. (CC BY 4.0; Stephen Contakes)

2.1: Prelude to Coordination Chemistry I - Structure and Isomers is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.1: Prelude to Coordination Chemistry I - Structure and Isomers** by Stephen M. Contakes is licensed CC BY 4.0.

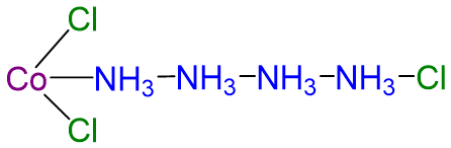
2.2: History

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; one of the oldest synthetic pigments is the blue pigment Egyptian blue, a copper complex of formula $CaCuSi_4O_{10}$ used by the Egyptians since the third Millenium B.C. (in ancient China the Ba analogue, Han blue, was discovered independently). The blue color of Egyptian blue is due to interlocked $Cu(Si_2O_7)_4$ units in which each copper is coordinated by four O atoms in a square planar arrangement. Later, in 1706, the Berlin painter Diesbach would discover another deep blue pigment, Prussian blue: $KFe_2(CN)_6$.

Despite their long use, the chemical nature of coordination compounds was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF_3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds. Of these the most influential was the Blomstrand-Jørgensen chain theory of bonding in coordination compounds, which predicted the "Chattanooga choo-choo" model for $CoCl_3{\cdot}4NH_3$ shown in Scheme 2.2.I.



Scheme 2.2.I. Blomstrand-Jørgensen chain theory model of bonding in $CoCl_3{\cdot}4NH_3$.

Nevertheless, this theory was not wholly illogical and, in fact, explained much of the analytical data on coordination compounds available to chemists of the time. This data included the electrical conductivity of aqueous solutions of these compounds, which was roughly proportional to the number of ions formed per mole, and the number of free chloride ions present, which could be determined by precipitating them gravimetrically as AgCl. In the case of $CoCl_3{\cdot}4NH_3$, two ions and one chloride were produced when the compound was dissolved in water, which Jørgensen was able to explain using the chain structure shown above by postulating that chlorides attached to NH_3 could dissociate while those attached to Co could not. The modern theory of coordination chemistry, which overthrew the chain theory, is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table 2.2.1. Werner's data on $PtCl_4{\cdot}6NH_3$ in Table 2.2.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$, was a neutral molecule that did not give free chloride ions when dissolved in water.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 2.2.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (oxidation state) that corresponds to the positive charge on the metal ion and (2) a secondary valence (coordination number) that is the total number of ligands bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq) \quad (2.2.1)$$

$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq) \quad (2.2.2)$$

$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq) \quad (2.2.3)$$

$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq) \quad (2.2.4)$$

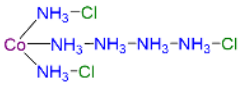
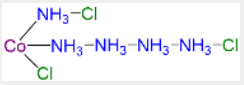
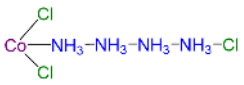
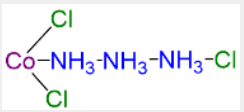
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq) \quad (2.2.5)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

? Exercise 2.2.1. The $CoCl_3 x NH_3$ series.

The series $CoCl_3 \cdot xNH_3$ was particularly important in establishing the correctness of Werner's coordination theory over the rival chain theory. By ~1900 conductivity measurements suggested that the members of the series gave the number of ions shown in Table 2.2.1.

Table 2.2.1. The CoCl3·xNH3 series according to coordination theory, chain theory, and experiment.

Compound	**Color**	**Werner formulation**	**Blomstrand-Jørgensen chain theory formulation**	**Number of ions in solution**
$CoCl_3 \cdot 6NH_3$	yellow	$[Co(NH_3)_6]Cl_3$		4
$CoCl_3 \cdot 5NH_3$	violet	$[Co(NH_3)_5Cl]Cl_2$		3
$CoCl_3 \cdot 4NH_3$	green	$[Co(NH_3)_4Cl_2]Cl$		2
$CoCl_3 \cdot 3NH_3$	orange	$[Co(NH_3)_4Cl_3]$		0

What does this data suggest about the relative explanatory power of Werner's coordination theory and chain theory? Explain.

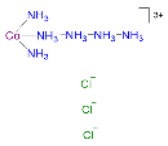
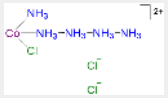
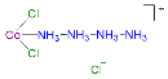
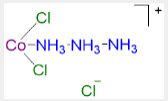
Answer

Remember that

- chain theory predicts that the number of ions is the number formed when the Cl atoms bound in a chain with NH_3 dissociate.
- coordination theory predicts the number of ions based on the number of complex ions and their counterions.

Based on this the predictions of coordination theory and chain theory can be compared with the experimental data, as is done in Table 2.2.2

Table 2.2.2: Comparison of ions predicted for the $CoCl_3 \cdot xNH_3$ series by coordination theory and chain theory with the number observed experimentally.

Compound	Color	Ions predicted by Werner's coordination theory	Number of ions predicted by coordination theory	Ions predicted by Blomstrand-Jørgensen chain theory	Number of ions predicted by chain theory	Observed Number of ions in solution
$CoCl_3 \cdot 6NH_3$	yellow	$[Co(NH_3)_6]^{3+}$ Cl^- Cl^- Cl^-	4		4	4
$CoCl_3 \cdot 5NH_3$	violet	$[Co(NH_3)_5Cl]^{2+}$ Cl^- Cl^-	3		3	3
$CoCl_3 \cdot 4NH_3$	green	$[Co(NH_3)_4Cl_2]^+$ Cl^-	2		2	2
$CoCl_3 \cdot 3NH_3$	orange	None	0		2	0

As can be seen by comparing the number of ions predicted by coordination and chain theory in Table 2.2.2 coordination theory successfully explains all the observed ion counts, while chain theory fails to explain the lack of ions observed for $CoCl_3 \cdot 3NH_3$.

Nevertheless, as is often the case when developing theoretical models using data from real experimental investigations, these observations did not convince Jørgensen, who could point to the experimental difficulty of determining the number of ions present from solution conductivity data.

What ultimately convinced Jørgensen of the correctness of Werner's coordination model over his own chain theory was how Werner's explanation of the structure of cobalt coordination complexes using an octahedral coordination geometry explained the existence of isomers in Co complexes containing Cl and NH_3 ligands. In the case of $[Co(NH_3)_4Cl_2]Cl$ two isomers were known: one red and the other green. Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, stereoisomers (Figure 2.2.1). His conclusion was also corroborated by the existence of two and only two stereoisomers of the next compound in the series: $Co(NH_3)_3Cl_3$.

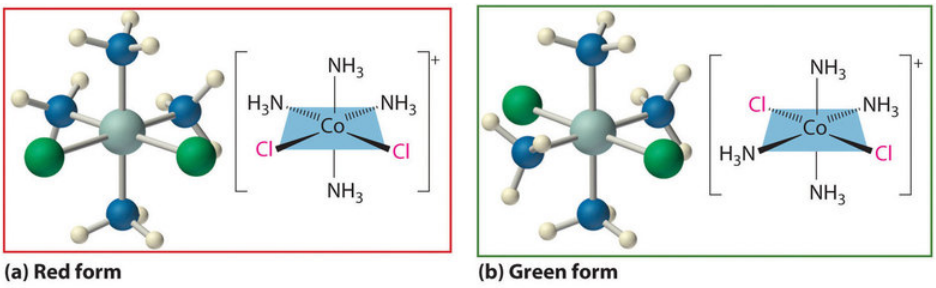


Figure 2.2.1. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other (*cis*), the complex is red (a), but if they are opposite each other (*trans*), the complex is green (b).

Example 2.2.1: Why did Werner propose an octahedral geometry for 6-coordinate complexes?

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning that this suggests these complexes possess an octahedral geometry, calculate the maximum number of different structures possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures the ligands will form about the central metal - a hexagon, a trigonal prism, and an octahedron.

Assuming that the absence of evidence for additional compounds in this case serves as reasonable circumstantial evidence for their absence, what does the fact that no more than two forms of any MA_4B_2 complex were known suggest about the three-dimensional structures of these complexes?

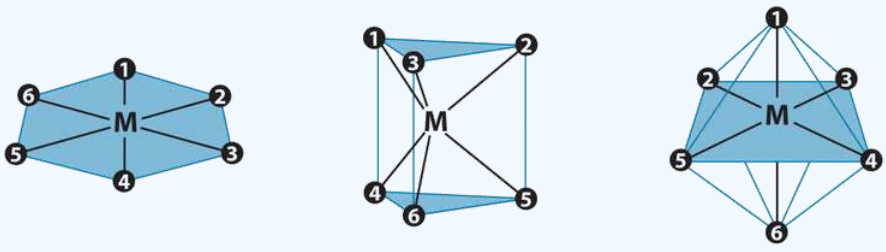
Solution

In this problem you are given

- the stochiometry of the complexes, MA_4B_2
- three possible coordination geometries - hexagonal, trigonal prismatic, and octahedral.

In order to calculate the number of isomers that could be present for each geometry it is best to follow a systematic approach. Since there are fewer B type ligands than A type ligands, the easiest way to do this for each geometry is to start by placing a B ligand at one vertex and then to determine how many different positions are available for the second B ligand.

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now **three** possible places for the second B ligand:

- position 2 (or 6)
- position 3 (or 5)
- position 4

The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand. Those of you who remember your ogranic chemistry might recognize that this situation is formally analogous to the *ortho*-, *meta*-, and *para*-isomerism in disubstituted benzenes.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand:

- at position 2 or 3 on the same triangular face
- position 4 (on the other triangular face but adjacent to 1)
- position 5 or 6 (on the other triangular face but not adjacent to 1).

The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand:

- position 2 (or 3 or 4 or 5)
- position 6.

In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

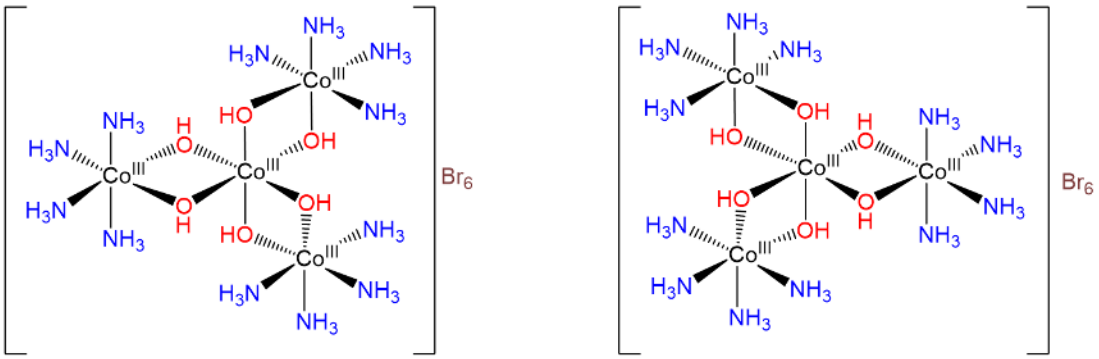
? Exercise 2.2.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Even Werner's explanation of isomerism in coordination complexes in terms of octahedral and other recognized coordination geometries did not convince all chemists until he was able to resolve a racemic mixture of *d*- and *l*-$[Co\{Co(NH3)_4(OH)_2\}_3]$ into its enantiomers, which are shown in Scheme 2.2.II. By doing so Werner demonstrated to chemists of his time (virtually none of whom knew group theory) that tetrahedral carbon atoms were not required for chirality; D_3 octahedral complexes were also chiral.



Scheme 2.2.II : d- and l-enantiomers of $[Co\{Co(NH3)_4(OH)_2\}_3]$, colloquially referred to as hexol. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.2: History is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **24.1: Werner's Theory of Coordination Compounds** by Anonymous is licensed CC BY-NC-SA 4.0.

2.3: Nomenclature and Ligands

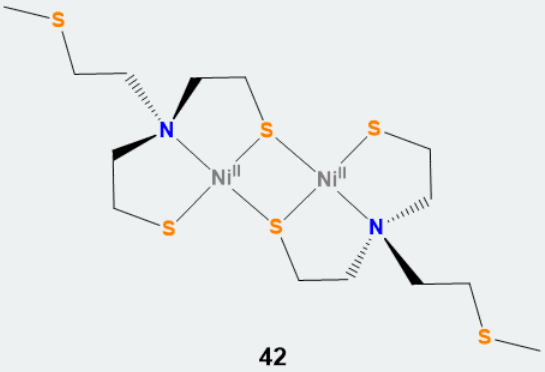
Systems of nomenclature and formulae are intended as tools, to be employed insofar as they are useful

There are well-established rules for both naming and writing the formulae of coordination compounds. The purpose of these rules is to facilitate clear and precise communication among chemists. As with all such rules, some are more burdensome than others to employ, and some serve more crucial roles in the communication process while others are more peripheral - and all are poorly used in the service of pedantic tyranny, especially when used against those who are otherwise doing good work. For this reason, you are urged to approach the rules in a spirit of generosity towards others in

- naming and writing formulas as reasonably accurately as you can so that ligands and metals are where readers expect them and thus can understand what you mean more easily.
- being gracious towards the many professional inorganic chemists who adhere loosely to some of the rules you are about to learn.
- recognizing that in cases when a structure is particularly complex and a picture may make be particularly useful, you should supply one (See the note below).

Note 2.3.1: Sometimes the most helpful name to give a compound is 42.

Even though the IUPAC nomenclature rules permit specification of even the most complex structures, it is often much easier and more effective to supply a numbered structure that can be referred to instead of the IUPAC name. Consider bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. Which is easier, to expect readers and hearers to work out the structure from that name or to just refer them to compound **42** in Scheme 2.3.1?



42

Scheme 2.3.1. Structure of bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. The authors of the synthesis of this compound in Inorganic syntheses1 may have had to figure out an IUPAC name for this compound but if you have this scheme in your paper and your instructor is OK with it you can just call it **42**

Coordination Complexes are named as the ligand derivatives of a metal

A variety of systems have been used for naming coordination compounds since the development of the discipline in the time of Alfred Werner. In this section the most common approaches as they are currently used by practicing chemists will be described. Those who need a more thorough and accurate acquaintance with the full IUPAC nomenclature rules are encouraged to consult the IUPAC brief guide to inorganic nomenclature followed by complete guidelines, commonly known as the IUPAC red book. If those are still not enough a careful read of note 2.3.1 is suggested.

The systems for naming coordination compounds used at present are additive, meaning that they consider coordination compounds as comprising a central metal to which are added ligands. To specify the structure and bonding in this metal-ligand complex then involves:

1. when there are several different ways of attaching the metal and ligands, specifying the structural or stereoisomer
2. systematically listing the ligands in a way that, as necessary, conveys information about how they are linked to the metal and their stereochemistry

3. providing the identity of the metal and its oxidation state, or if the oxidation state is unclear, at least the overall charge on the complex
4. specifying any counterions present

Since the stereochemistry of coordination compounds forms the subject of the next section, in this section it will be addressed by simply giving the prefixes that designate stereochemistry as if they were self-evident. Do not worry about these for now. They will make sense after you have learned more about stereochemistry in the next section. At that time, you can go back over the examples in that section to solidify your understanding of how to name coordination compounds.

However, in order to name coordination compounds accurately you will need to learn how to think about and name ligands first.

Ligands

Ligands are classified based on whether they bind to the metal center through a single site on the ligand or whether they bind at multiple sites. Ligands that bind through only a single site are called **monodentate** from the Latin word for tooth; in contrast, those which bind through multiple sites are called **chelating** after the Greek $\chi\alpha\lambda\epsilon$ for "claw". These relationships are summarized in Figure 2.3.1.

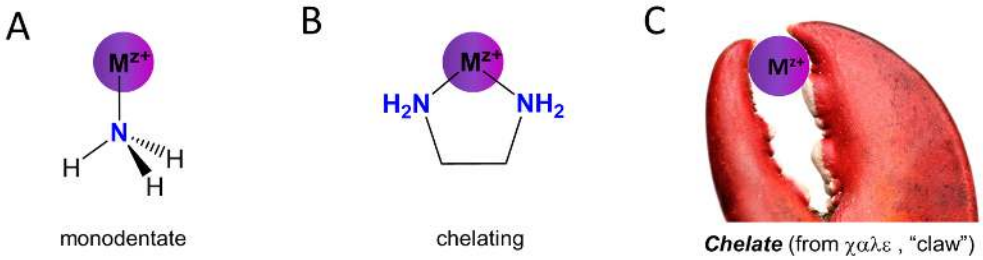
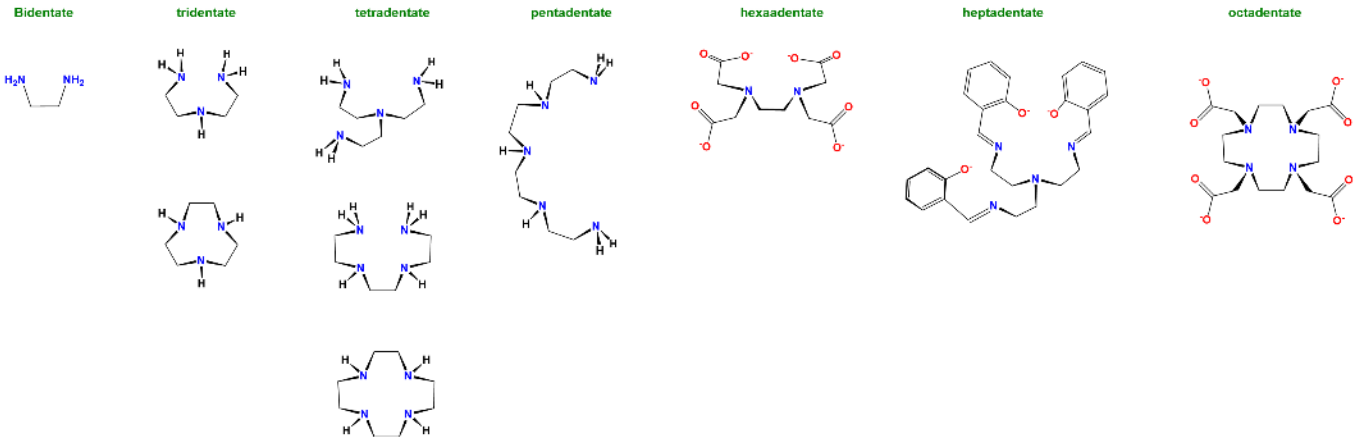


Figure 2.3.1. (A) Ammonia is a monodentate ligand while (B) ethylene diamine is a chelating ligand owing to its capacity to bind metals via its two amine functional groups. (C) Chelating ligands act like a lobster claw in attaching to the metal via multiple sites. The lobster claw image is adapted from https://www.clipart.email/download/1127636.html. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Following naturally from the classification of non-chelating ligands as monodentate, chelating ligands are further classified according to the number of sites which they can use to bind a metal center. This number of binding sites is called the denticity and ligands are referred to as monodentate (non- chelating), bidentate, tridentate, etc., based on the number of sites available. Ligands with two binding sites have a denticity of two and are said to be bidentate; those with three are tridentate, four tetradentate, and so on. To illustrate this classification system examples of chelating ligands classified according to denticity are given in Scheme 2.3.I.

Scheme 2.3.I. A selection of chelating ligands classified according to denticity.

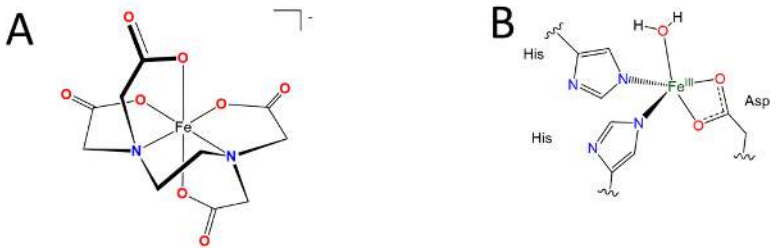


Scheme 2.3.IIA. Because only one oxygen per carboxylate *typically* binds, only one is counted when assigning a ligand's denticity. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

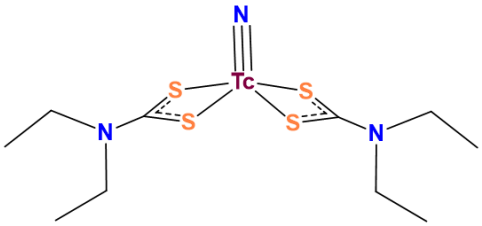
Although only one carboxylate oxygen *usually* binds to a metal, it is still possible to bind for both oxygens to bind to a single metal. As shown in Scheme 2.3.IIB, complexes in which both carboxylates bind to a metal are known, and in fact are common in

the active sites of some enzymes. It is just that the binding of both oxygens gives a strained four-membered ring that is usually unstable.

Scheme 2.3.II. (A) Only one oxygen per carboxylate counts towards the denticity of EDTA since on binding the other oxygen generally points away from the metal center, as in the structure of $Fe(EDTA)^-$. (B) In some enzyme active sites both oxygens of a carboxylic acid (aspartate or Asp in this example) bind to a metal. The aspartate carboxylic acid group is bidentate while the EDTA carboxlic acid groups in A are monodentate. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.



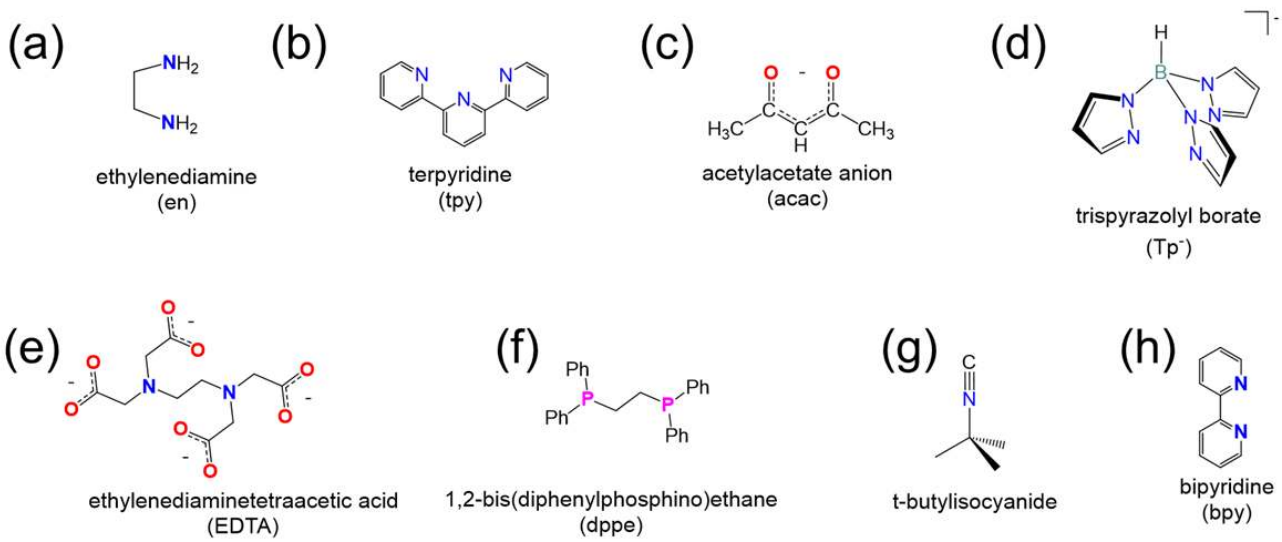
Scheme 2.3.III. As in this complex, dithiocarbamates commonly bind metals through both sulfur atoms. Consequently, dithiocarbamates are classified as bidentate. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.



Because of these factors it is technically more correct to say that carboxylates *usually act as* monodentate ligands and dithiocarbamates bidentate ones than it is to say that carboxylates *are* monodentate ligands and dithiocarbamates bidentate ones. So in other words the ligand classifications presented here just represent common binding modes.

Exercise 2.3.1

Determine the denticity of each ligand in the list below and classify them as monodentate, tridentate, etc.



Answer

(a) bidentate

(b) tridentate

(c) bidentate

(d) tridentate (only the lower N on each ring has a lone pair that can be used to bind the metal)

(e) hexadentate (remember that each carboxylate only counts as one point of attachment)

(f) bidentate

(g) monodentate (through the lone pair on the isocyanide C)

(h) bidentate

This experimentally-based classification of dithiocarbamates as bidentate and carboxylates as monodentate can be confusing to a beginner. Fortunately, such experimentally based classifications are embedded in the lists of common monodentate ligands as given in Table 2.3.1 and common chelating ligands in Table 2.3.2.

A perusal of the ligands in Table 2.3.1 reveals that several can bind to a metal in multiple ways. For example, thiocyanate, SCN^- can bind metals through its S or N atoms. Such ligands are called **ambidentate ligands**. In naming an ambidentate ligand, the atom through which it attaches to the metal is commonly specified after the ligand name using the italicized element symbol or, more formally, a κ followed by the italicized element symbol. An example is given in Scheme 2.3.1.[2]

Scheme 2.3.1. Two possible binding modes of nitrite acting as a ligand.[3]

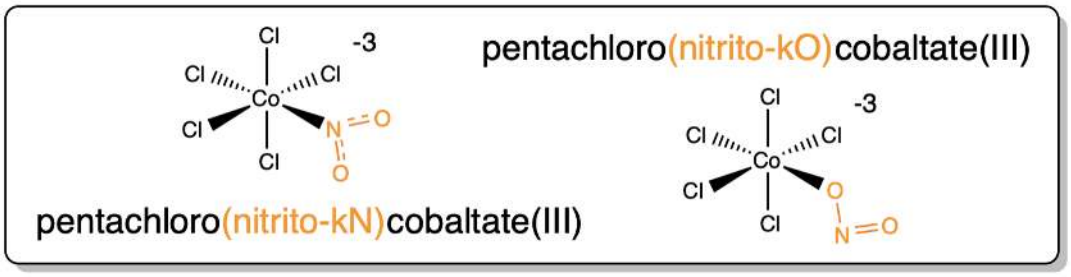
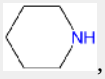
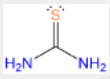


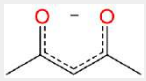
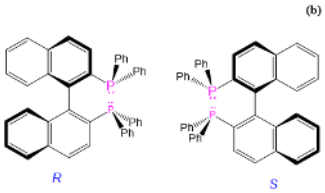
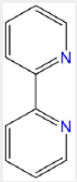
Table 2.3.1. Common monodentate ligands. Most chemists still prefer common names over the IUPAC ones.

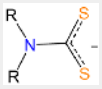
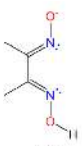
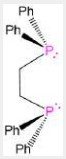
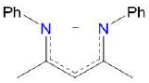
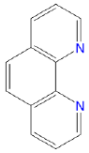
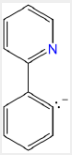
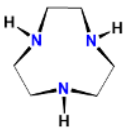
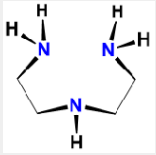
Ligand	Common name	IUPAC name
H^- (H ligands are always considered anions for naming purposes)	hydrido	hydrido
F^-	fluoro	fluorido
Cl^-	chloro	chlorido
Br^-	bromo	bromido
I^-	iodo	iodido
CN^-, as M-CN	cyano	cyanido or cyanido-κC or cyanido-*C*
CN^-, as M-NC	isocyano	isocyanido or cyanido-κN or cyanido-*N*
CH_3NC	methylisocyanide	methylisocyanide
N_3^-	azido	azido
SCN^-, *e.g.* thiocyanate as M-SCN	thiocyanato	thiocyanato-κS or thiocyanato-*S*
NCS^-, *e.g.* thiocyanate as M-NCS	isothiocyanato	thiocyanato-κN or thiocyanato-*N*
$CH_3CO_2^-$	acetato	ethanoato

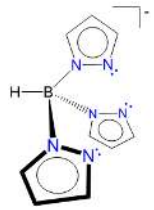
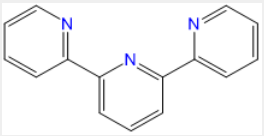
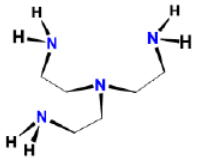
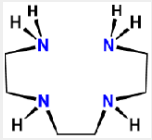
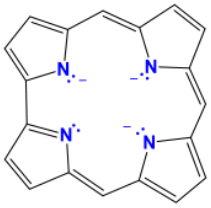
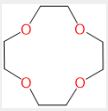
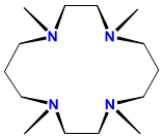
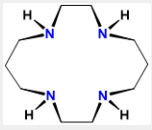
Ligand	Common name	IUPAC name
N^{3-}	nitrido	nitrido
NH^{2-}	imido	azanediido
NH_2^-	amido	azanido
NH_3	ammine	ammine
RNH_2, R_2NH, R_3N	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)
 , piperidine, abbreviated pip	piperidine	piperidine
 , pyridine, abbreviated py	pyridine	pyridine
CH_3CN, acetonitrile, abbreviated MeCN	acetonitrile	acetonitrile
P^{3-}	phosphido	phosphido
PH_3	phosphine	phosphane
PR_3	trialkylphosphine (*e.g.* trimethylphosphine for Me_3P)	trialkylphosphane (*e.g.* trimethylphosphane for Me_3P)
PAr_3	triarylphosphine (*e.g.* triphenylphosphine for Ph_3P)	triarylphosphine (*e.g.* triphenylphosphane for Ph_3P)
 , dimethylsulfoxide or DMSO or dmso	dimethylsulfoxide (sometimes called dimethylsulfoxo but this usage is rare and violates the nomenclature rules for neutral ligands)	(methanesulfinyl)methane or dimethyl(oxido)sulfur
 , thiourea or tu	thiourea	thiourea
O^{2-}	oxo	oxido
OH^-	hydroxo	hydroxido
H_2O	aqua	aqua
S^{2-}	sulfo	sulfo
HS^-	hydrosulfido	hydrosulfido
RS^-	alkanethiolate (*e.g.* ethanthiolate for EtS^-)	thioalkanoate
H_2S	hydrogen sulfide	hydrogen sulfide
R_2S	alkylsulfanylalkane (*e.g.* ethylsulfanylethane for Et_2S)	dialkyl sulfide
O_2	dioxygen	dioxygen
O_2^-, superoxide	superoxido	dioxido(1-) or superoxido
O_2^{2-}, peroxide	peroxido	dioxido(2-) or peroxido
N_2	dinitrogen	dinitrogen

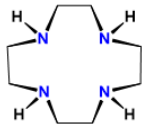
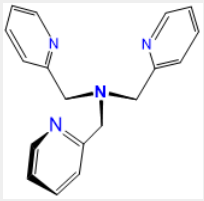
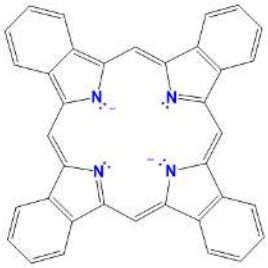
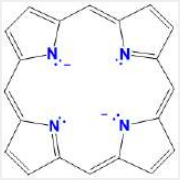
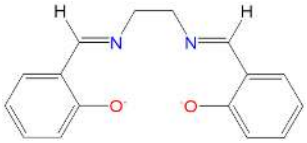
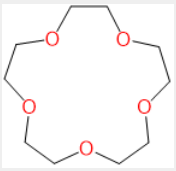
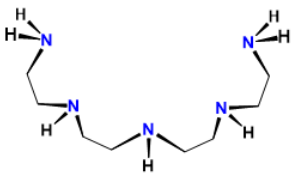
Ligand	Common name	IUPAC name
NO (are always considered neutral for naming purposes)	nitrosyl	nitrosyl
CO	carbonyl	carbonyl
CS	thiocarbonyl	thiocarbonyl
SO, as M-SO	sulfino	sulfur monoxide-κS or sulfur monoxide-*S*
NO_2, as M-NO_2	nitryl	nitrogen dioxide-κN or nitrogen dioxide-*N*
CO_3^{2-}	carbonato	carbonato
NO_2^-, as M-NO_2	nitro or nitrito-*N*	nitrito-κN or nitrito-*N*
NO_2^-, as M-ONO	nitrito or nitrito-*O*	nitrito-κO or nitrito-*O*
NO_3^-	nitrato	nitrato
SO_3^{2-}	sulfito	sulfito
SO_4^{2-}	sulfato	sulfato
$S_2O_3^{2-}$, as M-S-SO_2-O^-	thiosulfato-*S*	thiosulfato-κS or thiosulfato-*S*
$S_2O_3^{2-}$, as M-O-SO_2-S^-	thiosulfato-*O*	thiosulfato-κO or thiosulfato-*O*

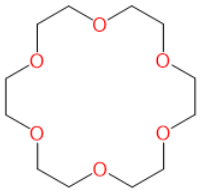
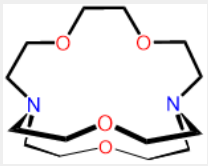
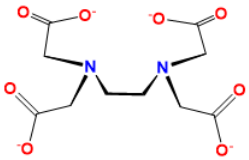
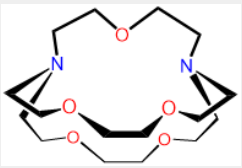
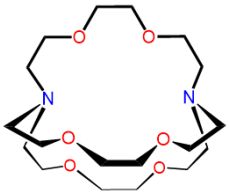
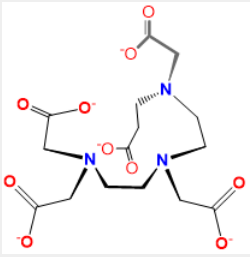
Table 2.3.2. Common chelating ligands organized by denticity. Most chemists use the common names and abbreviations to describe these ligands.

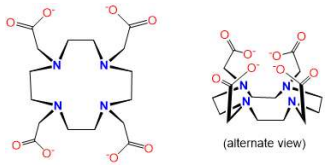
Common Ligand name	**IUPAC ligand name**	**abbreviation (if applicable)**	**structure or representative/parent structure (shown in the ionization state in which they bind to a metal)**
bidentate ligands			
acetylacetonato	2,4-pentanediono	acac	
R-BINAP and *S*-BINAP	*R*- or *S*-2,2'-bis(diphenylphosphino)-1,1'-binapthyl	BINAP	
2,2'-bipyridine	2,2'-bipyridine	bpy or bipy	
cyclooctadiene	1,5-cyclooctadiene	COD	 (binding to the metal occurs through the alkene π cloud)

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
dialkyldithiocarbamato	dialkylcarbamodithiolato	$R_2NCS_2^-$ or dtc	
dimethylgloximato	butanedienedioxime	Hdmg or DMG	 DMG  often forms bis(DMG) complexes
diphenylphosphinoethane or 1,2-(diphenylphosphino)ethane	Ethane-1,2-diylbis(diphenylphosphane)	dppe	
ethylenediamine	Ethane-1,2-diamine	en	
ethylenedithiolato	Ethane-1,2-dithiolato	$C_2H_2S_2^{2-}$	
nacnac	*N*,*N*′-diphenyl-2,4-pentanediiminato	nacnac	
oxalato	oxalato	ox	
1,10-phenanthroline or *o*-phenanthroline	1,10-phenanthroline	phen or *o*-phen	
phenylpyridinato	2-phenylpyridinato-C^2,*N* or 2-phenylpyridinato-κC^2,*N*	ppy	
tridentate ligands			
triazacyclononane	1,4,7-triazacyclononane	tacn	
diethylenetriamine	1,4,7-triazaheptane	dien	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
pyrazoylborato (scorpionate)	hydrotris(pyrazo-1-yl)borato	Tp	
terpyridine or 2,2';6',2"-terpyridine	$1^2,2^2:2^6,3^2$-terpyridine or 2,6-bis(2-pyridyl)pyridine, tripyridyl, 2,2′:6′,2″-terpyridine	tpy or terpy	
tetradentate ligands			
β, β', β"-triaminotriethylamine	β, β', β"-tris(2-aminoethyl)amine	tren	
triethylenetetramine	1,4,7,10-tetraazadecane	trien	
corroles	variable and generally not used	cor or Cor	
12-crown-4	1,4,7,10-tetraoxacyclododecane	12-crown-4	
tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC or cyclam	
cyclam	1,4,8,11-tetraazacyclotetradecane	cyclam	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
cyclen	1,4,7,10-tetraazacyclododecane	cyclen	
tris(2-pyridylmethyl)amine	1-pyridin-2-yl-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine	tpa or TPA	
phthalocyanines	variable and generally not used	variable, usually a modified Pc	
porphyrins	variable and generally not used	variable, usually a modified por, Por, or P (e.g. TPP = tetraphenylporphyrin)	
salen	2,2'-ethylenebis(nitrilomethylidene) diphenoxido	salen	
pentadentate ligands			
15-crown-5	1,4,7,10,13-Pentaoxacyclopentadecane	15-crown-5	
tetraethylenepentamine	1,4,7,10,13-pentaazatridecane	tepa or TEPA	
hexadentate ligands			

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane	18-crown-6	
2,1,1-cryptand	4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]icosane	2,1,1-crypt or [2.1.1]-cryptand kryptofix 211 and variations thereof	
ethylenediaminetetraaceto	2,2′,2″,2‴-(Ethane-1,2-diyldinitrilo)tetraaceto	EDTA, edta, Y^{4-}	
heptadentate ligands			
2,2,1-cryptand	4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]icosane	2,2,1-crypt or [2.2.1]-cryptand kryptofix 221 and variations thereof	
octadentate ligands			
2,2,2-cryptand	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan	2,2,2-crypt or [2.2.2]-cryptand kryptofix 222 and variations thereof	
pentetato acid or diethylenetriaminepentaacetato or DTPA	2-[bis[2-[bis(carboxylatomethyl)amino]ethyl]amino]acetato	DTPA	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
DOTA or tetraxetan	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid	Dota, DOTA	

Rules for Naming Coordination Compounds

As explained above, the name of a coordination compound communicates

- as appropriate, information about isomerism
- systematically listing the ligands in a way that as necessary conveys information about their oxidation state and how they are linked to the metal
- the identity of the metal and its oxidation state
- any counterions present

Before going into these rules it is worth pointing out a few things.

1. It is easiest to learn these rules by starting with one or two of the rules, learning how to apply them, and then adding additional rules one at a time. To that end, instructors who wish to use a more programmed approach may find it convenient to first direct their students to this page which focuses on getting the names of the ligands and metal right, without worrying about isomerism or stereochemistry.

2. The rules also assume some familiarity with common coordination geometries and patterns of isomerism in metal complexes. Thus it might be easiest to learn about common coordination geometries first, followed by common patterns of isomerism in metal complexes before beginning this section. If you decide to dive right in to this section you might find it helpful to know that when applying nomenclature and formula rules most textbooks *assume*

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four are tetrahedral

Like all assumptions these don't always work in real life but they should be good enough to get you through your first inorganic chemistry course.

For the pedants among you, note that the complexes given as examples and in exercises on this page have been selected for pedagogical utility. Although many are well-known compounds, others are hypothetical.

Now on to the rules.

Rule 1: If ions are present, name the cation first, followed by the anion.

Examples:

$K_2[Pt^{II}Cl_4]$ potassium tetrachloroplatinate(2-)

$[Co^{III}(NH_3)_6](NO_3)_3$ hexaamminecobalt(3+) nitrate

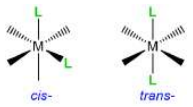
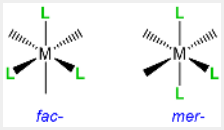
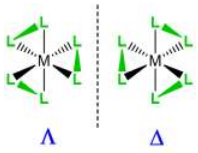
$[Co^{III}(NH_3)_6][Cr^{III}(C_2O_4)_3]$ hexaamminecobalt(3+) tris(oxalato)chromium(3-)

Rule 2: When multiple isomers are possible, designate the particular isomer in italics at the front of the name of each complex

If you have not yet learned about isomerism in coordination compounds skip this rule for now and return to it after you have.

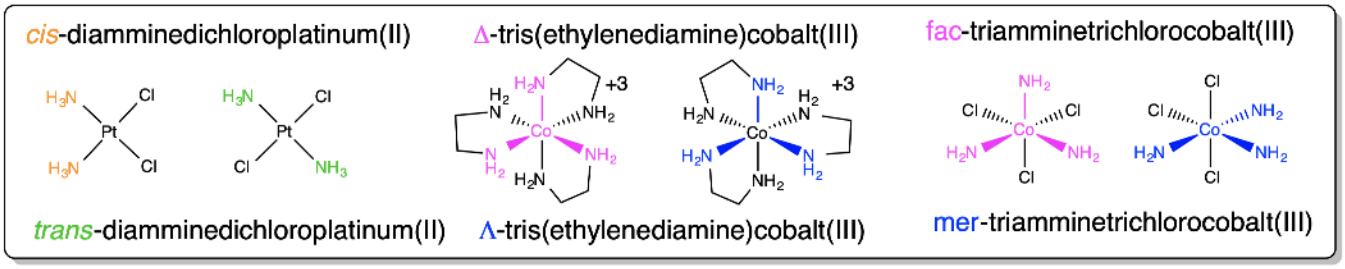
When a complex might exist as one of two stereoisomers, prefixes are commonly used to designate which isomer is present. The most common cases are listed in Table 2.3.3.

Table 2.3.3. Prefixes used to specify isomerism about a metal center when naming and writing coordination compounds' formulae.

Type of isomerism	Graphical reminder	Prefixes
Geometric, *cis-* , *trans-*		*cis-* or *trans-*
Geometric, *fac- /mer-*		*fac-* or *mer-*
Enantiomers, Λ-, Δ-		Λ- or Δ-

Examples of how isomerism about a metal center is designated are given in Scheme 2.3.II.

Scheme 2.3.II. Application of nomenclature rules for stereosimerism about a metal.[3]



There are a number of other cases where it might be advisable to specify the stereochemistry of a complex. These cases involve specifying

- the coordination geometry about a metal center (octahedral, trigonal prismatic, tetrahedral, square planar, etc.)
- the geometry cannot be unambigouously described by a single *cis/trans* or *fac/mer* relaionship of ligands

These cases may also be handled by using a designator to specify the coordination geometry and, as necessary, giving the position of ligated atoms in terms of designated numbered positions for that geometry. See the IUPAC red book for details as such cases fall outside the scope of what is normally advisable for an undergraduate course.

Rule 3: Specify the identity, number, and as appropriate, isomerism of the ligands present in alphabetical order by ligand name.

Before specifying the metal, the ligands are written as prefixes of the metal.

In specifying the ligands several rules are followed.

1. The ligands are written in alphabetical order by the ligand name only; symbols are not considered and prefixes do not count in determining alphabetical order.

   Example: In the name of the complex ion $[Co(NH_3)_5Cl]^{2+}$, pentamminechlorocobalt(II), the ammine ligand is named before the chloro ligand because the order is alphabetical by the ligand name by virtue of which ammine comes before chloro.

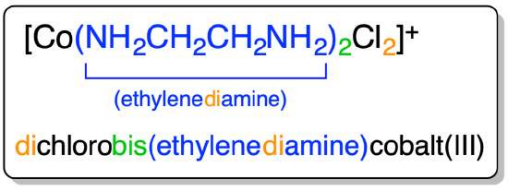
2. Prefixes are used to indicate the number of each ligand present. Specifically, *di-*, *tri-*, *tetra-* , *penta-*, *hexa-*, *etc.* prefixes are used to indicate multiple ligands of the same type EXCEPT when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc. In that case *bis-*,*tris-*, *tetrakis-*, etc. are used instead. These prefix rules are summarized in Table 2.3.3.

Table 2.3.3. Prefixes used to specify the number of a given ligand present.

Number of identical ligands	prefix used when the ligand name is simple	prefix used when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc.
2	di-	bis-
3	tri-	tris-
4	tetra-	tetrakis-
5	penta-	pentakis-
6	hexa-	hexakis-
7	hepta-	heptakis-
8	octa-	octakis-
9	nona-	nonakis-
10	deca-	decakis-

An example of the application of the prefix rule is given in Scheme 2.3.III.

Scheme 2.3.III . Example of the use of prefixes to specify the number of ligands of each type in a complex.[3]



3. Ligand names are based on their charge.
   - Neutral and cationic ligand names are the same as the names of their neutral compounds with two caveats:
     i. names that involve spaces should either be put in parentheses or the spaces should be eliminated (preferred)

        Example: cis-dichlorobis(**dimethyl sulfoxide**)platinum(II) or *cis*-dichlorobis(**dimethylsulfoxide**)platinum(II)

     ii. A few ligands are given common names.
        - H_2O = aqua
        - NH_3 = ammine (notice that there are two n's)
        - CO = carbonyl
        - CS = thiocarbonyl
        - NO = nitrosyl
   - For anionic ligands, the vowel at the end of their anion names is changed to an -"o"

     Examples: Cl^- = chloro, NH_2^- = amido, N_3^- = azido

     Caveat: some anionic ligands have common names that may also be used

     Examples:

     I^- = iodo or iodino

     CN^- = cyano or cyanido

     O^{2-} = oxo or oxido

   The IUPAC and common names of many ligands are given in Tables 2.3.1. and 2.3.2.
4. When an ambidentate ligand is present, the atom through which it is bound to the metal is indicated by giving either its element symbol or a κ and its element symbol in italics after the ligand name.

   Example:

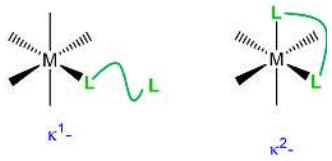
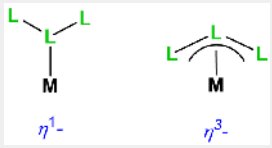
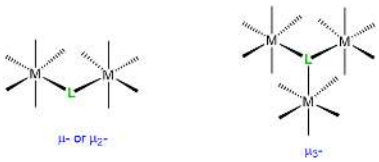
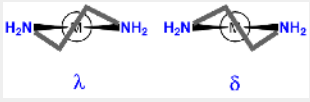
M-SCN is thiocyanato-*S* or thiocyanato-κS

M-NCS = thiocyanato-*N or* thiocyanato-κN

The use of κ and an element symbol to indicate how a ligand and metal are linked is called a **k-term**. More complex k-terms might also involve specifying the atoms by number, though their use is outside the scope of this text.

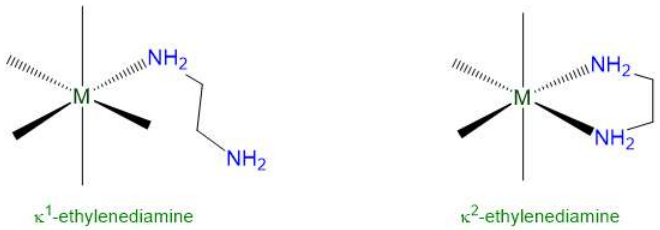
5. As appropriate, additional information about the way a ligand is bound to the metal center and/or its stereochemistry is specified using a prefix. The prefixes to provide linkage and stereochemistry for ligands are given in Table 2.3.4.

Table 2.3.4. Prefixes used to specify ligands' isomerism when naming and writing coordination compounds' formulae. Some of these types of isomerism will be discussed in later pages.

Type of isomerism	Graphical reminder	Prefixes
when a multidentate ligand binds through less than the full number of atoms		κ^n where n is the number of attached atoms; used when the attached atoms are not directly connected by a chemical bond. The metal-ligand bonding usually involves σ-type coordination.
hapticity		η^n where n is the number of attached atoms; used when the coordinated atoms are all connected by bonds. Usually the metal-ligand bonding involves π-type coordination. In speech, η^1=monohapto; η^2=dihapto; η^3=trihapto, etc.
bridging ligands		μ_n where n is the number of atoms bridged. The number n is usually omitted when n =2.
chelating ligand ring twist		λ- or δ-

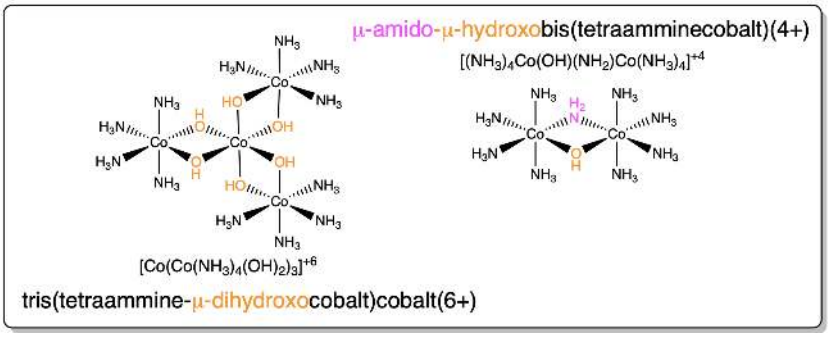
A example showing how the nomenclature rule is applied to a ligand that can have two coordination modes is given in Scheme 2.3.IV.

Scheme 2.3.IV. Use of the κ notation to specify the number of attached groups in a multidentate ligand.



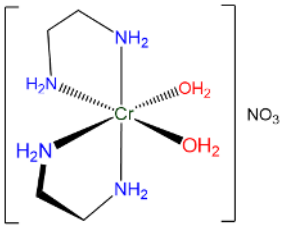
Scheme 2.3.V. The names of the complexes follow the rules described in 9.2.6: multinuclear coordination complexes.

Scheme 2.3.V. Use of the μ notation to specify bridging ligands in metal complexes.[3]



6. If desired, parentheses *may* be used to delineate a ligand name to make it easier to identify in the name of the complex. This can be particularly helpful when the entire name contains a lot of information to keep track of. An example is given in Scheme 2.3.VI.

Scheme 2.3.VI. When naming the complex shown, *cis*-diaquabis(ethylenediamine)chromium(III) nitrate is easier to read than *cis*-diaquabisethylenediaminechromium(III) nitrate.



Rule 4: Specify the identity of the metal

- In neutral and cationic complexes the metal's name is used directly

  - *e.g.* as in hexammineruthenium(III) for $[Ru(NH_3)_6]^{3+}$

- In anionic complexes, *-ate* replaces *-ium*, *-en*, or *–ese* or adds to the metal name,

  e.g., as in hexachloromanganate(IV) for $MnCl_6^{2-}$

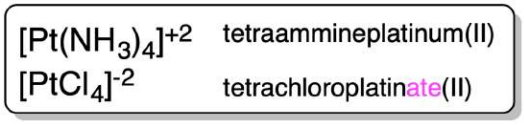
- In anionic complexes of some metals a Latin-derived name is used instead of the element's English name. These names are given in Table 2.3.5.

Table 2.3.5. Latin terms for select metal Ions. Redrawn from this page describing the nomenclature of coordination complexes.

Transition Metal	Latin
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Silver	Argentate
Tin	Stannate

An example of the application of the metal naming rules is given in Scheme \sf{\PageIndex{VII}}\).

Scheme 2.3.VII. Example of the application of the metal specification rules to a cationic and an anionic platinum complex.[3]



Rule 5: Specify the oxidation state of the metal.

Two different systems are used to specify the oxidation state of the metal.

1. In the **Stock system** the metal's oxidation state is indicated in Roman numerals after the metal name.

   Examples:

   $[CoCl(NH_3)_5]Cl_2$ = pentamminechlorocobalt(III) chloride

   $[PtBr_2(bpy)]$ = dibromobipyridineplatinium(II)

   $K[Ag(SCN)_2]$ = potassium di-*S*-thiocyanatoargentate(I)

2. In the **Ewing-Bassett system** the charge on the complex is specified in Arabic numerals after the complex name. This provides a way of specifying a complex even when the oxidation state of the metal isn't known and, in cases where it is known, the value of the metal's oxidation state may be inferred from the complex ion's charge.

   $[CoCl(NH_3)_5]Cl_2$ = pentamminechlorocobalt(2+) chloride

   $[PtBr_2(bpy)]$ = dibromobipyridineplatinium(0)

   $K[Ag(SCN)_2]$ = potassium di-*S*-thiocyanatoargentate(1-)

Summary of rules for naming coordination complexes.

A graphical summary of the **rules for naming complexes** along with a few examples that you can use to review the nomenclature rules is given in Figure 2.3.1. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

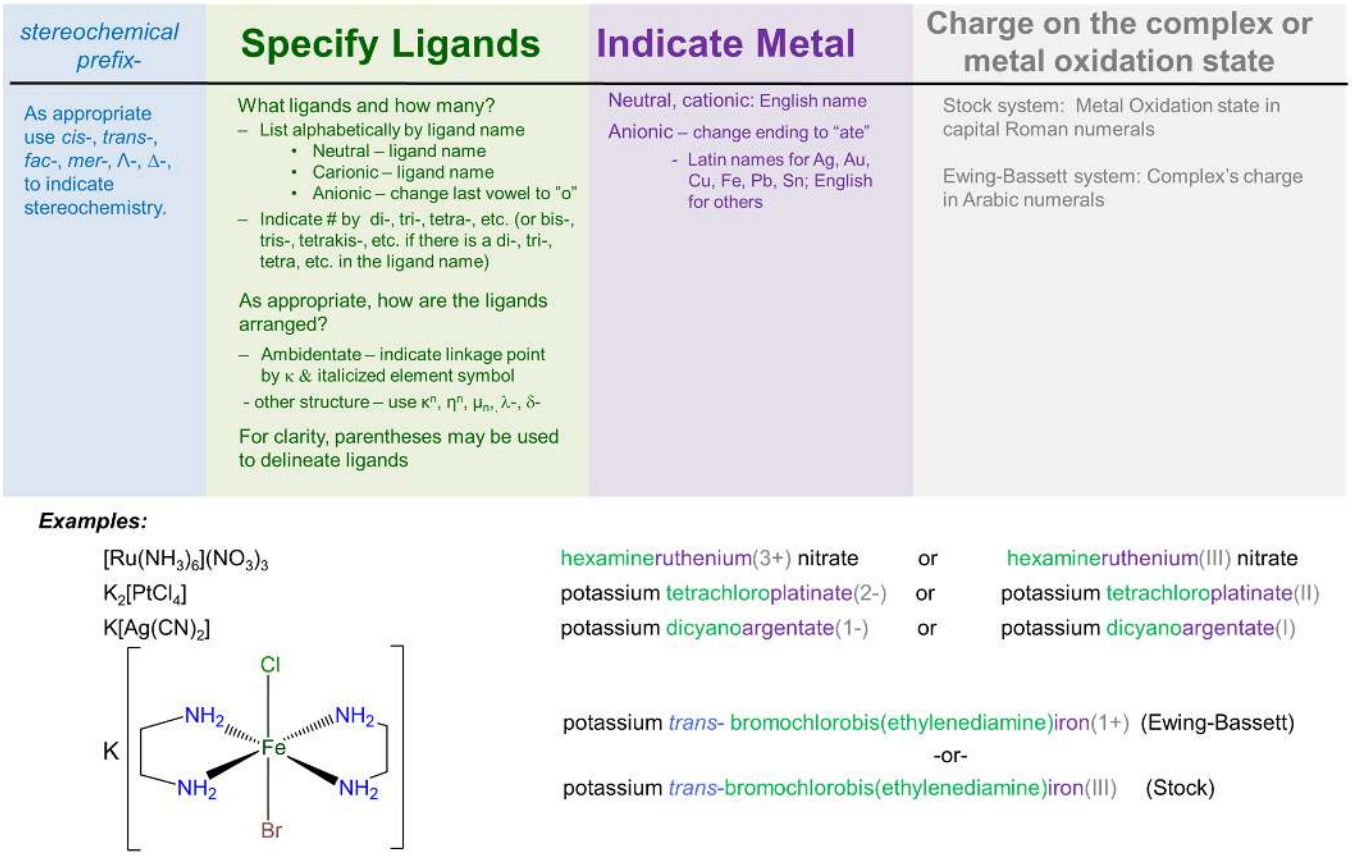


Figure 2.3.1. Summary of nomenclature rules for coordination complexes along with a few examples of their application.

When learning chemical nomenclature, practice makes perfect. The following examples and exercises are provided to give you this practice. Additional examples and exercises on the https://chem.libretexts.org/ site include a set of simple examples with explained solutions, a set of simple exercises with solutions, and a set of more challenging exercises without solutions.

Exercise 2.3.2. Assigning metal oxidation states in a complex

In order to name a complex in the Stock system it is necessary to assign a formal oxidation state to the metal. For this reason it is important to be able to assign the oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state the ligands can be treated as having an oxidation state equal to their charge - *i.e.*, the charge they possess in the form in which they coordinate the metal, so if they need to lose a proton to bind, don't forget to account for that.

Given the above, assign the oxidation state of the metal in the following real and hypothetical complexes.

a. $K_3[Fe(CN)_6]$
b. $[CoCl(NH_3)_5](NO_3)_2$
c. $K_2[PtCl_4]$
d. [MnCl(por)]
e. $[Ru(bpy)_3]Cl_2$
f. $[PdCl_2(dppe)]$
g. $[Mn(en)_2(SCN)_2]$

Answer for $K_3[Fe(CN)_6]^{3-}$.

This contains $[Fe(CN)_6]^{3-}$; so $O.S._{Fe}$ + 6 x (-1) (for CN^-) = -3 (the complex's charge) so $O.S._{Fe}$ = +3 or Fe^{3+}.

Answer for $[CoCl(NH_3)_5](NO_3)_2$.

This contains $[CoCl(NH_3)_5]^{2+}$; so $O.S._{Co}$ + 1 x (-1) (for Cl^-) + 0 x 5 (for NH_3) = +2 (the complex's charge) so $O.S._{Co}$ = +3 or Co^{3+}.

Answer for $K_2[PtCl_4]$.

This contains $2K^+$ and $[PtCl_4]^{2-}$; so $O.S._{Pt}$ + 4 x (-1) (for Cl^-) = -2 (the complex's charge) so $O.S._{Pt}$ = +2 or Pt^{2+}.

Answer for [MnCl(por)].

$O.S._{Pt}$ + 1 x (-2) (for por; see table 9.2.2) + 1 x (-1) (for Cl^-) = +0 (the complex's charge) so $O.S._{Mn}$ = +3 or Mn^{3+}.

Answer $[Ru(bpy)_3]Cl_2$.

The complex is $[Ru(bpy)3]^{2+}$ so $O.S._{Ru}$ + 0 x 3 (for bpy) = +2 (the complex's charge) so $O.S._{Ru}$ = +2 or Ru^{2+}.

Answer $[PdCl_2(dppe)]$.

$O.S._{Pd}$ + 2 x (-1) (for Cl^-) + 0 x 3 (for dppe) = +0 (the complex's charge) so $O.S._{Pd}$ = +2 or Pd^{2+}.

Answer $[Mn(en)_2(SCN)_2]$.

$O.S._{Mn}$ + (2 x 0) (for en) + 2 x (-1) (for SCN^-) = +0 (the complex's charge) so $O.S._{Mn}$ = +2 or Mn^{2+}.

Exercise 2.3.3: Simple Nomenclature Problems.

Name the following compounds in both the Stock and Ewing-Bassett systems:

a. $[Ru(NH_3)_6](NO_3)_3$
b. $K_2[PtCl_4]$
c. $K[Ag(CN)_2]$
d. $Cs[CuBrCl_2F]$
e. $[Cu(acac)_2]$

Answer

	Complex	Stock system name	Ewing-Bassett System name
a	$[Ru(NH_3)_6](NO_3)_3$	hexammineruthenium(III) nitrate	hexammineruthenium(3+) nitrate

	Complex	Stock system name	Ewing-Bassett System name
b	$K_2[PtCl_4]$	potassium tetrachloroplatinate(II)	potassium tetrachloroplatinate(2-)
c	$K[Ag(CN)_2]$	potassium dicyanoargentate(I)	potassium dicyanoargentate(1-)
d	$Cs_2[CuBrCl_2F]$	cesium bromodichlorofluorocuprate(II)	cesium bromodichlorofluorocuprate(2-)
e	$[Cu(acac)_2]$	bis(acetylacetonato)copper(II)	bis(acetylacetonato)copper(0)

? Exercise 2.3.4: More simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems.

a. $Cu(OH)_4^-$
b. $[AuXe_4]^{2+}$
c. $AuCl_4^-$
d. $Fe(CN)_6^{3-}$
e. $K_4[Fe(CN)_6]$
f. *trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)
g. cis-$IrCl_2(CO)(PPh_3)$ (ignore stereochemistry)
h. $IrCl(PPh_3)_3$

Answer

	Compound	Stock System Name	Ewing-Bassett System Name
a	$Cu(OH)_4^-$	tetrahydroxidocuprate(III) or tetrahydroxidocuprate(III)	tetrahydroxidocuprate(1-) or tetrahydroxidocuprate(1-)
b	$[AuXe_4]^{2+}$	tetraxenongold(II)	tetraxenongold(2+)
c	$AuCl_4^-$	tetrachloroaurate(III)	tetrachloroaurate(1-)
d	$Fe(CN)_6^{3-}$	hexacyanoferrate(III) or hexacyanidoferrrate(III)	hexacyanoferrate(3-) or hexacyanidoferrate(3-)
e	$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II) or potassium hexacyanidoferrrate(II)	potassium hexacyanoferrate(4-) or potassium hexacyanidoferrrate(4-)
f	*trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)	bis(ethylenediamine)bisnitrocopper(II) or bis(ethylenediamine)bis(nitrito-κN)copper(II)	bis(ethylenediamine)bisnitrocopper(0) or bis(ethylenediamine)bis(nitrito-κN)copper(0)
g	*cis*-$IrCl_2(CO)(PPh_3)$	*cis*-dichlorocarbonyltriphenylphosphineiridium(I) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(I)	*cis*-dichlorocarbonyltriphenylphosphineiridium(0) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(0)

	Compound	Stock System Name	Ewing-Bassett System Name
h	$IrCl(PPh_3)_3$	chlorotris(triphenylphosphine)iridium(I)	chlorotris(triphenylphosphine)iridium(0)

Exercise 2.3.5: Even more simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

a. $Fe(acac)_3$
b. $K_2[CuBr_4]$
c. ReH_9
d. $[Ag(NH_3)_2]BF_4$
e. $[Ag(NH_3)_2][Ag(CN)_2]$
f. $[Ni(CN)_4]^{2-}$
g. $[Co(N_3)(NH_3)_5]SO_4$
h. $[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)

Sample Answers

	Complex	Stock system name	Ewing-Bassett System name
a	$Fe(acac)_3$	tris(acetoacetato)iron(III)	tris(acetoacetato)iron(0)
b	$Na_2[CuBr_4]$	sodium tetrabromocuprate(II)	sodium tetrabromocuprate(2-)
c	$[Co(NH_3)_6][Co(ox)_3]$	hexamminecobalt(III) tris(oxalato)cobalt(III)	hexamminecobalt(3+) tris(oxalato)cobalt(3-)
d	$[Ag(NH_3)_2]BF_4$	diamminesilver(I) tetrafluoroborate	diamminesilver(1+) tetrafluoroborate
e	$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I) or diamminesilver(I) dicyanidoargentate(I)	diamminesilver(1+) dicyanoargentate(1-) or diamminesilver(1+) dicyanidoargentate(1-)
f	$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) or tetracyanonickelate(II) ion	tetracyanonickelate(2-) or tetracyanonickelate(2-) ion
g	$[Co(N_3)(NH_3)_5]SO_4$	pentammineazidocobalt(III) sulfate	pentammineazidocobalt(2+) sulfate
h	$[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)	ammineaquabromochlorocobalt(III) iodide	ammineaquabromochlorocobalt(1+) iodide

Exercise 2.3.6: Nomenclature problems, some of which involve consideration of isomerism.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

a. *trans*-$[Cu(dppe)_2(NO_2)_2]$ (the N is bound to Cu)
b. $[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN
c. $[Mn(CO)_6]BPh_4$ (BPh_4 = tetraphenylborate)
d. $Rb[AgF_4]$
e. K_2ReH_9

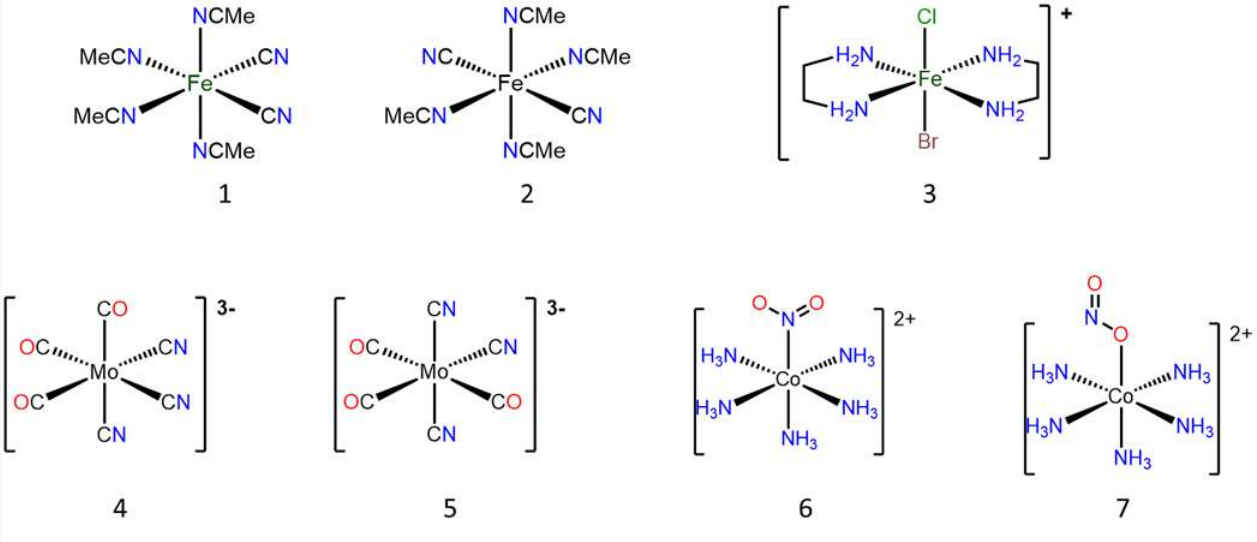
f. K_3CrCl_6
g. $[Ru(H_2O)_6]Cl_2$
h. [*cis*-$Fe(CO)_4I_2$]
i. K_2[*trans*-$Fe(CN)_4(CO)_2$]
j. [*cis*-$MnCl(H_2O)_4(NH_3)$](NO_3)
k. K_3[*fac*-$RuCl_3(PMe_3)_3$]

Answer

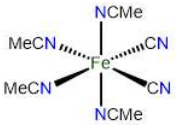
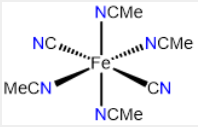
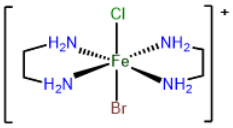
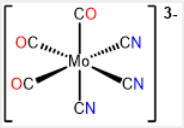
	Complex	Stock system name	Ewing-Bassett System name
a	*trans*-[$Cu(dppe)_2(NO_2)_2$]	*trans*-bis(diphenylphosphinoethane)bisnitrocopper(II) or *trans*-bis(diphenylphosphinoethane)bis(nitrito-κN)copper(II)	*trans*-bis(diphenylphosphinoethane) bisnitrocopper(0) or *trans*-bis(diphenylphosphino)ethane bis(nitrito-κN)copper(0)
b	[$Pd(en)_2(SCN)_2$], with the thiocyanates bound Pd-SCN	bis(ethylenediamine)bisthiocyanatopalladium(II) or bis(ethylenediamine)bis(thiocyanato-*S*)palladium(II) or bis(ethylenediamine)bis(thiocyanato-κS)palladium(II)	bis(ethylenediamine)bisthiocyanatopalladium(0) or bis(ethylenediamine)bis(thiocyanato-*S*)palladium(0) or bis(ethylenediamine)bis(thiocyanato-κS)palladium(0)
c	[$Mn(CO)_6$]BPh_4	hexacarbonylmanganese(I) tetraphenylborate	hexacarbonylmanganese(1+) tetraphenylborate
d	Rb[AgF_4]	rubidium tetrafluoroargentate(III)	rubidium tetrafluoroargentate(1-)
e	K_2ReH_9	potassium nonahydridorhenium(VII)	potassium nonahydridorhenium(2-)
f	K_3CrCl_6 or K_3[$CrCl_6$]	potassium hexachlorochromium(III) or potassium hexachloridochromium(III)	potassium hexachlorochromium(3-) or potassium hexachloridochromium(3-)
g	[$Ru(H_2O)_6$]Cl_2	hexaaquaruthenium(II) chloride	hexaaquaruthenium(2+) chloride
h	[*cis*-$Fe(CO)_4I_2$]	*cis*-tetracarbonyldiiodoiron(II)	*cis*-tetracarbonyldiiodoiron(0)
i	K_2[*trans*-$Fe(CN)_4(CO)_2$]	potassium *trans*-dicarbonyltetracyanoferrate(II)	potassium *trans*-dicarbonyltetracyanoferrate(2-)
j	[*cis*-$MnCl(H_2O)_4(NH_3)$](NO_3)	*cis*-amminetetraaquachloromanganese(0) nitrate	*cis*-amminetetraaquachloromanganese(1+) nitrate
k	K[*fac*-$RuCl_3(PMe_3)_3$]	potassium *fac*-trichlorotris(triphenylphosphine)ruthenium(II)	potassium *fac*-trichlorotris(triphenylphosphine)ruthenium(1-)

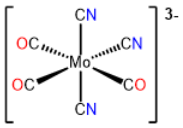
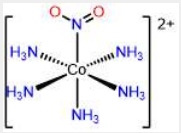
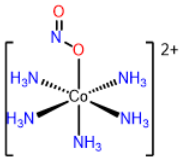
Exercise 2.3.7

Name the compounds and ions below using both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.



Answer

#	Structure	Stock system name	Ewing-Bassett system name
1		*cis*-tetraacetonitriledicyanoiron(II) or *cis*-tetraacetonitriledicyanidoiron(II)	*cis*-tetraacetonitriledicyanoiron(0) or *cis*-tetraacetonitriledicyanidoiron(0)
2		*trans*-tetraacetonitriledicyanoiron(II) or *trans*-tetraacetonitriledicyanidoiron(II)	*trans*-tetraacetonitriledicyanoiron(0) or *trans*-tetraacetonitriledicyanidoiron(0)
3		*trans*-bromochlorobis(ethylenediamine)iron(III) or *trans*-bromidochloridobis(ethylenediamine)iron(III)	*trans*-bromochlorobis(ethylenediamine)iron(1+) or *trans*-bromidochloridobis(ethylenediamine)iron(1+)
4		*fac*-tricarbonyltricyanomolybdate(0) or *fac*-tricarbonyltricyanidomolybdate(0)	*fac*-tricarbonyltricyanomolybdate(3-) or *fac*-tricarbonyltricyanidomolybdate(3-)

#	Structure	Stock system name	Ewing-Bassett system name
5		*mer*-tricarbonyltricyanomolybdate(0) or *mer*-tricarbonyltricyanidomolybdate(0)	*mer*-tricarbonyltricyanomolybdate(3-) or *mer*-tricarbonyltricyanidomolybdate(3-)
6		pentamminenitrito-*N*-cobalt(III), pentamminenitrito-κN-cobalt(III), or pentamminenitrocobalt(III)	pentamminenitrito-*N*-cobalt(2+), pentamminenitrito-κN-cobalt(2+), or pentamminenitrocobalt(2+)
7		pentamminenitrito-*O*-cobalt(2+), pentamminenitrito-κO-cobalt(2+), or pentamminenitritocobalt(2+)	pentamminenitrito-*O*-cobalt(2+), pentamminenitrito-κO-cobalt(2+), or pentamminenitritocobalt(2+)

Exercise 2.3.8

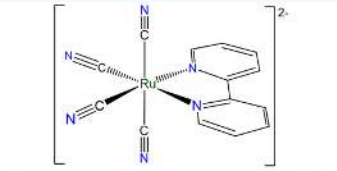
Draw structural formulae for the following compounds and ions. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

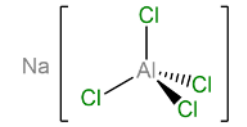
a. (2,2'-bipyridine)tetracyanoruthenium(2-)
b. sodium tetrachloroaluminate (note that since Al is a main group metal with a generally fixed oxidation state no oxidation state is given)
c. pentaamminechlorocobalt(2+) sulfate
d. carbonylhydridotris(triphenylphosphine)rhodium(I) (the ligands in this complex occupy sterically preferred positions)
e. bromotrichlorocobaltate(III)
f. hexaaquacopper(2+) sulfate
g. sodium tris(oxalato)cobalt(III)
h. *fac*-(1,10-phenanthroline)tricarbonylchlororhenium(I)
i. *mer*-triaquatrichlorochromium(III)
j. *trans*-dichlorobis(ethylenediamine)platinum(IV)

Answers

a

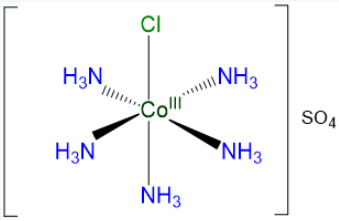

(2,2'-bipyridine)tetracyanoruthenium(2-)

b



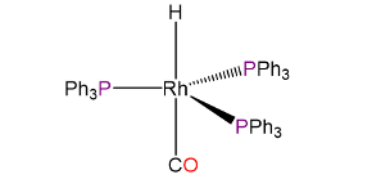
Sodium tetrachloroalumnate

c



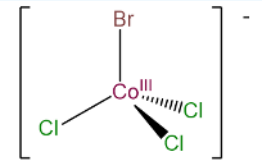
pentaamminechlorocobalt(2+) sulfate

d



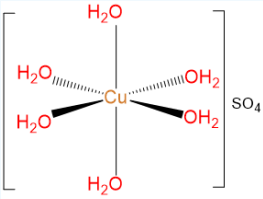
carbonylhydridotris(triphenylphosphine)rhodium(I)

e



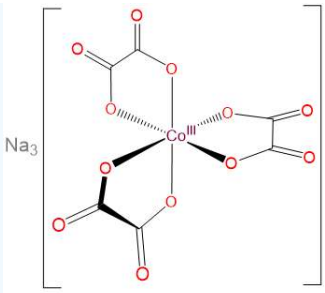
bromotrichlorocobaltate(III)

f



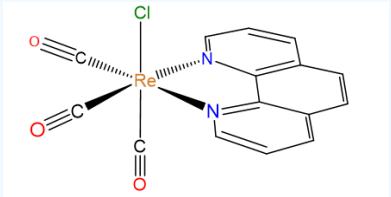
hexaaquacopper(2+) sulfate

g



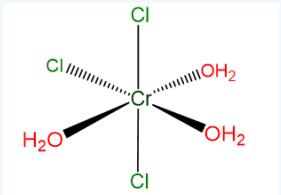
sodium tris(oxalato)cobalt(III)
Λ-enantiomer shown

h



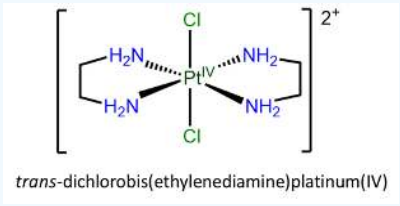
fac-(1,10-phenanthroline)tricarbonylchlororhenium(I)

i



mer-triaquatrichlorochromium(III)

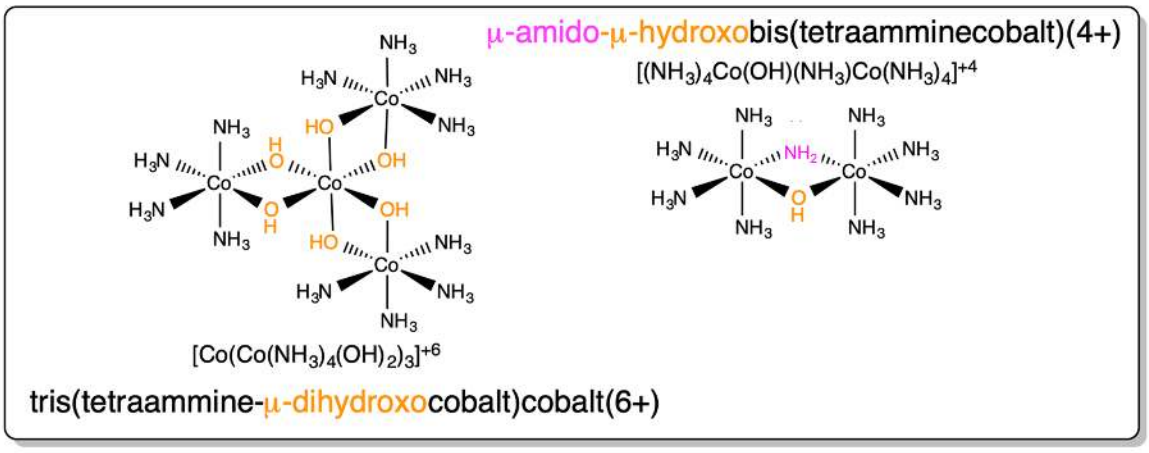
j



trans-dichlorobis(ethylenediamine)platinum(IV)

Exercise 2.3.9.

The name of the structure named tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) in Scheme 2.3.III (reproduced below) is incomplete. Give the complete name of the structure in both the Stock and Ewing-Basset systems.



Answer

Δ-tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) or Δ-tris(tetraammine-μ-dihydroxocobalt(III)cobalt(III)

Note: Rules for Writing the Formulae of Coordination Copounds

Rules for writing the formulae of coordination compounds

As organized predictable formulae can be easier to read and understand than haphazardly written ones, the rules for writing the formulae of coordination compounds have value. To support those who wish to employ them they are given in this section. The rules as given here are adapted from a summary by Robert Lancashire.

The rules for writing the formulae of coordination compounds follow the same convention used to specify their names.

1. If there are multiple ions present list the cations before anions.
2. Enclose all the constituents of each complex ion in square brackets.
3. For each complex ion,
   - Give the **central metal** atom first.
   - Then **ligands** next, listed in alphabetical order, ignoring prefixes according to the first letters in the ligand's symbol as written. This is true regardless of whether the symbol is an element symbol (like C, N, O, etc.) or a symbol for the ligand name (bpy, en, MeCN, etc.). Contrary to widely-circulated myths, the ligand's charge does not matter.[4]
   - The formulae or abbreviations (*e.g.* en) for all polyatomic ligands should be enclosed in ordinary parentheses.
   - As appropriate, use italicized atom symbols to indicate linkage isomerism and prefixes such as *cis*-, *trans*-, *fac*-, *mer*-, Λ-, Δ-, κ^n, η^n , μ_n, λ-, or δ- to indicate stereochemistry.
   - When a ligand is bound to a metal through a particular atom, preferably place that atom closest to the metal - *e.g.*, $[Fe(CN)_6]^{3-}$ not $[Fe(NC)_6]^{3-}$ (Note: this rule is used primarily for ambidentate ligands; although IUPAC recommends that aqua ligands be written as OH_2 when the O would be closest to its coordinated metal, they are still usually written as H_2O).

These rules are graphically summarized in Figure 2.3.2.

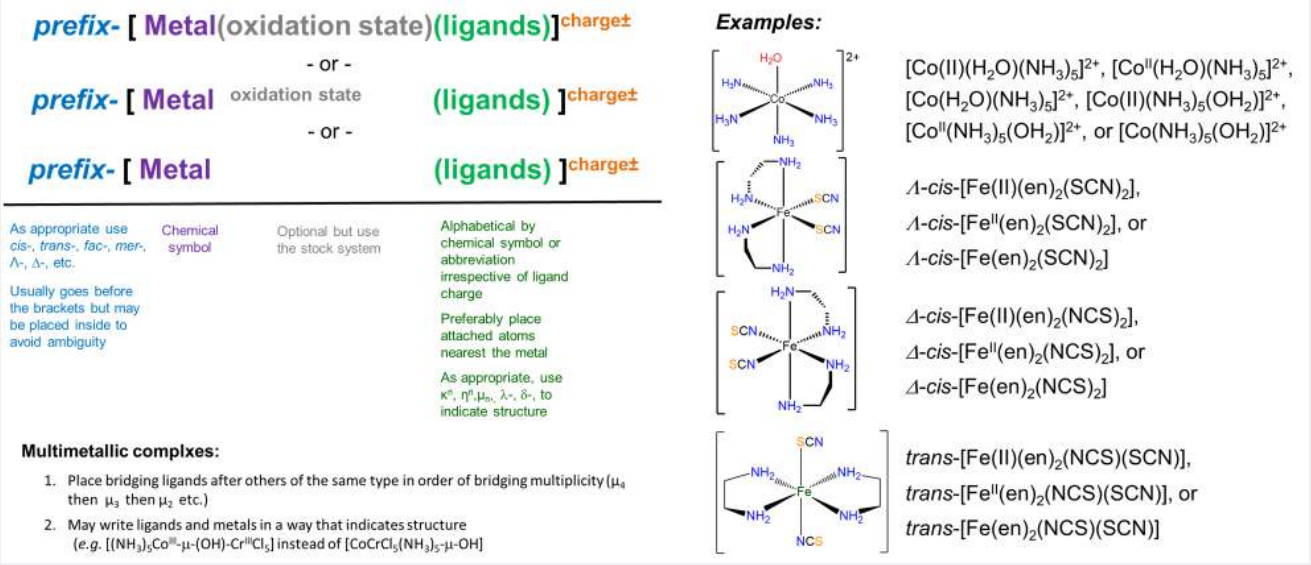
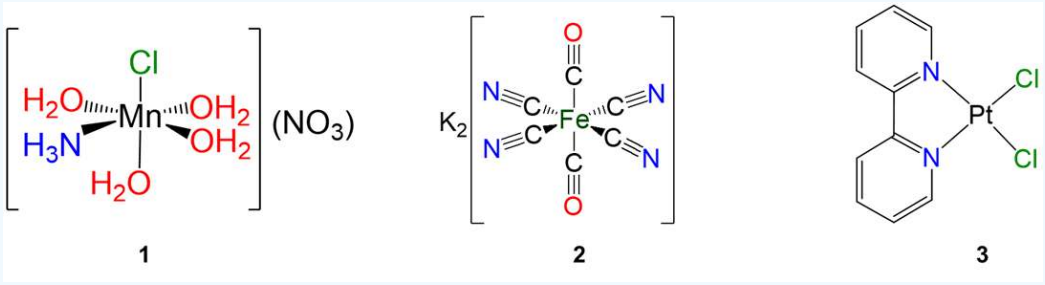


Figure 2.3.2. Summary of the rules for writing the formula of a coordination complexes along with a few examples of their application. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

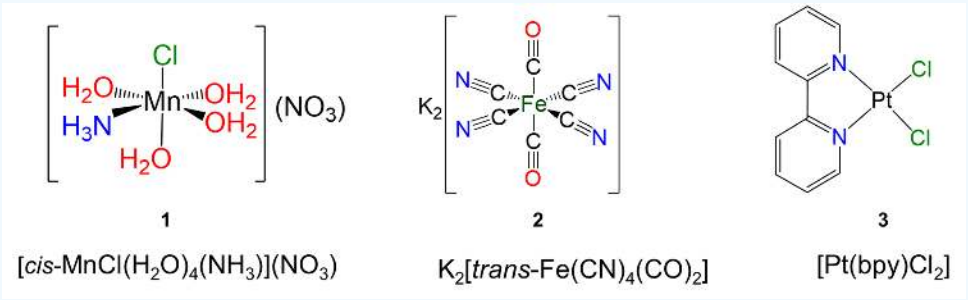
Exercise 2.3.10

Give the formulae of the following complexes.



.

Answer

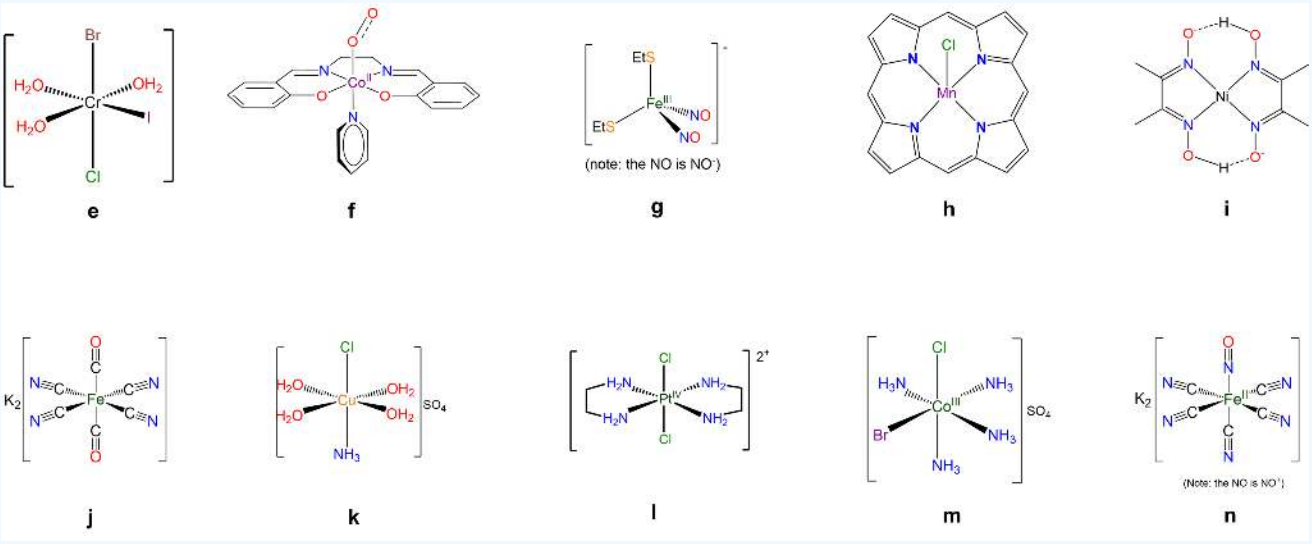


Exercise 2.3.11

Write formulae for each of the following compounds and ions. When multidentate ligands are present use suitable abbreviations.

a. pentaamminechlorocobalt(2+) sulfate
b. Δ-diamminebis(oxalato)manganate(III)
c. *trans*-tetraacetonitriledicyanoiron(II)

d. tricarbonyldichlorobis(triphenylphosphine)molybdenum



Answers

a.

$[CoCl(NH_3)_5](SO_4)$

b.

Δ-$[Mn(NH_3)_2(ox)_2]^-$

c.

trans-$[Fe(CN)_2(NCMe)_4]$

d.

$[MoCl_2(CO)_3(PPh_3)]$ or $MoCl_2(CO)_3(PPh_3)$

e.

mer-$[CrBrCl(H_2O)_3I]$

f.

$[Co(O_2)py(salen)]$

g.

$[Fe(NO)_2(SEt)_2]^-$

h.

$[MnCl(por)]^-$ or $[MnCl(porphyrin)]^-$

i.

$[Ni(DMG)_2]$ or $[Ni(Hdmg)_2]$

j.

potassium *trans*-$[Fe(CN)_2(CO)_4]$

k.

trans-$[CuCl(H_2O)_4(NH_3)]SO_4$

l.

trans-$[PtCl_2(en)_2]^{2+}$

m.

cis-$[CoBrCl(NH_3)_4]SO_4$

n.

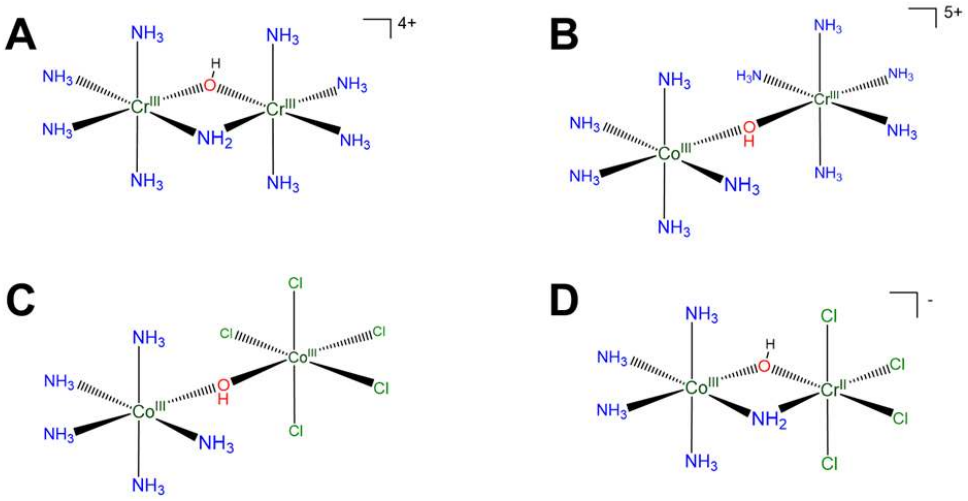
$K_2[Fe(CN)_5NO]$

Multinuclear coordination complexes

Multinuclear coordination complexes contain multiple metals connected by one or more bridging ligands. The structures of bridging complexes can usually be inferred from their μ-tagged ligands in their names and formulae. For the benefit of instructors who wish to have their students name multinuclear complexes, the rules are presented below.

Multinuclear complexes are named differently depending on whether the groups on either side of the bridging ligands are identical or different, as shown in Scheme 2.3.VIII

Scheme 2.3.VIII. Multinuclear coordination complexes may be named differently depending on whether the groups on either side of the bridging ligands are the same or different. The groups are the same if the metal, ligands, and ligand arrangement are identical. This is true in A but in B the metals differ, in C the ligands differ, and in D both the metal and ligands differ.



Naming multinuclear complexes

Let's look at the rules for naming symmetric and asymmetric multinuclear complexes.

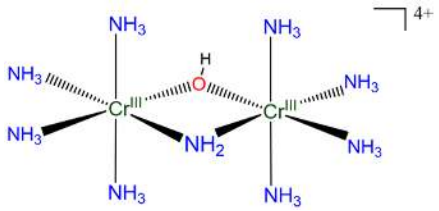
Application of the IUPAC system and variants thereof to symmetric complexes

The IUPAC naming system helpfully avoids the sort of ambiguities and *ad hoc* choices involved in most textbook-level nomenclature systems for multimetallic complexes. Unfortunately, it is correspondingly difficult for beginners to employ. Thus it will only be applied in depth to the case of symmetric complexes. Symmetric complexes are particularly easy to name in the IUPAC system and several of its variants that find common use. In these

1. The ligands are given in alphabetical order. When there are bridging and non-bridging ligands of the same type the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.*, μ_4-, μ_3-, μ_2-), the bridging ligands are specified in decreasing order of bridging multiplicity, *e.g.*, μ_3 -sulfido-di-μ-sulfido.
2. The groups bridged are given afterwards using names that follow the ordinary rules. Generally this involves either
    a. naming all the ligands followed by all the metals, in both cases using prefixes to indicate the number of each, or
    b. naming each group of atoms individually as in the less formal naming system, using prefixes to indicate the number of ligands (this is an unofficial variant of the IUPAC system that some textbook authors seem to prefer).

These two rules are sufficient to describe simple symmetric bridging complexes.

Example: The compound in Scheme 2.3.VIIIA



may be named

[μ-amido-μ-hydroxo-octaamminedichromium(4+)] ion

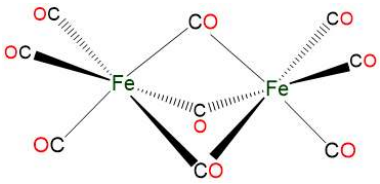
or

[μ-amido-μ-hydroxo-bis(tetraamminechromium(III))] ion

or

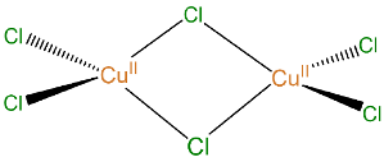
[μ-amido-μ-hydroxo-bis(tetraamminechromium)(4+)] ion

Example: The complex[5]



may be named [tri-μ-carbonyl-bis(tricarbonyliron)(0)], [tri-μ-carbonyl-bis(tricarbonyliron(0))], or [tri-μ-carbonyl-hexacarbonyldiiron)(0)]

Example: The complex



may be named di-μ-chlorido-tetrachloridodicopper(II), di-μ-chlorido-bis(dichlorocopper(II)), or di-μ-chlorido-bis(dichlorocopper)(0)

A note on the application of the IUPAC system and variants thereof to asymmetric complexes

For a symmetrical complex like the [$Cu_2Cl_4(\mu\text{-}Cl)_2$] considered above it is enough to specify the existence of the two bridging and four terminal chloro ligands; there is no need to number the chloro ligands or to specify exactly which ones are involved in bridging or to clarify that the bridging involves κ^2 coordination of the chloro ligands. In cases where the two metal centers or the chloro ligands differ it is necessary to specify the exact ligands and metals involved and how they are connected.

For example, a more extensive IUPAC name for [$Cu_2Cl_4(\mu\text{-}Cl)_2$] in which the chloro ligands are individually and more completely specified would read di-μ_2-chlorido-tetrachlorido-1κ^2Cl,2κ^2Cl-dicopper(II).

Even more extensive systems would involve numbering the metals and specifying how they are connected together too. The details of how this is done are typically beyond the level of most undergraduate and graduate courses in inorganic chemistry. Those who want to know the details should consult the red book. In many cases it is sufficient to reserve the use of formal IUPAC names for use in publications and to employ a convenient shorthand naming system for everyday use. An example of one type of system that is sometimes employed is given next.

Unofficial but commonly used methods applicable to complexes in which the groups bridged are identical or different.

It can be quite complicated to use the IUPAC system to name asymmetric multinuclear coordination complexes. Fortunately it is rarely necessary and there are a variety of simpler somewhat *ad hoc* methods that work well for such cases. Since these methods

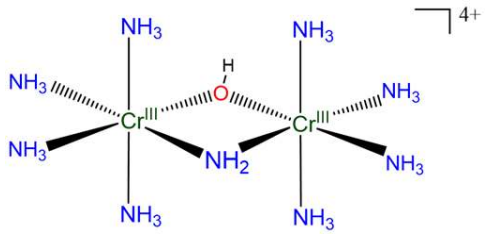
are commonly used by textbooks and inorganic instructors it is likely worth your while to learn about their general features. In these methods

1. A multinuclear complex is named as a derivative of one of the metal centers and the other metal centers and their ligands are treated as ligands to the prioritized metal center.
2. Unfortunately, most of the time the choice of which metals are part of the ligands and which one is central is made haphazardly. In other words, there is no agreed upon system for assigning which metal center is the central metal and which should be regarded as part of the ligands around it. One way to be more systematic about the selection of the central and ligand-embedded metals is to assign the central metal as the metal of highest priority in the IUPAC priority rules. In the IUPAC priority rules, the central metal is the highest priority metal alphabetically by name; then if there is a tie the ligands on each tied metal center are ranked alphabetically and the tied metal center with the highest priority (or most highest priority) ligands wins.
3. The metal centers not chosen as the primary metal center and all ligands around them, including those bridging to the winning metal center, are then treated as a single ligand that coordinates the winning metal center.
4. When naming the ligands and the overall complex, again there is much that is haphazard. However, in the best systems each coordination sphere is named using the same rules as for mononuclear complexes - *i.e.*, the ligands are given in alphabetical order, etc.

    - This is true of any metal center-containing ligands.
    - When there is a bridging and non-bridging ligand of the same type, the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.* μ_4-, μ_3-, μ_2-), the ligands are specified in decreasing order of bridging multiplicity, *e.g.* μ_3 -sulfido-di-μ-sulfido.

Let's apply these rules to the examples in Scheme 2.3.VIII

Compound A:



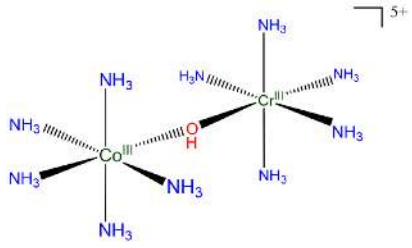
Using hydroxo for the OH^-, it may be named

[(μ-amido-tetraammine-μ-hydroxochromium(III))tetraamminechromium(III)] ion

or

[(μ-amido-tetraammine-μ-hydroxochromium)chromium(4+)] ion

Compound B:



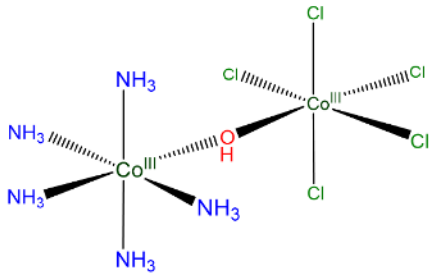
Using hydroxo for the OH^-, it may be named

[(pentaammine-μ-hydroxocobalt(III))tetraamminechromium(III)] ion

or

[(pentaammine-μ-hydroxocobalt)tetraamminechromium(5+)] ion

Compound C:



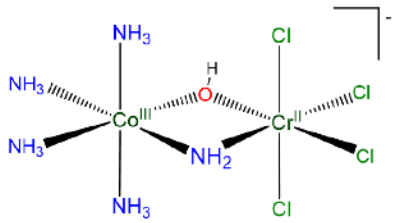
Using hydroxo for OH^-, it may be named

[pentaammine(pentachloro-μ-hydroxocobalt(III))cobalt(III)]

or

[pentaammine(pentachloro-μ-hydroxocobalt)cobalt](0)]

Compound D:



Using hydroxo for OH^- and chloro for Cl^-, it may be named

[pentaammine(pentachloro-μ-hydroxocobalt(III))chromate(III)] ion

or

[(tetrammine-μ-ammine-μ-hydroxocobalt)tetrachlorochromate](1-)] ion

As can be seen from the examples above this system gives serviceable names for multimetallic complexes but those names are not the IUPAC names and so should not be used to describe complexes outside of pedagogical and informal settings.

Writing and interpreting formulae for multinuclear complexes

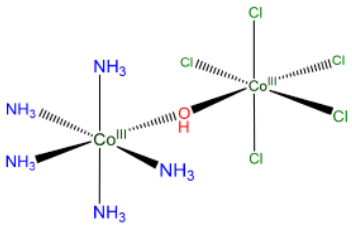
The rules for writing formulae for multinuclear complexes are the same as for mononuclear ones with two added details:

1. Write bridging ligands after nonbridging ligands of the same type. For example, Cu_2Cl_6 should be written as $[Cu_2Cl_4(\mu\text{-}Cl)_2]$
2. However, you may ignore that and other rules if you find it helpful to keep groups of metals and ligands together in a way that better conveys how the atoms are connected. Just as the structure of ethane may be more clearly conveyed as H_3CCH_3 instead of CH_3CH_3, the complex $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ may be written as $[(Cl_2Cu)(\mu\text{-}Cl)_2(CuCl_2)]$.

Other Examples:

For dichromate write, $[Cr_2O_6(\mu\text{-}O)]^{2-}$ or $[O_5Cr\text{-}\mu\text{-}O\text{-}CrO_5]^{2-}$

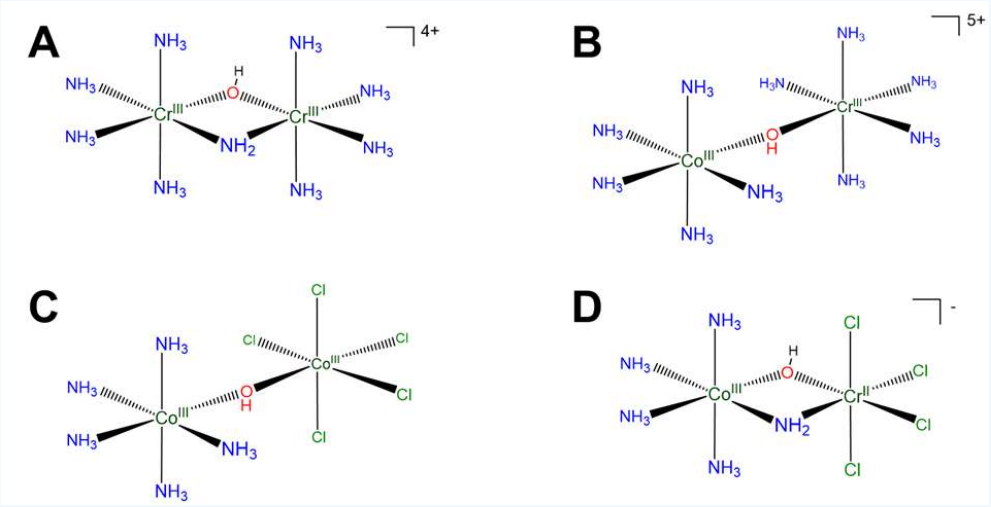
For compound C of Scheme 2.3.VIII



write $[Co_2Cl_5(NH_3)_5(\mu\text{-}OH)]$ or, even better, $[(H_3N)_5Co(\mu\text{-}OH)CoCl_5]$.

Exercise 2.3.10

Write reasonable formulae for complexes A, B, and D in Scheme 2.3.VIII, which for convenience is reproduced below.



Sample answers for A

$[Cr_2(NH_3)_8\text{-}\mu(NH_2)\text{-}\mu(OH)]^{4+}$ or $[(H_3N)_4Cr^{III}\text{-}\mu(NH_2)\text{-}\mu(OH)\text{-}Cr^{II}(NH_3)_4]$ and variants thereof involving writing the H_3N as NH_3, μ as μ_2, etc.

Sample answers for B

$[CoCr(NH_3)_{10}\text{-}\mu(OH)]^{5+}$ or, better, $[(H_3N)_5Co^{III}\text{-}\mu(OH)\text{-}Cr^{III}(NH_3)_5]^{5+}$

Sample answers for C

This was already done as an example above, $[Co_2Cl_5(NH_3)_5\text{-}\mu(OH)]$ or, better, $[(NH_3)_5Co^{III}\text{-}\mu(OH)\text{-}Co^{III}Cl_5]$ and variants thereof

Sample answers for D

$[CoCrCl_4(NH_3)_4\text{-}\mu(NH_2)\text{-}\mu(OH)]$ or, better, $[(H_3N)_4Co^{III}\text{-}\mu(NH_2)\text{-}\mu(OH)\text{-}Cr^{II}Cl_4]$

References

1. International Union of Pure and Applied Chemistry *Nomenclature of Inorganic Chemistry* Cambridge, UK, 2005.

2. The structure and name is taken from Choudhury, S. B.; Allan, C. B.; Maroney, M.; Wodward, A. D.; Lucas, C. R. *Inorg. Synth.* **1998**, *32*, 98-107.

3. Haas, K. Naming Transition Metal Complexes. https://chem.libretexts.org/Courses/Saint_Mary's_College%2C_Notre_Dame%2C_IN/CHEM_342%3A_Bio-inorganic_Chemistry/Readings/Week_2%3A_Introduction_to_Metal-Ligand_Interactions_and_Biomolecules/2.1_Transition_metal_complexes/2.1.6%3A_Naming_Transition_Metal_Complexes

4. There is a widely-circulated myth that anionic ligands should be named before neutral ones. This myth is false. According to the IUPAC red book (bolding mine):

> IR-2.15.3.4: Ordering ligands in formulae and names in formulae of coordination compounds,
>
> The formulae or abbreviations representing the ligands **are cited in alphabetical order as the general rule**. Bridging ligands are cited immediately after terminal ligands of the same kind, if any, and in increasing order of bridging multiplicity. (See also Sections IR-9.2.3 and IR-9.2.5.)
>
> IR-9.2.3.1 Sequence of symbols within the coordination formula
>
> (i) The central atom symbol(s) is (are) listed first.

(ii) The **ligand symbols (line formulae, abbreviations or acronyms) are then listed in alphabetical order** (see Section IR-4.4.2.2).5 Thus, CH_3CN, MeCN and NCMe would be ordered under C, M and N respectively, and CO precedes Cl because single letter symbols precede two letter symbols. **The placement of the ligand in the list does not depend on the charge of the ligand.**

(iii) More information is conveyed by formulae that show ligands with the donor atom nearest the central atom; this procedure is recommended wherever possible, even for coordinated water.

5. Technically organometallic complexes are named according to slightly different rules but the coordination compound naming system works here. Note that this complex was once thought to possess an Fe-Fe bond, in accordance with the predictions of the 18-electron rule. Consequently, older sources often give an [*Fe-Fe*] after the name to reflect the presence of that bond. However, as the complex is no longer thought to possess an Fe-Fe bond it is omitted here.

Contributors and Attributions

Stephen Contakes, Westmont College, to whom comments, corrections, and criticisms should be addressed.

with some examples taken from Naming Transition Metal Complexes by Kathryn Haas.

Consistent with the policy for original artwork made as part of this project, all unlabeled drawings of chemical structures are by Stephen Contakes and licensed under a Creative Commons Attribution 4.0 International License.

2.3: Nomenclature and Ligands is shared under a not declared license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.3: Nomenclature and Ligands** by Stephen M. Contakes has no license indicated.

2.4: Isomerism

Metal complexes present a rich, interesting, and diverse structural chemistry. Major points of variation in the structural chemistry of metal complexes include

1. **coordination number** and **coordination geometry**, which involve differences in how many ligands surround a central metal and their overall geometric arrangement. Examples of the latter include the tetrahedral and square planar geometries commonly observed for four-coordinate metal centers. Tetrahedral, square planar, and octahedral coordination serve as a backdrop to the discussion of isomerism on this page. Readers who are unfamiliar with these structures might consider reading the section on coordination geometries before this one.
2. **structural iosmerism** involves differences in how potential ligand atoms are bound to metals in a complex. Possibilities for structural isomerism include
   - linkage or ambidentate isomerism
   - hydrate/solvate isomerism
   - ionization isomerism
   - coordination isomerism.

   Of these, linkage isomerism should always be considered when working with ambidentate ligands. As classifications, the last three forms of structural isomerism are mainly of academic interest since they represent permutations of ordinary structure patterns for solvates, salts, and coordination complexes, respectively.
3. **stereochemistry**, which includes
   - which coordination geometry is adopted for a metal with a given set of ligands in a particular oxidation state. For instance, $[Ni^{II}Cl_4]^{2-}$ is tetrahedral while $[Pt^{II}Cl_4]^{2-}$ is square planar. Since this geometry is usually fixed by the metal and ligands it is typically not a source of stereoisomeric varierty.
   - metal-centric stereoisomerism involving possible variations in where ligands are located relative to one another around the metal. The possibilities depend on the coordination number, geometry, and number of different types of ligands. For instance, square planar complexes can exhibit *cis-/trans-* isomerism while tetrahedral ones cannot. Tetrahedral complexes with four different ligands exhibit *R* and *S* chirality but complexes of that type are relatively rare. The more common cases include *cis* and *trans* isomerism in square planar complexes and *cis* & t*rans-*, *mer* & *fac-*, and Λ & Δ isomerism in octahedral ones, although some multidentate ligands present additional possibilities for stereochemical variation
   - Stereoisomerism centered on the ligands bound to a metal center. Possibilities include
     - stereoisomerism inherent to a ligand. This would include cases where the ligand itself is chiral or, as in the case of amines, exists as a rapidly interconverting mixture of isomers. Thus this sort of stereoisomerism is an extension of the isomerism encountered in ordinary organic and other main group compounds. The main new issues introduced by binding of such ligands to a metal center involve the creation of new possibilities for diastereoisomerism based on the stereochemistry of the metal center and the freezing out of stereocenter inversion on binding to a metal. The latter is particularly important for amines, which as free amines racemize rapidly by nitrogen inversion.
     - or conformational isomerism involving five-membered **chelate rings** created when a multidentate ligand binds to a metal. This isomerism is often called chelate ring twist since individual rings can exhibit one of two conformations depending on how they twist on binding.

A summary of these forms of isomerism is given in Figure 2.4.1.

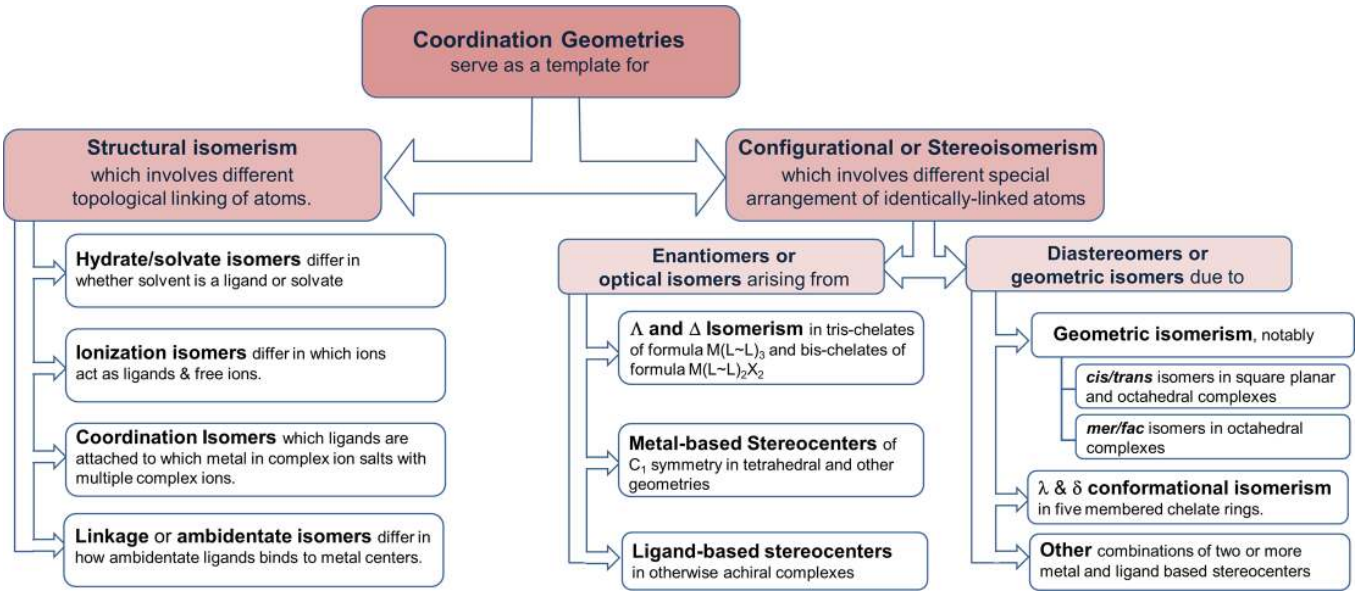


Figure 2.4.1. Relationship among the common types of isomerism in metal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Structural isomers

Structural isomerism involves different topological linkages of atoms. Differences in atomic linkages distinctive to coordination chemistry involve the linkages between metals and ligands. The main variations are:

1. Hydrate/solvate isomerism

Solvate isomers differ in terms of whether a molecule acts as a ligand or whether it acts as a solvate by occupying a lattice site in the crystal. Among solvate isomers, the case in which water is the ligand or solvate is the best known. The resulting isomers are called **hydrate isomers** after the term for water acting as a solvate, hydrate. A well-known example that illustrates how solvate isomerism works is the series $[CrCl_x(H_2O)_{6-x}]Cl_{3-x}{\cdot}xH_2O$, for which x = 0-2. The structures of the complex ions involved in this series are shown in Figure 2.4.2.[1]

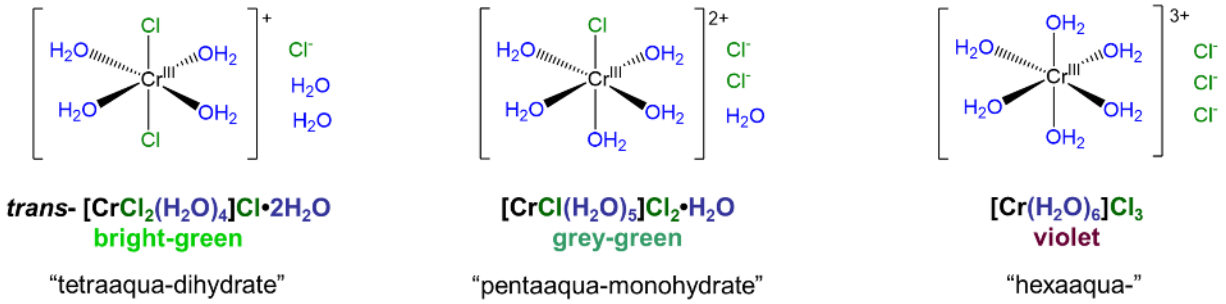


Figure 2.4.2. Complexes of the hydrate isomer series $[CrCl_x(H_2O)_{6-x}]Cl_{3-x}{\cdot}xH_2O$ (x = 0-2). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen from the compounds in Figure 2.4.2, hydrate isomers differ both in terms of whether water acts as a ligand or hydrate *and* in terms of whether a potential counterion acts as a counterion or ligand. Thus, in *trans*-$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ two chlorides act as chloro ligands and four waters as aqua ligands while in $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$ five water molecules act as aqua ligands while only one chloride acts as a chloro ligand. In this way, solvate isomers simply represent cases in which two or more of the possible permutations for metal ligand binding among a set of solvent and counterion molecules are stable.

2. Ionization isomerism

In **ionization isomerism** there are two or more potential ions that can act as ligands. The ionization isomers differ in terms of which of these ions act as counterions and which act as ligands. Consider, for instance, the complexes shown in Figure 2.4.3. These complexes differ in terms of whether the chloride or sulfate acts as a ligand, with the other acting as a counterion.

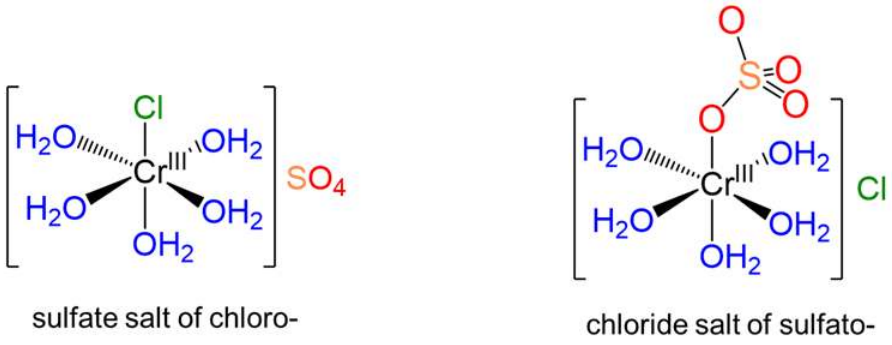


Figure 2.4.3. Ionization isomers comprising a pentaaquachromium(III) fragment and the anions chloride and sulfate. As with all ionization isomers, the isomers differ in terms of which anion acts as a ligand and which a counterion. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

3. Coordination isomerism

Coordination isomers exist in compounds containing two or more complexes, each of which possesses a different set of ligands that can in principle be swapped with a ligand of the other complex. An example involves $[Co^{III}(NH_3)_6][Cr^{III}(ox)_3]$, depicted in Figure 2.4.4A[1] Coordination isomers of this complex involve swapping the ammine ligands around the Co^{3+} center for oxalato ligands surrounding the Cr^{3+} center. For instance, swapping all the ammine and oxalato ligands between the metal centers gives the coordination isomer $[Cr^{III}(NH_3)_6][Co^{III}(ox)_3]$ shown in Figure 2.4.4B.

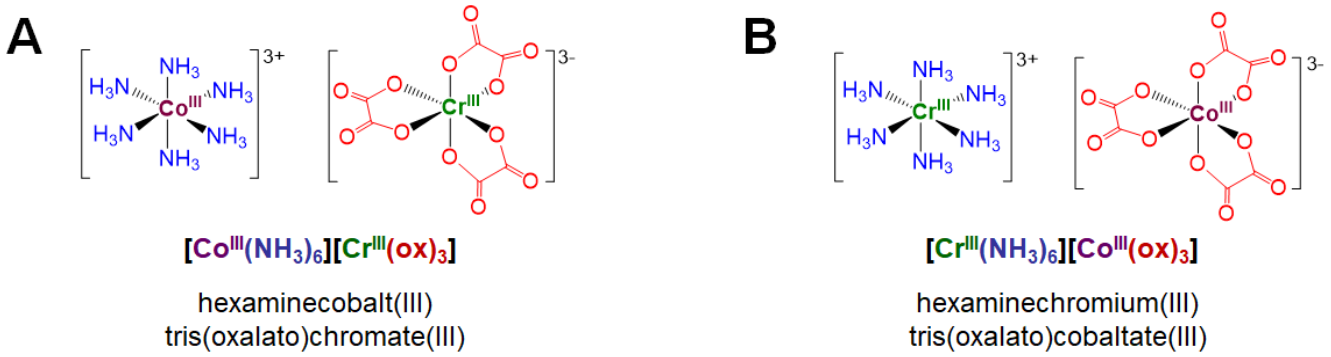
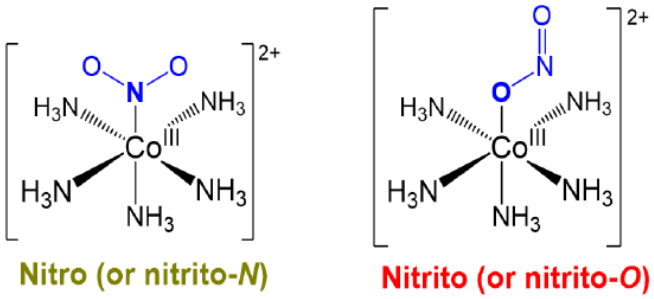


Figure 2.4.4. Two coordination isomers comprising a Co^{3+} ,Cr^{3+}, six NH_3. and three oxalato ligands. The isomers differ in terms of which ligand type is bound to which metal. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As classifications, hydrate/solvate, ionization, and coordination isomerism represent permutations of ordinary structure patterns for solvates, salts, and coordination complexes, respectively. As a result these forms of isomerism are rarely used as independent conceptual frameworks when thinking and talking about the structure of coordination compounds. Not so the final type of structural isomerism, linkage isomerism. That is because linkage isomerism has to do with the special *capacity* of ambidentate ligands to bind metals in multiple ways.

4. Linkage or ambidentate isomerism

Linkage or ambidentate isomers differ in how one or more ambidentate ligands bind to metal centers in a complex. The classic example dating from the work of Jørgensen and Werner is given in Scheme 2.4.1.



Scheme 2.4.1. Linkage isomers of penaamminenitritocobalt(III) ion. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Just as alkenes exist as *E* and *Z* isomers, compounds possessing ambidentate ligands exist as one among the possible linkage isomers. As such, when working with ambidentate ligands the particular linkage isomer formed should be determined experimentally and considered when interpreting the complex's chemical and physical behavior.

The main ambidentate ligands which give rise to linkage isomerism are

- cyanide, CN^-
- thiocyanate, SCN^-, and the O and Se analogues, OCN^- and $SeCN^-$
- nitrite, NO_2^-
- sulfite, SO_3^-
- nitrosyl, NO

Although ambidentate ligands can bind metals in multiple ways, most exhibit a preferred binding mode (*i.e.*, prefer to bind metal centers in one of the possible ways). For instance, cyanide almost always binds through its carbon atom and thiocyanate almost always binds through its nitrogen (μ-*N*). However, the other binding mode can sometimes be formed kinetically or by using conditions that particularly favor its formation. Thus thiocyanate forms M-SCN^- linkages in the presence of exceptionally soft metal centers or in hard polar solvents (in which Lewis acid groups can stablize the terminal nitrogen of a bound thiocyanate ligand).

Ambidentate ligands are of significant research interest because many don't just bind to metal centers in two ways; the linkage isomers sometimes have significantly different physical properties. In addition, the possibility of two binding modes introduces the possibility of exploiting linkage isomerism to take advantage of some of these ligands:

a. different structural chemistry in different coordination modes. In mononuclear complexes the coordination mode influences which side of the ligand faces away from the complex and might be susceptible to stabilization by interaction with solvent. Additionally, the orientation of the ligand relative to the metal center might differ between one coordination mode and another. For instance, as predicted from the minor contributor to its resonance structure, thiocyanate binds nonlinearly via its S atom and linearly via its N (Figure 2.4.5). Because of this the apparent steric bulk of the ligand around the metal center might differ between forms.

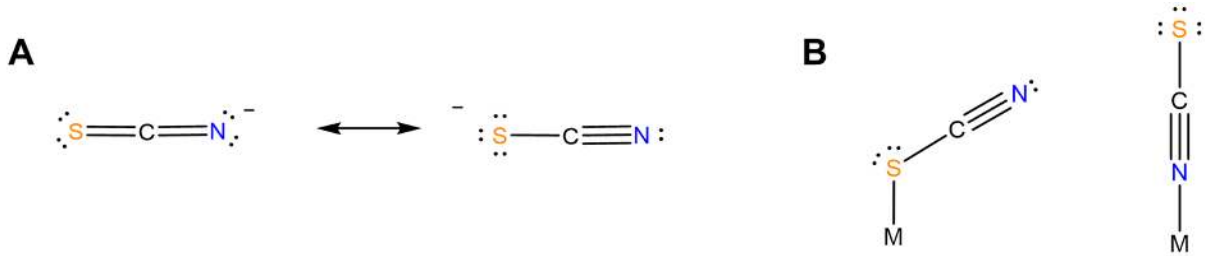


Figure 2.4.5. Thiocyanate generally prefers to bind metals nonlinearly but in some cases forms linear M-SCN bonds. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

b. bind two different metal centers at the same time, linking them together. Perhaps the best-known examples involve thiocyanate and cyanide. The latter forms linkages of the type M-C≡N-M'. In the dye Prussian blue these take the form Fe^{II}-C≡N-Fe^{III}. An example from the author's graduate research involved tetrahedral clusters containing four metal atoms linked by six cyano ligands, as shown in Figure 2.4.6.

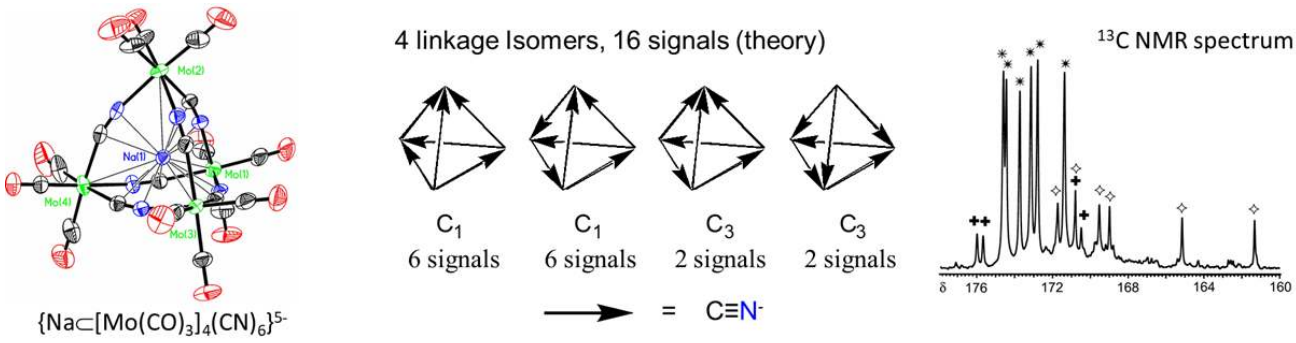


Figure 2.4.6. (A) Structure of $\{Na@[Mo(CO)_3]_4(CN)_6\}$ showing the linking of four Mo centers by six CN ligands. Thermal ellipsoids for the C atoms are shown in black; those of the N atoms in blue. (B) The complex exists as a mixture of four linkage isomers in which the bridging CN^- ligands are oriented in different ways, as may be seen from the presence of the expected sixteen signals in its ^{13}C NMR spectrum. Based on work reported in reference 2.

c. can be induced to change from one binding mode to another in response to a stimulus. The classic example involves the light-driven transformation of the thermodynamically more stable yellow nitro complex of pentamminecobalt(III), $[Co(NH_3)_5NO_2]^{2+}$ to the less stable red *O*-nitrito complex, $[Co(NH_3)_5ONO]^{2+}$. Less stable cyanometallate coordination networks like those in the red $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ transform into the more stable green $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ form on heating, as shown in Figure 2.4.7.[3]

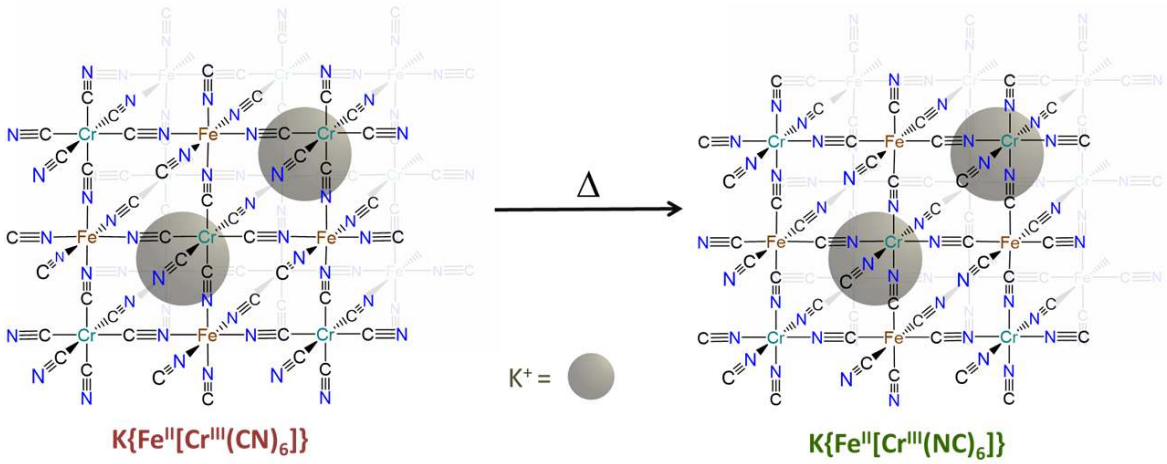


Figure 2.4.7. Thermally-induced transformation of one $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ into its more stable green linkage isomer $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ involves "flipping" the cyano ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

? Exercise 2.4.1: Bridging ambidentate ligands and the Hard-Soft Acid- Base Principle.

The hard-soft acid-base principle helps explain the preference of bridging ambidentate ligands for particular binding modes. How might the greater stability of the green $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ over red $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ be explained in terms of the hard and soft acid-base concept?

Answer

The greater stability of $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ over $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ reflects the greater stability of the Fe^{II}-CN-Cr^{III} linkages in the former over the Fe^{II}-NC-Cr^{III} linkages in the latter. This is consistent with the preference for hard-hard and soft-soft Lewis acid-base interactions of the Hard-Soft Acid-Base Principle.

The Fe^{II}-CN-Cr^{III} linkages are more stable because they possess bonds between

- the softer Lewis acid (Fe^{II}) and Lewis base (the C end of CN^-)
- the harder Lewis acid (Cr^{III}) and Lewis base (the N end of CN^-)

In contrast, the Fe^{II}-NC-Cr^{III} linkages in the less stable linkage isomer involve bonds between

- the softer base (the C end of CN^-) and harder acid (Cr^{III})

- the harder base (the N end of CN^-) and softer acid (Fe^{II})

Stereoisomerism

Optical Isomerism/Chirality

Molecules of D_n, C_n, or C_1 symmetry with only proper rotation axes (including $E = C_1$) are chiral and exhibit optical isomerism. As described in Figure 2.4.1, the main sources of such optical isomerism in coordination chemistry are:

1. Chirality inherent to an organic or main group ligand.

   This type of isomerism is just an extension of the sort described in undergraduate organic texts and consequently does not merit separate discussion here, other than to note that some forms of optical isomerism which are of little importance in organic chemistry lead to optical activity in coordination compounds. In particular, the nitrogen inversion process which serves to rapidly racemize chiral amines is frozen out on formation of a metal-ligand bond. Because of this chiral amine, ligands bound to a metal form non-interconvertible *R* and *S* enantiomers, as shown in Figure 2.4.8.

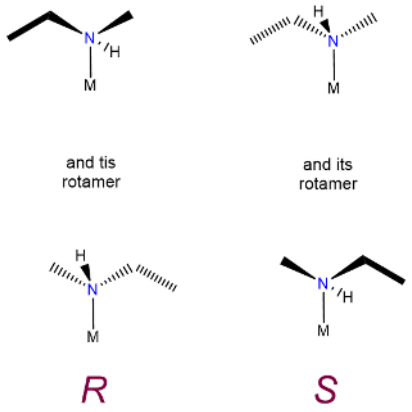


Figure 2.4.8. Two views of *R* and *S* enantiomers formed when the chiral amine ethylmethylamine binds a metal that are commonly used to represent chiral amines in complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2. Chirality arising from the symmetry of ligands about a metal center.

   The two common situations through which such chirality arises involve:

   i. Chirality at a tetrahedral metal center surrounded by four different ligand attachment points.

      Such cases are often referred to as MABCD or Mabcd where M stands for the metal and a, b, c, and d the four different ligand attachment points. An example of such a complex is given in Figure 2.4.9A. The chirality of such complexes is analogous to the chirality arising from a tetrahedral carbon stereocenter. There are two caveats, though. First, it is not enough to have a four-coordinate complex; the metal must possess tetrahedral symmetry since, as shown in Figure 2.4.9B, square planar M complexes with four different ligands are identical to their mirror images. Second, such chirality is most easily realized using macrocyclic ligands like proteins. Metal ligand bonds involving sterically unhindered monodentate complexes like that in the example of Figure 2.4.9A are in general weaker and more flexible than analogous carbon-carbon bonds. Consequently, in such cases it is likely that the enantiomers would interconvert through a fluxional process, making their resolution difficult if not impossible.

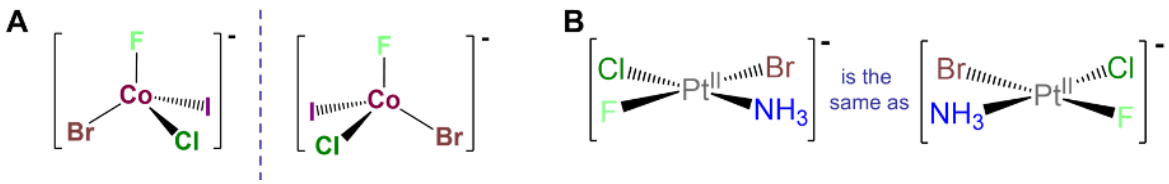


Figure 2.4.9. (A) In principle tetrahedral metal centers surrounded by four different ligands (Mabcd) exhibit chirality analogous to the chirality of tetrahedral carbon stereocenters; (B) in contrast, square planar Macbd complexes like $[PtBrClF(NH_3)]^-$ are not chiral since they are the same as their mirror images. (It is easiest to see this by either working out its point group (C_s) or by rotating the left $[PtBrClF(NH_3)]^-$ structure clockwise 180 degrees to give its mirror image. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

ii. Λ and Δ isomerism at octahedral metal centers surrounded by two or three chelating ligands.

Specifically,

a. Octahedral tris-chelates of formula $M(L\sim L)_3$ exhibit D_3 symmetry.
b. cis-octahedral bis-chelates of formula $M(L\sim L)_2XY$ exhibit C_2 or C_1 symmetry: C_2 if X = Y and C_1 if X ≠ Y.

As shown in Figure 2.4.10A, octahedral tris-chelates like $[V(ox)_3]^{3-}$ are chiral and can exist as nonsuperimposable Λ and Δ enantiomers. The chirality of these tris-chelates is analogous to that of pinwheels. As shown in Figure 2.4.10B, when looking directly at the head of any individual pinwheel from above, the blades will be angled from back to front going around the pinwheel in either the clockwise or counterclockwise direction. As shown in Figure 2.4.10C, the case for which the blades are angled in the clockwise direction is analogous to the Λ enantiomer and the case when they are angled in the counterclockwise direction the Δ.

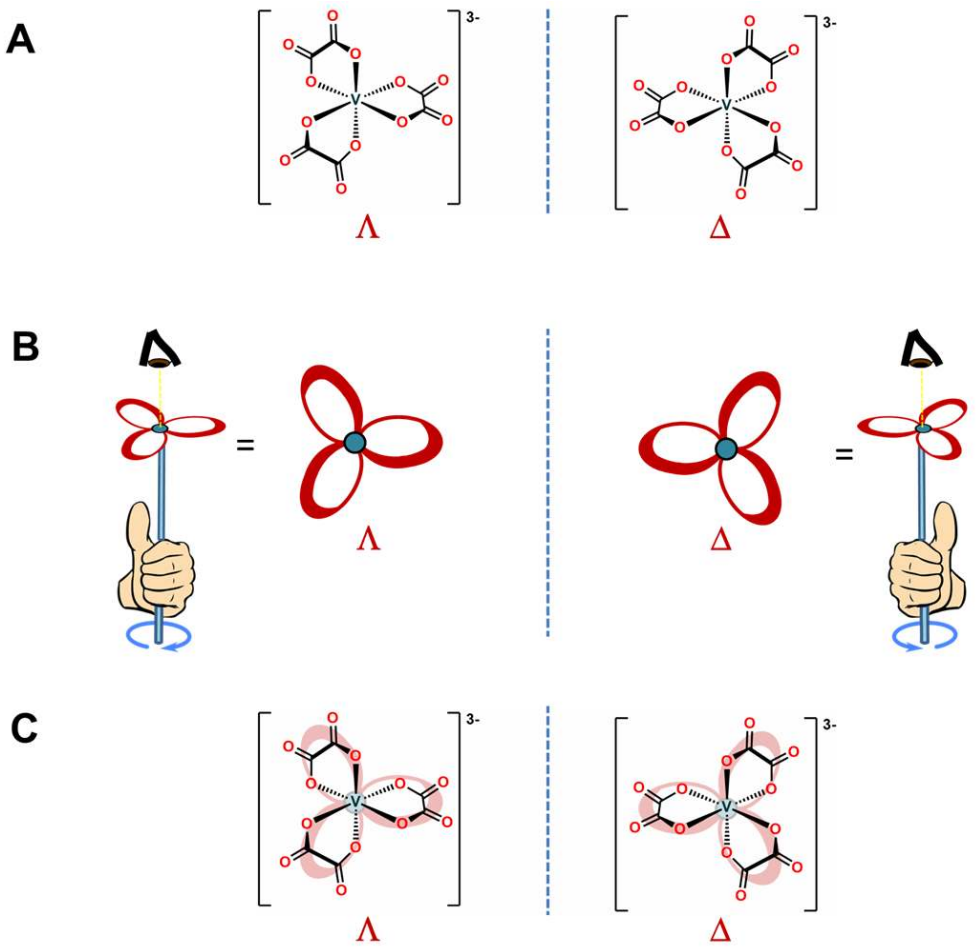


Figure 2.4.10. (A) Octahedral tris-chelates like $[V(ox)_3]^{3-}$ are chiral and can exist as Λ and Δ enantiomers. (B) The chirality in these systems is analogous to that of a pinwheel, with the Λ enantiomer exhibiting the symmetry of a left-handed pinwheel and the Δ enantiomer that of a right handed one. (C) The pinwheel-like nature of Λ and Δ enantiomers is easiest to see by overlaying the structures of $[V(ox)_3]^{3-}$ from A with the pinwheel structures of B. One way to recognize Λ and Δ enantiomers is to draw them in these projections. If a left hand is curled around the Λ enantiomer with the thumb facing up the curl of the fingers will flow from the back of each ligand towards the front. The same will be true if the right hand is curled around the Δ enantiomer. Credits: Although the image is largely an original drawing, the hand images used in part B are adapted from an image by SVGguru / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0). Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The Λ and Δ chirality in octahedral bis-chelates is analogous to that in the tris-chelates except this time the third chelating ligand is replaced by an arbitrary pair of ligands. This lowers the symmetry of the complex to either C_2 or C_1, as shown for the C_2 complex $[CoCl_2(en)_2]^+$ in Figure 2.4.11A. In either case the result is that such complexes exist as Λ and Δ enantiomers analogous to those in the metal tris-chelates, as shown in Figure 2.4.11B.

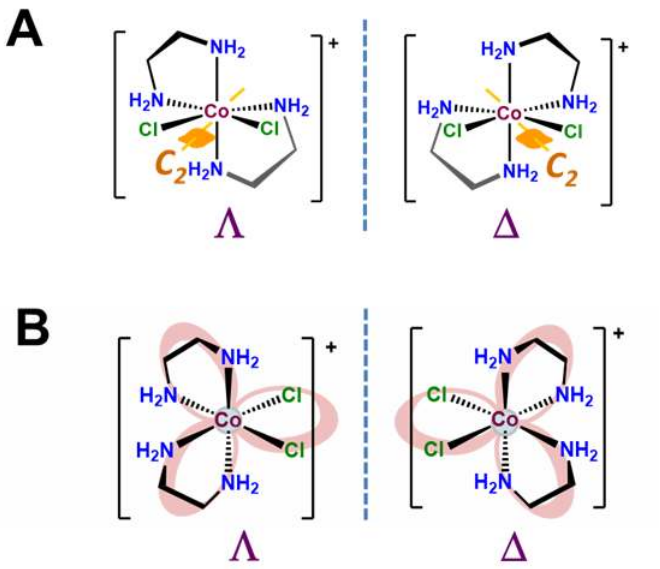


Figure 2.4.9C. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Octahedral complexes containing ligands with denticities of four or more also exhibit Λ and Δ chirality; it is just that in such cases the bound ligand defines multiple rings within the complex that can be defined as existing in either Λ or Δ orientations relative to each other. The procedure for making these assignments is beyond the scope of most introductory inorganic courses but the result is that such complexes are designated as ΛΛ, ΔΔ, ΔΛ, ΔΔΔ, etc., depending on the number of relationships involving the rings defined by the bound ligand. Interested readers should consult reference 4 for more details.

Circular dichroism may be used to characterize optically active metal complexes.

At the present the most definitive way to determine the absolute configuration of an optically active coordination compound is to determine its 3D molecular structure using single crystal X-ray crystallography.[5] However, as that is not always possible or convenient, the optical activity of coordination complexes is also commonly studied using circular dichroism (CD) spectroscopy. CD spectroscopy is used because, unlike most chiral organics, optically active coordination complexes possess low-energy electronic transitions that occur in the far UV and visible range. This means that it is often convenient to use the ability of a complex to refract and absorb different circular polarizations of light to derive information about both the configuration of an optically active complex and its electronic structure. The focus of this section will be to explain how the determination of absolute configuration by circular dichroism and optical rotatory dispersion work, as well as the relationship of these techniques to the more ordinary sort of polarimetry used to measure optical rotation in organic systems. Only brief notes will be made about the instrumental and electronic structure applications of these techniques since the electronic spectra of metal complexes will be discussed in Chapter 11: Coordination Chemistry III - Electronic Spectra and the instrumental aspects of CD are well-treated elsewhere.

Both polarimetry and circular dichroism spectroscopy are grounded in the recognition that plane polarized light is equivalent to a superposition of left and right circularly polarized light, as shown in Figure 2.4.12

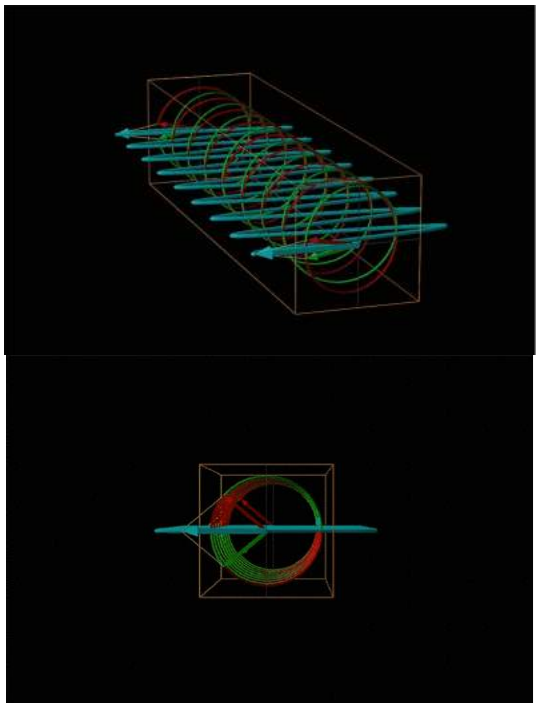


Figure 2.4.12. Angled and front view of plane polarized light (light blue) as the vector sum of left circularly polarized light (red) and right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

When plane polarized light passes through a chiral medium, its left and right circularly polarized components move at different rates (*i.e.*, have different indices of refraction). This causes the plane of polarization to rotate in the direction of the faster component according to the relationship

$$\alpha = \frac{n_l - n_r}{\lambda}$$

where α is the angle of rotation, λ the light's wavelength, and n_l and n_r the refractive indices experienced by left and right circularly polarized light.

An example of such a rotation is shown in Figure 2.4.13.

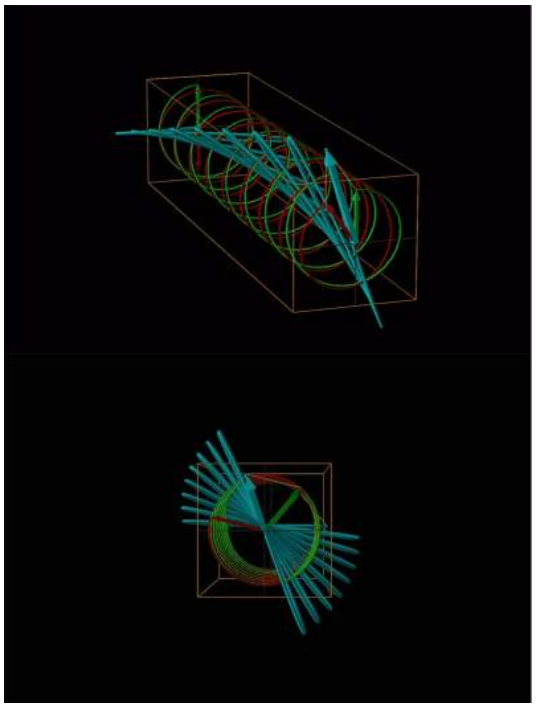


Figure 2.4.13. Angled and front view of plane polarized light (light blue) as it passes through a medium (represented by the orange box) in which left circularly polarized light (red) experiences a higher refractive index (and so moves slower) than right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim) with a refractive index of 1.05 for left circularly polarized light and 1.00 for right circularly polarized light. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Chemists typically call this rotation of light by a chiral medium optical rotation. In organic chemistry it is common to measure the optical rotation at the sodium D wavelength of 589.29 nm, a much longer wavelength than most organics are able to absorb. Because of this the optical rotations commonly measured by organic chemists are largely independent of absorption and mainly serve as a characteristic physical property similar to melting points or are used to establish the purity of a mixture of enantiomers. The sort of spectroscopic data used to characterize chiral coordination compounds more commonly makes use of the relationship between absorption and optical rotation.

In coordination chemistry the wavelength-dependence of optical rotation is used to discern information about compounds' electronic spectra. This measurement of the wavelength dependence of optical rotation is called **optical rotatory dispersion (ORD)** and the resulting plots are called optical rotatory dispersion or ORD spectra or curves. Such ORD curves are useful for characterizing the chiral environment in a coordination complex because the ORD curves exhibit a characteristic shape. This characteristic shape is because according to the **Cotton Effect,** the optical rotation changes sign at the absorption maximum of a chromophore in the compound. For one configuration the rotation will go from negative to positive with increasing wavelength and is called a **positive cotton effect**; for the other configuration the rotation will go from positive to negative or exhibit a **negative cotton effect**. This behavior is summarized in the top two curves of Figure 2.4.14.

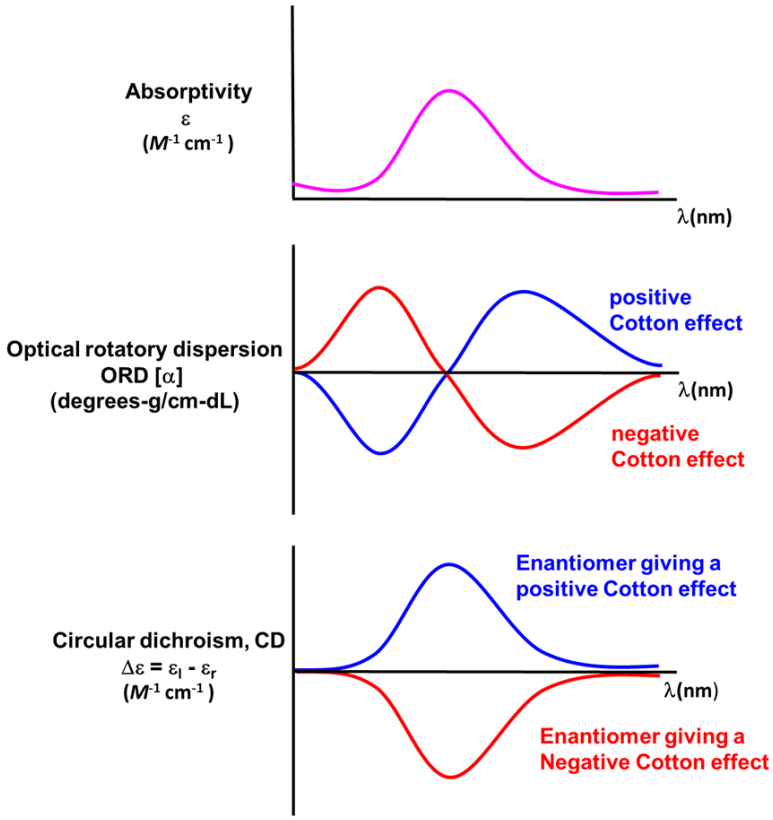


Figure 2.4.14. Idealized relationship between absorbance, ORD, and CD spectra for enantiomers exhibiting a positive and negative Cotton effect. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

A technique used even more often than ORD is **circular dichroism (CD)**, represented by the lowest spectrum in Figure 2.4.14. Circular dichroism arises from the differential absorption of left and right circularly polarized light by a chiral compound. This gives elliptically polarized light as shown in Figure 2.4.15.

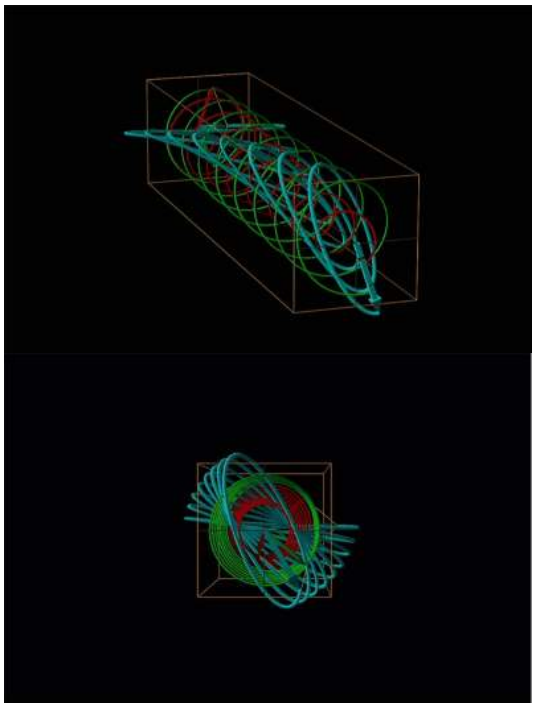


Figure 2.4.15. Angled and front view of plane polarized light (light blue) as it passes through a medium (represented by the orange box) in which left circularly polarized light (red) both experiences a higher refractive index and greater absorption than right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim) with a refractive index of 1.05 and an extinction coefficient of 0.05 for left circularly polarized light and a refractive index of 1.00 and extinction coefficient of 0 for right circularly polarized light. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In circular dichroism (CD) spectroscopy a sample is irradiated with polarized light resulting in the transmission of elliptically polarized light due to differential refraction and absorption of the polarized light's left and right circularly polarized components. For achiral molecules the handedness doesn't affect absorbance, but for chiral molecules, which chiral ground and excited states the handedness of an EM wave affects can determine how readily that wave can distort the chiral ground state into the chiral excited one. For this reason chiral molecules absorb left and right circularly polarized light differently.

In CD spectroscopy the magnitudes of the left and right circularly polarized components of light that is transmitted by the sample are measured and used to determine how much light of each was absorbed (just as in regular absorbance spectroscopy). The difference in absorption between left and right circularly polarized light constitutes the primary signal in CD spectroscopy. More specifically, circular dichroism spectra (CD spectra) show the difference in extinction coefficients for left and right circularly polarized light, $\Delta\epsilon$, as a function of wavelength, where

$$\Delta\epsilon = \epsilon_l - \epsilon_r$$

where ϵ_l and ϵ_r are the extinction coefficients observed with left and right circularly polarized light, respectively.

As with ORD spectra, the signs of the features in CD spectra like that of Δ–$[Co(en)_3]Cl_3$ given in Figure 2.4.16 are enantiomer-dependent. As illustrated in the lower spectrum in Figure 2.4.14, the CD spectra of enantiomers mirror one another. Because of this difference in behavior it is possible in principle to determine the absolute configuration of a complex from its CD spectrum.

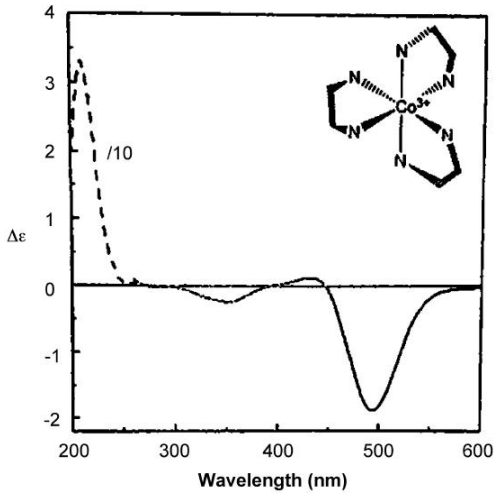


Figure 2.4.16. CD spectrum of Δ–[Co(en)$_3$]Cl$_3$. Taken from reference 6.

There are several ways that ORD and CD spectra can be useful for determining the absolute configuration of a chiral complex.

1. First, the sign of the Cotton effect and peaks in CD spectra exhibited by a given absolute configuration is often consistent across a series of compounds. Thus if a new member of the series is isolated, its configuration can be determined based on which enantiomer has the same Cotton effect. For instance, if both the Λ isomer of a metal diimine complex like [Ru(bpy)$_3$]$^{2+}$ exhibit a positive Cotton effect and a newly resolved metal diimine exhibits a negative Cotton effect it might reasonably be inferred that the newly-resolved complex is in the opposite or Δ configuration.
2. Second, for some systems the expected sign of the Cotton effect and CD peaks for each enantiomer may be predicted semi-empirically based on the spatial locations of substituents relative to the chromophore (the part of the molecule that changes electronic structure during the transition), although the details are beyond the scope of the present discussion.
3. Consideration of interactions between multiple chromophores in a compound can be used to infer absolute configuration. Again, the details are beyond the scope of the present discussion. Interested readers are referred to reference 7 for details.

Common patterns of Diastereomerism

Geometric isomerism

Geometric isomerism involves differences in the geometric placement of atoms in a compound. In coordination chemistry, geometric isomerism involves differences in the relative placement of a set of ligands about a metal center. There are two main types:

cis and *trans* isomerism

This type of isomerism has to do with how two ligands are oriented relative to one another in a square planar or octahedral complex. As shown in Figure 2.4.17, ligands that are next to one another with a L-M-L bond angle of 90° are said to be *cis*; those on opposite sides of the metal with a L-M-L bond angle of 180° are in the *trans* arrangement.



Figure 2.4.17. *cis* and *trans* arrangement of ligands around (A) square planar and (B) octahedral metal centers. Since both types of complexes feature 90° L-M-L bond angles, the arrangements are fundamentally the same in both cases. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Simple *cis* and *trans* geometric isomers can be identified when there are two identical ligands (A) or chelating ligands with distinguishable attachment points (A~B) oriented about either a square planar or octahedral center. Examples are given in Figure 2.4.18. Notice from the example given in Figure 2.4.18C that multidentate ligands have the potential to constrain complexes to adopt a particular geometry.

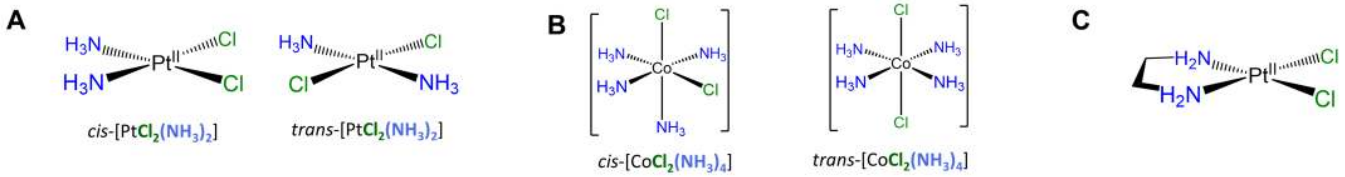


Figure 2.4.18. Examples of square planar and octahedral *cis* and *trans* isomers. (A) *cis* and *trans* isomers of $[PtCl_2(NH_3)_2]$; the former is medicinally important. Sold under the name cisplatin, the *cis* isomer is used as a chemotheraphy against various forms of cancer. (B) *cis* and *trans* isomers of $[CoCl_2(NH_3)_4]$, a compound of more academic interest. (C) $PtCl_2$(en) only exists as the *cis* isomer because the chelating en ligand can only bind in a *cis* arrangement. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Slightly more involved examples involve perturbations of the simple cases above in which there are multiple distinguishable *cis* and/or *trans* relationships. Two square planar examples are given in Figure 2.4.19.

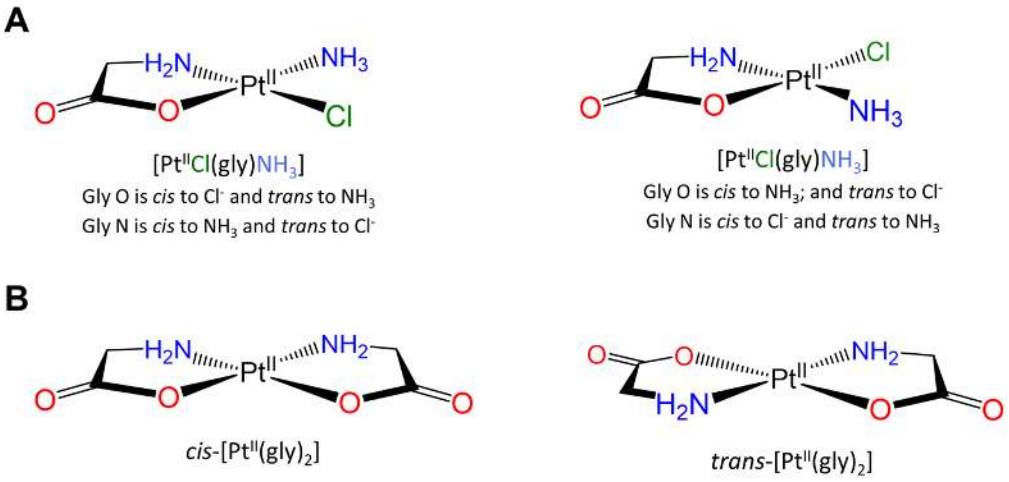


Figure 2.4.19. Examples of more complex square planar systems. (A) Geometric isomers of $[PtCl(gly)NH_3]$, a MA_2BC system for which A = gly^-, B = Cl^-, and C = NH_3. Swapping of the ammine and chloro ligands changes both the *cis* and *trans* relationships involving the Gly ligand. (B) Geometric isomers of $[Pt(gly)_2]$, an $M(A\sim B)_2$ system for which A = the κO glycine carboxy group and B its κN amine. The only possible geometric isomerism involves swapping the orientation of one glycine relative to the other. For this reason the two complexes shown can be designated as *cis* and *trans* isomers based on whether the κO and κN ends of the glycine are *cis* or *trans* to one another. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

More complex examples of *cis* and *trans* relationships between ligands in octahedral complexes are given in the exercises that conclude this page, which also demonstrates how a systematic approach may be used to identify isomers.

mer and *fac* isomerism

This type of isomerism has to do with how three ligands are oriented relative to one another in an octahedral complex. The arrangements are represented in Figure 2.4.20.

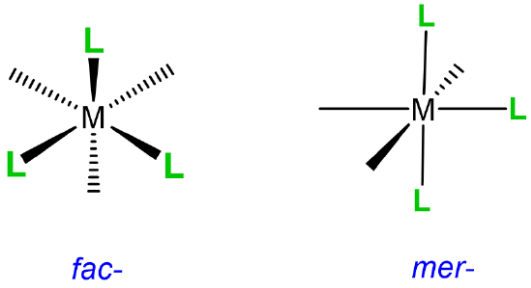


Figure 2.4.20. Simple representation of the *fac* and *mer* arrangements of ligands around an octahedral metal center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Since it can help to visualize the *mer* and *fac* geometry from multiple points of view, several representations are given in Figure 2.4.21. As shown in Figure 2.4.21, in ***fac*** or **facial arrangements**, the ligands occupy the same "face" of the octahedral

coordination sphere, while in the ***mer*** or **meridional geometry** the ligands form a T shape in the same plane or its "meridian."[8]

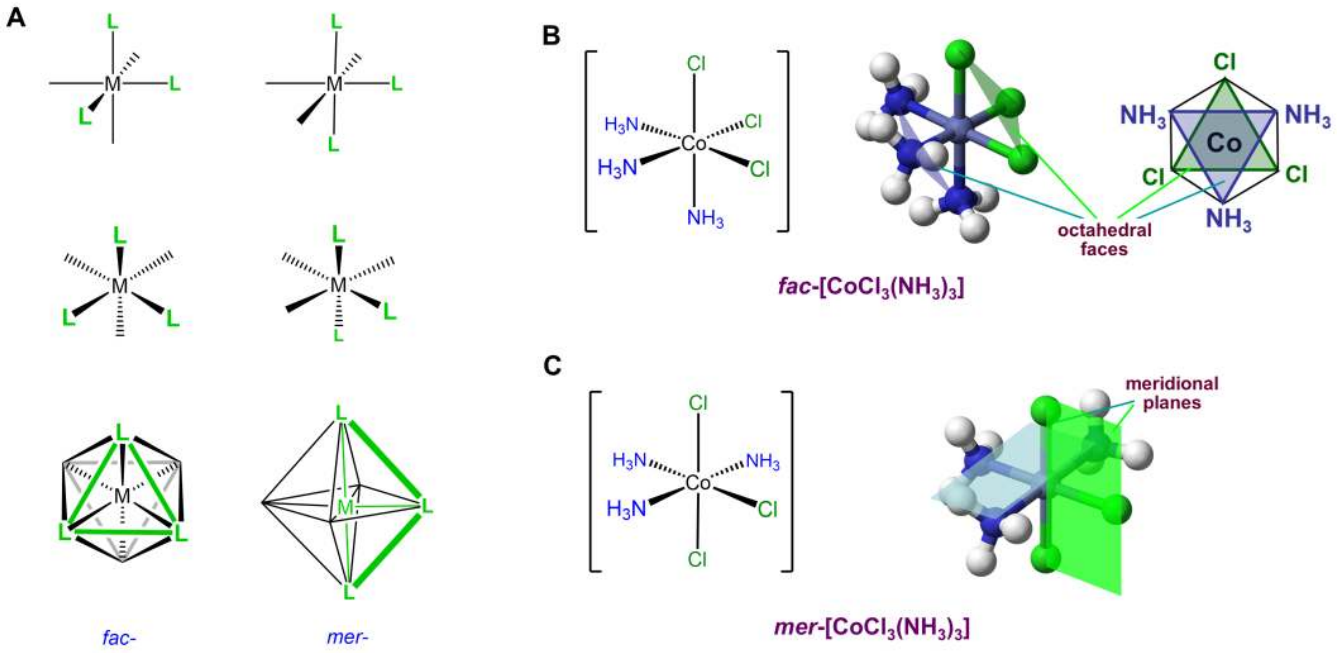


Figure 2.4.21. (A) Three projections of *fac* and *mer* arrangements of ligands around an octahedral metal center emphasizing that in the *fac* arrangement the ligands are oriented along a face of the octahedron while in the *mer* arrangement they are oriented in a plane. (B) Structure of *fac*-$[CoCl_3(NH_3)_3]$ showing the octahedral faces occupied by the chloro and amine ligands. (C) Structure of *mer*-$[CoCl_3(NH_3)_3]$ showing the planar arrangement of the chloro and ammine ligands. The ball and stick models are modified from images by Benjah-bmm27 - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=1874872 and curid=1874873. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Octahedral complexes with three identical ligands oriented about an octahedral center can only exist in *mer* and *fac* arrangements. Consequently, such complexes can be designated as *mer* and *fac* isomers. Examples are given in Figure 2.4.22.

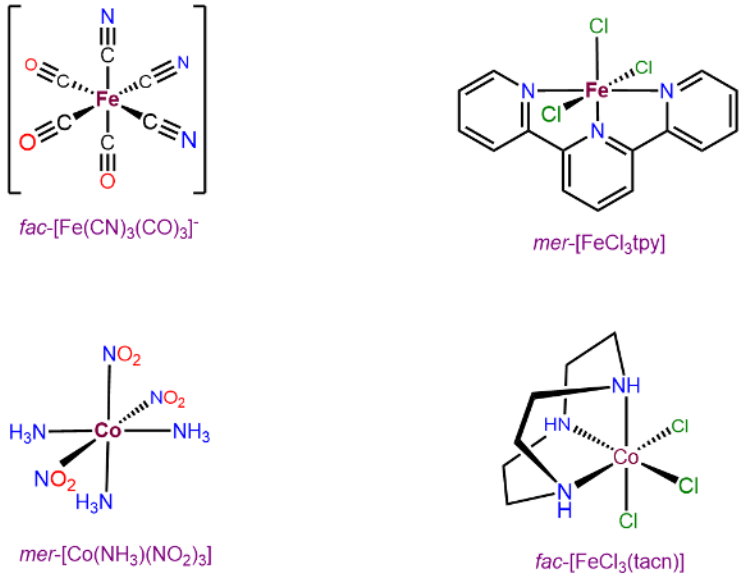


Figure 2.4.22. Examples of *fac* and *mer* octahedral complexes. Note how some chelating ligands preferentially bind to the metal in a *fac* or *mer* arrangement and, in so doing, force the other ligands to also form a *mer* or *fac* arrangement. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Diastereomerism arising from multiple ligand-associated chiral centers

Diastereomerism can also arise when two or more chiral ligands bind to a metal center. Such cases typically give rise to a complex mixture of isomers, as shown by the example in Figure 2.4.23. As may be seen from Figure 2.4.23, the differences between these

isomers can arise from both changes in the stereochemical configuration of the ligand and the relationship of particular ligand centers relative to one another. For instance, the leftmost two structures in Figure 2.4.23 possess one *R* and *S* nitrogen center each but differ in whether the centers are oriented so that the *R* and *S* centers on the two ligands are *trans* or *cis* to one another.

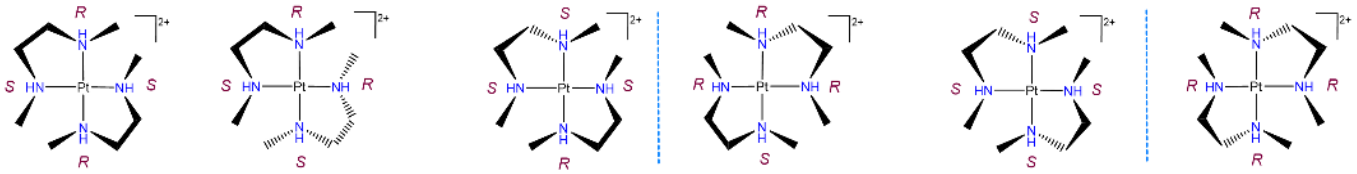


Figure 2.4.23. Diastereomers that can in principle be formed when two *N*,*N*′-dimethylethylenediamine ligands coordinate a Pt^{2+} center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Diastereomerism arising from λ and δ ring conformation isomerism.

Chelate rings are formed when a chelating ligand binds a metal

As may also be seen from the structures in Figure 2.4.23, when a multidentate ligand coordinates a metal, the ligand and metal center comprise one or more **chelate rings**. Examples of such chelate rings are shown in Figure 2.4.24.

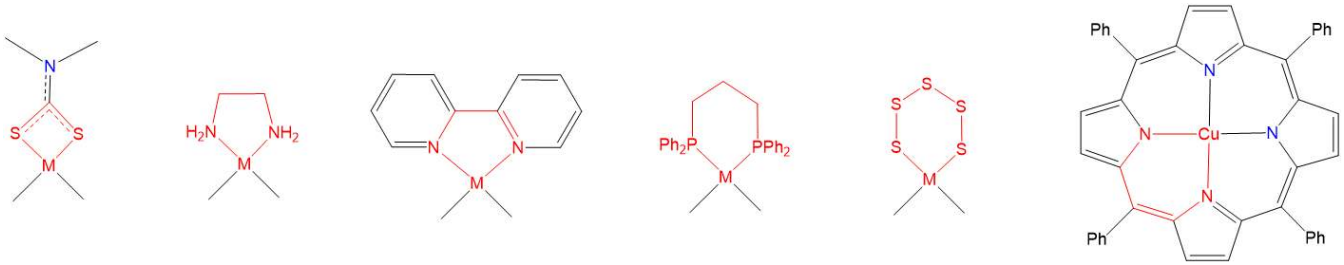


Figure 2.4.24. Four, five, and six-membered chelate rings (shown in red) formed by coordination of selected bidentate ligands to a metal center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As may be inferred from the examples in Figure 2.4.24, chelate rings may be of different sizes, although four, six, and especially five-membered rings are particularly common. Exactly which ring sizes will be more stable for a given system depends on the coordination geometry and, due to differences in M-L bond lengths, to a lesser degree on the metal. As a result, for octahedral and square planar complexes with 90° L-M-L bond angles between *cis* ligands, *five-membered rings tend to be especially stable* (Figure 2.4.25).

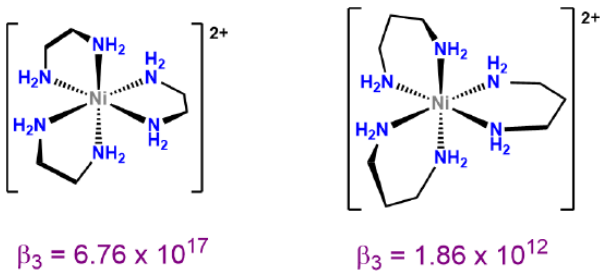


Figure 2.4.25. The greater stability of five-membered chelate rings involving Ni^{2+} and organic ligands is reflected in the higher overall formation constant (β_3) for the five-membered chelate rings contained in $[Ni(en)_3]^{2+}$ compared to that of $[Ni(et)_3]^{2+}$, which has six-membered rings. The data in this figure is taken from Stability of Metal Complexes and Chelation by Robert Lancashire. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Not all metal chelates prefer to form five-membered rings. The steric requirements of chelate rings depend on both the preferred coordination geometry of the metal center and the stereochemistry of the ligand. Both of these effects are typically considered in terms of preferred L-M-L bond angles. From the perspective of the metal center, the preferred bond angle is determined by the coordination geometry. Octahedral and square planar metals prefer 90° L-M-L bond amgles, trigonal bipyramidal systems 90 and 120° L-M-L bond angles, and tetrahedral complexes 109.5° L-M-L angles. The larger preferred bond angles in tetrahedral and trigonal bipyramidal systems often require the formation of larger six or seven-membered chelate rings for maximum stability. The size of the chelate ring actually formed between a metal and ligand is determined by the ligand's structure. As the contributor of all the atoms in the chelate ring but one, the ligand directly determines the chelate ring size. More subtly, ligands naturally prefer to coordinate metals at a particular L-M-L angle, called the **bite angle**, as shown in Figure 2.4.26A. Ligands with bite angles corresponding to the ideal L-M-L angle for a metal's preferred geometry tend to form more stable complexes, although in turn

ligand bite angles can cause metals with a weak coordination geometry preference to adopt the ligand's preferred geometry instead.[10] As may be seen from the values in Figure 2.4.26B, bite angles roughly increase with the size of the chelate ring formed but are also influenced by the types of structures used to connect the ligand's Lewis base sites. This facilitates the use of diphosphine ligands to tailor the structure and reactivity of phosphine-containing organometallic catalysts.

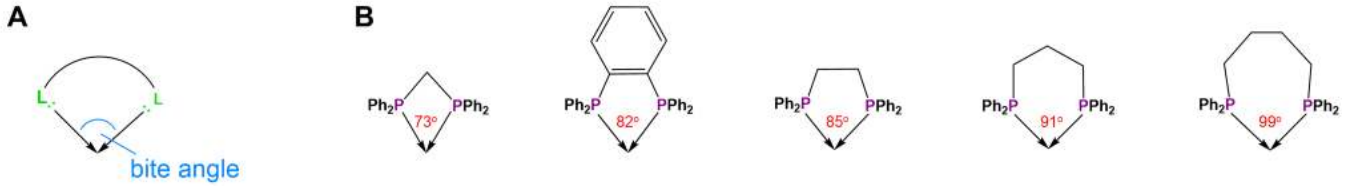


Figure 2.4.26. (A) Definition of the bite angle as the angle at which the ligand's preferred L-M-L angle when coordinating a metal center. (B) Bite angles of selected diphosphines.[9] The bite angles of many such diphosphines have been determined to facilitate the design of phosphine-containing organometallic catalysts. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

λ and δ isomerism involves differences in the conformation of nonplanar five-membered chelate rings

As shown in Figure 2.4.27, some chelate ring systems are planar while others are not.

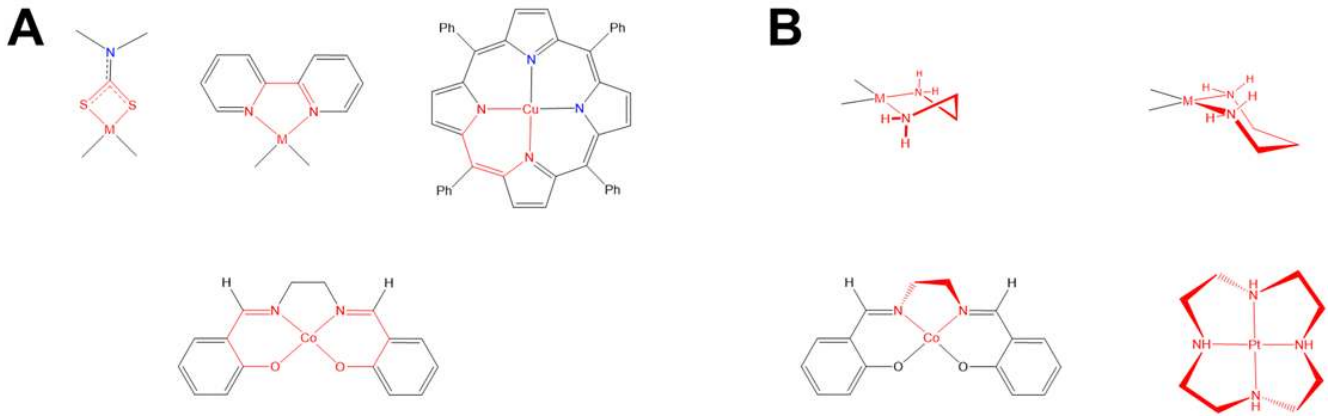


Figure 2.4.27. (A) Planar and (B) Nonplanar chelate rings shown highlighted in red. Notice how [Co(salen)] possesses a nonplanar chelate ring and two planar ones. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Among the nonplanar chelate ring systems are ligands like en and dppe, which contain tetrahedral C, N, O, P, and S atoms. Because these atoms create kinks in the chelate ring they introduce additional opportunities for diastereomerism due to differences in the chelate ring conformation, called **ring twist**. Ring twist in nonplanar systems has been most extensively explored for five-membered chelates like those formed by dppe and by en and other chelating amines. Unlike the more rigid four-membered chelate rings, five-membered chelates tend to be conformationally flexible, but not so conformationally flexible that their conformers are rapidly interconverting at room temperature (at least not when the rings are substituted to introduce additional steric strain). This balance between flexibility and rigidity enables some five-membered chelate rings to exist as mixtures of distinguishable conformational isomers at room temperature.

To understand the two most stable conformers that five-membered chelates rings tend to form, it is helpful to think of five-membered chelate rings as involving two components (Figure 2.4.28):

- a planar L-M-L group, where L are the atoms directly attached to the metal, M, and
- the remaining two ring atoms, E, which form a rigid E-E bar across the back of the chelate ring.

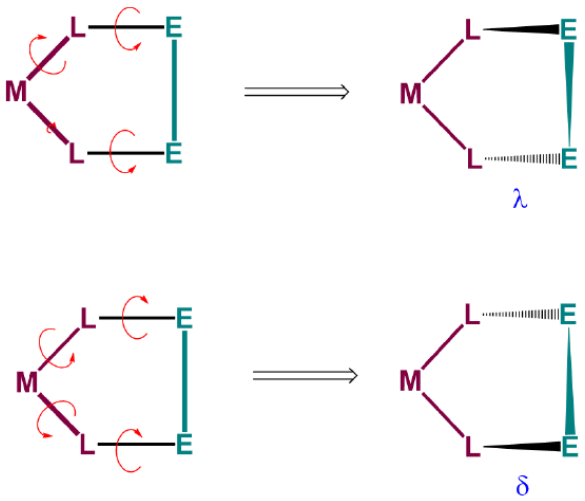


Figure 2.4.28. Five-membered chelate rings consist of a planar L-M-L group connected to a rigid E-E bar. Conformers arise as rotation about the M-L and L-E bonds causes twisting of the E-E bar relative to the L-M-L plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen from Figure 2.4.28, rotation about the M-L and L-E bonds causes twisting of the E-E bar relative to the L-M-L plane. The two most stable conformers produced by these motions are the λ or δ conformations as shown in Figures 2.4.29 and 2.4.29.

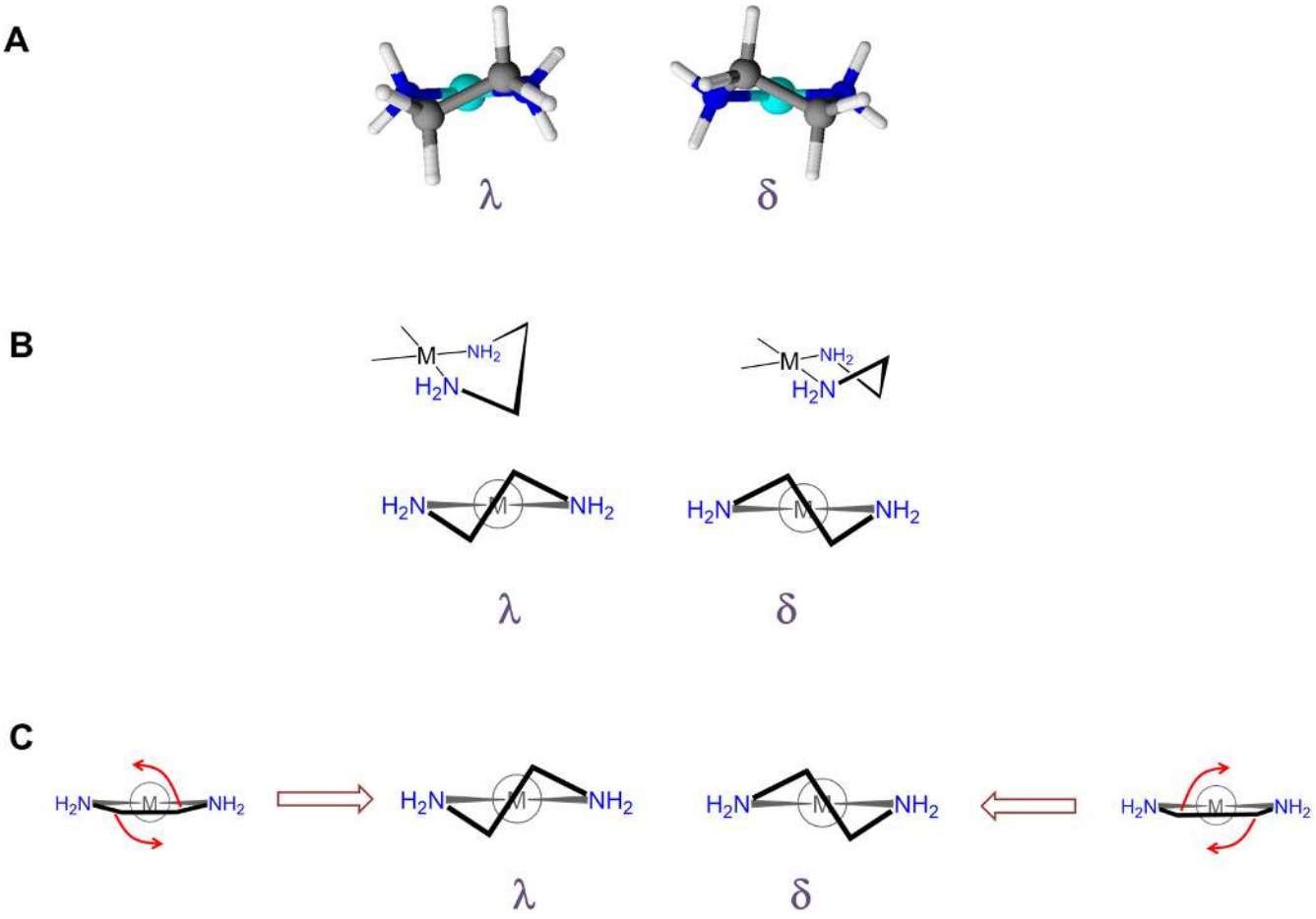


Figure 2.4.29. (A) λ and δ ring twist in a square planar metal ethylenediamine complex (B) along with several ways to represent it in line drawing form. (C) Of these, the projection looking down an axis bisecting the chelate ring makes it easiest to see that, starting with a planar chelate ring the λ conformer corresponds to a counterclockwise twist of the CH_2CH_2 bond relative to the N-M-N plane and the δ conformer a clockwise twist relative to the N-M-N plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The relative stability of the λ and δ conformers will depend on the configuration of any stereocenters present and steric factors. As with organic ring systems, steric effects tend to favor conformers in which bulky groups are placed in the less sterically strained equatorial positions while the configuration of the stereocenters present can serve to restrict the allowable ring twist conformations, as illustrated in Figure 2.4.30. A detailed treatment of such systems is beyond the scope of this page. Interested readers are referred to reference 12 for more details.

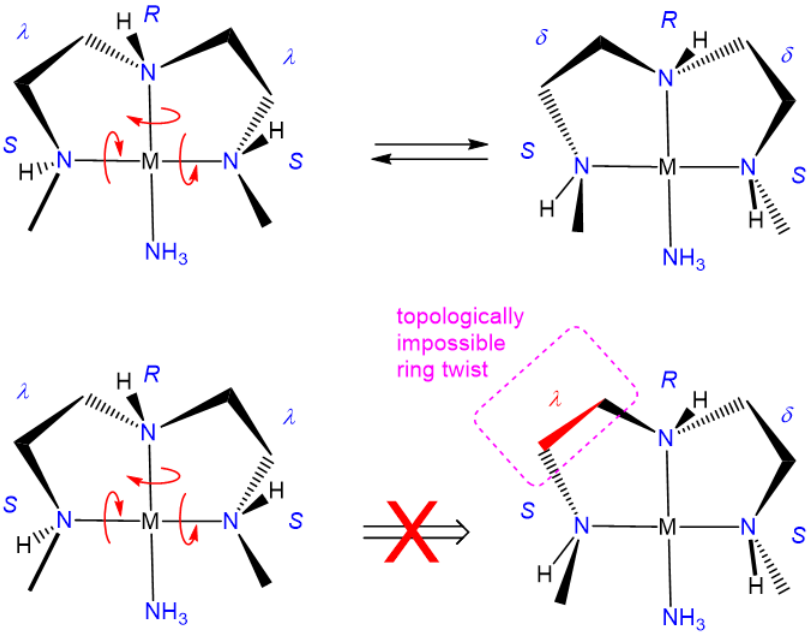


Figure 2.4.30. The configurations at nitrogen in the complex shown restrict the chelate ring conformations to either a $\lambda\lambda$ or $\delta\delta$ conformation because the rotations needed to enable a $\lambda\delta$ configuration are topologically impossible. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In closing, it should be noted that it might seem to be making much of small effects in pointing out that one source of diastereomerism in metal complexes involves the freezing out of chelate ring conformations. However, that would be to mistake the impacts that ring conformations can have on the steric accessibility of a coordination site and shaping the course of processes that might occur there. As illustrated in Figure 2.4.31, a simple shift in the conformation of one ring in a square planar, pyramidal, or octahedral complex containing coplanar ethylene diamine ligands can exert a significant effect on the steric profile of the complex perpendicular to the MN_4 square plane. Because of effects like these, ring conformation isomerism plays a role in the design of stereoselective transition metal catalysts.

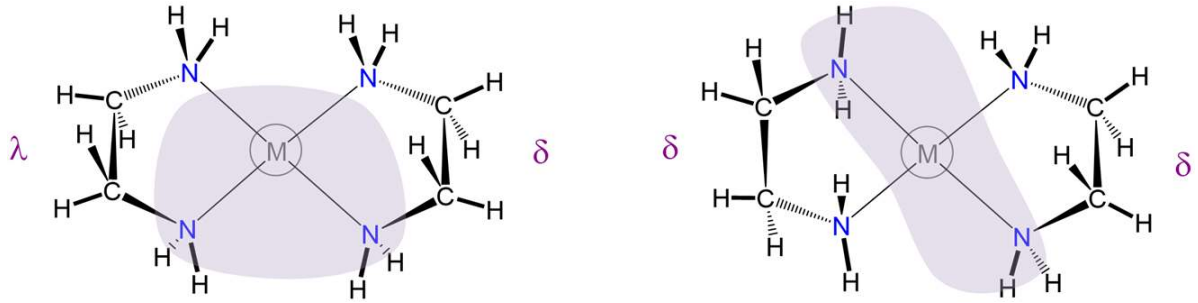


Figure 2.4.31. Schematic illustrating how the conformation of ethlyenediamine ligands bound to a metal center affects the steric accessibility of the metal (shown shaded in violet) to potential ligands attempting to bind from above the MN_4 plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Exercises

? Exercise 2.4.1. Identify the type of isomerism

What type of isomers are

a. $[CoCl(NH_3)_5](NO_3)$ and $[Co(NH_3)_5(N\text{-}NO_2)]Cl$?
b. $[Co(NH_3)_5\text{-}CN\text{-}Ru(NH_3)_5]^{4+}$ and $[Co(NH_3)_5\text{-}NC\text{-}Ru(NH_3)_5]^{4+}$
c. $[Cr(CN)_5\text{-}CN\text{-}Co(NH_3)_5]$ and $[Co(CN)_5\text{-}CN\text{-}Cr(NH_3)_5]$
d. *cis*-$[Mn(en)_2(CN)_2]$ and *trans*-$[Mn(en)_2(CN)_2]$

Answer a.

Ionization isomers.

Answer b.

Linkage isomers.

Answer c.

Coordination isomers.

Answer d.

Geometric isomers, specifically *cis*/*trans* isomers.

? Exercise 2.4.2. Assigning metal oxidation states in a complex

Many properties of transition metal complexes depend on the metal's oxidation state. For instance,

- octahedral complexes of Co^{II} lose and gain ligands rapidly
- octahedral complexes of Co^{III} lose and gain ligands very slowly
- four-coordinate complexes are generally tetrahedral
- EXCEPT four-coordinate complexes of metals like Pt^{II} , Pd^{II} , Rh^{I}, and Ir^{I}, among others, are square planar

For this reason it is important to be able to estimate the formal oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state, the ligands can be treated as having an oxidation state equal to their charge - *i.e.*, the charge they possess in the form in which they coordinate the metal - so if they need to lose a proton to bind, don't forget to account for that.

Given the above, estimate the oxidation state of the metal in the following real and hypothetical complexes.

a. $Na_4[Fe(CN)_6]$
b. $[Cu(phen)_2]BF_4$
c. $[PtF_4(NH_3)_2]$
d. $[Ni(en)_2]SO_4$
e. $Co(acac)_3$
f. [MnCl(O)(salen)]

Answer for $Na_4[Fe(CN)_6]$.

This contains $[Fe(CN)_6]^{4-}$; so $O.S._{Fe}$ + 6 x (-1) (for CN^-) = -4 (the complex's charge) so $O.S._{Fe}$ = +2 or Fe^{2+}.

Answer for $[Cu(phen)_2]BF_4$.

Since tetrafluoroborate is a monoanion, the complex is $[Cu(phen)_2]^+$ so $O.S._{Cu}$ + 0 x 2 (for phen) = +1 (the complex's charge) so $O.S._{Cu}$ = +1 or Cu^+.

Answer for $[PtF_4(NH_3)_2]$.

$O.S._{Pt}$ + 4 x (-1) (for F^-) + 0 x 2 (for NH_3) = +0 (the complex's charge) so $O.S._{Pt}$ = +4 or Pt^{4+}.

Answer $[Ni(en)_2]SO_4$.

The complex is $[Ni(en)_2]^+$ so $O.S._{Ni}$ + 0 x 2 (for en) = +2 (the complex's charge) so $O.S._{Ni}$ = +2 or Ni^{2+}.

Answer $Co(acac)_3$.

$O.S._{Co}$ + 3 x (-1) (for acac; see table 9.2.2) = +0 (the complex's charge) so $O.S._{Co}$ = +3 or Co^{3+}.

Answer [MnCl(O)(salen)].

$O.S._{Mn}$ + 1 x (-1) (for Cl^-) + 1 x (-2)(for oxo) + 1 x (-2) (for salen; see table 9.2.2) = +0 (the complex's charge) so $O.S._{Mn}$ = +5 or Mn^{5+}.

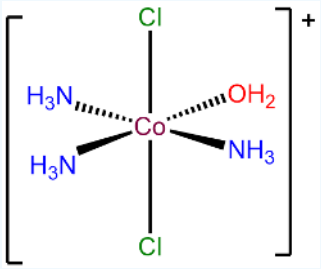
Exercise 2.4.3. Drawing isomers from descriptions

Draw structures that match the descriptions given, assuming that

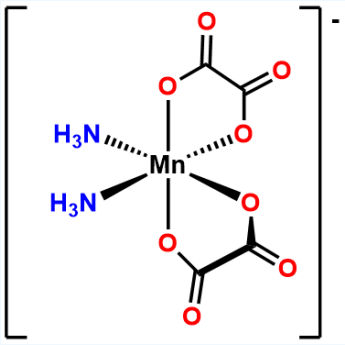
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. *mer*-triammineaqua-*trans*-dichlorocobalt(III) ion
b. Δ-diaminebis(oxalato)manganate(III)
c. $[CoCl_4]^{2-}$
d. *trans*-diamminebis(ethylenediamine)Nickel(2+) tetracyanopalladate(2-)
e. Λ-bis(ethylenediamine)cobalt(III)- μ-amido μ-hydroxo-Δ-bis(ethylenediamine)cobalt(III)

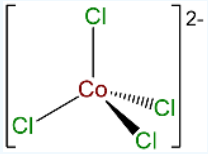
Answer a. *mer*-triammineaqua-*trans*-dichlorocobalt(III) ion.



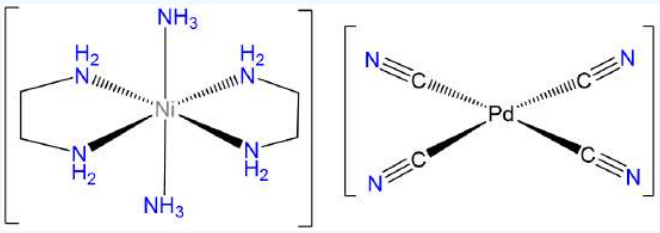
Answer b. Δ-diaminebis(oxalato)manganate(III).



Answer c. $[CoCl_4]^{2-}$.

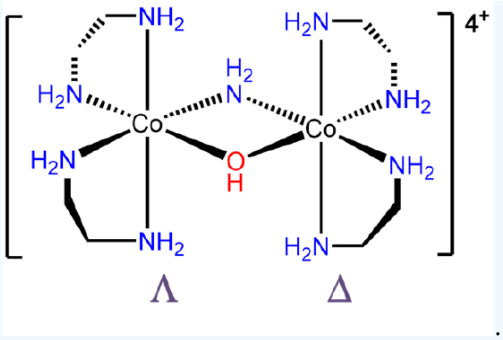


Answer d. *trans*-diamminebis(ethylenediamine)Nickel(2+) tetracyanopalladate(2-).



Note that since the Pd in $[Pd(CN)_4]^{2-}$ is Pd^{2+} it will be square planar.

Answer e. Λ-bis(ethylenediamine)cobalt(III)- μ-amido μ-hydroxo-Δ-bis(ethylenediamine)cobalt(III).



Exercise 2.4.4. Stereoisomers of complexes containing only monodentate ligands.

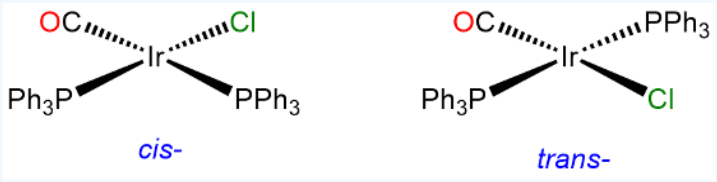
Draw all the stereoisomers of the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[IrCl(CO)(PPh_3)_2]$
b. $[CoCl_3(NH_3)_3]$
c. $[CoCl_2(H_2O)_2(NH_3)_2]^+$
d. $[CoBrCl(H_2O)_2(NH_3)_2]^+$
e. $[CoBrClI(NH_3)_3]$

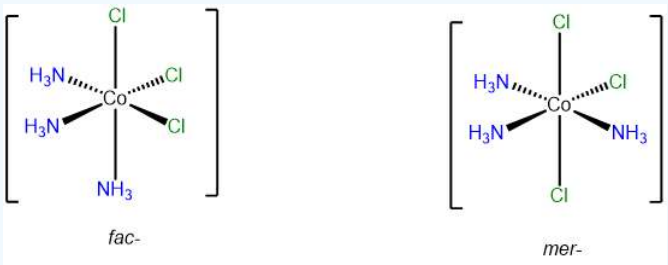
Answer a. $[IrCl(CO)(PPh_3)_2]$

This is a 4-coordinate Ir^{I} complex and, as such will be square planar. Since two of the ligands are identical, it will have *cis* and *trans* isomers. The *trans* isomer is famous for its ability to form adducts and is called Vaska's complex.



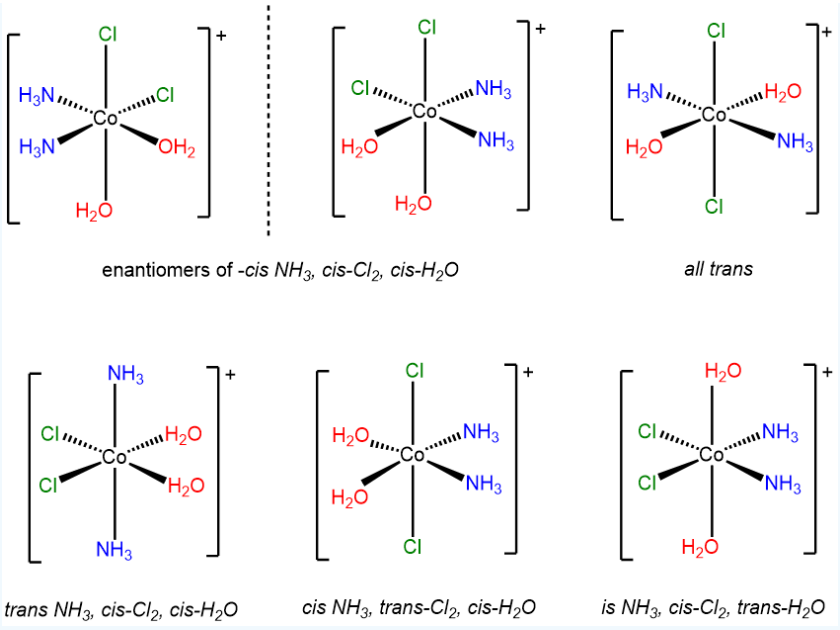
Answer b. $[CoCl_3(NH_3)_3]$

This complex contains three ammine and three chloro ligands and so will have *fac* and *mer* isomers.



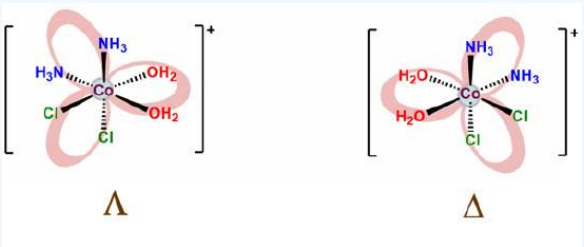
Answer c. $[CoCl_2(H_2O)_2(NH_3)_2]^+$

This is a case of an $MA_2B_2C_2$ system (A = Cl^-, B = H_2O, C = NH_3) involving multiple *cis* and *trans* relationships. The six stereoisomers are shown below.



Since it may not be obvious how to arrive at a set of isomers like the ones above, it is worth considering how one might work through the possibilities for a system of ligands like this one. Several systems may be used to systematically identify isomers. Once approach is the Macbdef system described in Note 2.4.1 at the end of these exercises. The solutions presented here and in subsequent problems employ a variant of that approach.

- Start by fixing one set of ligands. In this case the chloro ligands were first fixed as *cis* to one another. Then the remaining ligands might be *cis* or *trans* to one another, although since the *chloro* ligands are already *cis*, the ammine and aqua ligands cannot both be *trans* at the same time. Thus for *cis* chloro ligands the possibilities for the others are:
  - *cis*-H_2O ,*cis*-NH_3,
  - *cis*--H_2O, *trans*-NH_3
  - *trans*-H_2O, *cis*-NH_3
- Swap the configuration of the ligand set you started with. In this case it means placing the chloro ligands *trans* to one another. From that configuration, the possibilities for the ammine and aqua ligands are
  - *cis*-H_2O ,*cis*-NH_3,
  - *trans*-H_2O, *trans*-NH_3
- Check for enantiomers and create mirror images of any chiral complexes you drew. The easiest way to do this is to assign point groups. However, it turns out that the octahedral all-*cis* case is D_3 and formally equivalent to the symmetry of a tris chelate, as shown below.

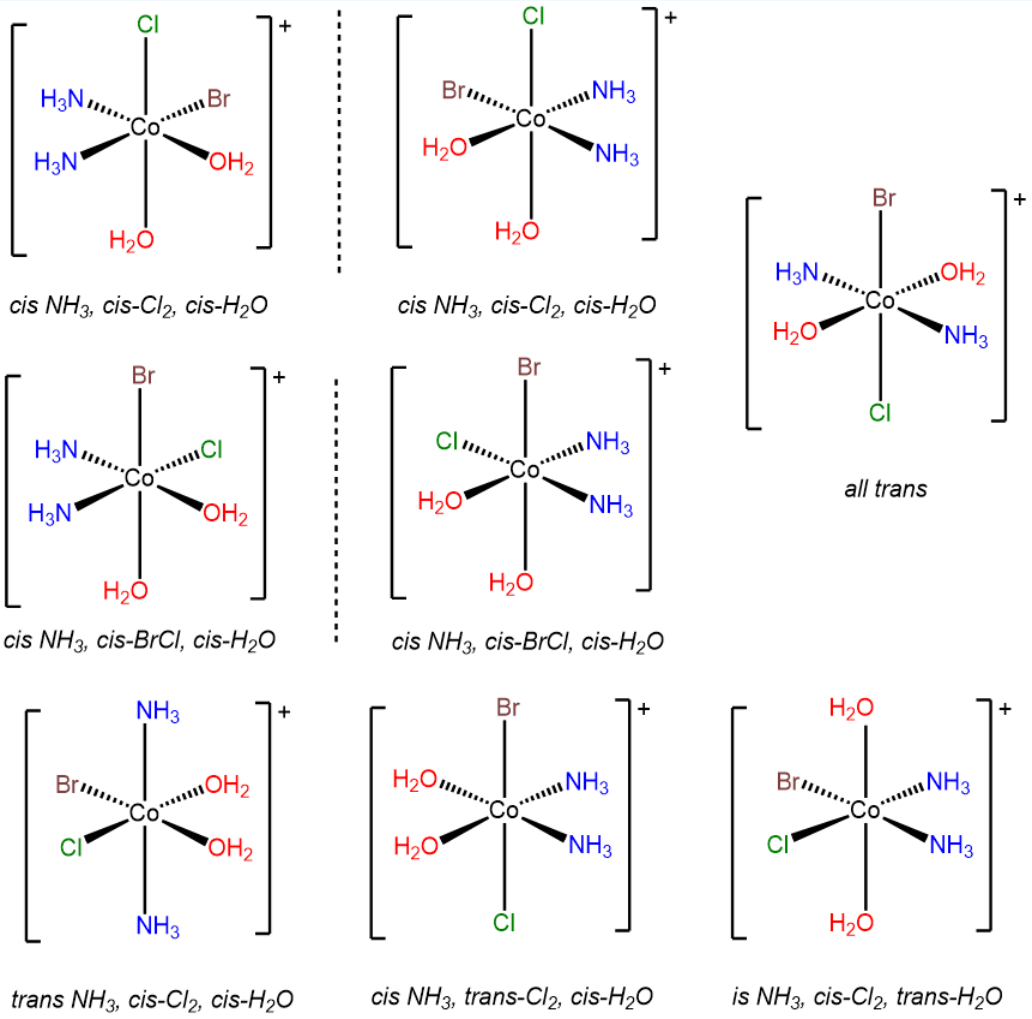


- finally, check to make sure you didn't include the same complex twice. Humans do make mistakes after all.

Answer d. $[CoBrCl(H_2O)_2(NH_3)_2]^+$

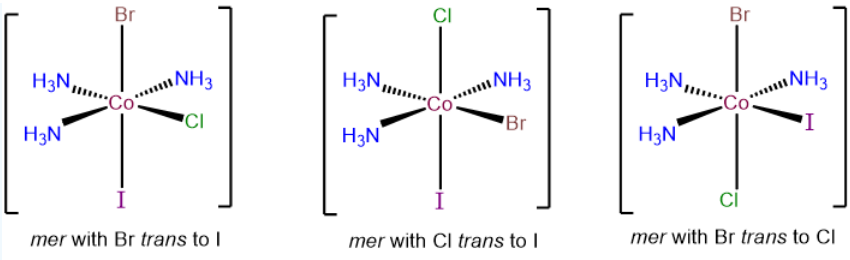
This problem is analogous to the one above except that this complex contains a bromo and chloro ligand in place of the two chloro ligands in $[CoCl_2(H_2O)_2(NH_3)_2]^+$. Consequently, when the bromo and chloro ligands are *cis* to one

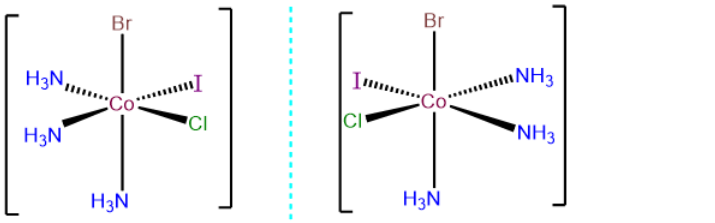
another, additional possibilities for isomers arise based on whether ammine or aqua ligands are *trans* to the chloro and bromo. The result is eight isomers.



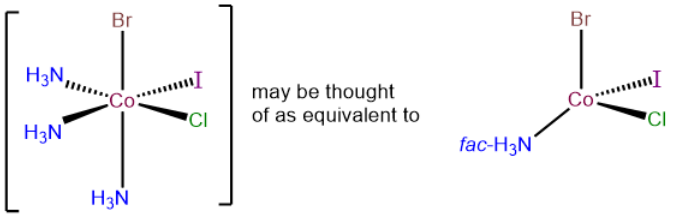
Answer e. $[CoBrClI(NH_3)_3]$

There are two possibilities for this complex - a *fac*-$(NH_3)_3$ and a *mer*-$(NH_3)_3$ arrangement. These may be taken as starting points for examining the possible permutations for the Cl^-, Br^-, and I^- ligands. The top row presents the three possibilities within the *mer*-$(NH_3)_3$ arrangement; each corresponds to a different ligand *trans* to an ammine ligand. The bottom row presents the two possible isomers with a *fac*-$(NH_3)_3$ arrangement. In each, the Cl^-, Br^-, and I^- ligands are *trans* to ammine ligands. However, the complexes possess C_1 symmetry and so are chiral and exist as enantiomers.





(C_1 symmetry or it you think of the *fac*-$(H_3N)_3$ as being "one uniform group" then the symmetry is equivalent to that of a chiral carbon)



Exercise 2.4.5. Stereoisomers of complexes with bidentate ligands (ignoring ring twist).

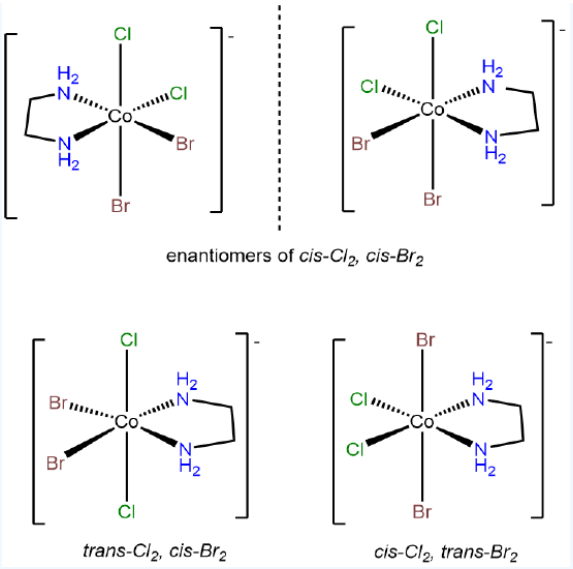
Ignoring ring twist, draw all the stereoisomers of the following real and hypothetical octahedral complexes.

a. $[CoBr_2Cl_2(en)]^-$
b. $[CoBrCl(en)_2]^+$
c. $[CoBrCl(gly)_2]^-$
d. $[Co(en)_3]^{3+}$
e. $[Co(gly)_3]$

Answer a. $[CoBr_2Cl_2(en)]^-$

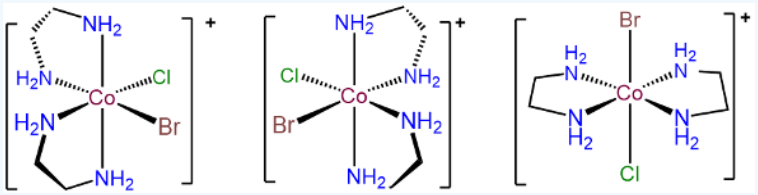
This complex is analogous to $[CoCl_2(H_2O)_2(NH_3)_2]^+$ in possessing pairs of identical ligating groups. The main difference is that in $[CoBr_2Cl_2(en)]^-$ the two amine ligating group of the en ligand are restricted to a *cis* arrangement. Under the MABCDEF system explained in Note 2.4.1, $[CoCl_2(H_2O)_2(NH_3)_2]^+$ may be $MA_2B_2C_2$, but this complex, $[CoBr_2Cl_2(en)]^-$, is $M(AA)B_2C_2$. The isomers are:

https://chem.libretexts.org/@go/page/429156



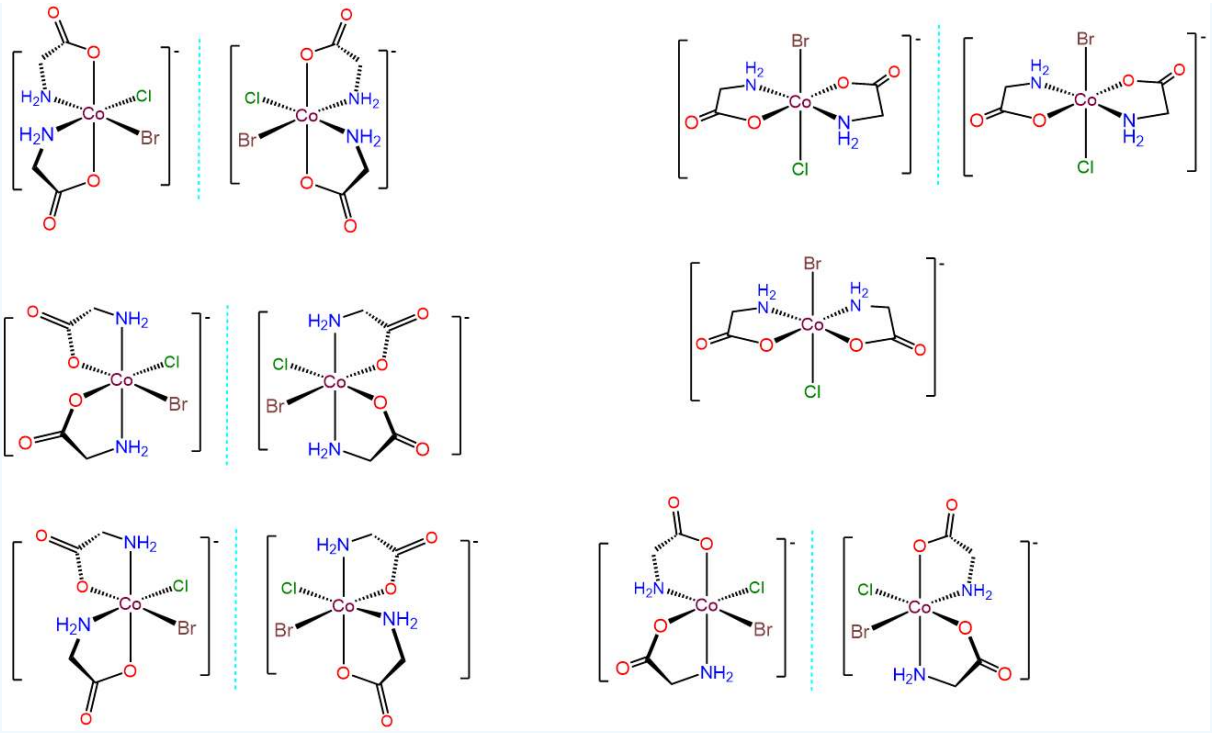
Answer b. $[CoBrCl(en)_2]^+$

The key to problems like this is to focus on the unique ligands, in this case Br^- and Cl^-. These can exist in either a *cis* or *trans* arrangement. The *trans* form is achiral, but in the case where Br^- and Cl^- are *cis*, Λ and Δ enantiomers are possible. The result is three isomers.



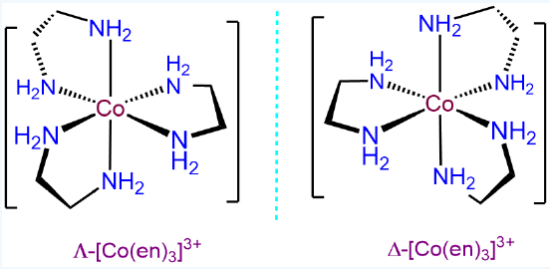
Answer c. $[CoBrCl(gly)_2]^-$

This case is analogous to the one above, but this time the bidentate ligand, gly, possesses distinguishable binding sites. Thus there are additional permutations involving how the gly ligands are bound relative to one another and/or whether the O or N end of the gly is bound *trans* to Br or Cl. The result is 11 different isomers, which are given below.



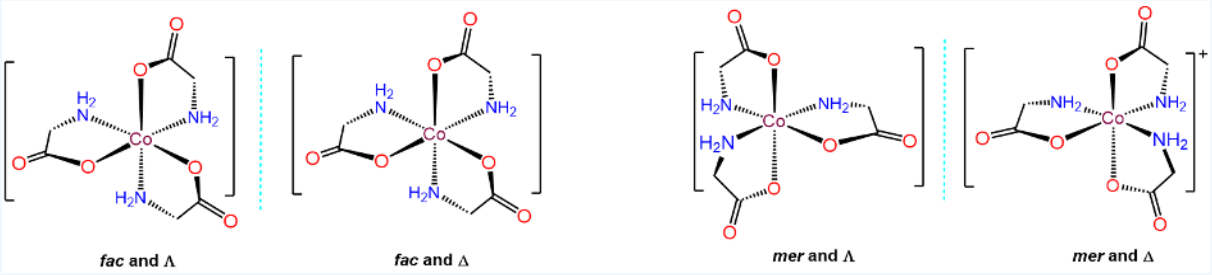
Answer d. $[Co(en)_3]^{3+}$

As a tris-chelate of symmetric bidentate ligands, ignoring ring twist, $[Co(en)_3]^{3+}$ will only exhibit Λ and Δ isomerism.



Answer e. $[Co(gly)_3]$

Since there are three gly ligands, each of which have carboxy and amine ends, the allowable arrangements involve whether the resulting three carboxy and three amine ends are oriented in a *mer* or *fac* arrangement. This gives two possibilities, each of which can exist as either the Λ or Δ enantiomer, for a total of four isomers, which are given below.



https://chem.libretexts.org/@go/page/429156

Exercise 2.4.6. More stereoisomers: Now featuring linkage isomerism

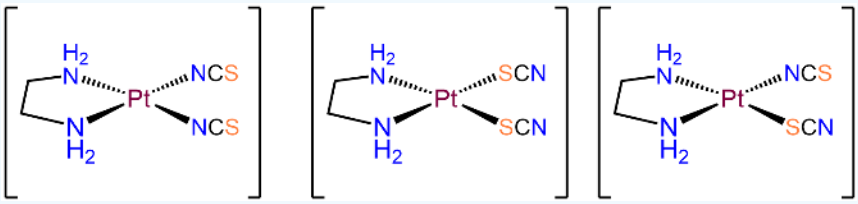
Ignoring ring twist, draw all chemically reasonable stereoisomers for the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[Pt(en)(SCN)_2]$
b. $[Pt(NH_3)_2(SCN)_2]$
c. $[Co(en)_2(SCN)_2]^+$

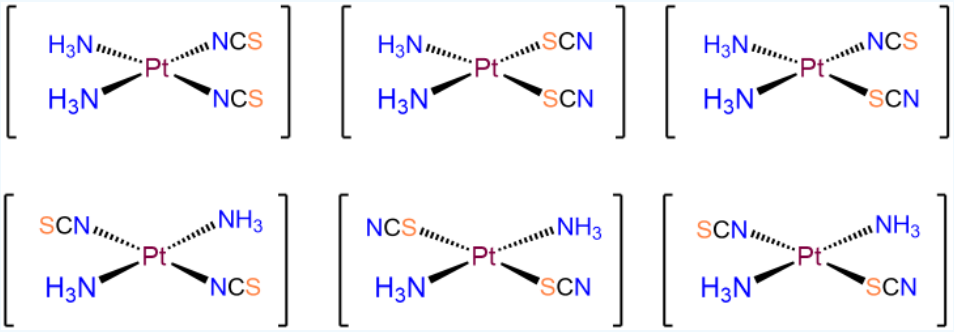
Answer a. $[Pt(en)(SCN)_2]$

The Pt in this neutral complex must be Pt^{2+} to balance the negative charges of the two SCN^- ligands. Complexes of Pt^{2+} are square planar and four coordinate, consistent with the bidentate en and two thiocyanato ligands. Of the ligands, the en ligand must bind in a *cis* arrangement. Consequently, the two SCN^- ligands will be in a *cis* arrangement as well. The isomers will therefore only differ in whether the two SCN^- bind κN or κS. The possibilities are:



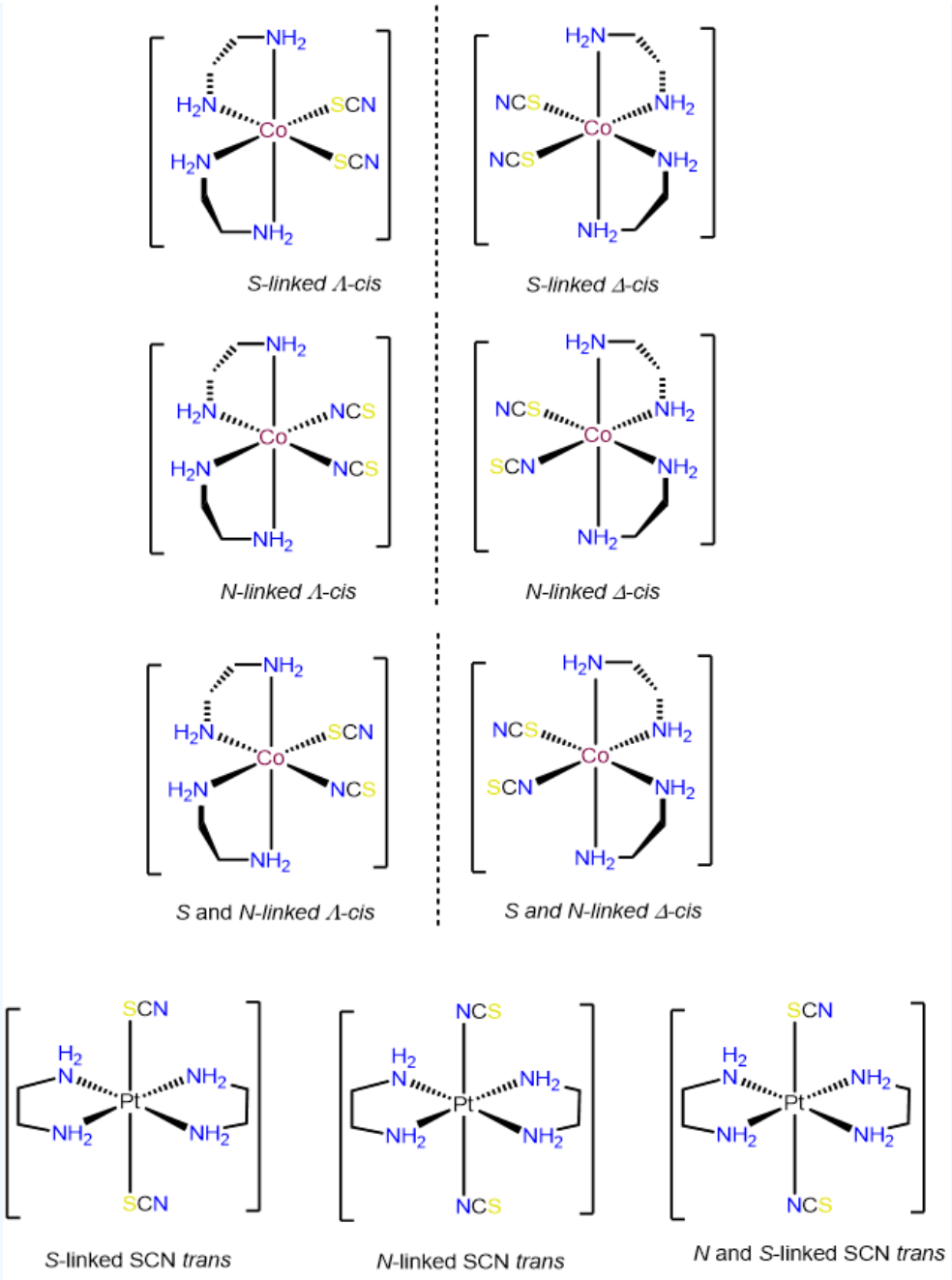
Answer b. $[Pt(NH_3)_2(SCN)_2]$

As with the preceding example, this will be a square planar Pt^{2+} complex. The main difference is that this time the coordinated nitrogens are not constrained to adopt a *cis* arrangement so there will be both *cis* and *trans* isomers.



Answer c. $[Co(en)_2(SCN)_2]^+$

https://chem.libretexts.org/@go/page/429156



? Exercise 2.4.7. Stereoisomer free for all.

Ignoring ring twist, draw all chemically reasonable stereoisomers for the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

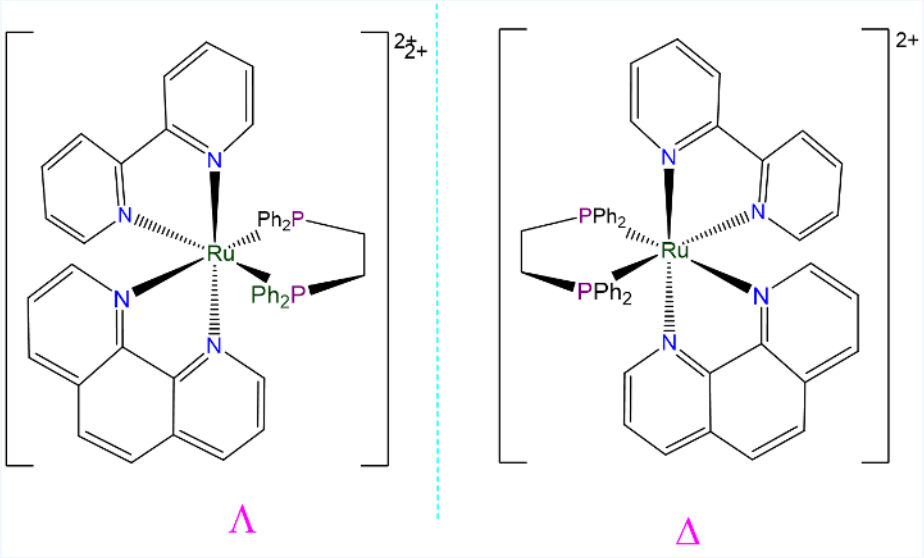
a. $[Ru(bpy)(phen)(dppe)]^{2+}$
b. $[CoClF(PPh_3)(py)]^{-}$
c. $[Ni(en)_2(NO_2)_2]$

https://chem.libretexts.org/@go/page/429156

d. $[Fe(H_2O)_3(SCN)_3]$
e. $[PtClF(PPh_3)(py)]$
f. $[CoBr_2Cl(NH_3)_3]$

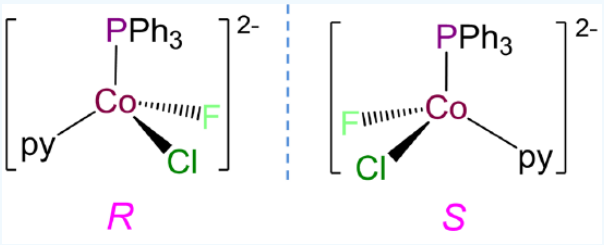
Answer a. $[Ru(bpy)(phen)(dppe)]^{2+}$

This complex is an octahedral tris-chelate containing symmetric ligands. As such it will exhibit Λ and Δ isomers:



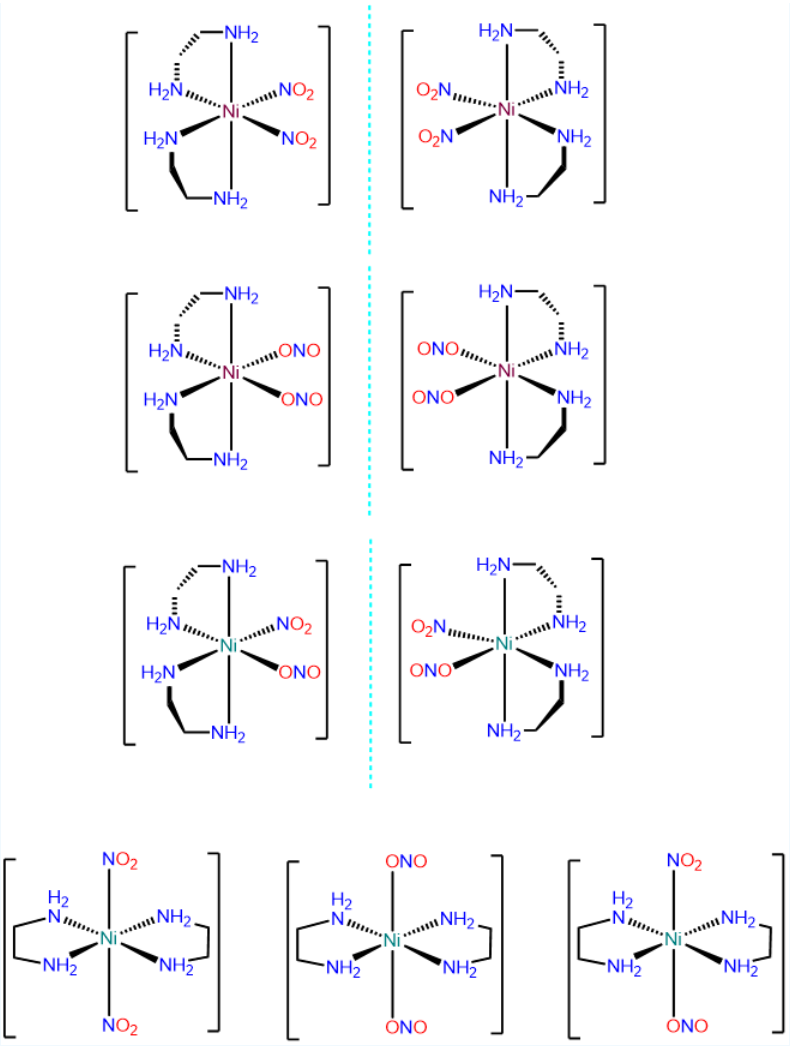
Answer b. $[CoClF(PPh_3)(py)]^-$

This complex has a coordination number of 4 and contains a Co^{2+} ion with a d^7 electron configuration, so a tetrahedral geometry is expected. Tetrahedral complexes like this one with four different ligands are chiral and can form *R* and *S* enantiomers.



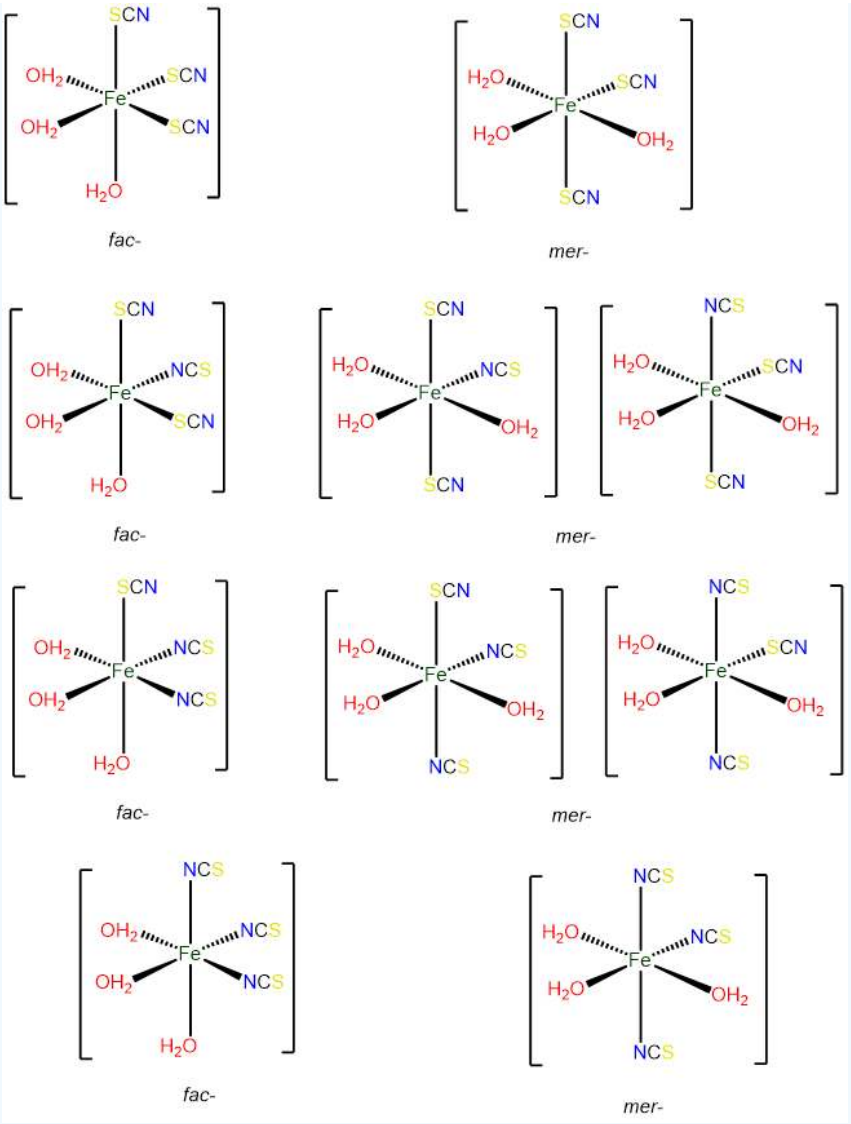
Answer c. $[Ni(en)_2(NO_2)_2]$

This is an octahedral bis-chelate and will exist in Λ and Δ configurations. Within each configuration the NO_2^- ligands can exist as *κN* and *κO*, leading to the following possibilities:



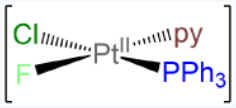
Answer d. $[Fe(H_2O)_3(SCN)_3]$

As an octahedral complex with three identical ligands it can exist in *mer* and *fac* configurations, with the ambidentate SCN ligand providing additional possibilities for isomerism.



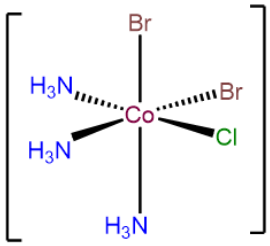
Answer e. $[PtClF(PPh_3)(py)]$

As a square planar complex with four nonidentical ligands, this complex exists as a single isomer.

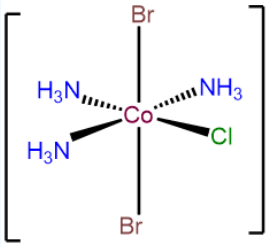


Answer f. $[CoBr_2Cl(NH_3)_3]$

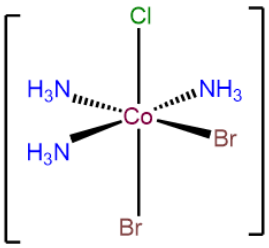
As an octahedral complex with three identical ligands it will exhibit *mer* and *fac* isomerism. In addition, it will have two *mer* configurations that differ in terms of the cis and trans relationships between the bromo and chloro ligands.



fac



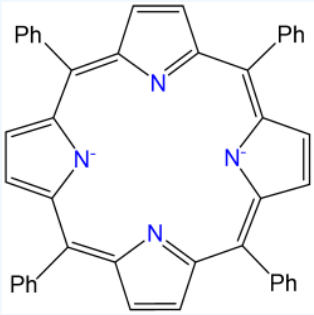
mer with Br *trans* to Br



mer with Cl *trans* to Br

Exercise 2.4.8

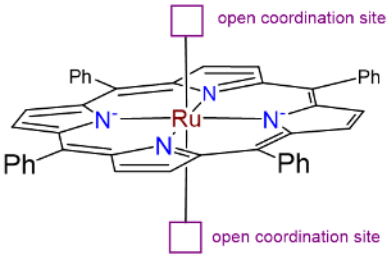
Complexes of formula Ru(TPP)py_2 have been prepared, in which TPP is tetraphenylporphyrin, which binds metals in the form given below. Draw all isomers of Ru(TPP)py_2.

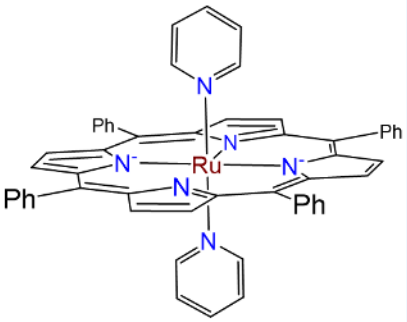


Answer

There is only one isomer. While normally complexes containing two identical ligands (in this case py) can exhibit *cis* and *trans* isomerism, in this case the planar tetraphenylporphyrin ring ligates the Ru^{2+} ion in a square planar arrangement, as shown at left in the image below. This leaves only a pair of *trans* coordination sites for the chloro ligands to occupy, giving the isomer shown at right below.

When TPP ligates Ru^{2+} it leaves only *trans* open coordination sites so only the *trans* isomer can form.

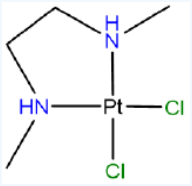




trans-[Ru(py)$_2$(TPP)]

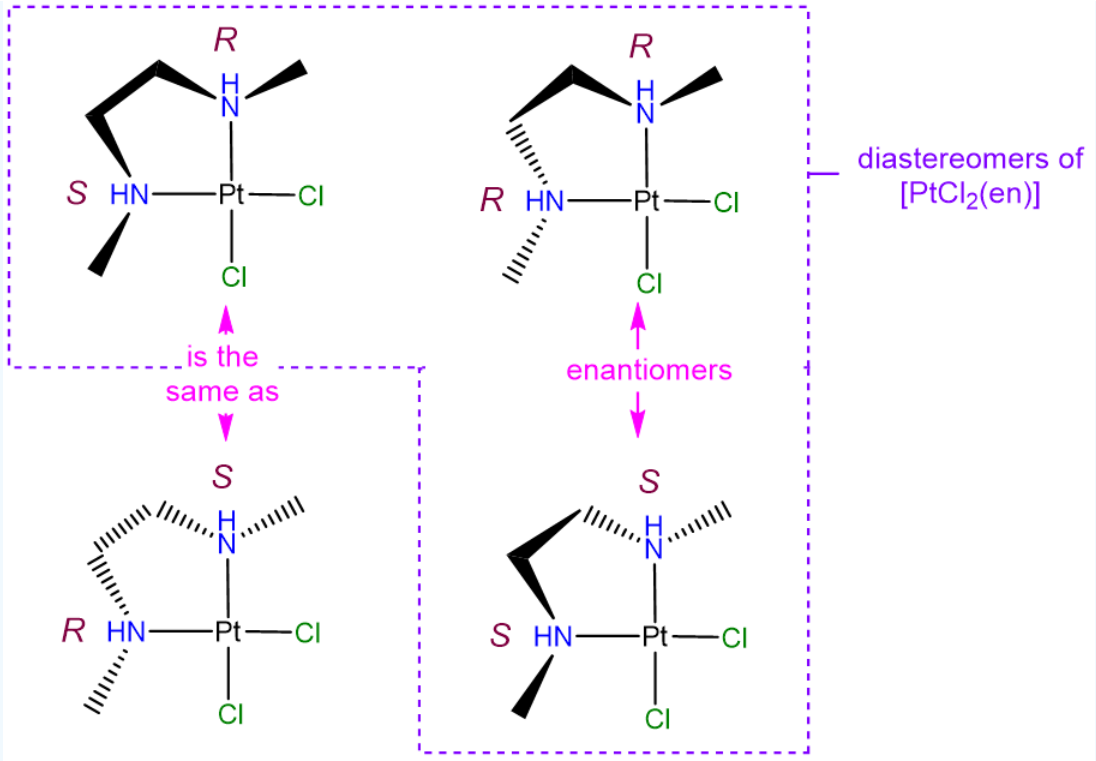
Exercise 2.4.9

Draw the diastereomers formed due to the chirality of the amine nitrogen atoms in [$PtCl_2$(*N*,*N*'-dimethylethane-1,2-diamine)] which has the atomic connectivity represented below



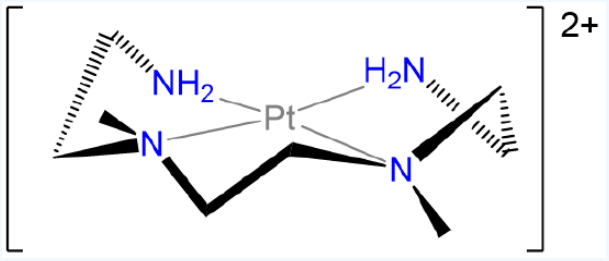
Answer

The diastereomers will differ in whether the N atoms adopt an *R* or *S* configuration at the nitrogen atoms. The possible permutations are (*R*,*R*), (S,*S*), (*R*,*S*), and (S,*R*). However, as may be seen from the image below, the (*R*,*S*) and (S,*R*) configurations are identical (the two projections shown can be interconverted through a C_2 rotation along an axis bisecting the Cl-Pt-Cl unit). As a result there are only three unique isomers. Of these, the (*R*,*R*) and (S,*S*) configurations are enantiomers (they are mirror images by reflection in the $PtCl_2N_2$ plane). Note that in solving problems like this one it can be helpful to keep track of possible isomers by assigning the stereochemistry at each chiral center as *R* or *S* using the Cahn-Ingold-Prelog-convention, though it is not strictly necessary to do so.

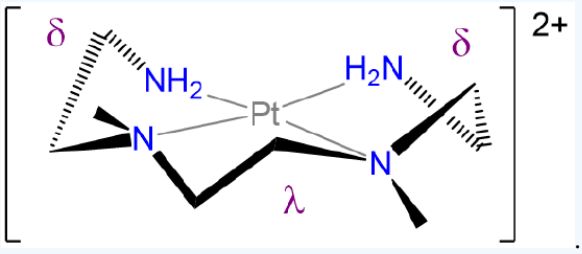


Exercise 2.4.10

Label the conformations of all chelate rings in the structure below.



Answer



https://chem.libretexts.org/@go/page/429156

Appendix: The MABCDEF bookkeeping system for identifying isomers

The Mabcdef or MABCDEF system is one method for identifying the number of isomers in an octahedral complex, although since it is really just a bookkeeping and organizational system it can easily be extended to other geometries as well. The M in Mabcdef stands for metal and the other letters are used to stand in for ligands. The basic approach involves

- classifying the ligands as A, B, C, D, E, or F in order of multiplicity. Thus for

  $[Cr(NH_3)_6]^{3+}$ A = NH_3; there are no B, C, D,E, or F ligands; and the complex is classified as MA_6

  $[CoCl(NH_3)_5]^{2+}$ A = NH_3, B = Cl^-, and the complex is MA_5B

  $[CrCl_2(H_2O)_2(NH_3)_2]^+$ A = Cl^-, B = H_2O, C = NH_3, and the complex is $MA_2B_2C_2$

- in the classification above, multidentate ligands are typically classified before monodentate ones and are designated AA, AB, ABC, ABA, etc. based on the symmetry of the attachment points. Thus

  en has identical attachment amine points and is AA

  gly has a carboxy and amine attachment points and is AB

  trien is ABA

  $CoCl_2(en)_2^+$ is $M(AA)_2B_2$

  $CoCl_2(gly)_2^-$ is $M(AB)_2C_2$

  $CoCl_2(en)(gly)$ is $M(AA)(AB)C_2$

- Systematically list out the possible *trans* arrangements of ligands by
  1. assigning one pair of ligands to be *trans* to one another.
  2. Then systematically list out the other possible *trans* pairs by permuting the remaining trans arrangements. It can help to organize the permutations in a table, such as that shown below for an MABCDEF complex where A and B are assigned *trans*. In looking at the table notice how the second set of trans permutations is systematically varied. This helps ensure that no possibility is skipped.
  3. Go through the list of isomers and remove any duplicates you generated so far. For instance, notice in the table below that the last three stereoisomers are identical with the first three (*e.g.*, stereoisomer 4 is identical to stereoisomer 3, 5 with 2, and 6 with 1).

Stereoisomer 1	Stereoisomer 2	Stereoisomer 3	Stereoisomer 4 (same as isomer 3)	Stereoisomer 5 (same as isomer 2)	Stereoisomer 6 (same as isomer 1)
trans AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)
trans CD	*trans* CE	*trans* CF	*trans* DE	*trans* DF	*trans* EF
trans EF	*trans* DF	*trans* DE	*trans* CF	*trans* CE	*trans* CD

  4. If the complex possesses multidentate ligands that demand that certain groups exist and *cis* pairs, then also remove any configurations which do not agree with the known binding capability of the ligand (*e.g.*, the two amine groups of ethylenediamine cannot be *trans* to one another, so if you have an en ligand, remove configurations like that from the list).
  5. Next, swap or permute the original *trans* pair and repeat the process you just followed. In the case of Mabcdef this gives the following results:

Isomer	"fixed" trans pair	Additional trans pairs	
1	AB	CD	EF
2	AB	CE	DF
3	AB	CF	DE
4	AC	BD	EF

5	AC	BE	BF
6	AC	BF	DE
7	AD	BC	EF
8	AD	BE	CF
9	AD	BF	CE
10	AE	BC	DF
11	AE	BD	CF
12	AE	BF	CD
13	AF	BC	DE
14	AF	BD	CE
15	AF	BE	CD

- Since the procedure explained above only identifies isomers based on unique *trans* pairings, **it does not identify when a configuration is chiral and corresponds to a pair of enantiomers.** Any enantiomers can be identified by drawing out the complexes and either classifying their point groups or by drawing their mirror images and checking if they are superimposable. In the MABCDEF case - *i.e.*, where all the ligands are different - all of the isomers identified have C_1 symmetry so are chiral. This means there will be a pair of enantiomers for each, giving 15 x 2 = 30 different stereoisomers.

References

1. These examples are taken from http://wwwchem.uwimona.edu.jm/courses/inorgnom.html

2. Contakes S. M.; Rauchfuss, T.B. *Chem. Commun.* 2001, 553-554.

3. Shriver, D. F.; Shriver, S. A.; Anderson, S. E., *Inorg. Chem.* 1965, *4(5)*, 725-730.

4. Zelewsky, A. v., *Stereochemistry of Coordination Compounds* Wiley, 1996.

5. In the past it was difficult to determine absolute configurations from X-ray data alone, but recent advances have made it easier to do so.

6. Pavan M. V. Raja & Andrew R. Barron "Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species" in *Physical Methods in Chemistry and Nano Science* https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/07%3A_Molecular_and_Solid_State_Structure/7.07%3A_Circular_Dichroism_Spectroscopy_and_its_Application_for_Determination_of_Secondary_Structure_of_Optically_Active_Species

7. Berova, N.; Bari, L. D.; Pescitelli, G., *Chemical Society Reviews* 2007, 36 (6), 914-931.

8. Of course, if one set of ligands occupies a meridional plane, then the other three ligands will be oriented in an equatorial one. The reason they may both be considered meridional is because if the complex were rotated, the equatorial plane would be meridional and vice versa. From that point of view both might be considered meridional planes - albeit not at the same time.

9. Bite angles are taken from Mansell, S. M., Catalytic applications of small bite-angle diphosphorus ligands with single-atom linkers. Dalton Transactions 2017, 46 (44), 15157-15174.

10. Hancock, R. D., The pyridyl group in ligand design for selective metal ion complexation and sensing. Chemical Society Reviews 2013, 42 (4), 1500-1524.

11. Sasi, D.; Ramkumar, V.; Murthy, N. N., Bite-Angle-Regulated Coordination Geometries: Tetrahedral and Trigonal Bipyramidal in Ni(II) with Biphenyl-Appended (2-Pyridyl)alkylamine N,N'-Bidentate Ligands. ACS Omega 2017, 2 (6), 2474-2481.

12. Ehnbom, A.; Ghosh, S. K.; Lewis, K. G.; Gladysz, J. A., Octahedral Werner complexes with substituted ethylenediamine ligands: a stereochemical primer for a historic series of compounds now emerging as a modern family of catalysts. Chemical Society Reviews 2016, 45 (24), 6799-6811.

2.4: Isomerism is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.4: Isomerism** by Stephen M. Contakes is licensed CC BY 4.0.

2.5: Coordination Numbers and Structures

2.5.1 Why do coordination complexes form the structures they do?

As with all chemical structure, coordination complexes form the structures they do so as to best stabilize the metal center and ligands through the formation of metal-ligand bonds while avoiding destabilizing interactions like steric repulsions. The issue then is how many metal-ligand bonds should be formed and how those bonds should be arranged spatially to give the largest net stabilization possible. This question will eventually be considered in detail in connection with the nature of bonding in coordination compounds. For now, it will be helpful to think about it in terms of seven factors:

2.5.1.1 The stabilizing effect of metal-ligand bond formation.

The driving force for complex formation is the stabilization of electrons in covalent chemical bonds. In the vast majority of cases, this largely involves stabilization of the ligand lone pair as it experiences the effective nuclear charge of the metal, although a few instances involve stabilization of metal electrons by ligand nuclei (inverse ligand fields). Regardless, metal-ligand bond formation is stabilizing and classified by the way it preferences the addition of ligands to the complex.

2.5.1.2 Steric effects, specifically steric repulsions between ligands.

One reason coordination numbers do not increase indefinitely is that only so many ligands can fit around a metal. Exactly how many depends on

- *the size of the metal center.* This is one of the more important factors. Many metals tend to exhibit preferred coordination numbers, which depend on their oxidation state and size as shown in Figure 2.5.1. Larger inner transition metals like the Lanthanides and Actinides can accommodate 9-12 sterically undemanding ligands, while the smaller transition metals tend to accommodate up to six, although larger coordination numbers are more common for low valent metals and as size increases on moving from right to left across the transition metal block of the periodic table. Thus, the early transition metal molybdenum forms seven- and eight-coordinate $[Mo^{III}(CN)_7]^{4-}$ and $[Mo^{IV}(CN)_8]^{4-}$ with the sterically undemanding cyano ligand.
- *the size of the ligands.* As long as ligands are not excessively rigid and bulky, their size is less important than the size of the metal in determining the number of ligands that coordinate. Ligands' ability to donate electrons to the metal center also tends to influence coordination number more than ligand size. However, all other things being equal for a given metal and ligand donor ability, small ligands allow higher coordination numbers while fewer bulky ligands will fit around the metal center.
- *how the ligand bonds to the metal.* Again, all other things being equal, ligands that are more sterically demanding in the vicinity of the metal center tend to limit the ability of other ligands to bind more than those which bind through a small extended group. For example, a bulky isocyanide like t-BuCN will sterically crowd the metal less than a bulky phosphine like t-BuH_2P would. For this reason the effective size of a ligand is sometimes rated in terms of either a cone angle of space they are estimated to occupy around the metal (called the Tolman cone angle, it is commonly used to evaluate phosphines' steric bulk) or in terms of the percentage of the metal's coordination sphere the ligand occupies (called the percent buried volume, it is used to estimate the steric impact of *N*-heterocyclic carbenes).

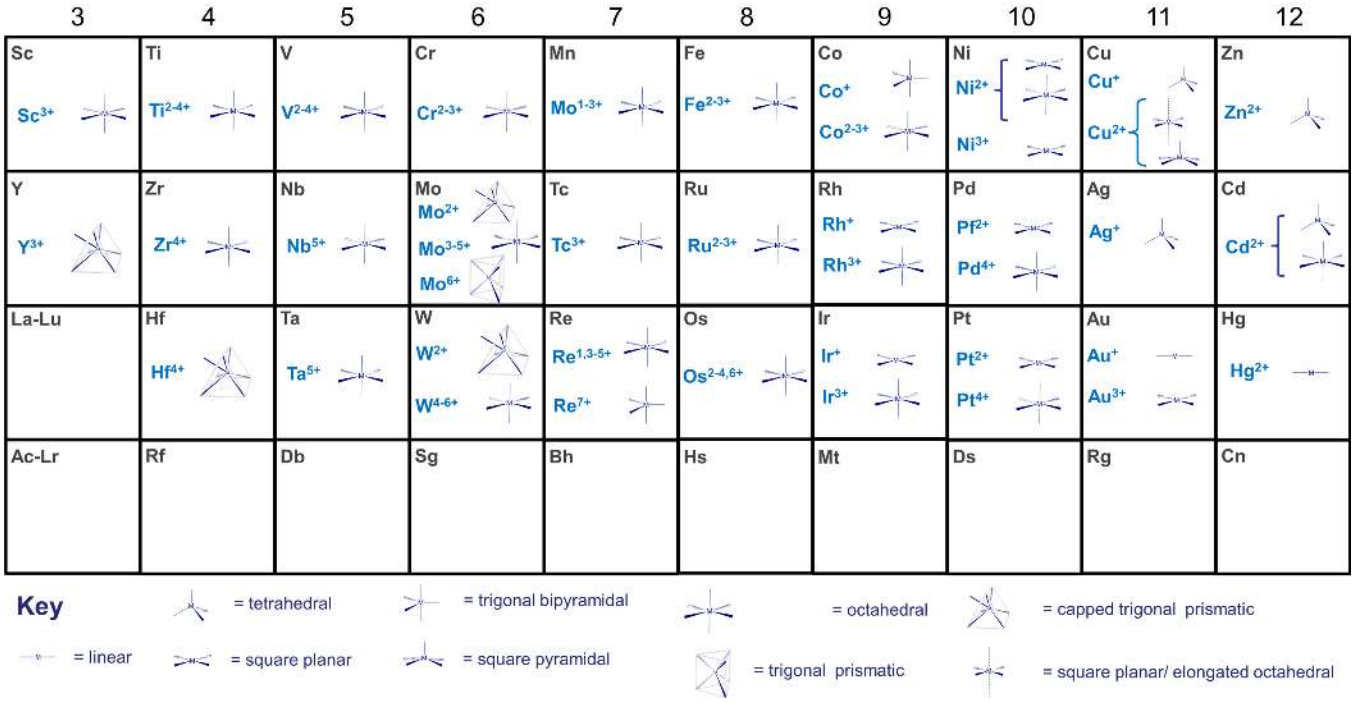


Figure 2.5.1. Preferred coordination geometries of the transition elements. Assignments are as reported in reference 1 except for Cu^{2+}, which is assigned above as square planar/elongated octahedral instead of the square planar assignment given in that work. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.1.3 Repulsion between M-L bonding electrons on different ligands.

For many complexes, steric effects are neither the only effects nor the most important. Among the additional factors that should be considered are the repulsions that occur between the electrons that different ligands donate to the metal-ligand bonding. These electron-electron repulsions affect the

a. **Coordination number.** When a ligand donates its electrons to a metal center to form a new metal-ligand bond, the electron density around the metal increases, raising the overall energy of the other M-L bonding electrons. This increased repulsion often limits the number of coordinated ligands. As more ligands are added, the electron-electron repulsions keep increasing until the lowering of energy of the ligand electrons in the new bond is insufficient to compensate for the raising of energy of the existing M-L bonding electrons. Based on this effect alone,
   - larger metals tend to achieve higher coordination numbers than smaller ones because the electron-electron repulsions are spread across a larger coordination sphere.
   - With a given metal, ligands that are more electron donating have a greater tendency to form complexes with lower coordination numbers with a given metal than similar neutral ones do. This is why anionic ligands (which tend to be better electron donors) tend to give lower coordination numbers than comparable neutral ligands (which tend to be weaker donors). Thus Co^{2+} forms $CoCl_4^{2-}$ with chloro ligands but $[Co(H_2O)_6]^{2+}$ with aqua ligands.

b. **Coordination geometry.** In the **Kepert model** for the shapes of coordination complexes, this intraligand repulsion determines the most stable coordination geometry by causing the ligands to move as far apart from one another on the metal's coordination sphere as possible.

Formally, according to the **Kepert model**

- any of the metal's valence electrons not involved in metal-ligand bonds occupy (n-1)*d* orbitals and function as core electrons. As core electrons they do not influence the molecular shape.
- electrons involved in bonding to a given ligand constitute an electron group that repels all other electron groups around the metal.
- all other things being equal, the complex will form the geometry that maximizes the intra-electron group repulsions.

Notice the similarities of these postulates to those of VSEPR theory. In predicting coordination geometries in terms of electron-electron repulsions, the Kepert model is just an extension of VSEPR theory to coordination compounds. The difference between

VSEPR theory and the Kepert model is that in the Kepert model, only electrons involved in metal-ligand bonds count.

Coordination geometries predicted by the Kepert model for coordination numbers two through nine are given in Figure 2.5.2. As may be seen from the geometries listed in Figure 2.5.2, these are just equivalent to VSEPR geometries for cases in which the number of electron groups is equal to the coordination number.

The difference between optimal and suboptimal coordination geometries is greater with few ligands, and becomes smaller as ligands become increasingly dispersed across the metal's coordination sphere. In complexes containing five, seven, eight, or higher coordinate metals, there are a number of geometries that are similar in energy to the preferred geometry. These geometries, which should be regarded as accessible, are also listed in Figure 2.5.2.

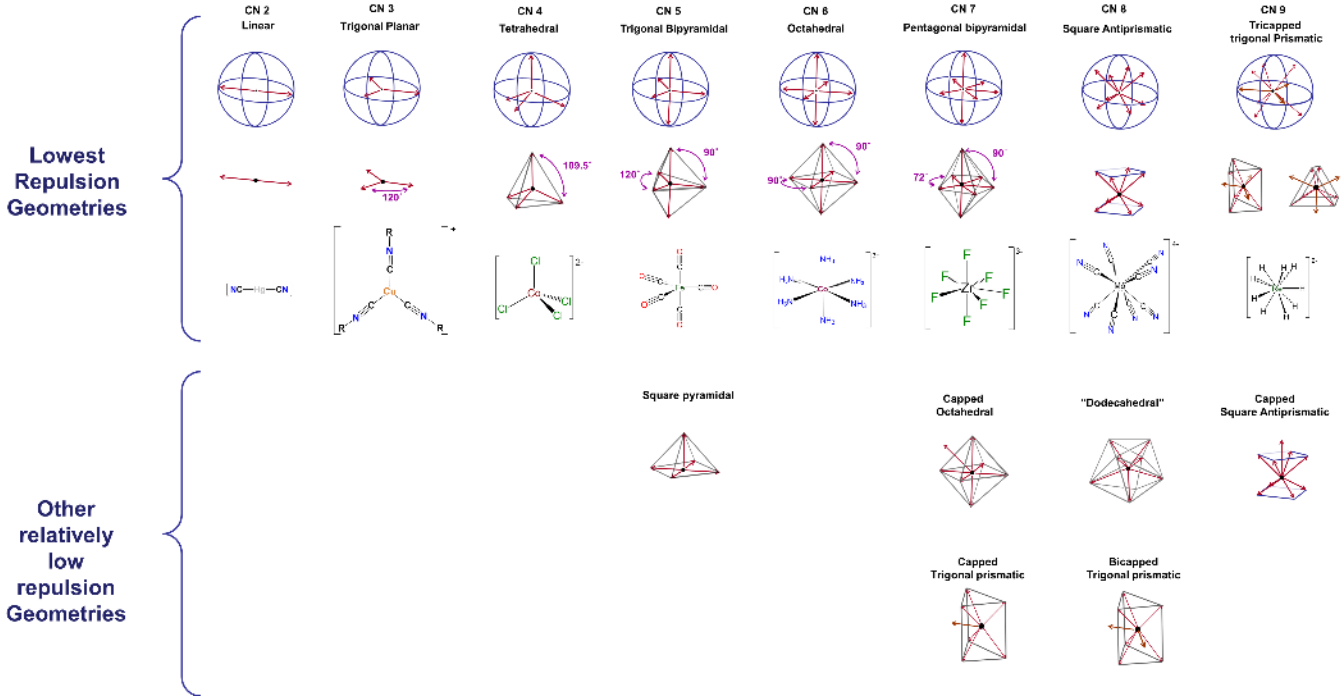


Figure 2.5.2. Coordination geometries predicted by the Kepert model for coordination numbers two through nine along with other coordination geometries similar in energy to the lowest repulsion geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.1.4 d-electron effects

A few coordination geometries are noticeably absent from the Kepert-preferred and Kepert-accessible geometries in Figure 2.5.1. These include the trigonal prismatic geometries formed by compounds like $W(CH_3)_6$ and the very common square planar geometry illustrated by complexes like $[PtCl_4]^{2-}$ and $[IrClH(PPh_3)_2]$. One of the reasons the Kepert model fails to predict the existence of such structures is its neglect of directional interactions involving *d* electrons on the metal center. Metal *d* electrons exert a profound influence on almost all properties of transition metal complexes, including their structures. The way in which this occurs will be explored at length in the next chapter. For now, it is enough to note that both the ligand-donated electrons surrounding a metal center and the electrons occupying particular *d* orbitals on that metal are oriented in specific directions relative to one another. Because of this, the strength of the interactions between the ligand and metal *d* electrons depends on the number of *d* electrons present, how strongly metal-ligand binding affects their energy, and how the ligands are arranged about the metal center. The impact of these effects, here termed ligand field effects, differs from case to case and can include

- distortions of the complex's geometry. For instance, an ideal octahedral coordination geoemtry might be tetragonally distorted by flattening or elongating it.
- imparting a strong preference for non-Kepert coordination geometries. This is why, for example, 2nd and 3rd row complexes in which the metal has a d^8 electron configuration are almost always square planar.
- stabilizing non-Kepert geometries enough to permit complexes to adopt them in the presence of a rigid or semirigid ligand that prefers to coordinate the metal in that geometry.[3]

Because of these effects, square planar and trigonal prismatic geometries are also observed, and the list of coordination geometries given in Figure 2.5.2 may be extended to that shown in Figure 2.5.3.

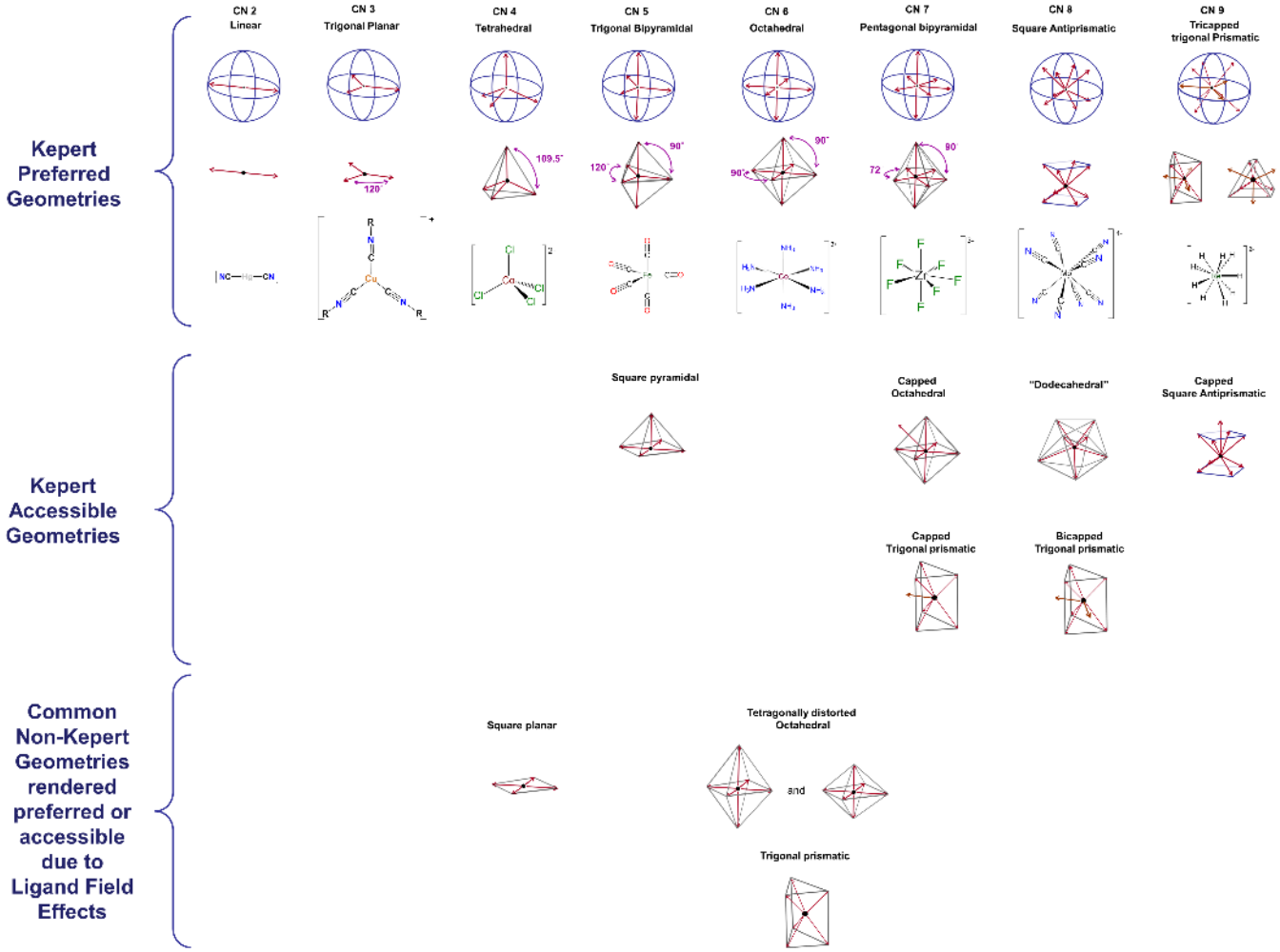


Figure 2.5.3. Coordination geometries accessible for 2-9 coordinate complexes even without constraint by rigid or semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.1.5 Ligand constraints imposed by rigid or semirigid ligands

Rigid or semirigid ligands influence the coordination geometry of metal complexes in two main ways:

a. Bulky rigid ligands that crowd the metal center prevent other ligands from binding. Thus such ligands are useful for preparing low-coordinate complexes.
b. Rigid and semirigid ligands can impose their preferred coordination geometry on a metal center. This is because these ligands energetically prefer to adopt a particular conformation when they bind a metal center. In doing so they shift the coordination geometry energy landscape toward that preferred geometry. If the shift is large enough relative to the native preference due to ligand repulsion and ligand field effects, the complex will either adopt the ligand-preferred geometry or be distorted in the direction of the ligand-preferred geometry. Examples are given in Figure 2.5.4.

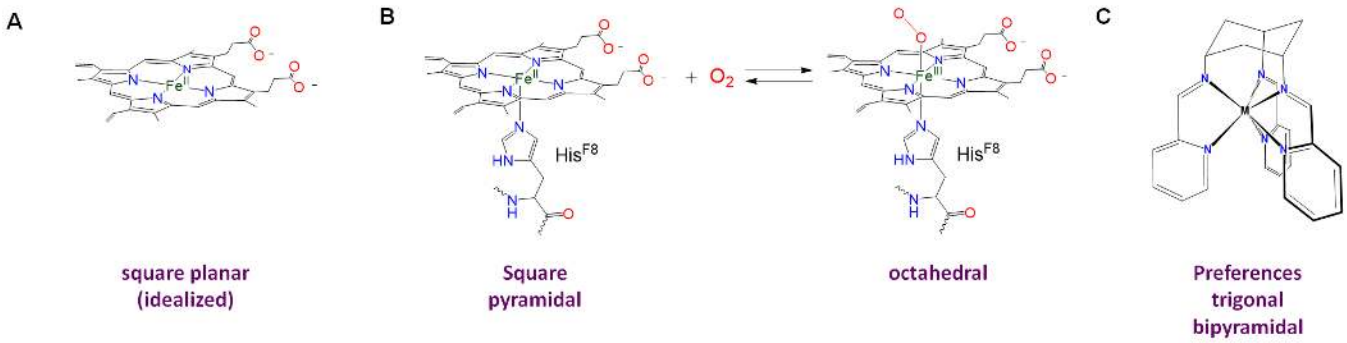


Figure 2.5.4. Examples of rigid/semirigid ligands that can impose their preferred coordination geometry on a metal center. Porphyrins, phyhalocyanines and related macrocycles tend to impose a slightly bent square planar coordination geometry, although (B) many such complexes, including the iron of myoglobin's heme cofactor, coordinate additional ligands to give square planar or octahedral complexes. (C) Synthetic multidentate ligands have been developed to preference trigonal prismatic coordination geometries, including the one shown here. It forms roughly trigonal prismatic complexes with Co^{II} and Zn^{II}, albeit imperfect ones.[3]
This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The influence of ligands on coordination geometry is important in living systems, in which proteins and nucleic acids can act as rigid or semirigid ligands. The ability of these ligands to distort the coordination geometries of metal atoms in ways that enable them to perform specific functions is so common that the resulting distorted geometries are termed entactic states. A particularly spectacular case of an entactic state involves the blue copper proteins azurin and plastocyanin, the structure of which is given in Figure 2.5.5.

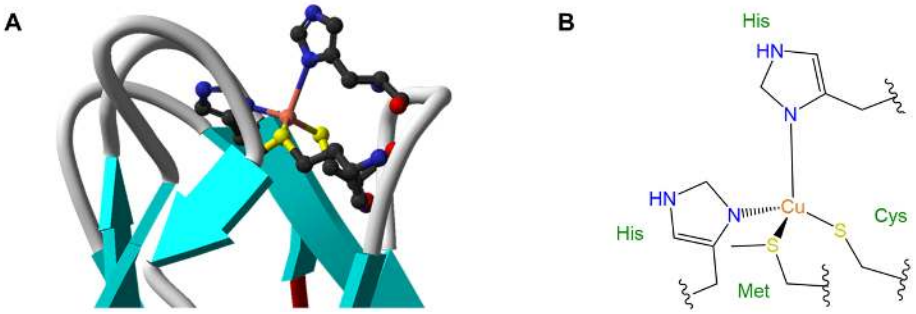


Figure 2.5.5. (A) Structure and (B) schematic of the plastocyanin active site showing the distorted tetrahedral coordination environment that the protein imposes on the copper center (tan), which is most evident from the long vertically oriented Cu-Histidine bond. The image in part A is cropped from an original image by Ben Mills - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=6202620. The image in part B is by Stephen Contakes and licensed under a Creative Commons Attribution 4.0 International License.

As may be seen from the structure in Figure 2.5.5, the copper in plastocyanin exibits a distorted tetrahedral coordination geometry. The protein is said to act like a medieval torture device called a rack in stretching the metal into its distorted geometry. This distortion makes it easier for the copper center to undergo facile redox reactions, enabling it to better function as an electron carrier.

2.5.1.6 Crystal packing effects, in which the energy-lowering packing of molecules and ions in a crystal drives the distortion of a complex's structure away from what it would adopt in the gas phase or solution

This effect is similar to that of ligand constraints except that in this case it arises not from the structure internal to a ligand but out of the forces involves in maximizing the stabilization energy of a crystal. With lower coordination number complexes, packing effects can shift the conformations of flexible ligands but only give rise to very small distortions of the overall coordination geometry. Packing effects can drive a shift in the overall coordination geometry of higher coordination number complexes, for which packing effects are significant relative to the small difference in energy between geometries. Thus while $[Mo(CN)_8]^{4-}$ has a square antiprismatic coordination geometry, in solution it exhibits a dodecahedral coordination geometry in the crystals of many of its salts.

2.5.1.7 Relativistic effects on orbital energies

The proximity of fast moving electrons to massive nuclei in the heavier transition elements results in relativistic expansion and contraction of orbitals. The net results are that

- heavier elements tend to be smaller than expected. This effect preferences lower coordination numbers.
- the relative energies of orbitals shift. Orbitals which become contracted are lowered in energy while those which are expanded increase in energy, as shown for the case of gold in Figure 2.5.6A

The combination of smaller sizes and altered orbital energies affects coordination preferences. Relativistic effects contribute to the greater tendency of Au^{I} relative to other group 11 metals to form linear two-coordinate complexes. As shown in Figure 2.5.6B, the relative closeness in energy of the 6*s* and 5*d* orbitals of gold makes mixing of these orbitals more favorable, facilitating the ability of gold to form two-coordinate complexes with strong sigma bonds oriented 180/(^{\circ}\) from one another.

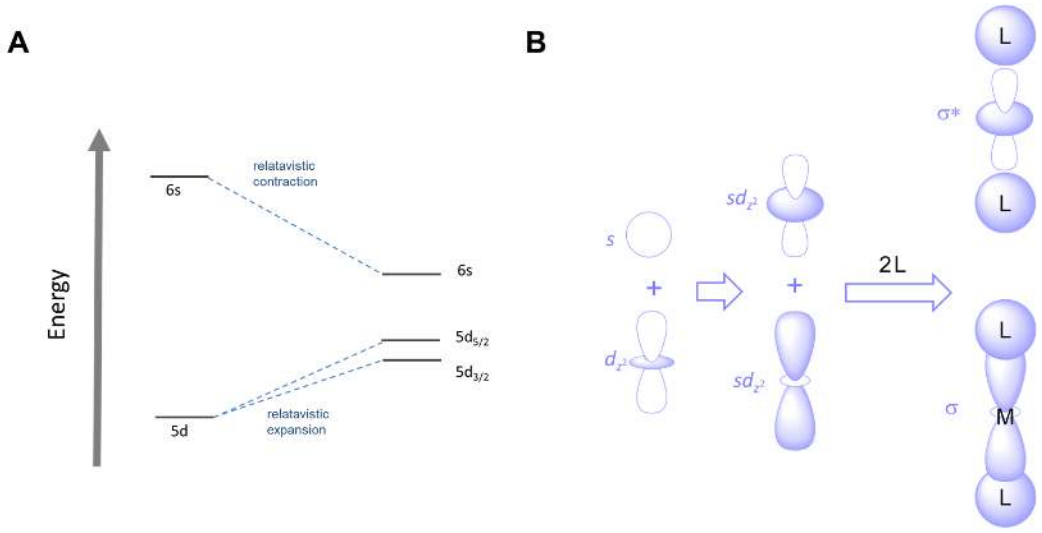


Figure 2.5.6. (A) Gold experiences relativistic expansion and contraction of its 5*d* and 6*s* orbitals, resulting in shifts to their relative energies. (B) This makes mixing of these orbitals more favorable, facilitating the ability of gold to form two-coordinate complexes with strong sigma bonds that involve considerable sd_{z^2} character. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2 What structures do coordination complexes form?

Metal complexes with coordination numbers ranging from one to 16 are known, although values greater than seven are rare for the transition metals. In this section, examples of common coordination geometries will be presented in order of coordination number.

2.5.2.1 Coordination Number 1.

Condensed phase monocoordinate complexes are unknown for the transition metals, although the post-transition metals Tl and In form monocoordinate complexes with the bulky ligands triazapentadienyl and 2,6-tris(2,4,6-triisopropylphenyl)benzene as shown in Figure 2.5.7.

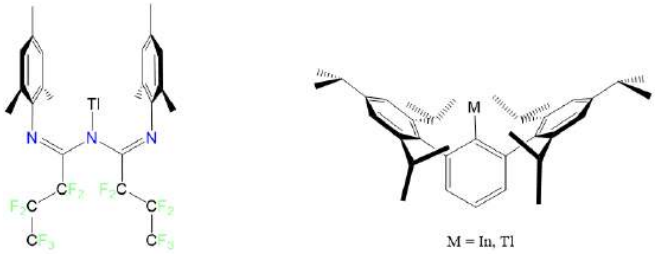
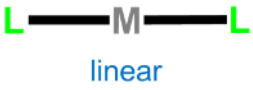


Figure 2.5.7. No monocoordinate transition metal complexes are known, but Tl^{+} and In^{+} form monocoordinate complexes with extremely bulky ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2.2 Coordination Number 2.

A coordination number of 2 is rare outside of ***d*^{10} complexes of the group 11 metals and mercury**, specifically, Cu^{+}, Ag^{+}, Au^{+}, and Hg^{2+}. In accordance with the predictions of the Kepert model these give **linear complexes.**



Among these,

- Cu^+ more commonly gives tetrahedral complexes but can be coaxed to give linear ones. The most prominent example is $[CuCl_2]^-$, which forms when CuCl is treated with concentrated HCl under anerobic conditions.
- Ag^+ also commonly forms tetrahedral or trigonal planar complexes but can give linear ones. The most prominent example is $[Ag(NH_3)_2]^+$, which can be formed by treating silver slats with concentrated aqueous or liquid ammonia.
- Au^+ almost always forms linear complexes, but many of these formally two-coordinate complexes associate as depicted in Figure 2.5.8. The ability of Au^+ to form linear complexes with cyanide is even used to selectively extract metallic gold from low grade ores. The stability of $[Au(CN)_2]^-$ means that the dissolution of metallic gold in aqueous cyanide is thermodynamically favorable under aerobic conditions.

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,[Au(CN)_2]^- + 4\,OH^-$$

- Hg^{2+}, like Au^+, benefits from relativistic effects and more commonly forms two-coordinate complexes with a linear geometry. Among these is $[Hg(CN)_2]$. However, its preference for linearity is not as rigid as for Au^+, and so complexes with a variety of coordination geometries are known.

And by means of honorary mention, the mercury(I) ion, Hg_2^{2+}, forms linear complexes of the type L-Hg-Hg-L, although since Hg_2^{2+} is often considered as a single unit, these aren't always considered to be two-coordinate complexes.

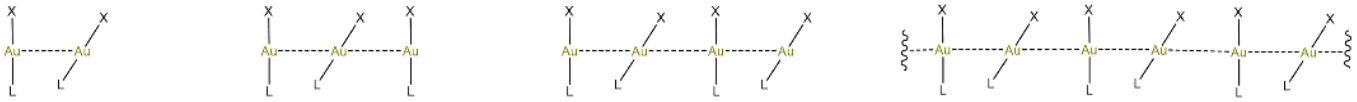


Figure 2.5.8. Many "linear" gold complexes associate side-on to form dimers, trimers, tetramers, and chains. Although in this chapter L is usually taken to represent a generic ligand, in this scheme L represents a neutral ligand that donates two electrons to the metal (py, PR_3, CO, etc.) and X an anionic one (*e.g.*, Cl^-, CN^-, etc.). Exactly which structure forms depends on the identity of L and X. Redrawn from reference 5. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Two-coordinate complexes may also be formed through the use of bulky ligands that only allow for the binding of two to the metal center. The classic examples are given in Figure 2.5.9.

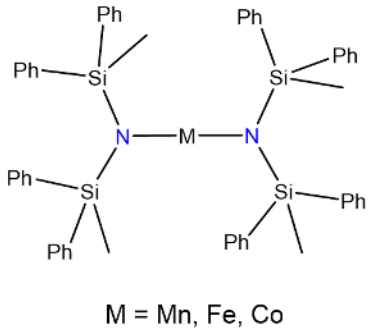


Figure 2.5.9. Two-coordinate complexes form between Mn^{2+}, Fe^{2+}, and Co^{2+} with $N(SiMePh_2)_2$.[6] This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2.3 Coordination Number 3

Three-coordinate complexes are similar to two-coordinate ones in that they are rare and, aside from the constraining influence of ligands, usually limited to d^{10} metal ions such as Cu^+ , Ag^+, Au^+, Hg^{2+}, and Pt(0). As expected from the Kepert model, in the absence of constraining ligands, three-coordinate complexes are trigonal planar.

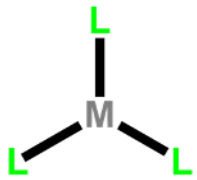


Figure 2.5.10.



Figure 2.5.10. Three-coordinate complexes prepared using bulky and semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

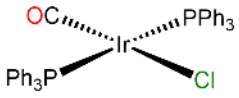
2.5.2.4 Coordination Number 4

The two common four-coordinate geometries are tetrahedral and square planar.



Tetrahedral complexes are commonly formed by metals possessing either a d^0 or d^{10} electron configuration. Monometallic examples of d^0 configurations include $TiCl_4$, VO_4^{3-}, WS_4^{2-}, MnO_4^-, CrO_4^{2-}, and OsO_4, while d^{10} examples are $[Ni(CO)_4]$, $[HgBr_4]^{2-}$, $[ZnCl_4]^{2-}$, and $[CdI_4]^{2-}$. For other electron configurations, tetrahedral complexes are known but much less common. Examples usually involve good donor ligands and include $[FeCl_4]^-$ (d^5), $[CoCl_4^{2-}]$ (d^6), and $[NiCl_4]^{2-}$ (d^7).

Second and third row transition metal centers with d^8 electron configurations like Rh^+, Ir^+, Pd^{2+}, Pt^{2+}, and Au^{3+} almost exclusively exhibit **square planar geometries**. Beyond this, square planar geometries are often formed by Ni^{2+} (d^8), Ni^{3+} (d^7), and Cu^{2+} (d^9). Examples of square planar complexes include $[Cu(acac)_2]$; $[PtCl_4]^{2-}$;Wilkinson's catalyst, $[RhCl(PPh_3)_3]$; and Vaska's complex, *trans*-$[Ir(CO)Cl(PPh_3)_2]$.



2.5.2.5 Coordination Number 5

The two common coordination geometries for five-coordinate complexes are trigonal bipyramidal and square pyramidal.



Figure 2.5.11.

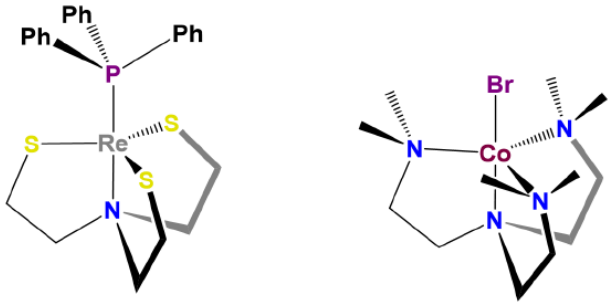


Figure 2.5.11. Some tripodal ligands preference the formation of trigonal bipyramidal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Homoleptic $[Ni(CN)_5]^{3-}$ possesses a square pyramidal structure, although the geometry is more common for macrocyclic complexes like the iron protoporphyrin of deoxymyoglobin shown in figure 2.5.4 and for complexes containing oxo and nitrido ligands, examples of which are shown in Figure 2.5.12

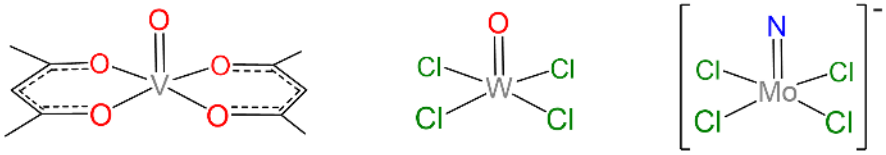


Figure 2.5.12. Some square pyramidal oxo and nitrido complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In the absence of rigid constraining ligands, the relatively low energy difference between the trigonal bipyramidal and square pyramidal coordination geometries provides a mechanism for interconversion of the axial and equatorial ligands in a trigonal planar complex. For example, pentacarbonyliron(0) exhibits fluxionality involving a square pyramidal intermediate via a Berry pseudorotation mechanism, as shown in Figure 2.5.13

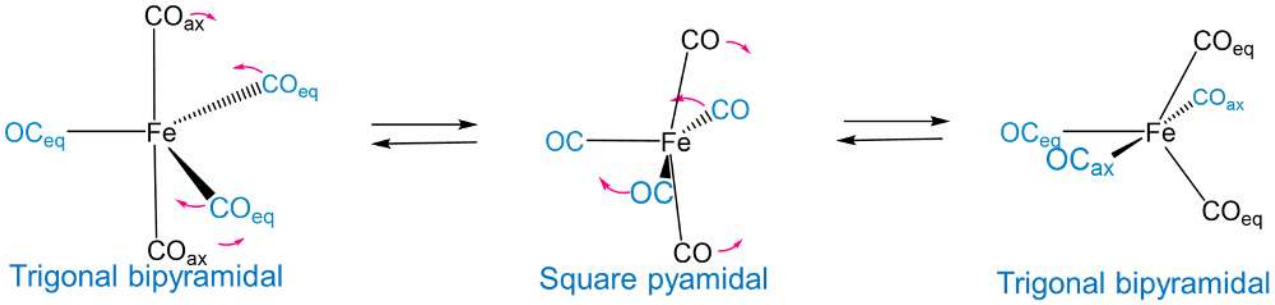


Figure 2.5.13. Fluxionality in pentacarbonyliron(0) involves exchange of axial and equatorial carbonyl ligands via Berry pseudorotation. Interconversion of the axial and equatorial carbonyl groups occurs faster than the NMR timescale at room temperature. As a result the ^{13}C NMR spectrum of $Fe(CO)_5$ exhibits a single signal rather than two separate signals for the axial and equatorial carbonyl carbons. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2.6 Coordination Number 6

The two common coordination geometries for coordination number 8 are octahedral and trigonal prismatic.

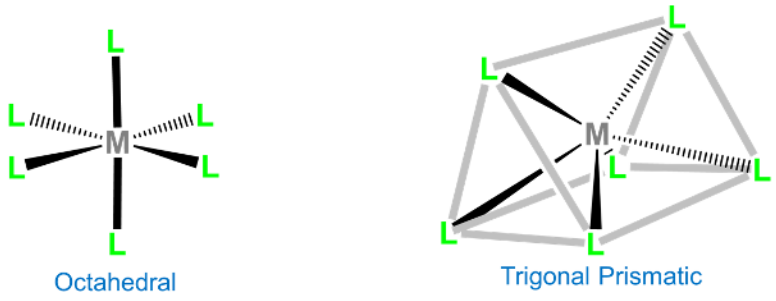


Figure 2.5.14.

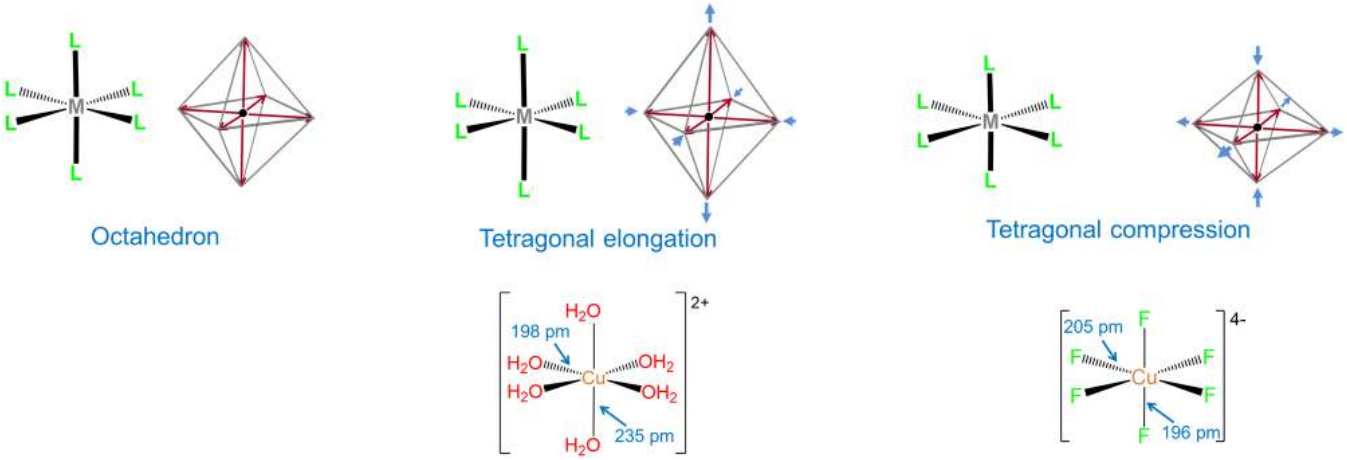


Figure 2.5.14. Tetragonal distortions commonly occur for d^4, d^7 , and d^9 octahedral complexes. The most common type involves axial elongation in which the octahedron is stretched along a single *trans*-L-M-L axis, but axial compressions in which the octahedron is compressed along such an axis instead are sometimes observed. An example of an axial elongated complex is $[Cu(H_2O)_6]^{2+}$ in solution, while $[CuF_6]^{4-}$ is axially compressed when doped into a Ba_2ZrF_6 lattice (it is elongated when doped into a -----. Bond distances are taken from references 7 and 8. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Trigonal prismatic coordination is related to octahedral coordination as shown in Figure 2.5.15. As may be seen in Figure 2.5.15, an octahedral coordination sphere is just a trigonal antiprism in which all edge lengths are identical. Rotation of one triangular face relative to its opposite until the two are eclipsed gives a trigonal prismatic geometry. In fact, since continuation of this rotation gives another octahedral complex, the trigonal prismatic geometry is an intermediate in isomerization reactions involving octahedral complexes.

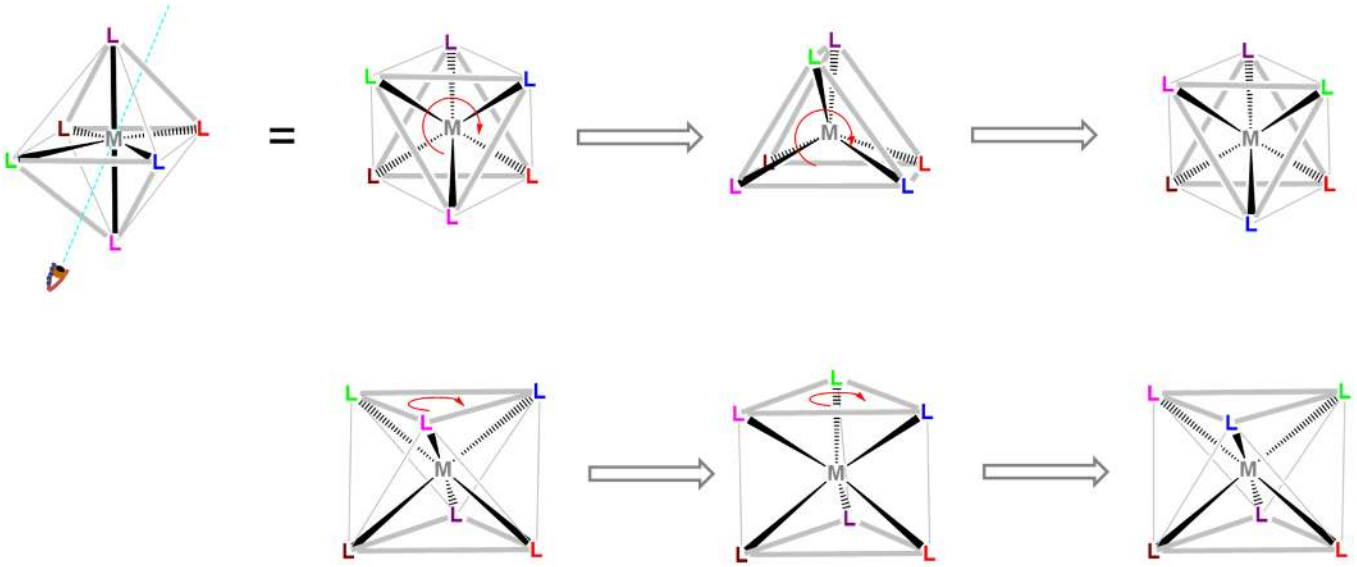


Figure 2.5.15. Since an octahedron is a trigonal antiprism, a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is thermally or photochemically accessible, such twists provide one pathway for isomerization reactions involving octahedral complexes. In tris- and bis-chelates, such isomerizations are said to occur by Bailar and Ray-Dutt twists, which differ only in the relationship between the chelate rings and the faces twisted. Top: View looking down an axis bisecting a pair of opposing faces. Bottom: View perpendicular to that shown at top. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In contrast to octahedral coordination geometries, trigonal prismatic coordination (and distorted versions thereof) are rare and occur mostly for d^0, d^1, and d^2 configurations. Examples of trigonal prismatic metal centers include the d^2 Mo^{4+} centers in MoS_2, d^1 $[Re(S_2C_2Ph_2)_3]^-$, and d^0 $[Ta(CH_3)_6]^-$, of which the latter two structures are given in Figure 2.5.16. Semirigid ligands like that shown in Figure 2.5.4C may be used to encourage the adoption of a trigonal prismatic geometry, although once the number of *d* electrons present exceeds two, the preference for octahedral coordination is too great for a trigonal prismatic geometry to occur.

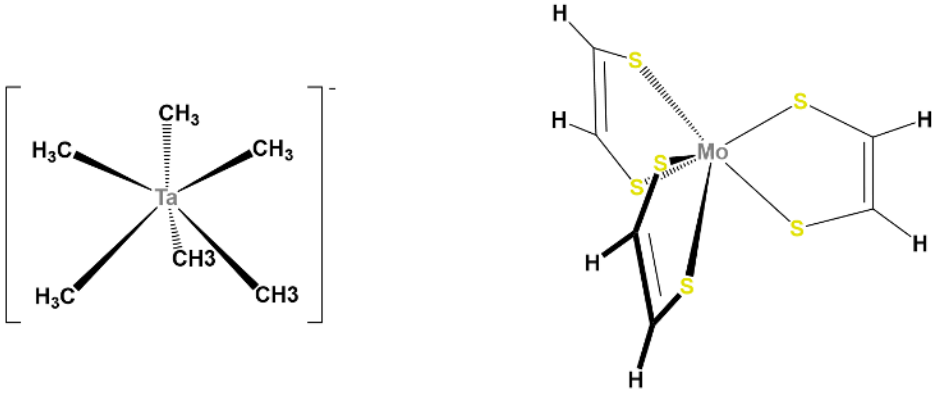
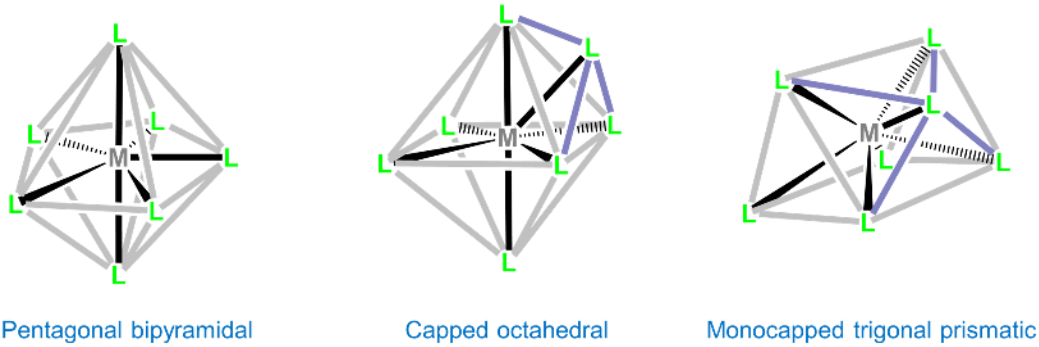


Figure 2.5.16. The complexes $[Ta(CH_3)_6]^-$ and $[Mo(S_2C_2H_2)_3]$ adopt a trigonal prismatic geometry. Trigonal prismatic coordination is common for d^0 and d^1 complexes with alkyl and dithiolene ligands. It is also typical for the dithiolene ligands to coordinate along the rectangular edges of the trigonal prism instead of the triangular ones. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2.7 Coordination Number 7

Seven-coordinate complexes are rare outside of the relatively large early transition metals, lanthanides, and actinides. The three common seven-coordinate geometries are pentagonal bipyramidal, monocapped octahedral, and monocapped trigonal prismatic. The latter two are often called capped octahedral and capped trigonal prismatic, with the mono- prefix being understood.



Although intraligand repulsions are smaller in the pentagonal bipyramidal coordination geometry than the capped octahedral and capped trigonal prismatic geometries, the difference is small, and the three structures are often close in energy. As a result the structure observed is often dependent on ligand-based constraints, crystal packing, and solvent effects that preference one geometry over the others.

Heptacyano complexes are often pentagonal bipyramidal. Examples include $[Mo(CN)_7]^{3-}$, $[W(CN)_7]^{3-}$, and $[Os(CN)_7]^{3-}$. Seven-coordinate complexes containing oxo ligands commonly are pentagonal bipyramidal with the oxo ligand(s) in the less sterically hindered axial position. Examples include $[NbOF_6]^{3-}$ and, for the inner transition metals, $[UO_2F_5]^{3-}$. Ligands that have been used to promote formation of seven-coordinate species include 15-crown-5 and 2,2':6',2":6",2"'-quaterpyridine. Representative complexes are given in Figure 2.5.17.

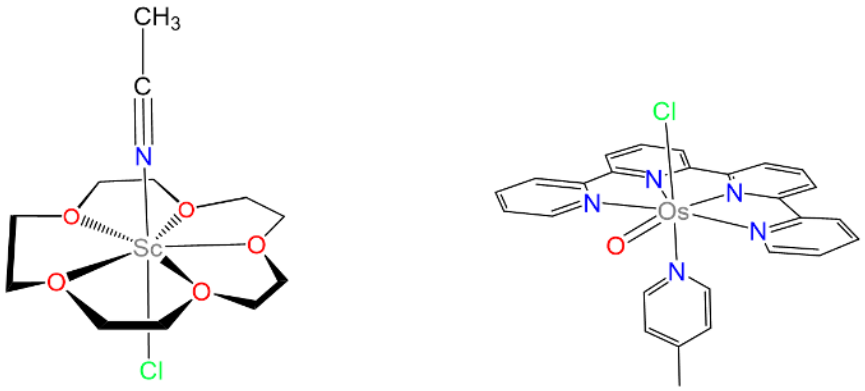


Figure 2.5.17. Seven-coordinate complexes containing ligands that encourage the formation of seven-coordinate geometries. Note that while in $[NbOF_6]^{3-}$ and $[UO_2F_5]^{3-}$ the oxo ligands occupy axial positions, the Osmium complex shown possesses an oxo ligand in an equatorial position. This is likely because the parent octahedral complex, in which the oxo ligand is not present, possesses an expanded outer N-Os-N angle of 121.655° that opens to 154.161° to accommodate the oxo group. Drawn based on the structures reported in references 9 and 10. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Capped trigonal prismatic geometries are common for complexes of the early transition metals. Examples include $[NbF_7]^{2-}$, $[TaF_7]^{2-}$, and $[ZrF_7]^{3-}$ in $(NH_4)_3[ZrF_7]$.

Capped octahedral geometries are found in $[MoMe_7]^-$, $[WMe_7]^-$, and $[WBr_3(CO)_4]$, which contains three pairs of *trans*-Br and CO with the final CO capping the octahedron's $(CO)_3$ face, as shown in Figure 2.5.18.

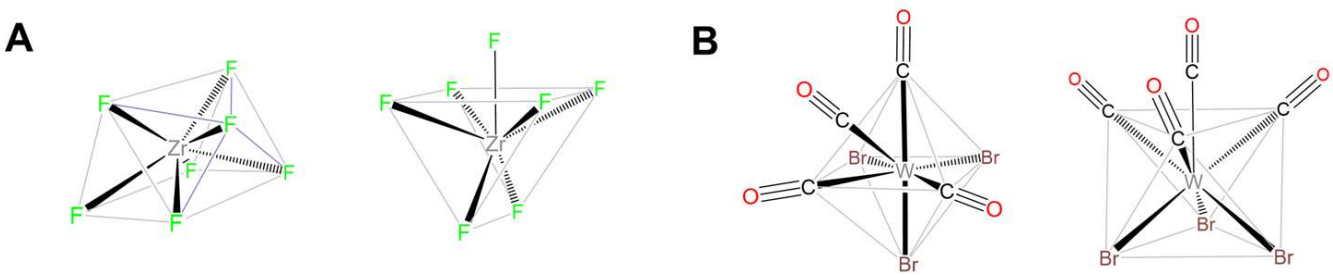


Figure 2.5.18. Examples of complexes that adopt monocapped triconal prismatic and monocapped octahedral geometries.(A) Two views of the structure of (A) capped trigonalprismatic $[ZrF_7]^{3-}$ and (B) capped octahedral $[WBr_3(CO)_4]$. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In seven- and higher-coordinate complexes, ligand and crystal packing effects frequently give distorted coordination geometries. These geometries are intermediate between two or more of the idealized seven coordinate geometries, making it difficult to tell exactly which structure they are a distortion of (Figure 2.5.19).

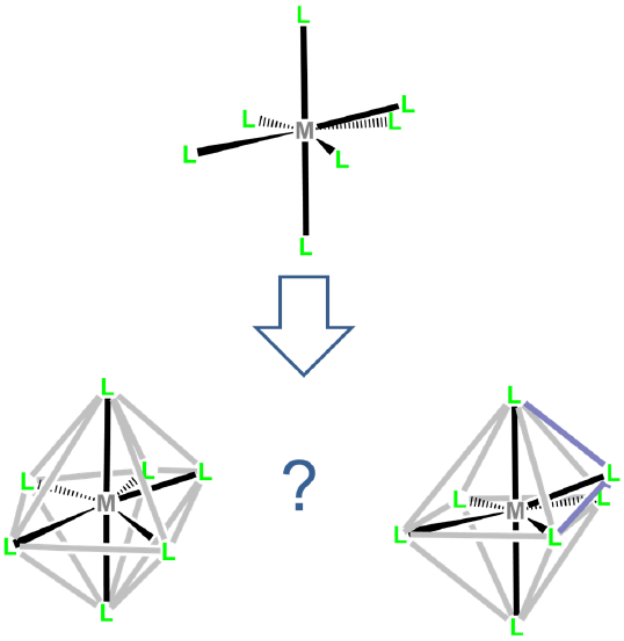


Figure 2.5.19. Many seven-coordinate structures are distorted and can be difficult to classify. For example, how should the geometry of this complex be described - as distorted trigonal bipyramidal or distorted monocapped octahedral? This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2.8 Coordination Number 8

Eight-coordinate complexes are rare and occurs in discrete molecules and ions only for the relatively large early transition metals, lanthanides, and actinides. The three common eight-coordinate geometries are square antiprismatic, dodecahedral, and bicapped trigonal prismatic. In contrast, the cubic coordination geometry is only found in ionic lattices like that of CsCl and in complexes of the inner transition metals such as $Na_3[UF_8]$.

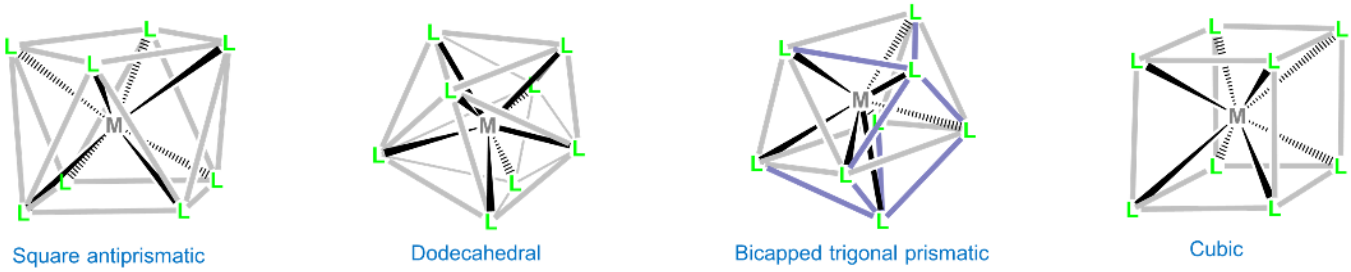


Figure 2.5.20. The square antiprism may be made by twisting one face of a cube relative to another, and the dodecahedron by folding opposing faces towards one another.

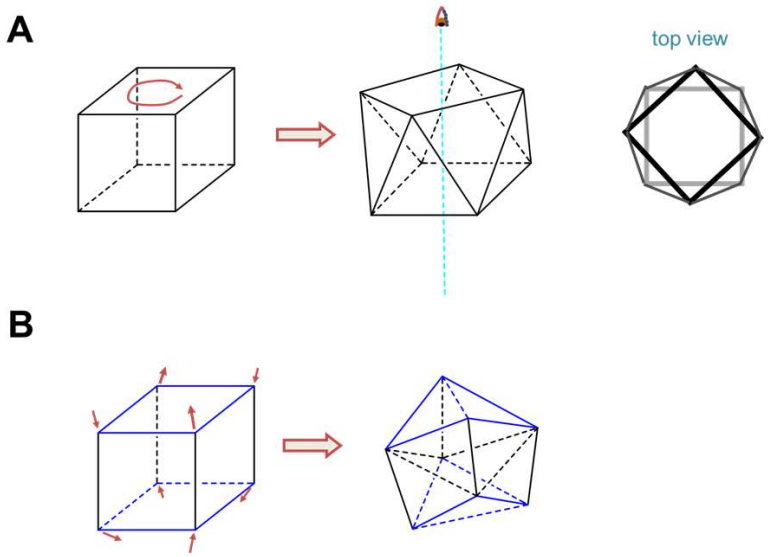


Figure 2.5.20. The (A) square antiprismatic and (B) dodecahedral coordination geometries are distorted cubic geometries. (A) The square antiprismatic coordination geometry is just a cubic coordination geometry in which one face has been rotated 45° relative to its opposite (and for which the distance between those faces need not be equal to the distance between adjacent atoms within a face) (B) The dodecahedral geometry may be thought of as a cube in which opposing faces are folded up and down relative to one another as shown. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As with other high-coordinate structures, the energy difference between these eightfold coordination geometries is small enough that packing effects can significantly influence the observed structure. For example, octacyanomolybdates commonly adopt a square antiprismatic coordination geometry but depending on the counterions present can give dodecahedral or bicapped trigonal prismatic complexes. Examples are given in Figure 2.5.21

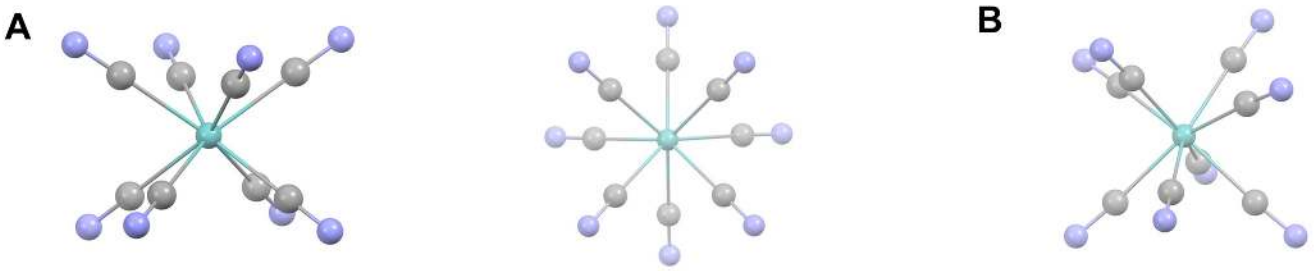


Figure 2.5.21: Structures reported for (A) square antiprismatic $[Mo(CN)_8]^{3-}$ as a solid 4,4'-Diazenediyldipyridinium salt and (B) dodecahedral $[Mo(CN)_8]^{4-}$ as a solid tetra-n-butylammonium salt.

2.5.2.9 Coordination Number 9

Again, nine-coordinate complexes typically require larger transition metals, lanthanides, and actinides. Coordination geometries are typically either tricapped trigonal prismatic or idiosyncratically determined by the ligands. Simple examples include the aqua complexes $[Sc(H_2O)_9]^{3+}$, $[Y(H_2O)_9]^{3+}$, and $[La(H_2O)_9]^{3+}$, as well as $[TcH_9]^{2-}$ and $[ReH_9]^{2-}$.

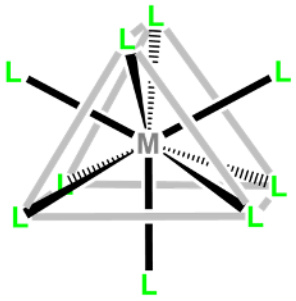


Figure 2.5.22.

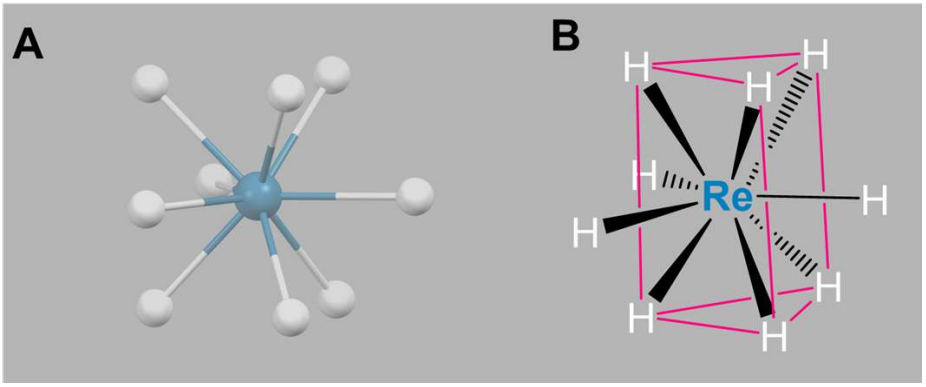


Figure 2.5.22. (A) Structure of $[ReH_9]^{2-}$ in $K_2[ReH_9]$ and (B) schematic showing how the structure maps onto a tricapped trigonal pyramidal coordination geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2.5.2.10 Coordination Numbers 10-16

Coordination numbers higher than nine are extremely rare for compounds that bind in κ fashion (form conventional metal-ligand bonds)[14] and usually involve some combination of large metals, sterically undemanding ligands, and special ligand structures that promote higher coordination. Noteworthy examples include

1. Twelve-coordinate $[Hf(BH_4)_4]$, which illustrates how small multidentate ligands promote higher coordination numbers. As shown in Figure 2.5.23, $[Hf(BH_4)_4]$ has a cubooctahedral structure in which BH_4^- acts as a tridentate ligand, with BH_3 units occupying triangular faces of the cubooctahedron to give a tetrahedron of BH_4^- ligands around the Hf.

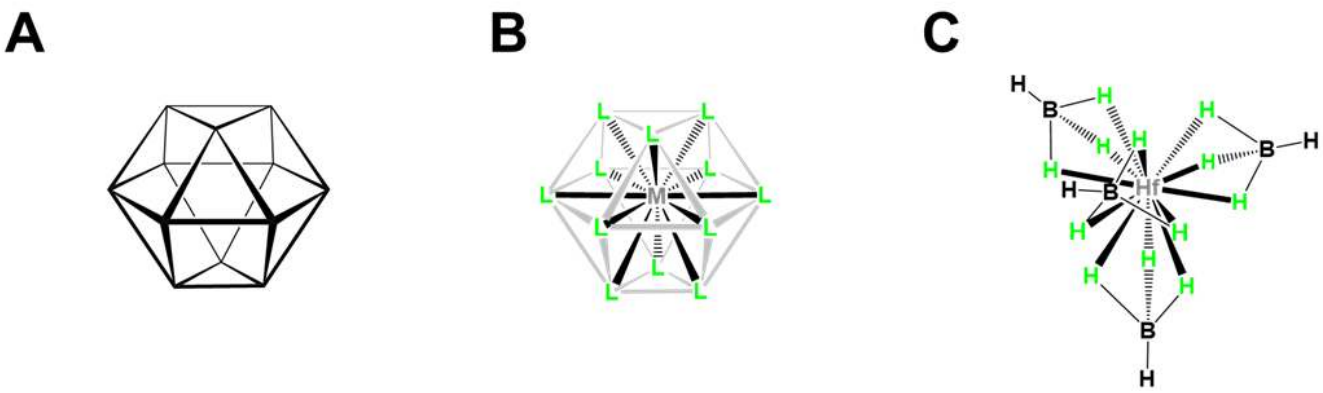


Figure 2.5.23. The anticubooctahedral coordination geometry is observed for $[Hf(BH_4)_4]$. (A) An anticubooctahedron consists of a hexagonal ring capped with antiparallel triangles above and below the ring. (B) Idealized anticubooctahedral complex. (C) Structure of $[Hf(BH_4)_4]$. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2. Twelve-coordinate $[Ce(NO_3)_6]^{2-}$, in which the nitrate oxygens define an icosahedral coordination geometry as shown in Figure 2.5.24. The nitrates in the structure bind the Ce center in bidentate fashion in an octahedral array.

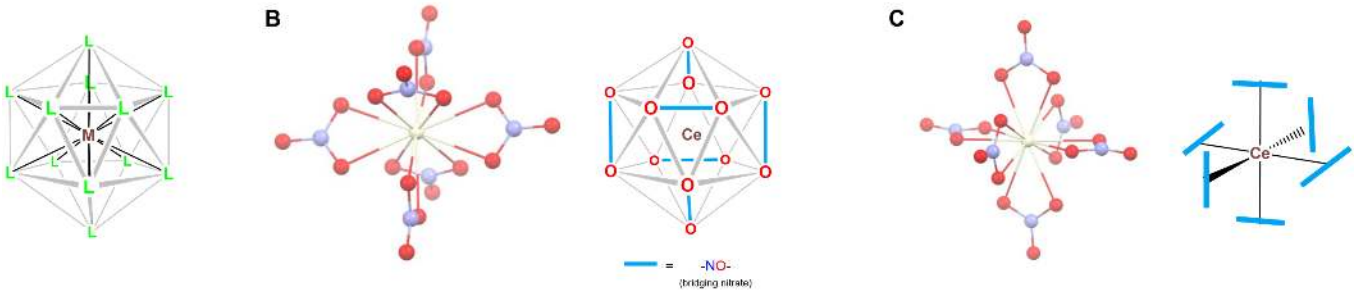


Figure 2.5.24. Coordination geometry of $[Ce(NO_3)_6]^{2-}$ in $[Mg(H_2O)_6][Ce(NO_3)_6]\cdot H_2O$. (A) Idealized icosahedral coordination. (B) View of the structure of $[Ce(NO_3)_6]^{2-}$ showing how it maps onto the icosahedral coordination geometry. (C) The structure may also be thought of as comprising an octahedral geometry in which each vertex of the octahedron is occupied by a κ^2-NO_3^-. The structure of $[Ce(NO_3)_6]^{2-}$ is rendered in Mercury from the cif data in reference 15. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

3. Fifteen-coordinate $[Th(H_3BNMe_2BH_3)_4]$, which also uses bridging H-B-H units that occupy little of the coordination sphere. In $[Th(H_3BNMe_2BH_3)_4]$, three of the four $H_3BNMe_2BH_3$ ligands bind in κ^4 fashion and one binds κ^3, giving the fifteen fold coordination.[16]
4. Sixteen-coordinate $[CoB_{16}]^-$, which possesses the highest coordination number yet observed. Its structure is given in Figure 2.5.25. The coordination geometry is an octahedral antiprism, and the complex should be considered to involve a Co center in the midst of a B_{16}^- "molecular drum" held together by cluster bonds.

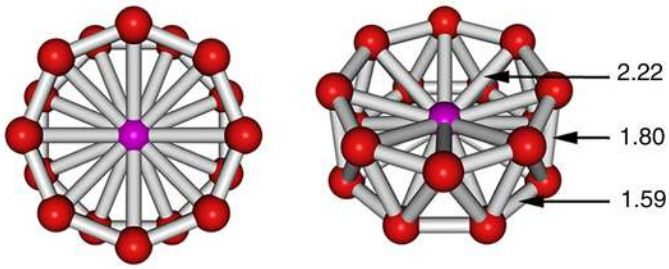


Figure 2A from Popov, I., Jian, T., Lopez, G. *et al.* Cobalt-centered boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015). https://doi.org/10.1038/ncomms9654, which is is licensed in that publication under a Creative Commons Attribution 4.0 International License.

2.5.3 References

1. Dudev, M.; Wang, J.; Dudev, T.; Lim, C., Factors Governing the Metal Coordination Number in Metal Complexes from Cambridge Structural Database Analyses. *The Journal of Physical Chemistry B* **2006**, *110(4)*, 1889-1895.
2. Kuppuraj, G.; Dudev, M.; Lim, C., Factors Governing Metal−Ligand Distances and Coordination Geometries of Metal Complexes. *The Journal of Physical Chemistry B* 2009, 113 (9), 2952-2960.
3. Cremades, E.; Echeverría, J.; Alvarez, S., The Trigonal Prism in Coordination Chemistry. *Chemistry – A European Journal* 2010, 16 (34), 10380-10396.
4. Xiong, X.-G.; Wang, Y.-L.; Xu, C.-Q.; Qiu, Y.-H.; Wang, L.-S.; Li, J., On the gold–ligand covalency in linear $[AuX_2]^-$ complexes. *Dalton Transactions* 2015, 44 (12), 5535-5546.
5. Concepción Gimeno, M. The Chemistry of Gold in Laguna, Antonio (ed.) *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications*. Wiley, 2008.
6. Andersen, R. A.; Faegri, K.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W. P.; Rypdal, K., Synthesis of bis[bis(trimethylsilyl)amido]iron(II). Structure and bonding in M[N(SiMe3)2]2 (M = manganese, iron, cobalt): two-coordinate transition-metal amides. *Inorganic Chemistry* 1988, 27 (10), 1782-1786.
7. Persson, I., Hydrated metal ions in aqueous solution: How regular are their structures? Pure and Applied Chemistry 2010, 82*(10)*, 1901.
8. Aramburu, J. A.; García-Fernández, P.; García-Lastra, J. M.; Moreno, M., Jahn–Teller and Non-Jahn–Teller Systems Involving CuF_6^{4-} Units: Role of the Internal Electric Field in Ba2ZnF6:Cu2+ and Other Insulating Systems. *The Journal of Physical Chemistry C* 2017, *121(9)*, 5215-5224.

9. Brown, M. D.; Levason, W.; Murray, D. C.; Popham, M. C.; Reid, G.; Webster, M., Primary and secondary coordination of crown ethers to scandium(iii). Synthesis, properties and structures of the reaction products of ScCl3(thf)3, ScCl3·6H2O and Sc(NO3)3·5H2O with crown ethers. Dalton Transactions 2003, (5), 857-865.
10. Liu, Y.; Ng, S.-M.; Lam, W. W. Y.; Yiu, S.-M.; Lau, T.-C., A Highly Reactive Seven-Coordinate Osmium(V) Oxo Complex: [OsV(O)(qpy)(pic)Cl]2+. Angewandte Chemie International Edition 2016, 55 (1), 288-291.
11. Popov, I., Jian, T., Lopez, G. *et al.* Cobalt-centred boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015). https://doi.org/10.1038/ncomms9654
12. The structures are rendered from cif data reported in the following publications: (A) square antiprismatic $[Mo(CN)_8]^{3-}$: Wen-Yan Liu, Hu Zhou, Ai-Hua Yuan, *Acta Crystallographica Section E: Structure Reports Online*, 2008, 64, m1151, (B) dodecahedral $[Mo(CN)_8]^{4-}$: B.J.Corden, J.A.Cunningham, R.Eisenberg, *Inorganic Chemistry*, 1970, 9, 356.
13. The structure of ReH_9^{2-} is rendered from the structure reported in Abrahams, S.C.; Ginsberg, A.P.; Knox, K. Transition metal-hydrogen compounds. II. The crystal and molecular structure of potassium rhenium hydride, K_2ReH_9 *Inorganic Chemistry*, **1964**, *3*, 558-567.
14. There are other complexes in which a metal may be said to interact with more than sixteen "ligand atoms", but these are not usually considered to possess a higher coordination number. For example, in some π complexes like η^5-Cp_4U, technically there are 20 C atoms fastened to the U, but these complexes are better considered as 12-coordinate than twenty (since each cyclopentadienyl ring is isolobal with a *fac*-coordinated set of 3 L ligands), while the metal centers in endohedral fullerene species like $La@C_{60}$ do not interact with all sixty carbon atoms at once, and so are better thought of as a metal trapped in a spacious sixty-carbon cage.
15. Zalkin, A.; Forrester, J.D.; Templeton, D.H. Crystal structure of cerium magnesium nitrate hydrate *Journal of Chemical Physics*, **1963**, *39*, 2881-2891.
16. Daly, S. R.; Piccoli, P. M. B.; Schultz, A. J.; Todorova, T. K.; Gagliardi, L.; Girolami, G. S., Synthesis and Properties of a Fifteen-Coordinate Complex: The Thorium Aminodiboranate [Th(H3BNMe2BH3)4]. Angewandte Chemie International Edition 2010, 49 (19), 3379-3381.
17. Popov, I., Jian, T., Lopez, G., Boldyrev, A. I.; Wang, L-S. Cobalt-centred boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015).

2.5: Coordination Numbers and Structures is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.5: Coordination Numbers and Structures** by Stephen M. Contakes is licensed CC BY 4.0.

2.6: Coordination Frameworks

Bridging ligands link metals in multicenter coordination complexes

Some ambidentate and multidentate ligands have the capacity to bridge two metal centers. For instance, the cyano ligands can bridge two metal centers by forming linear links of the type

$$M-CN-M'$$

Linkages like these can be used to bridge multiple metal centers in a cluster or network solid, the latter of which is sometimes called a coordination framework. When the cyano ligand is combined with octahedral metal centers possessing 90° L-M-L bond angles, a cubic coordination network results. An example is the Prussian Blue coordination framework, which possesses the unit cell depicted in Figure 2.6.1A.

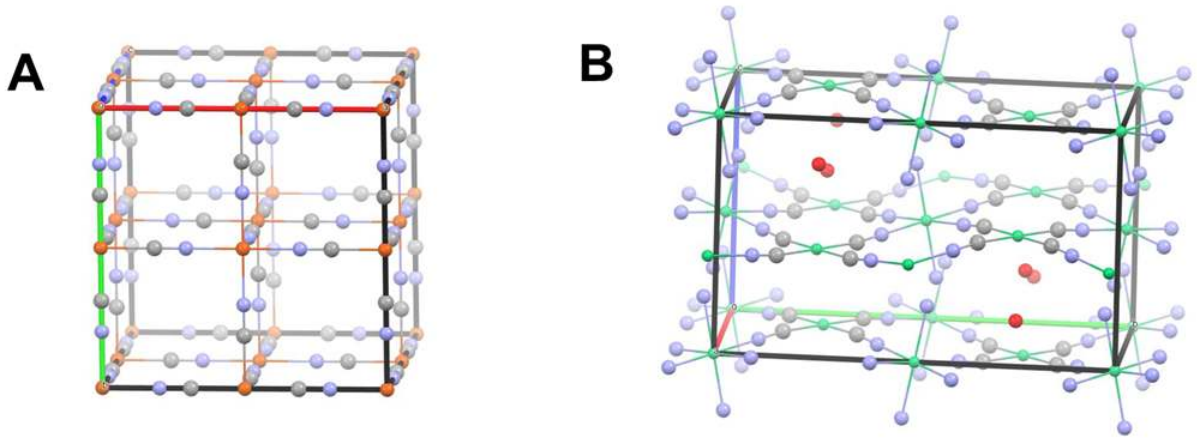


Figure 2.6.1. (A) Idealized unit cell of Prussian Blue showing the cubic coordination framework of interconnected $[Fe^{II}(CN)_6]^{4-}$ and Fe^{3+} units. Because the ratio of Fe^{3+} to $[Fe^{II}(CN)_6]^{4-}$ is 4:3, some of the $[Fe^{II}(CN)_6]^{4-}$ sites are occupied by aqua ligands. (B) Structure of a Hofmann-type clathrate consisting of layers of square planar $[Ni(CN)_4]^{2-}$ units linked by $Ni(NH_3)_2^{2+}$ units. In this structure water occupies the sites between the layers, but structures like these can adjust to accommodate a variety of organic molecules. Hydrogen atoms are omitted for clarity. Rendered from the structures reported in references 1. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The cubic network shown in Figure 2.6.1A reflects the 3D structure of the octahedron, in which the M-L bonds point along the x, y, and z axes. If a square planar metal center is used, a 2D coordination network comprising interlinked squares is produced instead. An example is the Hofmann clathrate shown in Figure 2.6.1B, which depicts a Hofmann clathrate in which square planar $[Ni(CN)_4]^{2-}$ units are linked by *trans*-$Ni(NH_3)_2^{2+}$ units (which are octahedral but have a square plane of open coordination sites perpendicular to the NH_3-Ni-NH_3 axis).

The structures of coordination polyhedra and frameworks reflect ligand and metal coordination geometries

As illustrated by the Prussian Blue and Hofmann clathrate coordination networks shown in Figure 2.6.1, the structures formed when a bridging ligand links multiple metal centers depends on the geometry of the centers, the ligand, and the metal-ligand bonds formed. Because the directionality of metal-ligand bonding in many types of complexes is well-characterized and predictable, it is possible to design metal complexes and linkers that can serve as building blocks for clusters and networks. In particular

- metal complexes with combinations of labile (substitutable) ligands in particular topologies. These insure that the linking ligand will be arranged around the metal center in those defined directions.
- Ligands that possess binding sites oriented in defined directions so that they link the metal centers together in particular topologies.

Examples of the sort of metal centers that can be used and examples of linking ligands are given in Figure 2.6.2.

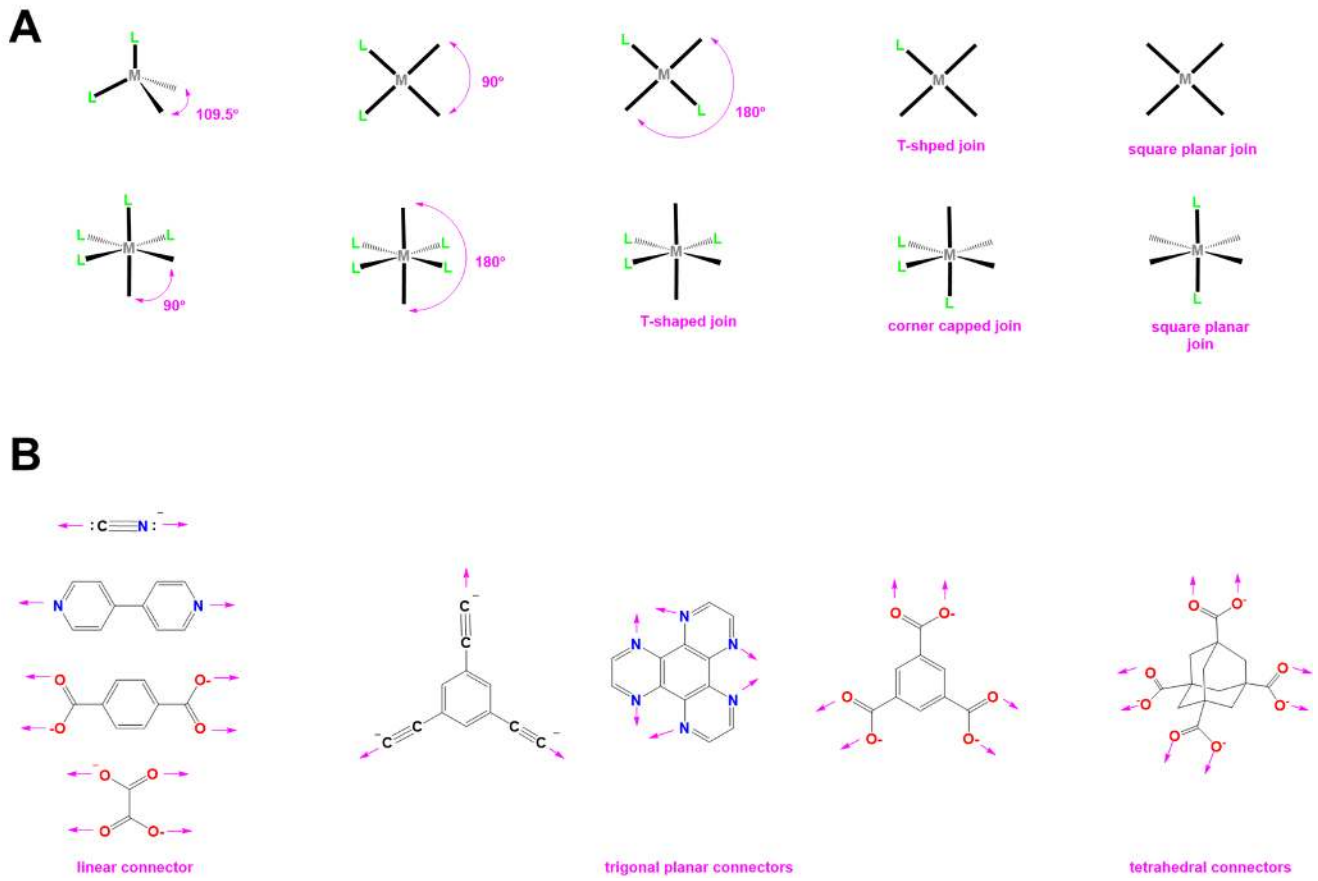


Figure 2.6.2. The directionality of M-L bonding permits the rational construction of structures using metal and ligand "building blocks". For example, (A) Tetrahedral, octahedral, and square planar metal centers alone can be used to connect sets of ligands at 90°, 109.5°, and 180° bond angles in a variety of arrangements while (B) the selection of organic linkers shown can be used as linear, trigonal planar, and tetrahedral linkers.

Examples of how the building blocks shown in Figure 2.6.2 might be used to prepare molecular polyhedra and coordination networks are depicted schematically as shown in Figure 2.6.3. Among the examples shown in Figure 2.6.3, those depicted on the right schematize the Hofmann clathrate (top) and Prussian Blue (bottom) coordination networks of Figure 2.6.1.

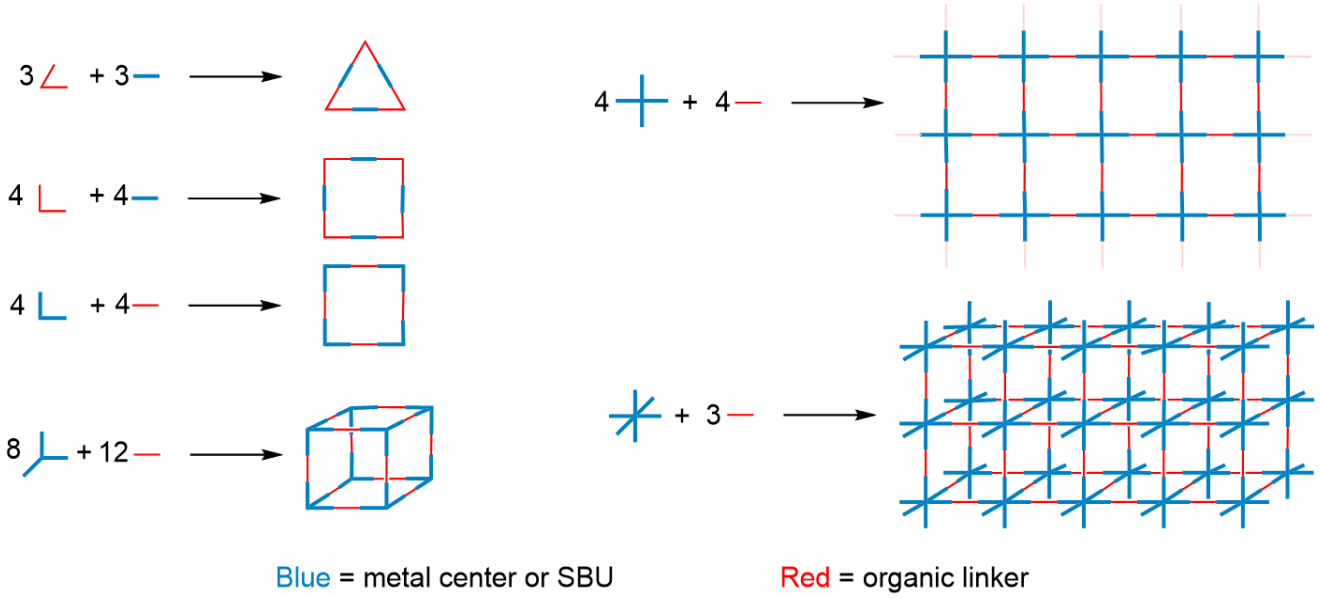


Figure 2.6.3. Examples illustrating how the combination of metal and organic linker units gives rise to polyhedral and network structures that reflect the geometry of the building blocks used.

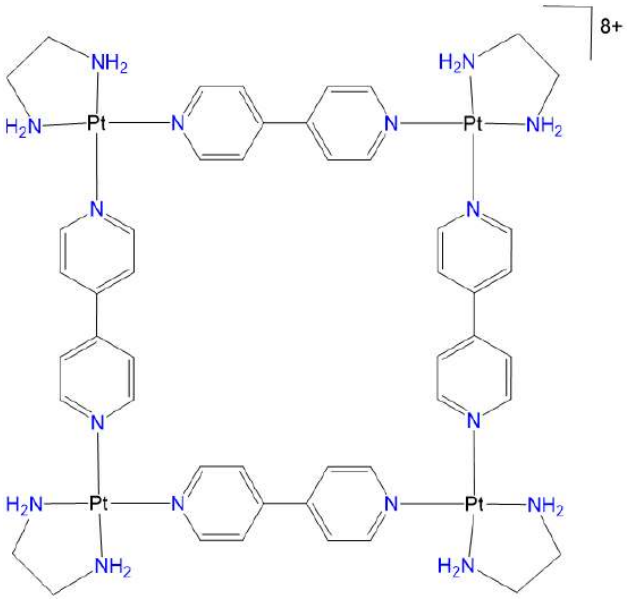


Figure 2.6.4. In its structure, the $Pt(en)^{2+}$ centers possess *cis*-90° coordination sites linked by the linear linker 4,4'-bipyridine.

A wider variety of structures are possible than those hinted at by the building blocks and structures shown in Figures 2.6.2 and 2.6.3. More may be obtained using the principles of molecular structure outlined in the sections on coordination geometry, ligands, and isomerism. In fact, one of the first coordination polyhedra prepared involved Jean-Marie Lehn's recognition that planar bidentate ligands in a tetrahedral bis-chelate are oriented perpendicular to one another, as shown in Figures 2.6.5A. This enabled him to prepare a molecular trigonal prism by combining a source of Cu^{2+} with the trigonal planar and linear-capable organic linkers that bind the Cu^{2+} in bidentate fashion, as shown in Figure 2.6.5B.

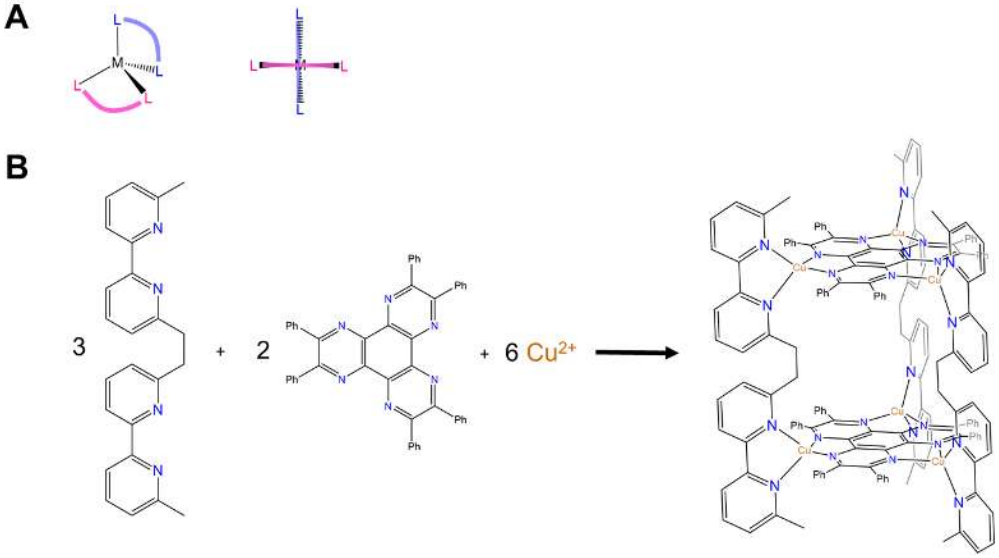


Figure 2.6.5. (A) When a tetrahedral metal center is coordinated by two planar bidentate ligands, the ligands are oriented at 90° to one another. (B) This permitted Jean Marie-Lehn and his cowokers to prepare a molecular trigonal prism consisting of six Cu^{2+} ions linked by the rigid and semirigid nitrogen-containing ligands on the prism's trigonal faces and rectangular edges as shown. Redrawn from structures given in reference 3.

Metal Organic Frameworks (MOFs) are porous coordination polymers in which metal "building units" are connected by rigid organic ligand "struts"

One class of coordination frameworks that has received much attention over the past 25 years is the metal organic frameworks (MOFs). These consist of metal centers linked by rigid organic ligands to give a porous structure similar to those of the aluminosilicate-based zeolites. The structure of one MOF, called MIL-53, is given in Figure 2.6.6A.

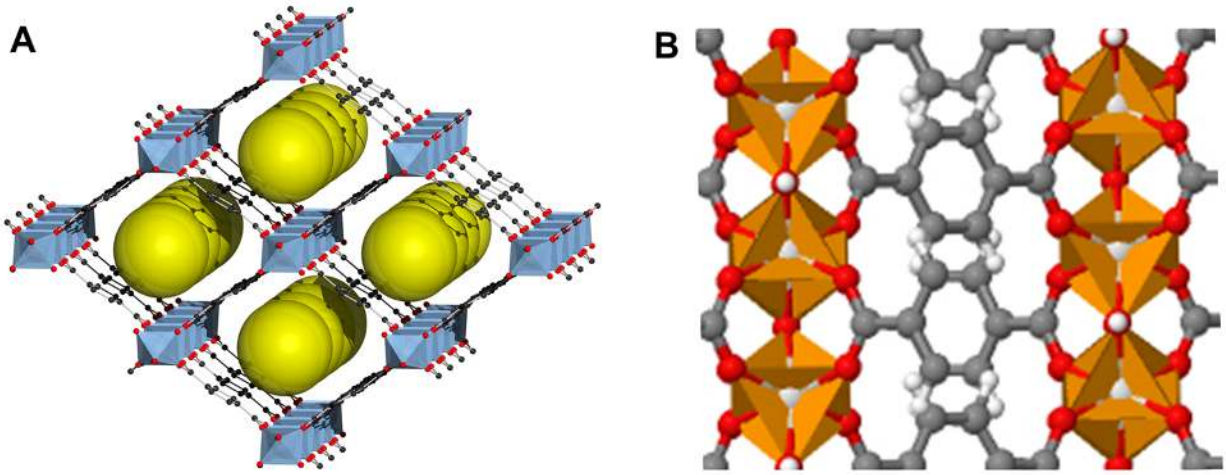


Figure 2.6.6. In metal organic frameworks containing carboxylate ligands, the two oxygens in each carboxylate usually bind to different metal centers. A simple example involves the structure of MIL-53, in which linear *p*-terephthalato (1,4'-benzenedicarboxylato or BDC) ligands bridge chains of linked MO_6 octahedra. (A) Structure of MIL-53 showing the open structure of the MOF, indicated by the yellow spheres. (B) Top-down image of an MIL-53 structure showing how the carboxylic acid oxygens in the BDC ligands coordinate two different metals. The image in part A is by Tony Boehle - Tony Boehle, Public Domain, https://commons.wikimedia.org/w/inde...curid=10328580 The image in part B is rendered from the jmol structure of MIL-53(Sc) at https://www.chemtube3d.com/mof-mil53sc-2/

As can be seen from the overall structure of MIL-53 depicted in Figure 2.6.6A, the structure possesses large rhombic prismatic voids, represented by the yellow spheres. These voids can in principle be occupied by small molecule substrates. Because of MOF's potential to bind and store substrates, there is considerable interest in developing MOFs that are useful for storing and separating particular gases.

A closer look at the structure of MIL-53 reveals that the carboxylate oxygens in the benzenedicarboxylato (BDU) linkers span two different metal centers rather than binding to only one. As explained in Figure 2.6.7, this binding mode enables the formation of rigid stable networks, although it requires the use of metal building blocks in which two or more metal centers are held in close proximity.

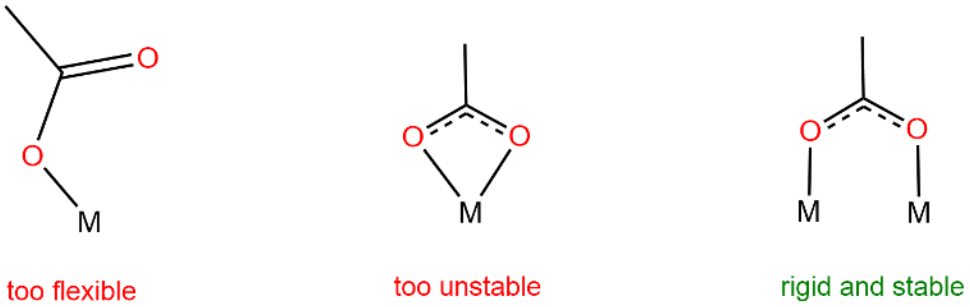


Figure 2.6.7. The carboxylate groups in the ligands of metal organic frameworks commonly bind κ^1 to two different metal centers rather than κ^1 or κ^2 to a single center because the single metal κ^1 binding mode is too flexible to give rigid networks while the small chelate rings and narrow bite angles of the κ^2 chelate rings make them less stable.

In MIL-53, the metal centers that the DBU ligands coordinate are chains of octahedral metal centers bridged by μ_2 hydroxo ligands. These chains form spontaneously as the network forms under the high temperature conditions of its synthesis. In other cases, metal secondary building units (SBUs) containing the necessary bridging dicarboxylate ligands are used. One common class of metal SBUs used is the paddlewheel carboxylates shown in Figure 2.6.8A. These consist of two metals spanned by a square plane of four carboxylates in a paddlewheel arrangment.

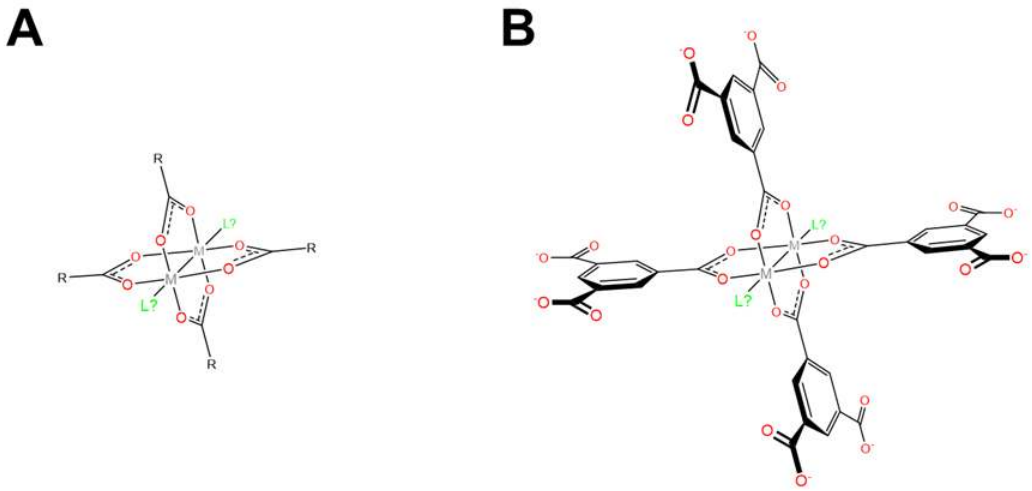


Figure 2.6.8. Metal organic frameworks do not use a metal center directly but instead employ a metal cluster as a secondary building unit (SBU). (A) Paddlewheel carboxylates are a common SBU. They consist of two metals surrounded by four carboxylato ligands in a square planar "paddlewheel" arrangement. (B) In complexes where the ligands contain additional carboxylates, they function as a planar center in a MOF. An example is the paddlewheel carboxylate present in the HKUST class of MOFs, in which each carboxylato ligand is capable of bridging to three dimetal units. Note that in the structures shown, the axial ligands shown in green may be present or absent depending on the specific metal carboxylate used and/or whether the ligand was removed during processing of the MOF.

The use of paddlewheel carboxylate metal SBUs and bridging organic carboxylate ligands enables the construction of coordination frameworks like that of HKUST-1 shown in Figure 2.6.9. The structure of these networks depends on the geometry of the linking ligand. For instance, in HKUST-1 the 1,3,5-benzenetricarboxylato bridging ligands each link three paddlewheel SBUs to give the cubic network shown in Figure 2.6.9. Other organic carboxylate ligands give different network topologies. In addition, the ability of some paddlewheel carboxylates to coordinate ligands perpendicular to the carboxylates, represented by the ligands marked L? in Figure 2.6.8, affords additional opportunities to use these networks to bind substrates that can coordinate those sites.

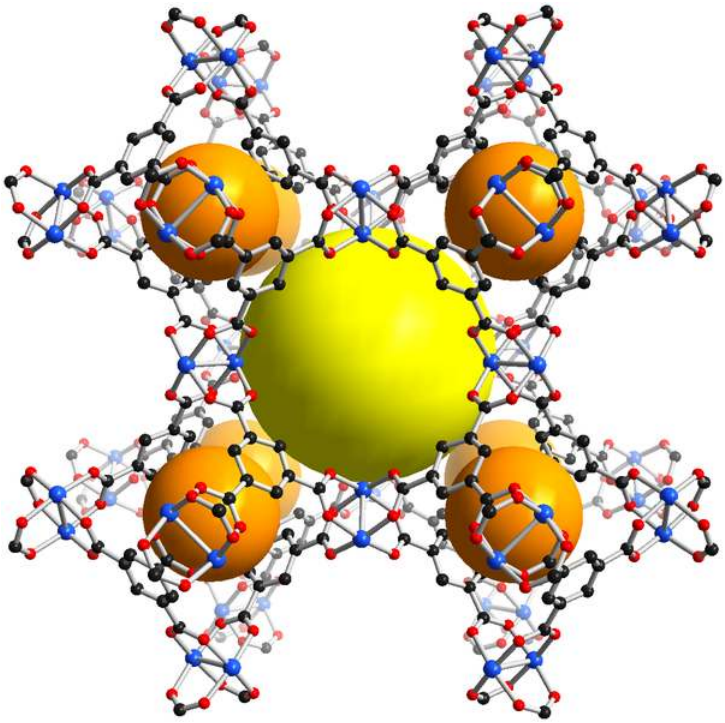


Figure 2.6.9. Desolvated HKUST-1 member of the HKUST class of MOFs showing open regions in the structure. The structure consists of paddlewheel carboxylates linked by trigonal planar tricarboxylate organic SBUs. The image is by Tony Boehle - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/inde...curid=27424501

Another common metal SBU is the basic zinc acetate structure shown in Figure 2.6.10. As shown in Figure 2.6.10A, the structure is analogous to those of the basic beryllium acetates and involves an OZn_4 tetrahedron in which the tetrahedrally arranged Zn^{2+} are connected by carboxylate ligands spanning the tetrahedron's six edges. When these carboxylate ligands are replaced by rigid dicarboxylates (Figure 2.6.10B), the result is that the Zn_4O core is surrounded by an octahedral coordination sphere of carboxylate ligands (Figure 2.6.10C).

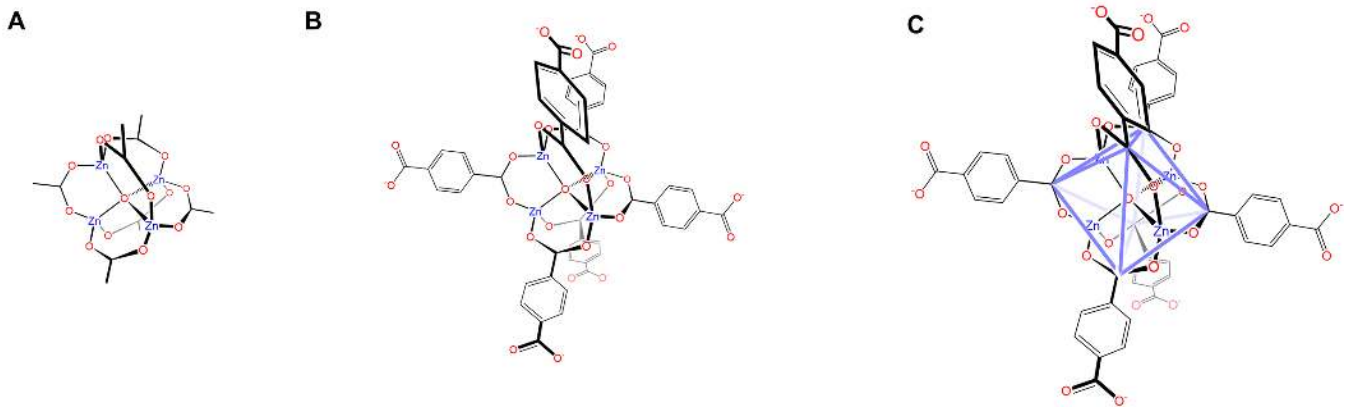


Figure 2.6.10 (A) Basic zinc acetate is a common SBU used as a pseudooctahedral center in MOFs. (B) Exchange of its acetate ligands with *p*-terephthalate (1,4-benzenedicarboxylate) linkers gives a complex in which the free dicarboxylates are oriented towards the vertices of an octahedron (C).

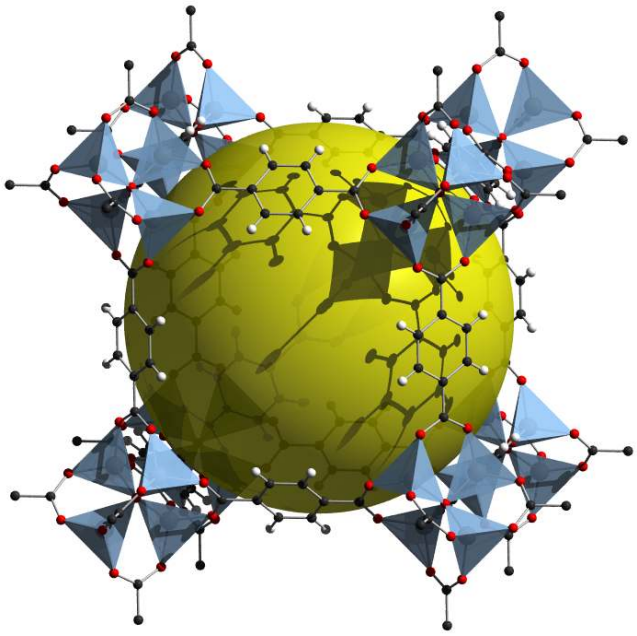


Figure 2.6.11. A cubic metal organic framework derived from the basic zinc acetate SBU. The structure is called MOF-5 and consists of Zn_4O^{6+} pseudooctahedra linked by linear *p*-terephthalate (1,4-benzenedicarboxylate) ligands. The large golden sphere inside the unit cell has a radius of 12 Angstroms (defined with the aromatic rings oriented as shown) and represents the space available for the framework to accommodate guest molecules. By Tony Boehle - Own work, Public Domain, https://commons.wikimedia.org/w/inde...curid=10319204.

The structure of MOF-5 also illustrates how the size of the pores in an MOF structure may be tailored by lengthening or shortening the organic linker. In particular, from Figure 2.6.11 it can be seen that the size of the MOF-5's cubic unit cell depends on the length of the organic portion of the carboxylate linker. In MOF-5 this linker consists of a single benzene unit and gives 9-Angstrom pores, while the use of two and three benzene rings increases the pore size to 13 and 16 Angstroms, respectively, as shown in 2.6.12.

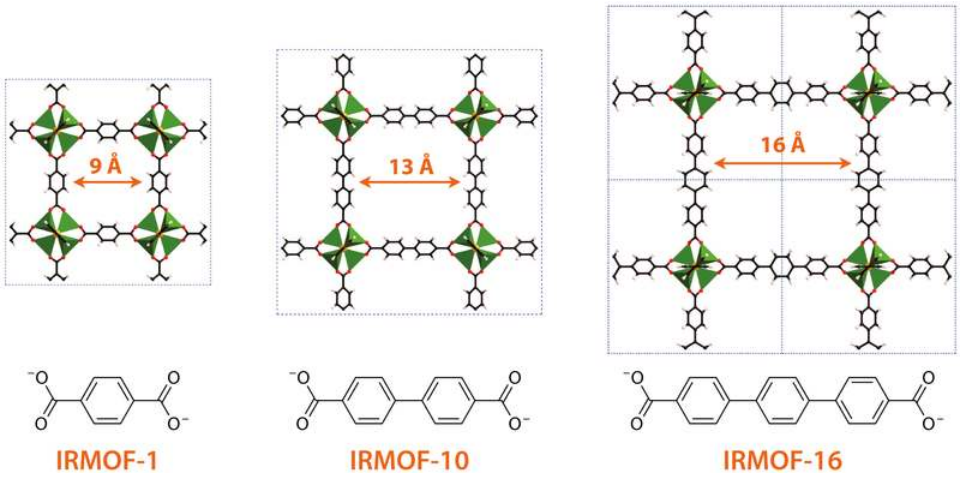


Figure 2.6.12. The spacing between metal centers in a coordination network may be tailored by the use of organic linkers of differing lengths. By François-Xavier Coudert - Own work, CC BY 4.0, https://commons.wikimedia.org/w/inde...curid=89656071

References

1. The structure of Prussian blue is rendered from that reported in Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A., The crystal structure of Prussian Blue: $Fe_4[Fe(CN)_6]_3.xH_2O$. *Inorganic Chemistry* 1977, *16(11)*, 2704-2710; to simplify depiction of the coordination framework, water molecules were removed. The structure of the Hofmann-type clathrate is rendered from that reported in Rayner, J. H.; Powell, H. M., 688. Crystal structure of a hydrated nickel cyanide ammoniate. *Journal of the Chemical Society (Resumed)* 1958, 3412-3418.

2. (a) Fujita, M.; Ogura, K., Transition-metal-directed assembly of well-defined organic architectures possessing large voids: From macrocycles to [2] catenanes. *Coordination Chemistry Reviews* 1996, *148*, 249-264. (b) Leininger, S.; Olenyuk, B.; Stang, P. J., Self-Assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals. *Chemical Reviews* 2000, *100(3)*, 853-908.

3. Machado, V. G.; Baxter, P. N. W.; Lehn, J.-M., Self-assembly in self-organized inorganic systems: a view of programmed metallosupramolecular architectures. Journal of the Brazilian Chemical Society 2001, 12, 431-462.

4. Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., Reticular synthesis and the design of new materials. Nature 2003, 423 (6941), 705-714.

2.6: Coordination Frameworks is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- **9.6: Coordination Frameworks** by Stephen M. Contakes is licensed CC BY 4.0.

2.P: Problems

19.1: Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Q19.1.1

Write the electron configurations for each of the following elements:

a. Sc
b. Ti
c. Cr
d. Fe
e. Ru

S19.1.1

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and sub-shells. The electron configuration of each element is unique to its position on the periodic table where the energy level is determined by the period and the number of electrons is given by the atomic number of the element. There are four different types of orbitals (s, p, d, and f) which have different shapes and each orbital can hold a maximum of 2 electrons, but the p, d and f orbitals have different sub-levels, meaning that they are able to hold more electrons.

The periodic table is broken up into groups which we can use to determine orbitals and thus, write electron configurations:

Group 1 & 2: S orbital

Group 13 - 18: P orbital

Group 3 - 12: D orbital

Lanthanide & Actinides: F orbital

Each orbital (s, p, d, f) has a maximum number of electrons it can hold. An easy way to remember the electron maximum of each is to look at the periodic table and count the number of periods in each collection of groups.

Group 1 & 2: 2 (2 electrons total = 1 orbital x max of 2 electrons = 2 electrons)

Group 13 - 18: 6 (6 electrons total = 3 orbitals x 2 electrons max = 6 electrons)

Group 3 - 12: 10 (10 electrons total = 5 orbitals x 2 electrons max = 10 electrons)

Lanthanide & Actinides: 14 (14 electrons total = 7 orbitals x 2 electrons max = 14 electrons)

Electron fills the orbitals in a specific pattern that affects the order in which the long-hand versions are written:

Electron filling pattern: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f

An easier and faster way to write electron configurations is to use noble gas configurations as short-cuts. We are able to do this because the electron configurations of the noble gases always have all filled orbitals.

$$\text{He: } 1s^2 2s^2$$

$$\text{Ne: } 1s^2 2s^2 2p^6$$

$$\text{Ar: } 1s^2 2s^2 2p^6 3s^2 3p^6$$

$$\text{Kr: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$$

$$\text{Xe: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$$

$$\text{Rn: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6$$

The most common noble gas configuration used is Ar. When you want to use the noble gas configuration short-cut, you place the noble gas's symbol inside of brackets:

$$[\text{Ar}]$$

and then write it preceding the rest of the configuration, which is solely the orbitals the proceed after that of the noble gas.

a. Sc

Let's start off by identifying where Scandium sits on the periodic table: row 4, group 3. This identification is the critical basis we need to write its electron configuration.

By looking at Scandium's atomic number, 21, it gives us both the number of protons and the number of electrons. At the end of writing its electron configuration, the electrons should add up to 21.

At row 4, group 3 Sc, is a transition metal; meaning that its electron configuration will include the D orbital.

Now, we can begin to assign the 21 electrons of Sc to orbitals. As you assign electrons to their orbitals, you move right across the periodic table.

Its first 2 electrons are in the 1s orbital which is denoted as

$$1s^2$$

where the "1" preceding the s denotes the fact that it is of row one, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 21-2=19 more electrons to assign.

Its next 2 electrons are in the 2s orbital which is denoted as

$$2s^2$$

where the "2" preceding the s indicates that it is of row two, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 19-2=17 more electrons to assign.

Its next 6 electrons are in the 2p orbital which is denoted as

$$2p^6$$

where the "2" preceding the p indicates that it is of row two, and it has an exponent of 6 because it fulfills the p orbital's maximum electron number. Now we have 17-6=11 more electrons to assign.

Its next 2 electrons are in the 3s orbital which is denoted as

$$3s^2$$

where the "3" preceding the s indicates that it is of row three, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 11-2=9 more electrons to assign.

Its next 6 electrons are in the 3p orbital which is denoted as

$$3p^6$$

where the "3" preceding the p indicates that it is of row three, and it has an exponent of 6 because it fulfills the p orbital's maximum electron number. Now we have 9-6=3 more electrons to assign.

Its next 2 electrons are in the 4s orbital which is denoted as

$$4s^2$$

where the "4" preceding the s indicates that it is of row four, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 3-2=1 more electron to assign.

Its last electron would be alone in the 3 d orbital which is denoted as

$$3d^1$$

where the "3" preceding the d indicates that, even though it is technically of row 4, by disregarding the first row of H and He, this is the third row and it has an exponent of 1 because there is only 1 electron to be placed in the d orbital. Now we have assigned all of the electrons to the appropriate orbitals and sub-orbitals, so that the final, entire electron configuration is written as:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$$

This is the long-hand version of its electron configuration.

So for Sc, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^2 3d^1$$

b. Ti

Start off by identifying where Titanium sits on the periodic table: row 4, group 4, meaning it has 22 electrons total. Titanium is one element to the right of the previous problem's Sc, so we will basically use the same method except, in the end, there will be 2 electrons remaining, so therefore the final orbital will be denoted as:

$$3d^2$$

If needed, look above to the exact steps for how to do it in detail again; the long-hand electron configuration for Titanium will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$$

So for Ti, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^2 3d^2$$

c. Cr

Start off by identifying where Chromium sits on the periodic table: row 4, group 6, that means it has a total of 24 electrons. But first, Cr, along with Mo, Nb, Ru, Rh, Pd, Cu, Sg, Pt and Au, is a special case. You would think that since it has 24 electrons that its configuration would look like:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$$

which is how we learned it earlier. However, this electron configuration is very unstable because of the fact that there are 4 electrons in its 3 d orbital. The most stable configurations are half-filled (d^5) and full orbitals (d^{10}), so the elements with electrons resulting in ending with the d^4 or d^9 are so unstable that we write its stable form instead, where an electron from the preceding s orbital will be moved to fill the d orbital, resulting in a stable orbital.

If needed, look above to the exact steps for how to do the beginning of the configuration in detail again. However we have to apple the new rule to attain stability so that the long-hand electron configuration for Chromium will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{4s^1 3d^5}$$

So for Cr, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^1 3d^5$$

d. Fe

Start off by identifying where Iron sits on the periodic table: row 4, group 8, meaning it has 26 electrons total. This is 5 elements to the right of the previous problem's Sc, so we will basically use the same method except, in the end, there will be 6 electrons remaining, so therefore the final orbital will be denoted as:

$$3d^6$$

If needed, look above to the exact steps for how to do it in detail again; the long-hand electron configuration for Iron will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$$

So for Fe, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^2 3d^6$$

e. Ru

Start off by identifying where Ruthenium sits on the periodic table: row 5, group 8, that means it has a total of 44 electrons. But first, as stated earlier, Ru, along with Cr, Mo, Nb, Rh, Pd, Cu, Sg, Pt and Au, is a special case. You would think that since it has 44 electrons that its configuration would look like:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \mathbf{5s^2\ 4d^6}$$

which is how we learned it earlier. However, this electron configuration is very unstable because of the fact that, even though there are 4 paired electrons, there are also 4 electrons unpaired. This results in a very unstable configuration, so to restore stability, we have to use a configuration that has the most paired electrons, which would be to take an electron from the s orbital and place it in the d orbital to create:

$$5s^1 4d^7$$

If needed, look above to the exact steps for how to do the beginning of the configuration in detail again. However we have to apple the new rule to attain stability so that the long-hand electron configuration for Ru will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \mathbf{5s^1 4d^7}$$

So for Cr, its short-hand version of its electron configuration would therefore be:

$$[Kr]\ 5s^1 4d^7$$

A19.1.1

a. Sc: $[Ar]4s^2 3d^1$
b. Ti: $[Ar]4s^2 3d^2$

c. Cr: [Ar]$4s^1 3d^5$
d. Fe: [Ar]$4s^2 3d^6$
e. Ru: [Kr]$5s^1 4d^7$ (anomalous configuration)

Q19.1.2

Write the electron configurations for each of the following elements and its ions:

a. Ti
b. Ti^{2+}
c. Ti^{3+}
d. Ti^{4+}

S19.1.2

Electrons are distributed into molecular orbitals, the $s, p, d, and f$ blocks. An orbital will have a number in front of it and a letter that corresponds to the block. The s block holds two electrons, the p block holds six, the d block holds ten, and the f block holds fourteen. So, based on the number of electrons an atom has, the molecular orbitals are filled up in a certain way. The order of the orbitals is $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p$An exponent will be put after the letter for each orbital to signify how many electrons are in that orbital. Noble gas notation can also be used by putting the noble gas prior to the element you are writing the configuration for, and then proceed by writing the orbitals filled after the noble gas. Metal ions of the d-block will have the two electrons removed from the s block prior to any electrons being removed from the proceeding d-block.

Solutions:

1. Ti

Titanium has an atomic number of 22, meaning it has 22 electrons. The noble gas prior to Titanium is Argon. Looking at row 4 of the periodic table, Titanium still has 4 electrons to be placed in orbitals since Argon has 18 electrons that are already placed. The remaining electrons will fill the $4s$ orbital and the remaining two electrons will go into the $3d$ orbital. [Ar]$4s^2 3d^2$

2. Ti^{+2}

This is an ion with a plus 2 charge, meaning 2 electrons have been removed. The electrons will be removed from the $4s$ orbital and the 2 remaining electrons will be placed in the $3d$ orbital. Like number 1, the prior noble gas is Argon. [Ar]$3d^2$

3. Ti^{+3}

This is an ion with a plus 3 charge, meaning 3 electrons have been removed. The first 2 electrons will be removed from the $4s$ orbital, and the third will be taken from the $3d$ orbital, and the 1 remaining electron will be placed in the 3d orbital. Like number 1, the prior noble gas is Argon. [Ar]$3d^1$

4. Ti^{+4}

This is an ion with a plus 4 charge, meaning 4 electrons have been removed. The first 2 electrons will be removed from the $4s$ orbital and the second 2 will be removed from the $3d$ orbital. This results in the ion having the same electron configuration as Argon. [Ar]

Answers:

1. $[Ar]4s^2 3d^2$
2. $[Ar]3d^2$
3. $[Ar]3d^1$
4. $[Ar]$

A19.1.2

a. $[Ar]4s^2 3d^2$
b. $[Ar]3d^2$
c. $[Ar]3d^1$
d. $[Ar]$

Q19.1.3

Write the electron configurations for each of the following elements and its 3+ ions:

a. La
b. Sm
c. Lu

https://chem.libretexts.org/@go/page/429159

S19.1.3

In order to write the electron configuration, we begin by finding the element on the periodic table. Since La, Sm, and Lu are all a period below the noble gas Xenon, we can abbreviate $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$as [Xe] when writing the orbital configurations. We then find the remaining of the orbital configurations using the Aufbau Principle. For other elements not just those in period 6, the shorthand notation using noble gases would be the noble gas in the period above the given element.

1. La has three additional electrons. Two of them fill the 6s shell and the other single electron is placed on the 5d shell.

La : [Xe] $6s^2 5d^1$

2. Sm has eight more electrons. The 6s orbital is filled as previously and the 4f orbital receives 6 electrons because pairing electrons requires lower energy on the 4f shell than on the 5d shell.

Sm : [Xe] $6s^2 4f^6$

3. Lu has seventeen more electrons. Two electrons fill the 6s orbital, 14 electrons fill the 4f orbital, and extra single electron goes to the 5d orbital .

Lu : [Xe] $6s^2 4f^{14} 5d^1$

To find the 3+ ion electron configuration, we remove 3 electrons from the neutral configuration, starting with the 6s orbital.

1. The ionization of La^{3+} removes the three extra electrons. So it reverts back to the stable Xenon configuration.

La^{3+} : [Xe]

2. The ionization of Sm^{3+} removes two electrons from the 6s shell and one from the outermost (4f) shell

Sm^{3+} : [Xe] $4f^5$

3. The ionization of Lu^{3+} removes its two 6s shell and one from the outermost (5d) shell, leaving only a full 4f shell

Lu^{3+} : [Xe] $4f^{14}$

A19.1.3

La: [Xe]6s ^{2}5d ^{1}, La^{3+}: [Xe]; Sm: [Xe]6s ^{2}4f ^{6}, Sm^{3+}: [Xe]4f ^{5}; Lu: [Xe]6s ^{2}4f ^{14}5d ^{1}, Lu^{3+}: [Xe]4f ^{14}

Q19.1.4

Why are the lanthanoid elements not found in nature in their elemental forms?

A19.1.4

Lanthanides are rarely found in their elemental forms because they readily give their electrons to other more electronegative elements, forming compounds instead of staying in a pure elemental form. They have very similar chemical properties with one another, are often found deep within the earth, and difficult to extract. They are the inner transition elements and have partially filled d orbitals that can donate electrons. Because of this, they are very reactive and electropositive.

Q19.1.5

Which of the following elements is most likely to be used to prepare La by the reduction of La_2O_3: Al, C, or Fe? Why?

S19.1.5

An **activity series** is a list of elements in decreasing order of their reactivity. Elements on the top of the list are good **reducing agents** because they easily give up an electron, and elements on the bottom of the series are good **oxidizing agents** because they are highly electronegative would really want to accept an electron.

Step 1: Compare Aluminum, Carbon, and Iron on an activity series. Many activity series include carbon and hydrogen as references. An activity series can be found here

The activity series goes in the order (from top to bottom): Aluminum, Carbon, and Iron.

Step 2: Identify which element is the best reducing agent.

Elements on the top of the list are the best reducing agents, because they give up electrons the best.

Aluminum is the best reducing agent of the options available.

Therefore aluminum will be the best reducing agent to prepare La by the reduction of La_2O_3 because it is the most reactive in the series amongst the three elements.

A19.1.5

Al is used because it is the strongest reducing agent and the only option listed that can provide sufficient driving force to convert La(III) into La.

Q19.1.6

Which of the following is the strongest oxidizing agent: VO_4^{3-}, CrO_4^{2-}, or MnO_4^-?

S19.1.6

Oxidizing agents oxidize other substances. In other words, they gain electrons or become reduced. These agents should be in their highest oxidation state. In order to determine, the strength of the compounds above as oxidizing agents, determine the oxidation numbers of each constituent elements.

VO_4^{3-}

We know that O has a -2 oxidation state and the overall charge of the ion is -3. We just need to determine Vanadate's oxidation number in this compound.

$V + -2(4) = -3$

$V = +5$

Vanadate has an oxidation number of +5, which is its highest possible oxidation state.

CrO_4^{2-}

Like in the previous calculation, O has a -2 oxidation state. The overall charge is -2. So calculate for chromium.

$Cr + -2(4) = -2$

$Cr = +6$

Chromium is in its highest possible oxidation state of +6 in this compound.

MnO_4^-

O has a -2 oxidation state and the overall charge is -1.

$Mn + -2(4) = -1$

$Mn = +7$

Manganese is also in its highest oxidation state, +7.

An oxidizing agent has to be able to gain electrons which, in turn, reduces its oxidation state. Here manganese has the greatest oxidation state which allows it to experience a greater decrease in its oxidation state if needed, meaning it can gain the most electrons. So among the three compounds, MnO_4^- is the strongest oxidizing agent. This method assumes the metals have similar electronegativities.

Alternatively, check a redox table.

A19.1.6

MnO_4^-

Q19.1.7

Which of the following elements is most likely to form an oxide with the formula MO_3: Zr, Nb, or Mo?

S19.1.7

Mo because Zr has an oxidation state of +4 and Nb has a oxidation state of +5 and those would not balance out the charge of 3 oxygens in the state of -2 which creates a charge of -6. Mo however has multiple oxidation states, the most common being +6 which balances out the -6 charge created by 3 oxygen ions. This is why its most likely to form an oxide with the formula MO_3 or MoO_3.

A19.1.7

Mo

Q19.1.8

The following reactions all occur in a blast furnace. Which of these are redox reactions?

a. $3\,Fe_2O_3(s) + CO(g) \longrightarrow 2\,Fe_3O_4(s) + CO_2(g)$

https://chem.libretexts.org/@go/page/429159

b. $Fe_3O_4(s) + CO(g) \longrightarrow 3\,FeO(s) + CO_2(g)$
c. $FeO(s) + CO(g) \longrightarrow Fe(l) + CO_2(g)$
d. $C(s) + O_2(g) \longrightarrow CO_2(g)$
e. $C(s) + CO_2(g) \longrightarrow 2\,CO(g)$
f. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
g. $CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$

S19.1.8

o identify redox reaction, we have to determine if have to see if the equation is an oxidation-reduction reaction-meaning that the species are changing oxidation states during the reaction, which involves the transfer of electrons between two species. If a species is losing electrons, then that species is being oxidized. If a species is gaining electrons, then that species is being reduced. A way to remember this is using the acronyms OIL RIG. **O**xidation **I**s **L**oss, and **R**eduction **I**s **G**ain, referring to electrons. Both of these must occur for an equation to be a redox reaction. Let's see if these equations are redox reactions or not:

a. In the reactants side Fe_2O_3, Fe is has an oxidation number of +3. In the product Fe_3O_4, Fe has an oxidation number of +2.67. Since Fe changed from +3 to +2.67, we can say that Fe had gained electrons and therefore reduced. In the reactant, CO, carbon has an oxidation number of +2, and in CO_2 (product) carbon has an oxidation number of +4. Therefore, carbon has lost electrons and it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

b. In the reactant, Fe_3O_4, Fe has an oxidation number of +2.67. In the product, FeO, Fe has an oxidation number of +2. Since the oxidation of Fe has changed from +2.67 to +2, electrons have been added therefore Fe has been reduced. In the reactant, CO, carbon has an oxidation number of +2, and in CO_2 (product) carbon has an oxidation number of +4. Therefore, carbon has lost electrons and it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

c. In the reactant side, in FeO, Fe has an oxidation number of +2 and in the products side Fe has an oxidation number of 0. Since the oxidation number of Fe changed from +2 to 0, electrons have been gained and therefore Fe has been reduced. In the reactant, CO, carbon has an oxidation number of +2, and in CO_2 (product) carbon has an oxidation number of +4. Therefore, carbon has lost electrons and it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

d. In the reactants C has an oxidation number of 0, and in the products side in CO_2, C has an oxidation number of +4. Since the oxidation number of C has changed from 0 to +4, we can say that C has been oxidized. In the reactants, in O_2 oxygen has an oxidation number of 0, and in the products CO2, oxygen has an oxidation number of -2. Since the oxidation number of oxygen has changed from 0 to -2, oxygen has been reduced. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

e. In the reactants CO_2 has an oxidation number of +4, and in the products side in CO, C has an oxidation number of +2. Since carbon went from +4 to +2, carbon has been reduced. In the reactants, in CO_2 oxygen has an oxidation number of -4 and in the products CO carbon has an oxidation number of -2. Since oxygen went from -4 to -2, it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

f. In the reactants, $CaCO_3$ Ca has an oxidation number of +2, and in products CaO Ca has an oxidation number of +2. Since the oxidization number doesn't change- we can conclude that this equation **is not a redox reaction.**

g. In the products CaO Ca has an oxidation number of +2, and in the products $CaSiO_3$ Ca has an oxidation number of +2. Since the oxidization number doesn't change- we can conclude that this equation **is not a redox reaction.**

A19.1.8

a, b, c, d, e

Q19.1.9

Why is the formation of slag useful during the smelting of iron?

S19.1.9

Slag is a substance formed as a byproduct of iron ore or iron pellets melting together in a blast furnace. Slag is also the byproduct that is formed when a desired metal has been separated from its raw ore. It is important to note that slag from steel mills is created in a manner that reduces the loss of the desired iron ore. The $CaSiO_3$ slag is less dense than the molten iron, so it can easily be separated. Also, the floating slag layer creates a barrier that prevents the molten iron from exposure to O_2, which would oxidize the Fe back to Fe_2O_3. Since Fe has a low reduction potential of -0.440 this means it has a high oxidation potential so it would easily oxidize in the presence of O2. Creating a barrier between iron and oxygen allows the maximum product of iron to be obtained in the end of smelting.

A19.1.9

The $CaSiO_3$ slag is less dense than the molten iron, so it can easily be separated. Also, the floating slag layer creates a barrier that prevents the molten iron from exposure to O_2, which would oxidize the Fe back to Fe_2O_3.

Q19.1.10

Would you expect an aqueous manganese(VII) oxide solution to have a pH greater or less than 7.0? Justify your answer.

S19.1.10

Manganese(VII) oxide, can be written as Mn_2O_7.

In relation to the Lewis acid-base theory, a Lewis acid accepts lone pair electrons, and is also known as the electron pair acceptor. Based on this theory, acidity can be measured by the element's ability to accept electron pairs. By doing the math, we find that Manganese has an oxidation state of +7 (Oxygen has an oxidation state of -2, and 2x-7=-14 **or this can be shown as $-7(2)+2(x)=0$ and $x=7$ since the whole compound has a charge of zero**, in order to balance the ion's charge, Mn must be +7). Therefore Mn has high capability of accepting electrons due to its high positive charge. For most metals, as the oxidation number increases, so does its acidity, because of its increased ability to accept electrons.

A19.1.10

In relation to the Lewis acid-base theory, the Lewis acid accepts lone pair electrons; thus, it is also known as the electron pair acceptor. This may be any chemical species. Acids are substances that must be lower than 7. Therefore, oxides of manganese is most likely going to become more acidic in (aq) solutions if the oxidation number increases.

Q19.1.11

Iron(II) can be oxidized to iron(III) by dichromate ion, which is reduced to chromium(III) in acid solution. A 2.5000-g sample of iron ore is dissolved and the iron converted into iron(II). Exactly 19.17 mL of 0.0100 *M* $Na_2Cr_2O_7$ is required in the titration. What percentage of the ore sample was iron?

S19.1.11

To answer this question, we must first identify the net ionic equation from the given half-reactions. We can write the oxidation and reduction half-reactions:

$$\text{oxidation: } \mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} \tag{2.P.1}$$

$$\text{reduction: } \mathrm{Cr_2O_7^{2-}} \rightarrow \mathrm{Cr}^{3+} \tag{2.P.2}$$

We can quickly balance the oxidation half-reaction by adding the appropriate number of electrons to get

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{e}^- \tag{2.P.3}$$

The first step in balancing the reduction half-reaction is to balance elements in the equation other than O and H. In doing so, we get

$$\mathrm{Cr_2O_7^{2-}} \rightarrow 2\ \mathrm{Cr}^{3+} \tag{2.P.4}$$

The second step would be to add enough water molecules to balance the oxygen.

$$\mathrm{Cr_2O_7^{2-}} \rightarrow 2\ \mathrm{Cr}^{3+} + 7\ \mathrm{H_2O} \tag{2.P.5}$$

Next, we add the correct amount of H^+ to balance the hydrogen atoms.

$$\mathrm{Cr_2O_7^{2-}} + 14\ \mathrm{H}^+ \rightarrow 2\ \mathrm{Cr}^{3+} + 7\ \mathrm{H_2O} \tag{2.P.6}$$

Finally, we add enough electrons to balance charge.

$$\mathrm{Cr_2O_7^{2-}} + 14\ \mathrm{H}^+ + 6\ \mathrm{e}^- \rightarrow 2\ \mathrm{Cr}^{3+} + 7\ \mathrm{H_2O} \tag{2.P.7}$$

The electrons involved in both half-reactions must be equal in order for us to combine the two to get the net ionic equation. This can be done by multiplying each equation by the appropriate coefficient. Scaling the oxidation half-reaction by 6, we get

$$6\ \mathrm{Fe}^{2+} \rightarrow 6\ \mathrm{Fe}^{3+} + 6\ \mathrm{e}^- \tag{2.P.8}$$

Now we can combine both half-reactions to get

$$6\ \mathrm{Fe}^{2+} + \mathrm{Cr_2O_7^{2-}} + 14\ \mathrm{H}^+ + 6\ \mathrm{e}^- \rightarrow 6\ \mathrm{Fe}^{3+} + 6\ \mathrm{e}^- + 2\ \mathrm{Cr}^{3+} + 7\ \mathrm{H_2O} \tag{2.P.9}$$

The electrons cancel out, so you get:

$$6\ \mathrm{Fe}^{2+} + \mathrm{Cr_2O_7^{2-}} + 14\ \mathrm{H}^+ \rightarrow 6\ \mathrm{Fe}^{3+} + 2\ \mathrm{Cr}^{3+} + 7\ \mathrm{H_2O} \tag{2.P.10}$$

From this we can see that the mole ratio of $Cr_2O_7^{2-}$ to Fe^{2+} is 1:6. Given that 19.17 mL (or 0.01917 L) of 0.01 M $Na_2Cr_2O_7$ was needed for titration we know that

$$0.01917\ \mathrm{L} \times 0.01\ \mathrm{M} = 1.917 \times 10^{-4}\ \mathrm{mol} \tag{2.P.11}$$

of $Na_2Cr_2O_7$ reacted. Also, since any number of moles of $Na_2Cr_2O_7$ produces the same number of moles of $Cr_2O_7^{2-}$ in solution

$$1.917 \times 10^{-4}\ \mathrm{mol\ of\ Na_2Cr_2O_7} = 1.917 \times 10^{-4}\ \mathrm{mol\ of\ Cr_2O_7^{2-}} \tag{2.P.12}$$

We can use the mole ratio of $Cr_2O_7^{2-}$ to Fe^{2+} to determine how many moles of iron (ii) was in the solution. The number of moles of iron (ii) is the same as the number of moles of pure iron in the sample since all of the iron was converted into iron (ii).

$$1.917 \times 10^{-4}\ \mathrm{mol\ of\ Cr_2O_7^{2-}} \times \frac{6\ \mathrm{mol\ of\ Fe}^{2+}}{1\ \mathrm{mol\ of\ Cr_2O_7^{2-}}} = 0.0011502\ \mathrm{mol\ of\ Fe}^{2+} \tag{2.P.13}$$

$$0.0011502\ \mathrm{mol\ of\ Fe}^{2+} = 0.0011502\ \mathrm{mol\ of\ Fe} \tag{2.P.14}$$

Now we can find the number of grams of iron that were present in the 2.5 g iron ore sample.

$$0.0011502\ \mathrm{mol\ of\ Fe} \times \frac{55.847\ \mathrm{g}}{1\ \mathrm{mol}} = 0.0642352194\ \mathrm{g\ of\ Fe} \tag{2.P.15}$$

Finally, we can answer the question and find what percentage of the ore sample was iron.

$$\frac{0.0642352194\ \mathrm{g}}{2.5\ \mathrm{g}} \times 100 \approx 2.57\% \tag{2.P.16}$$

So 2.57% of the ore sample was iron.

A19.1.11

2.57%

Q19.1.12

How many cubic feet of air at a pressure of 760 torr and 0 °C is required per ton of Fe_2O_3 to convert that Fe_2O_3 into iron in a blast furnace? For this exercise, assume air is 19% oxygen by volume.

S19.1.12

This question uses a series of unit conversions and the $PV = nRT$ equation.

The first step is to write out the balanced chemical equation for the conversion of Fe_2O_3 to pure iron.

$$2\ Fe_2O_3(s) \rightarrow 4\ Fe(s) + 3\ O_2(g) \tag{2.P.17}$$

Next, we need to analyze the original question to determine the value that we need to solve for. Because the question asks for a value of cubic feet, we know we need to solve for volume. We can manipulate $PV = nRT$ to solve for volume.

$$V = nRT/P \tag{2.P.18}$$

Now determine the known variables and convert into units that will be easy to deal with.

$$n = 2000\ lbs\ Fe_2O_3 \frac{453.592\ grams\ Fe_2O_3}{1\ lb\ Fe_2O_3} \frac{1\ mole\ Fe_2O_3}{159.69\ grams\ Fe_2O_3} \frac{3\ moles\ O_2}{2\ moles\ Fe_2O_3} \tag{2.P.19}$$

$$n = 8521\ moles\ of\ O_2 \tag{2.P.20}$$

Convert to atm for easier calculations

$$R = \frac{.0821\ L\ atm}{mol\ K} \tag{2.P.21}$$

$$T = 0^\circ C = 273\ K \tag{2.P.22}$$

$$P = 760\ torr = 1\ atm \tag{2.P.23}$$

Now plug the numbers into the manipulated gas law to get to an answer for V.

$$V = 190991.8\ liters\ of\ O_2 \tag{2.P.24}$$

From here we convert liters to cubic feet.

use the conversion

$$1\ L = .0353 ft^3 \tag{2.P.25}$$

thus we have 6744.811 ft^3 of O_2

We then refer back to the initial question and remember that this value is only 19% of the volume of the total air. So use a simple equation to determine the total volume of air in cubic feet.

$$6744.811 ft^3 = .19x \tag{2.P.26}$$

x=35499 ft^3 of air

A19.1.12

35499 ft^3 of air

Q19.1.13

Find the potentials of the following electrochemical cell:

Cd | Cd^{2+} (M = 0.10) ‖ Ni^{2+} (M = 0.50) | Ni

S19.1.13

Step 1 Write out your two half reactions and identify which is oxidation and which is reduction using the acronym OIL RIG to remember that oxidation is loss of electrons and reduction is gain of electrons

$Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^-$ (oxidation)

$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ (reduction)

Step 2 Write out complete balanced equation

$Cd(s) + Ni^{2+}(aq) \longrightarrow Cd^{2+}(aq) + Ni(s)$

Step 3 Find E^o_{cell}

$E^o_{cell} = E_{cathode} - E_{anode}$

oxidation: $Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^-$ E^o=-0.40V

reduction: $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ E^o=-0.26V

* E values come from standard reduction potentials table given above. Also, remember anode is where oxidation happens, and cathode is where reduction happens.

E^ocell=-0.26-(-.40)

E^o_{cell}=0.14V

Step 4 Find Q

Q=[products]/[reactants] (look at complete balanced equation) (remember that [x] means the concentration of x typically given in molarity and that we ignore solids or liquids)

$Q = [Cd^{2+}]/[Ni^{2+}]$

Q=0.10/0.50

Q=0.2

Step 5 Calculate E using E= E^{o}_{cell}-(.0592/n)logQ (n is number of moles of electrons transferred and in our case the balanced reaction transfers 2 electrons)

E= 0.14-(.0592/2)log(0.2)

E= 0.14-(-.207)

E=0.16 V

A19.1.13

0.16 V

Q19.1.14

A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

S19.1.14

A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

Assuming that metal chloride is XCl

The balance equation for the reaction would be:

$$XCl(aq) + AgNO_3(aq) \rightarrow XNO_3(aq) + AgCl(s) \tag{2.P.27}$$

The mass of AgCl = 3.03707g

To find the moles of AgCl present:

Next, we can determine the moles of AgCl present in the reaction since 1) the mass of the precipitate is given to us and 2) this value can help us determine the moles of alkali metal chloride compound present. Given the mass of AgCl is 3.03707g in the problem and the molecular mass of AgCl per mole is 143.32g, we can solve for how many moles of AgCl is in the reaction:

$$molesof\,Agcl = \frac{3.03707g}{143.32g/mol} = 0.0211mol \tag{2.P.28}$$

Since the molar ratio of the compounds are 1:1 so the number of moles of XCl used = 0.0211 mol

We can calculate the weight of Cl^- with the equation:

$$0.0211mol \times 35.5g/mol = 0.7490g \tag{2.P.29}$$

the amount of metal present in the original compound is the weight of the compound subtracted by weight of the Cl ion:

$$(2.5624 - 0.7490)g = 1.8134g \tag{2.P.30}$$

And the percentage can be calculate by

$$\frac{0.7490}{2.5624} \times 100 = 29.23\% \tag{2.P.31}$$

the molar ratio of XCl is 1:1 so then

Atomic mass of metal = $= \frac{1.8134\ g\ metal}{0.0211\ mol\ RbCl} = 85.943g/mol$

So the atomic mass is 85.943 g/mol which is of Rb hence the identity of the salt is RbCl

Q19.1.15

The standard reduction potential for the reaction $[Co(H_2O)_6]^{3+}(aq) + e^- \longrightarrow [Co(H_2O)_6]^{2+}(aq)$ is about 1.8 V. The reduction potential for the reaction $[Co(NH_3)_6]^{3+}(aq) + e^- \longrightarrow [Co(NH_3)_6]^{2+}(aq)$ is +0.1 V. Calculate the cell potentials to show whether the complex ions, $[Co(H_2O)_6]^{2+}$ and/or $[Co(NH_3)_6]^{2+}$, can be oxidized to the corresponding cobalt(III) complex by oxygen.

S19.1.15

To calculate the cell potential, we need to know the potentials for each half reaction. After doing so, we need to determine which one is being oxidized and which one is being reduced. The one that is oxidized is the anode and the one that is reduced is the cathode. To find the cell potential, you use this formula and the reduction potential values found in a reduction potential table. If $E°_{cell}$ is positive, ΔG is negative and the reaction is spontaneous.

$E°_{cell}$= E°cathode - E°anode

Because it states that $[Co(H_2O)_6]^{3+}$ will be oxidized, this means it is the anode.

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$ +1.229 V

O_2 is being reduced, so it is the cathode.

1.229V - 1.8V= -.571 V, or -0.6 V using significant figures. This cannot happen spontaneously because $E°_{cell}$ is negative.

For $[Co(NH_3)_6]^{3+}$, it is again being oxidized, meaning it's the anode.

1.229-.1= 1.129 V or 1.1 V using significant figures. This reaction is spontaneous because $E°_{cell}$ is positive.

A19.1.15

a) $E°$ = −0.6 V, $E°$ is negative so this reduction is not spontaneous.

b) $E°$ = +1.1 V, $E°$ is positive so this reduction is spontaneous.

Q19.1.16

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

a. $\mathrm{MnCO_3}(s) + \mathrm{HI}(aq) \longrightarrow$
b. $\mathrm{CoO}(s) + \mathrm{O_2}(g) \longrightarrow$
c. $\mathrm{La}(s) + \mathrm{O_2}(g) \longrightarrow$
d. $\mathrm{V}(s) + \mathrm{VCl_4}(s) \longrightarrow$
e. $\mathrm{Co}(s) + xs\mathrm{F_2}(g) \longrightarrow$
f. $\mathrm{CrO_3}(s) + \mathrm{CsOH}(aq) \longrightarrow$

S19.1.16

There is a myriad of reactions that can occur, which include: single replacement, double replacement, combustion, acid-base/neutralization, decomposition or synthesis. The first step to determine the products of a reaction is to identify the type of reaction. From then on, the next steps you take to predict the products will vary based on the reaction type.

1. This reaction is a **double displacement reaction**, in which the cations and anions of the reactants switch places to form new compounds. Writing out the equation in terms of it's aqueous ions will help you visualize what exactly is getting moved around:

$$2H^+(aq) + 2I^-(aq) \rightarrow 2H^+(aq) + CO_3^{2-}(aq) + Mn^{2+}(aq) + 2I^-(aq) \tag{2.P.32}$$

   In this case, the hydrogen cations will recombine with carbonate anions whilst manganese cations will recombine with iodide anions giving us the following equation:

$$\mathrm{MnCO_3}(s) + 2\,\mathrm{HI}(aq) \longrightarrow \mathrm{MnI_2}(aq) + \mathrm{H_2CO_3}(aq) \tag{2.P.33}$$

   This is still not the final answer however, as carbonic acid is unstable and decomposes to carbon dioxide and water under standard conditions. Taking this into account, our final equation is:

$$\mathrm{MnCO_3}(s) + 2\,\mathrm{HI}(aq) \longrightarrow \mathrm{MnI_2}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \tag{2.P.34}$$

2. This reaction is a **synthesis reaction**, in which two or more reactants combine to form a more complex compound. In this case we are also reacting a metal oxide with oxygen which would result in another metal oxide as the product. The resulting product would be the mixed valence oxide Co_3O_4 in which one cobalt atom has a +2 oxidation state whilst the other two have a +3 oxidation state. Now all is left is to balance the equation:

$$6\,\mathrm{CoO}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Co_3O_4}(s) \tag{2.P.35}$$

3. Like equation 2, this reaction is also a **synthesis reaction** involving a metal and oxygen which should result in the formation of a metal oxide. It is a matter now of balancing the oxidation states to attain a neutral compound. Oxygen will always hold a -2 oxidation state in compounds whilst lanthanum will always exhibit a +3 oxidation state. As such, a combination of 2 lanthanum atoms with a +3 oxidation state and 3 oxygen atoms with a -2 oxidation state will give us a molecule with an overall charge of 0 (3(-2)+2(+3)=0). We know our product now, La_2O_3, and now just need to balance the overall equation, giving us:

$$4\,\mathrm{La}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{La_2O_3}(s) \tag{2.P.36}$$

4. This reaction is slightly harder to define as it encapsulates both the properties of synthesis and decomposition reactions, wherein vanadium reacts with vanadium tetrachloride to produce vanadium trichloride. This reaction however is primarily a **synthesis reaction** since we are combining two reactants to produce one complex compound. With vanadium trichloride as our product, we can balance the equation:

$$\mathrm{V}(s) + 3\,\mathrm{VCl_4}(s) \longrightarrow 4\,\mathrm{VCl_3}(s) \tag{2.P.37}$$

5. This is another **synthesis reaction** combining cobalt and fluorine. This equation includes the "xs" notation in front of fluorine which is short for 'excess', meaning more fluorine than actually required is present in the reactants, ensuring the reaction goes to completion. Finding the products if a simple matter of combining the cobalt and fluorine into one molecule, which already leaves us with a balanced equation:

$$\mathrm{Co}(s) + xs\mathrm{F_2}(g) \longrightarrow \mathrm{CoF_2}(s) \tag{2.P.38}$$

6. It may not be obvious here, but the reaction we've been given here is actually an **acid-base/neutralization reaction**, with chromium trioxide acting as the acid and cesium hydroxide as the base. Chromium trioxide is referred to as an acidic oxide which means that it will react with water to form an acid. Note that this reaction can still proceed even if the reactants aren't in the same phases. The basic rule for acid-base/neutralization reactions is they form a salt (salt being the general term for any ionic compound formed from acid-base reactions) and water. Since we know water is one of our products, our other product must be a salt composed of cesium, chromium and oxygen. Thus, our other product should be cesium chromate, and you can now balance the equation accordingly:

$$\mathrm{CrO_3}(s) + 2\,\mathrm{CsOH}(aq) \longrightarrow \mathrm{Cs_2CrO_4}(aq) + \mathrm{H_2O} \tag{2.P.39}$$

A19.1.16

1. $\mathrm{MnCO_3}(s) + 2\,\mathrm{HI}(aq) \longrightarrow \mathrm{MnI_2}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$
2. $6\,\mathrm{CoO}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Co_3O_4}(s)$
3. $4\,\mathrm{La}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{La_2O_3}(s)$
4. $\mathrm{V}(s) + 3\,\mathrm{VCl_4}(s) \longrightarrow 4\,\mathrm{VCl_3}(s)$
5. $\mathrm{Co}(s) + xs\mathrm{F_2}(g) \longrightarrow \mathrm{CoF_2}(s)$
6. $\mathrm{CrO_3}(s) + 2\,\mathrm{CsOH}(aq) \longrightarrow \mathrm{Cs_2CrO_4}(aq) + \mathrm{H_2O}$

Q19.1.17

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

a. $\mathrm{Fe}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow$
b. $\mathrm{FeCl_3}(aq) + \mathrm{NaOH}(aq) \longrightarrow$
c. $\mathrm{Mn(OH)_2}(s) + \mathrm{HBr}(aq) \longrightarrow$
d. $\mathrm{Cr}(s) + \mathrm{O_2}(g) \longrightarrow$
e. $\mathrm{Mn_2O_3}(s) + \mathrm{HCl}(aq) \longrightarrow$
f. $\mathrm{Ti}(s) + xs\mathrm{F_2}(g) \longrightarrow$

S19.1.17

Predict the products of each of the following reactions.

- Fe(s)+H_2SO_4(aq)⟶ ?

  Whenever a metal reacts with an acid, the products are salt and hydrogen. Because Fe is lower on the activity series, we know that when it reacts with an acid it will result in the formation of Hydrogen gas. To simplify the equation is:

  $$Metal + Acid \longrightarrow Salt + Hydrogen \tag{2.P.40}$$

  The salt produced will depend on the metal and in this case, the metal is iron (Fe) so the resulting equation would be:

  $$\mathrm{Fe}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{FeSO_4}(aq) + \mathrm{H_2}(g) \tag{2.P.41}$$

This equation works out as the H2 is removed from H_2SO_2, resulting in a SO_4^{2-} ion where Fe will take on an oxidation state of Fe^{+2} to form $FeSO_4$ which will be the salt in this example.

But since $FeSO_4$ and $H2SO_4$ are aqueous, the reactants and products can also be written as its ions where the overall equation can be:

$$\mathrm{Fe}(s) + 2\,\mathrm{H_3O^+}(aq) + \mathrm{SO_2^{-4}}(aq) \longrightarrow \mathrm{Fe_2^+}(aq) + \mathrm{SO_2^{-4}}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(l) \tag{2.P.42}$$

- $FeCl_3$(aq)+NaOH(aq)⟶ ?

  In this case, adding a metal hydroxide (NaOH) to a solution with a transition metal ion (Fe) will form a transition metal hydroxide (XOH). As iron is bonded to three chlorine atoms in the reactants side, it has the oxidation state of +3 where three hydroxide ions (OH^-) are needed to balance out the charges when they are bonded in the products. The remaining ions are Na^+ and Cl^- where they bond together in a 1:1 ratio where there are 3 molecules of NaCl once the reaction is balanced.

  The overall reaction will be:

$$\mathrm{FeCl_3}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{Fe(OH)_3}(s) + 3\,\mathrm{NaCl}(aq) \tag{2.P.43}$$

  NOTE: $Fe(OH)_3$(s) is a solid as it is a rule that all all transition metal hydroxides are insoluble and a precipitate is formed.

  Since NaOH(aq) and NaCl(aq) are aqueous, we can write them out in their ion forms:

$$\mathrm{FeCl_3}(aq) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{OH^-}(aq) + \mathrm{Fe(OH)_3}(s) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{Cl^+}(aq) \tag{2.P.44}$$

- Mn(OH)2(s)+HBr(aq)⟶ ?

  This is an example of a metal hydroxide reacting with an acid where a metal salt and water will always be formed:

$$Metal Hydroxide + Acid \longrightarrow Metal Salt + Water \tag{2.P.45}$$

  When this rule is applied to this equation, we will get the following:

$$\mathrm{Mn(OH)_2}(s) + \mathrm{HBr}(aq) \longrightarrow \mathrm{MnBr_2}(aq) + 2\,\mathrm{H_2O}(l) \tag{2.P.46}$$

  But to follow through with this question, the aqueous solutions such as HBr(aq) and $MnBr_2$(aq) can be re-written as:

$$\mathrm{Mn(OH)_2}(s) + 2\,\mathrm{H_3O^+}(aq) + 2\,\mathrm{Br^-}(aq) \longrightarrow \mathrm{Mn_2^+}(aq) + 2\,\mathrm{Br^-}(aq) + 4\,\mathrm{H_2O}(l) \tag{2.P.47}$$

- Cr(s)+O_2(g)⟶ ?

  This is the general reaction of a metal reacting with oxygen which will always result in a metal oxide. However, the metal oxide is determined by the oxidation state of the metal so there may be several outcomes of this reaction such as:

$$4\,\mathrm{Cr}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Cr_2O_3}(s) \tag{2.P.48}$$

$$\mathrm{Cr}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CrO}(s) \tag{2.P.49}$$

$$\mathrm{Cr}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CrO_2}(s) \tag{2.P.50}$$

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{CrO_3}(s) \tag{2.P.51}$$

  However, Cr_2O_3 is the main oxide of chromium so it can be assumed that this is the general product of this reaction.

- Mn_2O_3(s)+HCl(aq)⟶?

  This follows the general reaction of a metal oxide and an acid will always result in a salt and water

$$Metal Oxide + Acid \longrightarrow Salt + Water \tag{2.P.52}$$

  Using this general reaction, similar to the general reactions above, the reaction will result in:

$$\mathrm{Mn_2O_3}(s) + \mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{MnCl_3}(s) + 9\,\mathrm{H_2O}(l) \tag{2.P.53}$$

  However, since HCl is an aqueous solution, the overall equation can also be re-written as:

$$\mathrm{Mn_2O_3}(s) + 6\,\mathrm{H_3O^+}(aq) + 6\,\mathrm{Cl^-}(aq) \longrightarrow 2\,\mathrm{MnCl_3}(s) + 9\,\mathrm{H_2O}(l) \tag{2.P.54}$$

- Ti(s)+xsF_2(g)⟶?

  Titanium is able to react with the halogens where there are two oxidation state that titanium can be: +3 and +4. The following reactions follow each oxidation state accordingly:

$$2\,\mathrm{Ti}(s) + 3\,\mathrm{F_2}(g) \longrightarrow 2\,\mathrm{TiF_3}(s) \tag{2.P.55}$$

$$\mathrm{Ti}(s)+2\,\mathrm{F}_2(g)\longrightarrow \mathrm{TiF}_4(s) \tag{2.P.56}$$

However, since there is the symbol "xs", this indicates that F_2 is added in excess so the second reaction is favored more as it drives the reaction to completion.

OVERALL:

\[\ce{Ti}(s)+\ce{xsF2}(g)⟶\ce{TiF4}(g)\]

A19.1.17

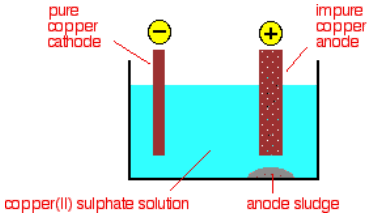
a. $\mathrm{Fe}(s)+2\,\mathrm{H_3O^+}(aq)+\mathrm{SO_4^{2-}}(aq)\longrightarrow \mathrm{Fe^{2+}}(aq)+\mathrm{SO_4^{2-}}(aq)+\mathrm{H_2}(g)+2\,\mathrm{H_2O}(l)$;
b. $\mathrm{FeCl_3}(aq)+3\,\mathrm{Na^+}(aq)+3\,\mathrm{OH^-}(aq)+\mathrm{Fe(OH)_3}(s)+3\,\mathrm{Na^+}(aq)+3\,\mathrm{Cl^+}(aq)$;
c. $\mathrm{Mn(OH)_2}(s)+2\,\mathrm{H_3O^+}(aq)+2\,\mathrm{Br^-}(aq)\longrightarrow \mathrm{Mn^{2+}}(aq)+2\,\mathrm{Br^-}(aq)+4\,\mathrm{H_2O}(l)$;
d. $4\,\mathrm{Cr}(s)+3\,\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{Cr_2O_3}(s)$;
e. $\mathrm{Mn_2O_3}(s)+6\,\mathrm{H_3O^+}(aq)+6\,\mathrm{Cl^-}(aq)\longrightarrow 2\,\mathrm{MnCl_3}(s)+9\,\mathrm{H_2O}(l)$;
f. $\mathrm{Ti}(s)+xs\mathrm{F_2}(g)\longrightarrow \mathrm{TiF_4}(g)$

Q19.1.18

Describe the electrolytic process for refining copper.

S19.1.18

By electrolysis, copper can be refined and purely made. The reason why copper needs to remove the impurities is because it helps increase the electrical conductivity in electrical wire. You can refine copper and remove the impurities through electrolysis. Pure copper is important in making electrical wire, because it creates better electrical conductivity when transferring electricity. In order for better electrical conductivity, the impurities needs to be removed and this can be done by firing the impure copper to remove the impurities, such as sulfur, oxygen, etc. and shaping them into electrical anodes that can be used in electrolysis. Then the copper electrodes are placed into an electrical cell (into separate beakers) where electrical current can pass through the beakers and onto the electrodes. Through this process, the copper is stripped off of the anode and deposited onto the cathode. This process helps remove the impurities and refine copper because all the copper has been deposited onto the cathode all in one electrode. This process increases the weight of the cathode due to copper being deposited onto the cathode. This is a prime example of how to tell if an electrode is a cathode or an anode, as stated in Q17.2.9 above.



Q19.1.19

Predict the products of the following reactions and balance the equations.

a. Zn is added to a solution of $Cr_2(SO_4)_3$ in acid.
b. $FeCl_2$ is added to a solution containing an excess of $\mathrm{Cr_2O_7^{2-}}$ in hydrochloric acid.
c. Cr^{2+} is added to $\mathrm{Cr_2O_7^{2-}}$ in acid solution.
d. Mn is heated with CrO_3.
e. CrO is added to $2HNO_3$ in water.
f. $FeCl_3$ is added to an aqueous solution of NaOH.

S19.1.19

1. Zn is added to a solution of $Cr_2(SO_4)_3$ in acid.
   - Oxidized half-reaction: $3Zn(s)\rightarrow 3Zn^{2+}(aq)+6e^-$
   - Reduction half reaction:
   - Overall reaction:
   - Chromium will precipitate out of the solution because it has a higher reduction potential than Zinc; the reaction is a single replacement.
2. $FeCl_2$ is added to a solution containing an excess of $\mathrm{Cr_2O_7^{2-}}$ in hydrochloric acid.
   - Dissociation reaction: $6FeCl_2(s)\rightarrow 6Fe^{2+}(aq)+12Cl^-(aq)$

https://chem.libretexts.org/@go/page/429159

- Oxidation half-reaction: $6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$
- Reduction half-reaction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- Overall reaction: 
- The reduction potential for permanganate is larger so the reaction is still favorable even when the oxidation of Fe^{2+} is negative.

3. Cr^{2+} is added to $Cr_2O_7^{2-}$ in acid solution.
   - Reduction half-reaction: 
   - Oxidation half-reaction: 
   - Overall reaction: $6Cr^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 8Cr^{3+}(aq) + 7H_2O(l)$
   - The reaction is favorable with a high positive E°
4. Mn is heated with CrO_3.
   - Reduction half-reaction: $8CrO_3(aq) + 24H^+ + 24e^- \rightarrow 4Cr_2O_3(aq) + 12H_2O(l)$
   - Oxidation half-reaction: $9Mn(s) + 12H_2O(l) \rightarrow 3Mn_3O_4(aq) + 24H^+(aq) + 24e^-$
   - Overall reaction: $8CrO_3(aq) + 9Mn(s) \rightarrow^{\Delta} 4Cr_2O_3(aq) + 3Mn_3O_4(aq)$
   - Heat creates a product with higher energy than both previous reactants.
5. CrO is added to HNO_3 in water.
   - Strong acid dissociation: $2HNO_3(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + 2NO_3^-(aq)$
   - Overall reaction: $2HNO_3(aq) + CrO(aq) \rightarrow Cr^{2+}(aq) + 2NO_3^-(aq) + H_2O(l)$
   - This reaction works by exchange of electrons to yield Chromium ions.
6. $FeCl_3$ is added to an aqueous solution of $NaOH$.
   - Overall reaction: $3NaOH(aq) + FeCl_3(s) \rightarrow 3Na^+(aq) + FeOH_3^-(s) + 3Cl^-(aq)$
   - Iron hydroxide will precipitate because the two metals will exchange anions.

A19.1.19

a. $\mathrm{Cr_2(SO_4)_3}(aq) + 2\ \mathrm{Zn}(s) + 2\ \mathrm{H_3O^+}(aq) \longrightarrow 2\ \mathrm{Zn^{2+}}(aq) + \mathrm{H_2}(g) + 2\ \mathrm{H_2O}(l) + 2\ \mathrm{Cr^{2+}}(aq) + 3\ \mathrm{SO_4^{2-}}(aq)$;
b. $4\ \mathrm{TiCl_3}(s) + \mathrm{CrO_4^{2-}}(aq) + 8\ \mathrm{H^+}(aq) \longrightarrow 4\ \mathrm{Ti^{4+}}(aq) + \mathrm{Cr}(s) + 4\ \mathrm{H_2O}(l) + 12\ \mathrm{Cl^-}(aq)$;
c. In acid solution between pH 2 and pH 6, $\mathrm{CrO_4^{2-}}$ forms $\mathrm{HrCO_4^-}$, which is in equilibrium with dichromate ion. The reaction is $2\ \mathrm{HCrO_4^-}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + \mathrm{H_2O}(l)$. At other acidic pHs, the reaction is $3\ \mathrm{Cr^{2+}}(aq) + \mathrm{CrO_4^{2-}}(aq) + 8\ \mathrm{H_3O^+}(aq) \longrightarrow 4\ \mathrm{Cr^{3+}}(aq) + 12\ \mathrm{H_2O}(l)$;
d. $8\ \mathrm{CrO_3}(s) + 9\ \mathrm{Mn}(s) \xrightarrow{\Delta} 4\ \mathrm{Cr_2O_3}(s) + 3\ \mathrm{Mn_3O_4}(s)$;
e. $\mathrm{CrO}(s) + 2\ \mathrm{H_3O^+}(aq) + 2\ \mathrm{NO_3^-}(aq) \longrightarrow \mathrm{Cr^{2+}}(aq) + 2\ \mathrm{NO_3^-}(aq) + 3\ \mathrm{H_2O}(l)$;
f. $\mathrm{CrCl_3}(s) + 3\ \mathrm{NaOH}(aq) \longrightarrow \mathrm{Cr(OH)_3}(s) + 3\ \mathrm{Na^+}(aq) + 3\ \mathrm{Cl^-}(aq)$

Q19.1.20

What is the gas produced when iron(II) sulfide is treated with a nonoxidizing acid?

S19.1.20

Formula for iron(II) sulfide:

$$FeS \tag{2.P.57}$$

Definition of non-oxidizing acid: A non-oxidizing acid is an acid that doesn't act the oxidizing agent. Its anion is a weaker oxidizing agent than H+, thus it can't be reduced. Examples of non-oxidizing acids:

$$HCl, HI, HBr, H_3PO_4, H_2SO_4 \tag{2.P.58}$$

Step 2: Choose one of the non-oxidizing acid, in this case HCl, and write the chemical reaction:

$$FeS(s) + 2HCl(aq) \rightarrow FeCl_2(s) + H_2S(g) \tag{2.P.59}$$

The gas produced when iron (II) sulfide treated with a non-oxidizing acid, HCl, is H_2S (dihydrogen sulfide) gas.

Q19.1.21

Predict the products of each of the following reactions and then balance the chemical equations.

a. Fe is heated in an atmosphere of steam.
b. NaOH is added to a solution of $Fe(NO_3)_3$.
c. $FeSO_4$ is added to an acidic solution of $KMnO_4$.
d. Fe is added to a dilute solution of H_2SO_4.

e. A solution of $Fe(NO_3)_2$ and HNO_3 is allowed to stand in air.
f. $FeCO_3$ is added to a solution of $HClO_4$.
g. Fe is heated in air.

S19.1.21

a. Steam is water (H_2O)

We can write out the reaction as:

$$Fe + H_2O \rightarrow ?$$

This is a single replacement reaction, so Fe replaces H_2. So, one of the products is Fe_3O_4 since it is a combination of iron(II) oxide, FeO, and iron(III) oxide, Fe_2O_3.

The Fe is heated in an atmosphere of steam. H_2 becomes neutrally charged and becomes another product.

After balancing the coefficients, the final reaction is:

$$3\,Fe(s) + 4\,H_2O(g) \rightarrow Fe_3O_4(s) + 4\,H_2(g)$$

b. $NaOH$ added to a solution of $Fe(NO_3)_3$ is a double replacement and precipitation reaction.

We can write out the reaction as:

$$NaOH + Fe(NO_3)_3 \rightarrow ?$$

The Na and Fe switch to form $Fe(OH)_3(s)$ and $NaNO_3(aq)$.

$Fe(OH)_3$ is solid because it is insoluble according to solubility rules.

After balancing the coefficients in the reaction, the final reaction is:

$$Fe(NO_3)_3(aq) + 3\,NaOH(aq) \rightarrow Fe(OH)_3(s) + NaNO_3(aq)$$

c. For instance, the acid used to make the acidic solution is H_2SO_4, then the reaction is:

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$$

Next, the net ionic reaction has to be written to get rid of the spectator ions in the reaction, this is written as:

$$Fe^{2+} + MnO_4^- + H^+ \rightarrow Fe^{3+} + Mn^{2+} + H_2O$$

As seen in the net ionic equation above, Fe^{2+} is oxidized to Fe^{3+} and MnO_4^- is reduced to Mn^{2+}. These can be written as two half reactions:

$$Fe^{2+} \rightarrow Fe^{3+}$$

$$MnO_4^- \rightarrow Mn^{2+}$$

To balance the oxidation half reaction, one electron as to be added to the Fe^{3+}, this is shown as:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

The reduction half reaction also has to be balanced, but with H^+ ions and H_2O, this is shown as:

$$MnO_4^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$$

After the charge of the Mn atoms are balanced, the overall charge has to be balanced on both sides because on the reactants side, the charge is $7+$, and the charge on the products side is $2+$. The overall charge can be balanced by adding electrons, this is shown as:

$$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$$

Now since both half reactions are balanced, the electrons in both half reactions have to be equal, and then the half reactions are added together. After this is done, the reaction looks like this:

$$MnO_4^- + 8\,H^+ + 5\,Fe^{2+} + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+} + 5\,e^-$$

The $5\,e^-$ on both sides cancel out and the final balanced reaction is:

$$MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \rightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+}$$

d. Fe added to a dilute solution of H_2SO_4 is a single replacement reaction.

The Fe is added to a dilute solution so the H_2SO_4 is written as separate ions.

We can write out the reaction as:

$$Fe(s) + 2\,H^+(aq) + (SO_4)^{2-}(aq) \rightarrow ?$$

The Fe replaces the H^+ ion, and becomes an Fe^{2+} ion.

H_2O is also a product because the solution is dilute.

Furthermore, the $FeSO_4$ also has to be separated into ions as a result of the Fe being added to a dilute solution.

After balancing all of the coefficients, the final reaction is:

$$Fe(s) + (2\,H_3O)^+(aq) + (SO_4)^{2-}(aq) \rightarrow Fe^{2+}(aq) + SO_4^{2-}(aq) + H_2(g) + 2\,H_2O(l)$$

Note: H^+ can also be written as the the hydronium ion, $(H_3O)^+$.

e. We initially can initially write out:

$$4\,Fe(NO_3)_2 + 4\,HNO_3 + O_2 \rightarrow ?$$

We write the oxygen term in the reactants because it is stated that the solution is allowed to stand in air.

We just have to analyze the possible products that can be formed and we can see that the hydrogen from nitric acid can combine with oxygen gas to form water and then combining everything together, we get the final reaction to be:

$$4\,Fe(NO_3)_2(aq) + 4\,HNO_3(aq) + O_2(g) \rightarrow 2\,H_2O(l) + 4\,Fe(NO_3)_3(aq)$$

f. When $FeCO_3$ is added to $HClO_4$, a double replacement reaction occurs.

The Fe^{2+} ion switches spots with the H^+ ion to form $Fe(ClO_4)_2$ as a product.

When the H^+ ion is added to the $(CO_3)^{2-}$ ion, H_2CO_3 is formed.

After balancing the coefficients, the final reaction is:

$$FeCO_3(s) + HClO_4(aq) \rightarrow Fe(ClO_4)_2(aq) + H_2O(l) + CO_2(g)$$

g. Air is composed of oxygen gas, which is a diatomic molecule, so it is O_2.

Adding Fe to O_2 will cause a synthesis reaction to occur forming Fe_2O_3.

After balancing coefficients, the final reaction is:

$$3\,Fe(s) + 2\,O_2(g) \rightarrow Fe_2O_3(s)$$

A19.1.21

a. $3\,Fe(s) + 4\,H_2O(g) \longrightarrow Fe_3O_4(s) + 4\,H_2(g)$;

b. $3\,NaOH(aq) + Fe(NO_3)_3(aq) \xrightarrow{H_2O} Fe(OH)_3(s) + 3\,Na^+(aq) + 3\,NO_3^-(aq)$;

c. $MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \rightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+}$

d. $Fe(s) + (2\,H_3O)^+(aq) + (SO_4)^{2-}(aq) \rightarrow Fe^{2+}(aq) + SO_4^{2-}(aq) + H_2(g) + 2\,H_2O(l)$

e. $4\,Fe(NO_3)_2(aq) + 4\,HNO_3(aq) + O_2(g) \rightarrow 2\,H_2O(l) + 4\,Fe(NO_3)_3(aq)$

f. $FeCO_3(s) + HClO_4(aq) \rightarrow Fe(ClO_4)_2(aq) + H_2O(l) + CO_2(g)$

g. $3\,Fe(s) + 2\,O_2(g) \rightarrow Fe_2O_3(s)$

Q19.1.22

Balance the following equations by oxidation-reduction methods; note that *three* elements change oxidation state.

$$Co(NO_3)_2(s) \longrightarrow Co_2O_3(s) + NO_2(g) + O_2(g) \tag{2.P.60}$$

S19.1.22

Balance the following equations by oxidation-reduction methods; note that three elements change oxidation state.

$$Co(NO_3)_2(s) \longrightarrow Co_2O_3(s) + NO_2(g) + O_2(g) \tag{2.P.61}$$

In this reaction, N changes oxidation states from +5 to +4 (reduced), Co changes oxidation states from +2 to +3 (oxidized), and O changes oxidation states from -2 to 0 (also oxidized).

First, split this reaction into an oxidation and reduction half reaction set, and balance all of the elements that are not hydrogen or oxygen (we will deal with these later):

$$Reduction: 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 \tag{2.P.62}$$

Now, for the oxidation reaction, we are only dealing with O_2 on the products side. In order to balance this, we will need to add water and hydrogen to both sides:

$$Oxidation: 2H_2O \rightarrow O_2 + 4H^+ \tag{2.P.63}$$

Balance the amount of oxygens on each side by adding the correct number of water molecules (H_2O), and balance the amount of hydrogen by adding the correct number of H^+ atoms:

$$Reduction: 2H^+ + 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + H_2O \tag{2.P.64}$$

$$Oxidation: 2H_2O \rightarrow O_2 + 4H^+ \tag{2.P.65}$$

Finally, balance the charges by adding electrons to each side of the equation. For the reduction reaction, we will add 2 electrons to balance out the $2H^+$, and to the oxidation reaction, we will add 4 electrons to balance out the $4H^+$. Remember, the goal of this step is to make sure that the charges are balanced, so we can cancel them out in the end.

$$Reduction: 2e^- + 2H^+ + 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + H_2O \tag{2.P.66}$$

$$Oxidation: 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2.P.67}$$

Multiply the reduction reaction by two, in order to balance the charges so there are 4 electrons on each side of the reaction.

$$Reduction: 2(2e^- + 2H^+ + 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + H_2O) \tag{2.P.68}$$

and combine both reactions which comes out to:

$$2H_2O + 4Co(NO_3)_2 + 4H^+ \rightarrow 2CO_2O_3 + 8NO_2 + 2H_2O + O_2 + 4H^+ \tag{2.P.69}$$

Cancel out like terms:

$$4Co(NO_3)_2(s) \rightarrow 2CO_2O_3(s) + 8NO_2(g) + O_2(g) \tag{2.P.70}$$

Both sides have overall charges of 0 and can be checked to see if they are balanced.

A19.1.22

$$4Co(NO_3)_2(s) \rightarrow 2CO_2O_3(s) + 8NO_2(g) + O_2(g) \tag{2.P.71}$$

Q19.1.23

Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

S19.1.23

Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

A: Step 1: look at the question and begin to write out a general product to reactant formula for this reaction.

Step 2: try to reason out why a precipitate will form but only for a finite period of time before reforming in an aqueous substance.

Step 3: With step 2 you should have noticed that the reaction is a multiple step reaction and using the rough formula that you derived in step 1, you should try and see what the series of steps are that lead to the overall product of liquid $AgCN_2$

In this reaction we see how NaCN is added to $AgNO_3$ .A precipitate forms but then disappears with the addition of even more NaCN, this must mean that its an intermediate reaction which will not appear as the final product. The silver and the cyanide temporarily bond, but the bond is too weak to hold them together so they are pulled apart again when NaCN is added because a new, more stronger and stable compound is formed: $[Ag(CN)_2]^-$ (aq).

The actual reaction equation when it is first taking place is

$$AgCl(aq) + NaCN(aq) \rightarrow AgCN(s) + NaCl(aq) \tag{2.P.72}$$

This can be written out in the following way: as CN^- is added, the silver and the cyanide combine : $Ag^+(aq)+CN^-(aq) \rightarrow AgCN\ (s)$

As more CN^- is added the silver and two cyanide combine to create a more stable compound: $Ag^+(aq)+2CN^-(aq) \rightarrow [Ag(CN)_2]^-$ (aq)

$AgCN(s) + CN^-(aq) \rightarrow [Ag(CN)_2]^-$ (aq)

A19.1.23

As CN^- is added,

$$Ag^+(aq) + CN^-(aq) \longrightarrow AgCN(s) \tag{2.P.73}$$

As more CN^- is added,

$$Ag^+(aq) + 2\,CN^-(aq) \longrightarrow [Ag(CN)_2]^-(aq) \tag{2.P.74}$$

$$AgCN(s) + CN^-(aq) \longrightarrow [Ag(CN)_2]^-(aq) \tag{2.P.75}$$

Q19.1.24

Predict which will be more stable, $[CrO_4]^{2-}$ or $[WO_4]^{2-}$, and explain.

S19.1.24

According to the rules associated with Crystal Field Stabilizing Energies, stable molecules contain more electrons in the lower-energy molecular orbitals than in the high-energy molecular orbitals. In this case, both complexes have O_4 as ligands, and both have a -2 charge. Therefore, you determine stability by comparing the metals. Chromium is in the 3d orbital, according to the periodic table. Tungsten (W) is in the 5d orbital. 3d is a lower energy level than 5d.Higher-level orbitals are more easily ionized, and make their base elemental form more stable. If the elemental form is more stable the oxidized form is less stable. Therefore, $[CrO_4]^{2-}$ is more stable than $[WO_4]^{2-}$.

A19.1.24

$[CrO_4]^{2-}$ is more stable because Chromium is in the 3d orbital while Tungsten is in the 4d orbital, which has a higher energy level and makes it less stable.

Q19.1.25

Give the oxidation state of the metal for each of the following oxides of the first transition series. (Hint: Oxides of formula M_3O_4 are examples of *mixed valence compounds* in which the metal ion is present in more than one oxidation state. It is possible to write these compound formulas in the equivalent format $MO{\cdot}M_2O_3$, to permit estimation of the metal's two oxidation states.)

a. Sc_2O_3
b. TiO_2
c. V_2O_5
d. CrO_3
e. MnO_2
f. Fe_3O_4
g. Co_3O_4
h. NiO
i. Cu_2O

S19.1.25

The first step to solving this problem is looking at the rules of Oxidizing states for various elements:

chem.libretexts.org/Core/Analytical_Chemistry/Electrochemistry/Redox_Chemistry/Oxidation_State

The main rules that will be used in these problems will be the oxidation state rule 6 which states that oxidation state for Oxygen is (-2) and rule 2 which is that the total sum of the oxidation state of all atoms in any given species is equal to the net charge on that species. Solving these problems requires simple algebra. The oxidation states of both elements in the compound is equal to zero, so set the unknown oxidation of the element that is not oxygen to a variable x, and the oxidation state of Oxygen equal to -2. Then multiply both oxygen states by the number of atoms of the element present. Add the values together, set the equation equal to zero and solve for x.

1. $Sc_2O_3 = 3(-2) + 2x = 0 \longrightarrow -6 + 2x = 0 \longrightarrow x = Sc = +3 \quad Sc^{3+}$
2. $TiO_2 = 2(-2) + x = 0 \longrightarrow -4 + x = 0 \longrightarrow x = Ti = +4 \quad Ti^{4+}$
3. $V_2O_5 = 5(-2) + 2x = 0 \longrightarrow -10 + 2x = 0 \longrightarrow x = V = +5 \quad V^{5+}$
4. $CrO_3 = 3(-2) + x = 0 \longrightarrow -6 + x = 0 \longrightarrow x = Cr = +6 \quad Cr^{6+}$
5. $MnO_2 = 2(-2) + x = 0 \longrightarrow -4 + x = 0 \longrightarrow x = Mn = +4 \quad Mn^{4+}$
6. $Fe_3O_4 = FeO \cdot Fe_2O_3 =$

$FeO = -2 + x = 0 \longrightarrow x = Fe = +2 \quad Fe^{2+}$

$Fe_2O_3 = 3(-2) + 2x = 0 \longrightarrow -6 + 2x = 0 \longrightarrow x = Fe = +3 \quad Fe^{3=}$

(One Fe Atom has an oxidation state of +2 and the other 2 Fe atoms have an oxidation state of +3)

7. $Co_3O_4 = CoO \cdot Co_2O_3 =$

$CoO = -2 + x = 0 \longrightarrow x = Co = +2 \quad Co^{2+}$

$Co_2O_3 = 3(-2) + 2x = 0 \longrightarrow -6 + 2x = 0 \longrightarrow x = Co = +3 \quad Co^{3+}$

(One Co Atom has an oxidation state of +2 and the other 2 Co atoms have an oxidation state of +3)

8. $NiO = -2 + x = 0 \longrightarrow x = Ni = +2 \quad Ni^{2+}$

9. $Cu_2O = -2 + 2x = 0 \longrightarrow -2 + 2x = 0 \longrightarrow x = Cu = +1 \quad Cu^{1+}$

A19.1.25

Sc^{3+}; Ti^{4+}; V^{5+}; Cr^{6+}; Mn^{4+}; Fe^{2+} and Fe^{3+}; Co^{2+} and Co^{3+}; Ni^{2+}; Cu^{+}

19.2: Coordination Chemistry of Transition Metals

Q19.2.1

Indicate the coordination number for the central metal atom in each of the following coordination compounds:

a. $[Pt(H_2O)_2Br_2]$
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, C_5H_5N)
c. $[Zn(NH_3)_2Cl_2]$
d. $[Zn(NH_3)(py)(Cl)(Br)]$
e. $[Ni(H_2O)_4Cl_2]$
f. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)

S19.2.1

First we must identify whether or not the ligand has more than one bonded atom (bidentate/polydentate). Using the table below we are able to do this.

Ligand	Number of bonded atoms
Ammine (NH_3)	monodentate
Aqua (H_2O)	monodentate
Bromo (Br)	monodentate
Chloro (Cl)	monodentate
Cyano (CN)	monodentate
Pyridine (C_5H_5N)	monodentate
Ethylenediamine ($C_2H_8N_2$)	bidentate

Now that we have identified the number of bonded atoms from each ligand, we can find the total number of atoms bonded to the central metal ion, giving us the coordination number.

a. $[Pt(H_2O)_2Br_2]$: We can identify the metal ion in the complex as Pt, platinum, as the other two are listed as ligands above and are nonmetallic. We can now use the number of ligands and their bonding atoms to find its coordination number. From the table above we see that H_2O has only one bonding atom and Br as well. So for each Br atom we have one bonding atom, and we have two of these, yielding 2 bonding atoms; this is the same for H_2O, giving us a total number of 4 bonding atoms, and therefore a coordination number of 4.
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, C_5H_5N): The metal ion in this complex, similarly to the first one, can be identified as Pt, platinum. The ligands can be identified as NH_3, pyridine, Cl, and Br, which are all monodentate ligands and have one bonding atom each. Since we have four ligands, each with one bonding atom, the total number of bonding atoms on the metal ion is 4, therefore the complex has a coordination number of 4.
c. $[Zn(NH_3)_2Cl_2]$: The metal ion in this complex can be identified as Zn, zinc, and the ligands can be identified as NH_3 and Cl. Since these two are both monodentate ligands they have one bonding atom each. Since we have a total of two NH_3 and two Cl ligands, we get a total of four monodentate ligands, giving us 4 bonding atoms and a coordination number of 4.
d. $[Zn(NH_3)(py)(Cl)(Br)]$: The metal ion in this complex can be identified as Zn, zinc, and the ligands can be identified as NH_3, pyridine, Cl, and Br, which are all monodentate ligands and have one bonding atom each. Since we have four ligands, each with one bonding atom, the total number of bonding atoms on the metal ion is 4, therefore the complex has a coordination number of 4.

e. $[Ni(H_2O)_4Cl_2]$: The metal ion in this complex can be identified as Ni, nickel, and we can now use the number of ligands and their bonding atoms to find its coordination number. From the table above we see that H_2O has only one bonding atom and Cl as well. So for each Cl atom we have one bonding atom, and we have two of these, yielding 2 bonding atoms. H_2O is the same, having only one bonding atom, but there are four of these. So this gives us a total number of 6 bonding atoms, and therefore a coordination number of 6.
f. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$): The metal ion in this complex can be identified as Fe, iron, and the ligands can be identified as (en) and CN. Since (en) is bidentate, meaning it has 2 bonding atoms, and there are two of these, the total number of bonding atoms from (en) is four. Since CN is monodentate, meaning it has one bonding atom, and there are two of these, the total number of bonding atoms from CN ligand is two. So, the total number of bonding atoms is 6, therefore the complex has a coordination number of 6.

A19.2.1

a. The 2 aqua and the 2 bromo ligands form a total of 4 coordinate covalent bonds and as a result the coordination number is 4.
b. The ammine, pyridine, chloro and bromo each form one coordinate covalent bond that gives a total of 4 and hence CN=4.
c. Two ammine and two chloro ligands give a total of 4 coordinate covalent bonds and a CN = 4.
d. One ammine, a pyrimidine, a chloro and a bromo ligand give a total of 4 covalent bonds, resulting in CN = 4.
e. Four aqua ligands and two chloro ligands form a total of 6 coordinate covalent bonds and a CN =6.
f. Ethylenediamine is a bidentate ligand that forms two coordinate covalent bonds; along with two cyano ligands, it forms a total of 6 bonds, and hence has a CN=6.

Q19.2.2

Give the coordination numbers and write the formulas for each of the following, including all isomers where appropriate:

a. tetrahydroxozincate(II) ion (tetrahedral)
b. hexacyanopalladate(IV) ion
c. dichloroaurate ion (note that *aurum* is Latin for "gold")
d. diamminedichloroplatinum(II)
e. potassium diamminetetrachlorochromate(III)
f. hexaamminecobalt(III) hexacyanochromate(III)
g. dibromobis(ethylenediamine) cobalt(III) nitrate

S19.2.2

To determine coordination numbers we must count the total number of ligands bonded to the central metal and distinguish monodentate and polydentate ligands. To determine the formulas, we use the nomenclature rules and work backwards.

1. "tetrahydroxo" = 4 hydroxide ligands; since hydroxide is a monodentate ligand, we have a total of 4 bonds to the central metal.
   Coordination Number: 4
   We review the basics of nomenclature and see that "tetra" = 4 and "hydroxo" = OH^-. Since the charge on zinc is 2+, which is given in the nomenclature by the Roman numerals, we can calculate the total charge on the complex to be 2-.
   Formula: $[Zn(OH)_4]^{2-}$
2. "hexacyano" = 6 cyanide ligands; since cyanide is a monodentate ligand, we have a total of 6 bonds to the central metal.
   Coordination Number: 6
   We review the basics of nomenclature and see that "hexa" = 6 and "cyano" = CN^-. Since the charge on Pd is 4+, which is given in the nomenclature by the Roman numerals, we can calculate the total charge on the complex to be 2-.
   Formula: $[Pd(CN)_6]^{2-}$
3. "dichloro" = 2 chloride ligands; since chloride is a monodentate ligand, we have a total of 2 bonds to the central metal.
   Coordination Number: 2
   We review the basics of nomenclature and see that "di" = 2 and "chloro" = Cl^-. Since the charge on Au is always 1+, we can calculate the total charge on the complex to be 1-.
   Formula: $[AuCl_2]^-$
4. "diammine" = 2 ammonia ligands and "dichloro" = 2 chloride ligands; since both ammonia and chloride ligands are monodentate, we have a total of 4 bonds to the central metal.
   Coordination Number: 4
   We review the basics of nomenclature and see that "di" = 2, "chloro" = Cl^- and "ammine" = NH_3. Since the charge on Pt is 2+, which is given in the nomenclature by the Roman numerals, we can calculate that the total charge is 0, so the complex is neutral.
   Formula: $[Pt(NH_3)_2Cl_2]$
5. "diammine" = 2 ammonia ligands and "tetrachloro" = 4 chloride ligands; since both ammonia and chloride ligands are monodentate, we have a total of 6 bonds to the central metal.
   Coordination Number: 6

We review the basics of nomenclature and see that "di" = 2, "ammine" = NH_3, "tetra" = 4 and "chloro" = Cl^-. Since the charge on the central metal, Cr, is 3+, which is given in the nomenclature by the Roman numerals, we can calculate that the total charge of the complex is 1-. The "potassium" at the front of the nomenclature indicates that it is the corresponding cation to this anionic complex.
Formula: $K[Cr(NH_3)_2Cl_4]$

6. Both of the metal complexes have "hexa" monodentate ligands, which means both have coordination numbers of 6.
Coordination Number: 6
We review the basics of nomenclature and see that "hexa" = 6, "ammine" = NH_3, and "cyano" = CN^-. Since the charge on Cr is 3+ and Co is 3+, which is given in the nomenclature by the Roman numerals, we find that these complexes' charges balance out.
Formula: $[Co(NH_3)_6][Cr(CN)_6]$
7. "dibromo" = 2 bromide ligands "bis(ethylenediamine)" = 2 (en) ligands; bromide is a monodentate ligand while (en) is a bidentate ligand. Therefore, we have a coordination number of 6.
Coordination Number: 6
We review the basics of nomenclature and see that "di" = 2, "bromo" = Br^-, "bis" = 2, and "ethylenediamine" = en. Since the charge on Co is 3+, which is given in the nomenclature by the Roman numerals, we find that the total charge of the complex is 1+. Nitrate is the corresponding anion to this cationic complex.
Formula: $[Co(en)_2Br_2]NO_3$

A19.2.2

a. 4, $[Zn(OH)_4]^{2-}$;
b. 6, $[Pd(CN)_6]^{2-}$;
c. 2, $[AuCl_2]^-$;
d. 4, $[Pt(NH_3)_2Cl_2]$;
e. 6, $K[Cr(NH_3)_2Cl_4]$;
f. 6, $[Co(NH_3)_6][Cr(CN)_6]$;
g. 6, $[Co(en)_2Br_2]NO_3$

Q19.2.3

Give the coordination number for each metal ion in the following compounds:

a. $[Co(CO_3)_3]^{3-}$ (note that CO_3^{2-} is bidentate in this complex)
b. $[Cu(NH_3)_4]^{2+}$
c. $[Co(NH_3)_4Br_2]_2(SO_4)_3$
d. $[Pt(NH_3)_4][PtCl_4]$
e. $[Cr(en)_3](NO_3)_3$
f. $[Pd(NH_3)_2Br_2]$ (square planar)
g. $K_3[Cu(Cl)_5]$
h. $[Zn(NH_3)_2Cl_2]$

S19.2.3

You can determine a compound's coordination number based on how many ligands are bound to the central atom.

1) In this compound, Cobalt is the central atom, and it has 3 CO_3^{2-} molecules attached to it. However, CO_3^{2-} is a bidentate ligand, which means it binds to the central atom in two places rather than one. This means that the coordination number of $[Co(CO_3)_3]^{3-}$ is 6. A coordination number of 6 means that the structure is most likely octahedral.

2) In this compound, Copper is the central atom. 4 ammonia molecules are attached to it. This means the coordination number is 4, and the structure is likely tetrahedral.

3) For this compound, we can ignore the $(SO_4)_3$ because it is not bound to the central atom. The central atom is cobalt, and it has 4 ammonia molecules and 2 bromine molecules bound to it. The coordination number is 6.

4) There are two compounds here, indicated by the brackets. The central atom for both is platinum. One of them has 4 ammonia molecules attached, and the other has 4 chlorine atoms attached. Both complexes have a coordination number of 4.

5) We can ignore $(NO_3)_3$ for this compound. The central atom is Chromium. There are 3 ethylenediamine molecules attached to the chromium. Ethylenediamine is a bidentate ligand, so the coordination number is 6.

6) Palladium is the central atom. 2 ammonia molecules and 2 bromine atoms are bound to the palladium atom. The coordination number is 4.

7) We can ignore the K_3 structure. Copper is the central atom, and there are 5 chlorine molecules attached to it. The coordination number is 5, so the structure is either trigonal bipyramidal or square pyramidal.

8) In this compound, zinc is the central atom. There are 2 ammonia molecules and 2 chlorine atoms attached. This means that the coordination number is 4.

Q19.2.4

Sketch the structures of the following complexes. Indicate any *cis*, *trans*, and optical isomers.

a. $[Pt(H_2O)_2Br_2]$ (square planar)
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)
c. $[Zn(NH_3)_3Cl]^+$ (tetrahedral)
d. $[Pt(NH_3)_3Cl]^+$ (square planar)
e. $[Ni(H_2O)_4Cl_2]$
f. $[Co(C_2O_4)_2Cl_2]^{3-}$ (note that $C_2O_4^{2-}$ is the bidentate oxalate ion, $-O_2CCO_2^-$)

S19.2.4

Cis and trans are a type of geometric isomer, meaning there is a difference in the orientation in which the ligands are attached to the central metal. In cis, two of the same ligands are adjacent to one another and in trans, two of the same ligands are directly across from one another.

Optical isomers → have the ability to rotate light, optical isomers are also chiral. Only chiral complexes have optical isomers

Chiral → asymmetric, structure of its mirror image is not superimposable

Enantiomers: chiral optical isomers (compound can have multiple enantiomers)

Tetrahedral complex with 4 distinct ligands → always chiral

- For tetrahedral, if 2 ligands are the same, then it cannot be chiral, has a plane of symmetry

Solutions:

a. $[Pt(H_2O)_2Br_2]$ (square planar)

This complex has 2 kinds of ligands. The matching ligands can either be adjacent to each other and be cis, or they can be across from each other and be trans.

b. $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)

This complex has 4 different ligands. There is no plane of symmetry in any of the enantiomers, making the structures chiral and therefore has optical isomers.

c. $[Zn(NH_3)_3Cl]^+$ (tetrahedral)

There is a plane of symmetry from NH_3 through Zn to the other NH_3, therefore it is not chiral.

d. $[Pt(NH_3)_3Cl]^+$ (square planar)

There is a plane of symmetry from NH_3 through Pt to the other NH_3, therefore it is not chiral.

e. $[Ni(H_2O)_2Cl_2]$

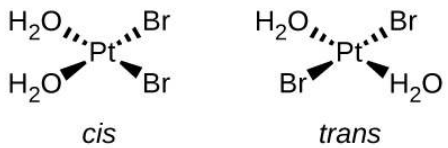
The Cl ligands can either be right next to each other, or directly across from one another allowing for both cis and trans geometries.

f. $[Co(C_2O_4)_2Cl_2]^-3$ (note that $C_2O_4^-2$ is the bidentate oxalate ion, $^-O_2CCO_2^-$

There is a plane of symmetry from Cl through Co to the other Cl in a "trans" chlorine configuration, therefore it is not chiral in a chlorine "trans" configuration. However, there is no symmetry in the chlorine "cis" configuration, indicating multiple "cis" isomers.

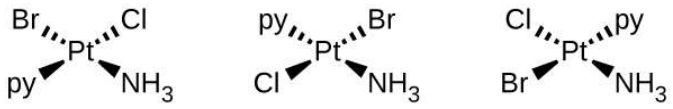
A19.2.4

a. $[Pt(H_2O)_2Br_2]$:

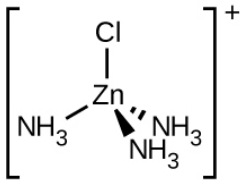


b. $[Pt(NH_3)(py)(Cl)(Br)]$:

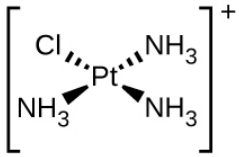
https://chem.libretexts.org/@go/page/429159



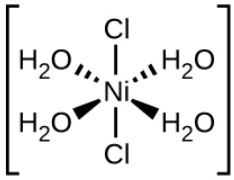
c. $[Zn(NH_3)_3Cl]^+$:



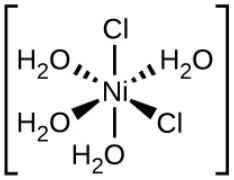
d. $[Pt(NH_3)_3Cl]^+$:



e. $[Ni(H_2O)_4Cl_2]$:

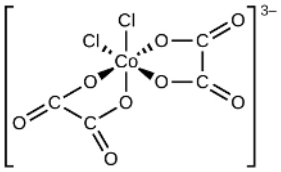


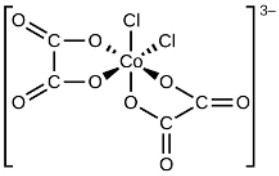
trans

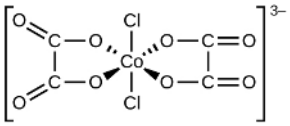


cis

f. $[Co(C_2O_4)_2Cl_2]^{3-}$:







Q19.2.5

Draw diagrams for any *cis*, *trans*, and optical isomers that could exist for the following (en is ethylenediamine):

a. $[Co(en)_2(NO_2)Cl]^+$
b. $[Co(en)_2Cl_2]^+$
c. $[Pt(NH_3)_2Cl_4]$
d. $[Cr(en)_3]^{3+}$
e. $[Pt(NH_3)_2Cl_2]$

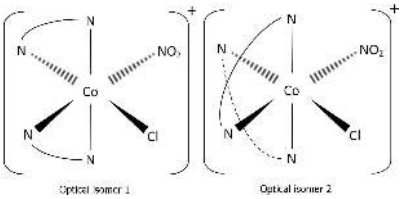
S19.2.5

We are instructed to draw all geometric isomers and optical isomers for the specified compound. Optical isomers exist when an isomer configuration is not superimposable on its mirror image. This means there are two distinct molecular shapes. Often a left and right hand are cited as an example; if you were to take your right hand and place it upon your left, you cannot make the major parts of your hand align on top of one another. The basic idea when deciding whether something is optically active is to look for a plane of symmetry--if you are able to bisect a compound in a manner that establishes symmetry, then the compound does not have an optical isomer.

Cis isomers exist when there are 2 ligands of the same species placed at 90 degree angles from each other. Trans isomers exist when there are 2 ligands of the same species placed at 180 degree angles from each other.

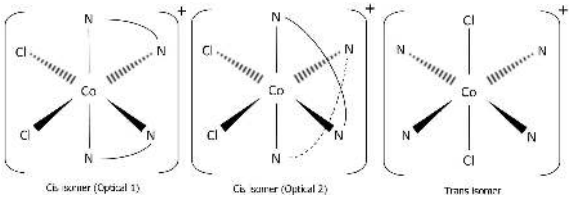
Problem 1

This compound is an octahedral molecule, so the six ligands (atoms in the complex that are not the central transition metal) are placed around the central atom at 90 degree angles. Two optical isomers exist for $[Co(en)_2(NO_2)Cl]^+$. The second isomer is drawn by taking the mirror image of the first.



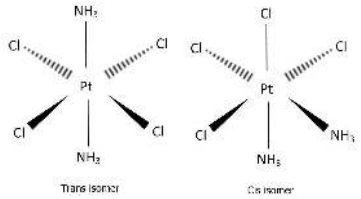
Problem 2

This compound is also an octahedral molecule. Two cis (optical) isomers and one trans isomer exist for $[Co(en)_2Cl_2]^+$. The trans isomer can be drawn by placing the chlorine ligands in positions where they form a 180 degree angle with the central atom. The first cis isomer can be drawn by placing the chlorine ligands in positions where they form a 90 degree angle with the central atom. The second cis isomer can be found by mirroring the first cis isomer, like we did in problem 1.



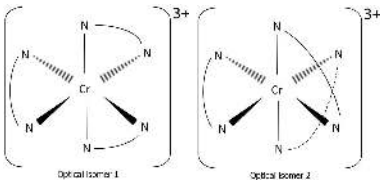
Problem 3

This compound is also an octahedral molecule. One trans isomer and one cis isomer of $[Pt(NH_3)_2Cl_4]$ exist. The trans isomer can be drawn by placing the ammonia ligands in positions where they form a 180 degree angle with the central atom. The cis isomer can be drawn by placing the ammonia ligands in positions where they form a 90 degree angle with the central atom.



Problem 4

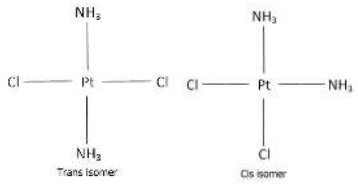
This compound is also an octahedral molecule. Two optical isomers for $[Cr(en)_3]^{3+}$ exist. The second optical isomer can be drawn by taking the mirror image of the first optical isomer.



Problem 5

This compound is a square planar complex, so the ligands are placed around the central atom in a plane, at 90 angles. A trans isomer and a cis isomer exist for the complex $[Pt(NH_3)_2Cl_2]$. The trans isomer can be drawn by placing the ammonia ligands in positions where they form a 180 degree angle in the plane with the central atom. The cis isomer can be drawn by placing the ammonia ligands in positions where they form a 90 degree angle in the plane with the central atom.

https://chem.libretexts.org/@go/page/429159



Q19.2.6

Name each of the compounds or ions given in Exercise Q19.2.3, including the oxidation state of the metal.

S19.2.6

Rules to follow for coordination complexes

1. Cations are always named before the anions.

2. Ligands are named before the metal atom or ion.

3. Ligand names are modified with an -o added to the root name of an anion. For neutral ligands the name of the molecule is used, with the exception of OH2, NH3, CO and NO.

4. The prefixes mono-, di-, tri-, tetra-, penta-, and hexa- are used to denote the number of simple ligands.

5. The prefixes bis-, tris-, tetrakis-, etc., are used for more complicated ligands or ones that already contain di-, tri-, etc.

6. The oxidation state of the central metal ion is designated by a Roman numeral in parentheses.

7. When more than one type of ligand is present, they are named alphabetically. Prefixes do not affect the order.

8. If the complex ion has a negative charge, the suffix –ate is added to the name of the metal.

9. In the case of complex-ion isomerism the names cis, trans, fac, or mer may precede the formula of the complex-ion name to indicate the spatial arrangement of the ligands. Cis means the ligands occupy adjacent coordination positions, and trans means opposite positions just as they do for organic compounds. The complexity of octahedral complexes allows for two additional geometric isomers that are peculiar to coordination complexes. Fac means facial, or that the three like ligands occupy the vertices of one face of the octahedron. Mer means meridional, or that the three like ligands occupy the vertices of a triangle one side of which includes the central metal atom or ion.

A19.2.6

a. tricarbonatocobaltate(III) ion;
b. tetraaminecopper(II) ion;
c. tetraaminedibromocobalt(III) sulfate;
d. tetraamineplatinum(II) tetrachloroplatinate(II);
e. *tris*-(ethylenediamine)chromium(III) nitrate;
f. diaminedibromopalladium(II);
g. potassium pentachlorocuprate(II);
h. diaminedichlorozinc(II)

Q19.2.7

Name each of the compounds or ions given in Exercise Q19.2.5.

S19.2.7

Given:

1. $[Co(en)_2(NO_2)Cl]^+$
2. $[Co(en)_2Cl_2]^+$
3. $[Pt(NH_3)_2Cl_4]$
4. $[Cr(en)_3]^{3+}$
5. $[Pt(NH_3)_2Cl_2]$

Wanted:

Names of the above compounds.

1. $[Co(en)_2(NO_2)Cl]^+$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Co: Cobalt

en: Ethylenediamine

NO_2: Nitro

Cl: Chloro

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(en)_2$: bis(Ethylenediamine)

Step 3: Find the charges of the ligands. Charges can be found here.

en: 0

NO_2: -1

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Co + 2(en) + (NO_2) + Cl = 1$

$Co +2(0) + (-1) + (-1) = 1$

$Co = 3$

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Chlorobis(ethylenediamine)nitrocobalt(III)

2. $[Co(en)_2Cl_2]^+$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Co: Cobalt

en: Ethylenediamine

Cl: Chloro

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(en)_2$: bis(Ethylenediamine)

Cl_2: dichloro

Step 3: Find the charges of the ligands. Charges can be found here.

en: 0

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Co + 2(en) +2(Cl) = 1$

$Co + 2(0) + 2(-1) = 1$

$Co = 3$

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Dichlorobis(Ethylenediamine)cobalt(III)

3. $[Pt(NH_3)_2Cl_4]$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Pt: Platinum

NH_3: Ammine

Cl: Chloro

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(NH_3)_2$: diammine

Cl_4: tetrachloro

Step 3: Find the charges of the ligands. Charges can be found here.

NH_3: 0

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Pt + 2(NH_3) + 4(Cl) = 0$

$Pt + 2(0) + 4(-1) = 0$

$Pt = 4$

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Diamminetetrachloroplatinum(IV)

4. $[Cr(en)_3]^{3+}$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Cr: Cromium

en: ethylenediamine

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(en)_3$: tris(ethylenediamine)

Step 3: Find the charges of the ligands. Charges can be found here.

en: 0

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Cr + 3(en) = 3$

$Cr + 3(0) = 3$

$Cr = 3$

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Tris(ethylenediamine)cromium(III)

5. $[Pt(NH_3)_2Cl_2]$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

NH_3: Ammine

Cl: Chloro

Pt: Platinum

Step 2: Add the appropriate pre-fixes to each ligand depending on the number.

$(NH_3)_2$: diammine

Cl_2: dichloro

Step 3: Find the charges of the ligands. Charges can be found here.

NH_3: 0

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Pt + 2(NH_3) + 2(Cl) = 0$

$Pt + 2(0) + 2(-1) = 0$

Pt = 2

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Diamminedichloroplatinum(II)

A19.2.7

1. Chlorobis(ethylenediamine)nitrocobalt(III)
2. Dichlorobis(Ethylenediamine)cobalt(III)
3. Diamminetetrachloroplatinum(IV)
4. Tris(ethylenediamine)cromium(III)
5. Diamminedichloroplatinum(II)

Q19.2.8

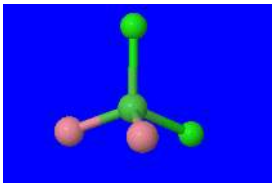
Specify whether the following complexes have isomers.

a. tetrahedral $[Ni(CO)_2(Cl)_2]$
b. trigonal bipyramidal $[Mn(CO)_4NO]$
c. $[Pt(en)_2Cl_2]Cl_2$

S19.2.8

Isomers are compounds that have the same number of atoms, but have different structures. Structural isomers (linkage, ionization, coordination) and stereoisomers (geometric and optical) can occur with several compounds.

1. tetrahedral $[Ni(CO)_2(Cl)_2]$

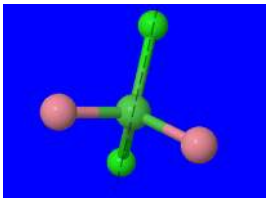


(Fig 1.) *In this model, nickel is the dark green central atom, carbonyl ligands are the pink atom, and chloro ligands are the light green atoms.*

Immediately, we can cancel out the possibility of linkage, ionization, and coordination isomers. There are no other coordination complexes for coordination isomerism, there is no ligand that can bond to the atom in more than one way for it to exhibit linkage isomerism, and there are no ions outside the coordination sphere for ionization isomerism.

This is a tetrahedral structure which immediately rules out any geometric isomers since they require 90° and/or 180° bond angles. Tetrahedral structures have 109.5° angles.

To confirm that the structure has no optical isomer, we must determine if there is a plane of symmetry. Structures that have no plane of symmetry are considered chiral and would have optical isomers.



(Fig 2.) *We can rotate the structure and find that there is indeed a plane of symmetry through the two chloro ligands and central atom and between the carbonyl ligands.*

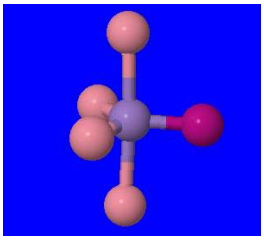
Since there is a plane of symmetry, we can conclude that there are no optical isomers.

Overall, there are no isomers that exist for this compound.

---

2. trigonal byprimidal $[Mn(CO)_4(NO)]$

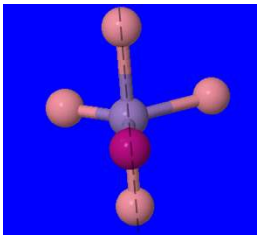
https://chem.libretexts.org/@go/page/429159



(Fig 3.) *The central purple atom is manganese, the carbonyl ligands are the pink atoms, and the nitrosyl ligand is the fuschia atom.*

There are no ions, other coordination complex, and ambidentate ligands. Therefore, no structural isomers exist for this structure.

Geometric isomers do not exist for this compound because there is only one nitrosyl ligand.



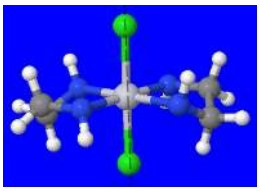
(Fig 4.) *Dashed line bisects molecule and shows plane of symmetry. The molecule is rotated in this image.*

In the image above, after the structure has been rotated, we can see that there is a plane of symmetry. Thus, there are no optical isomers.

No isomers (the ones mentioned above) exist for this compound.

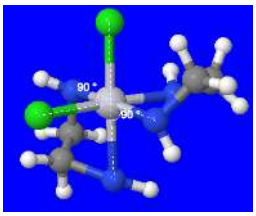
---

3. $[\mathrm{Pt(en)_2Cl_2}]\mathrm{Cl_2}$



(Fig 5.) *The green atoms are the chloro ligands, the the central atom is platinum, and the grey/blue atoms are ethyldiamine ligands.*

Coordination isomerism cannot exist for this complex because there are no other complexes. There are no linkage isomers because there are no ambidentate ligands. Ionization isomers cannot exist in this complex either, even though there is a neutral molecule outside the coordination sphere. If we exchange $\mathrm{Cl_2}$ with one ethyldiamine molecule, There would be 5 ligands in the coordination sphere instead of 4. This difference in the ratio of metal atom to ligands means that an ionization isomer cannot exist.



(Fig 6.) *Here, one chloro ligand exchanged places with the ethyldiamine so that it can be at a 90° angle with the other chloro ligand.*

The image above, shows the chloro and ethyldiamine ligands at a 90° angle with its other identical ligand. This is the *cis* isomer, while Fig. 5 shows the *trans* isomer.

Fig 5. shows that there is a plane of symmetry in the *trans* isomer. Therefore, that structure does not have an optical isomer. On the other hand, the *cis* isomer does not have a plane of symmetry and therefore has an optical isomer.

A19.2.8

none; none; The two Cl ligands can be *cis* or *trans*. When they are *cis*, there will also be an optical isomer.

Q19.2.9

Predict whether the carbonate ligand CO_3^{2-} will coordinate to a metal center as a monodentate, bidentate, or tridentate ligand.

S19.2.9

CO_3^{2-} can be either monodentate or bidentate, since two of its oxygen atoms have lone pairs as shown above and can form covalent bonds with a transition metal ion. In most cases carbonate is monodentate because of its trigonal planar geometry (there is 120 degrees between the oxygens so it's hard for both to bind to the same metal). However, in some cases it will bind to two different metals, making it bidentate.

A19.2.9

CO_3^{-2} will coordinate to a metal center as a monodentate ligand.

Q19.2.10

Draw the geometric, linkage, and ionization isomers for $[CoCl_5CN][CN]$.

S19.2.10

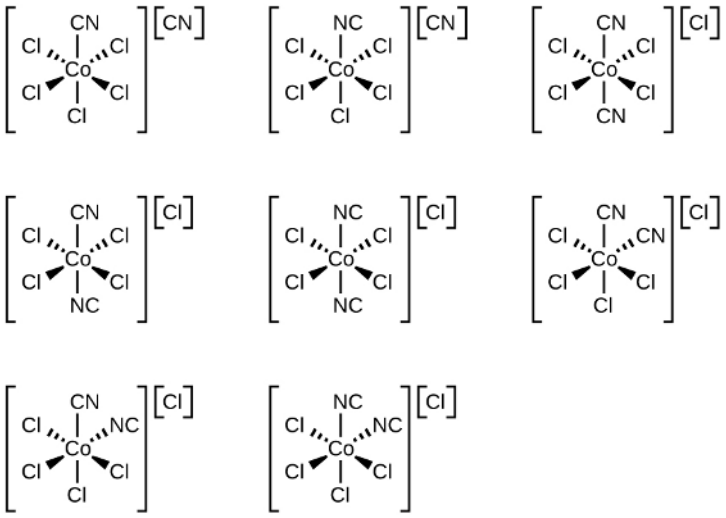
Isomers are compounds with same formula but different atom arrangement. There are two subcategories: **structural isomers**, which are isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another, and **stereoisomers**, isomers that have the same molecular formula and ligands, but differ in the arrangement of those ligands in 3D space.

There are three subcategories under structural isomers: **ionization isomers**, which are isomers that are identical except for a ligand has exchanging places with an anion or neutral molecule that was originally outside the coordination complex; **coordination isomers**, isomers that have an interchange of some ligands from the cationic part to the anionic part; and **linkage isomers**, in two or more coordination compounds in which the donor atom of at least one of the ligands is different.

There are also two main kinds of stereoisomers: **geometric isomers**, metal complexes that differ only in which ligands are adjacent to one another (cis) or directly across from one another (trans) in the coordination sphere of the metal, and **optical isomers**, which occurs when the mirror image of an object is non-superimposable on the original object.

Some of the isomers look almost identical, but that is because the CN ligand can be attached by both (but not at the same time) the C or N.

A19.2.10



19.3: Spectroscopic and Magnetic Properties of Coordination Compounds

Q19.3.1

Determine the number of unpaired electrons expected for $[Fe(NO_2)_6]^{3-}$and for $[FeF_6]^{3-}$ in terms of crystal field theory.

S19.3.1

- The crystal field theory is is a model that describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution.

- The degenerate d-orbitals split into two levels, e_g and t_{2g}, in the presence of ligands.
- The energy difference between the two levels is called the crystal-field splitting energy, $\Delta_\circ$.
- After 1 electron each has been filled in the three t_{2g} orbitals, the filling of the fourth electron takes place either in the e_g orbital or in the t_{2g}, where the electrons pair up. depending on whether the complex is high spin or low spin.
- If the $\Delta_\circ$ value of a ligand is less than the pairing energy (P), then the electrons enter the e_g orbital, but if the $\Delta_\circ$ value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.
- when the Δ_o is less than the pairing energy, the electrons prefer then e_g orbitals because there is not enough energy to pair the electrons together. It will be **high** spin
- when the Δ_o is more then the pairing energy, the electrons prefer the t_{2g} because there is enough energy to pair the electrons. It will be **low** spin.

Step 1: Determine the oxidation state of the Fe

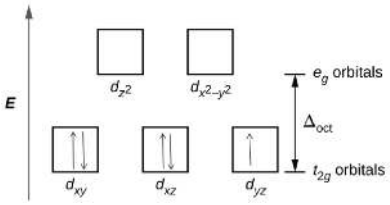
For $[Fe(NO_2)_6]^{3-}$ and $[FeF_6]^{3-}$, both NO_2 and F_6 have a charge of -1. Since there is 6 of them then that means the charge is -6 and in order for there to be an overall charge of -3, Fe has to have a +3 charge.

Step 2: Determine type of ligand

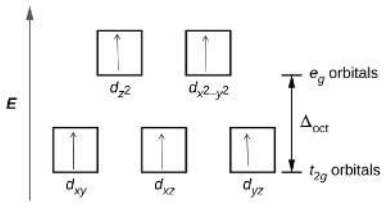
Based on the spectrochemical series we can see that NO_2^- is a stronger field ligand than F^-, and therefore is a low spin complex because it has a high $\Delta_\circ$ unlike F^- which is a high spin.

Step 3: Draw the crystal field

$[Fe(NO_2)_6]^{3-}$



$[FeF_6]^{3-}$



There is 1 unpaired electron for $[Fe(NO_2)_6]^{3-}$, and 5 for $[FeF_6]^{3-}$ based on the crystal field theory.

A19.3.1

$[Fe(NO_2)_6]^{3-}$:1 electron

$[FeF_6]^{3-}$:5 electrons

Q19.3.2

Draw the crystal field diagrams for $[Fe(NO_2)_6]^{4-}$ and $[FeF_6]^{2-}$. State whether each complex is high spin or low spin, paramagnetic or diamagnetic, and compare Δ_{oct} to P for each complex.

S19.3.2

a)

$$[Fe(NO_2)_6]^{-4} \tag{2.P.76}$$

- NO_2^- has a -1 charge. The overall ion has a -4 charge, therefore Fe must be +2 charge. (The math: $\boldsymbol{x+(6)(-1)=-4, x+-6=-4, x=+2}$ **or** 2+(6*-1)=-4)
- Fe^{2+} has 6 valence electrons.
- Next we look at the ligand bonded to Fe, which is NO_2^- . Based on the spectrochemical Series, NO_2^- is a strong field ligand meaning that it has a large **DELTA$_o$** large splitting energy in comparison to the pairing energy, P. So the electrons would rather pair up, as it takes the least amount of energy.

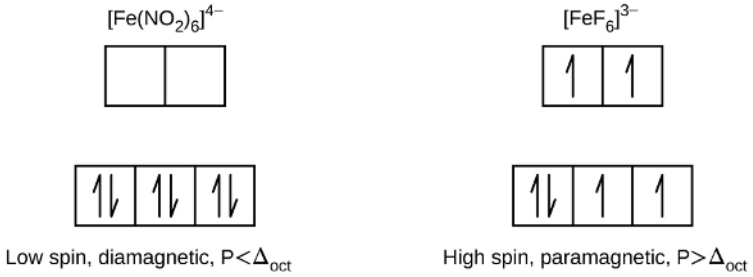
- So $[Fe(NO_2)_6]^{4-}$ is low spin.
- All 6 electrons are paired up, so it is diamagnetic.

b)

$$[FeF_6]^{-3} \tag{2.P.77}$$

- F^- has a -1 charge. The overall ion has a -3 charge, therefore Fe must be +3 charge. (The math: $x+(-1)(6)=-3, x+-6=-3, x=+3$ **or** 3+(6*-1)=-3)
- F^{3+} has 5 valence electrons.
- Next we look at the ligand bonded to Fe, which is F^- . Based on the Spectrochemical Series, F^- is a weak field ligand, meaning that it has a small $DELTA_o$ or small splitting energy in comparison to the pairing energy, P. So the electrons would rather split up and move up to the higher energy level, rather than pairing up, as it takes the least amount of energy.
- So $[Fe(NO_2)_6]^{4-}$ is high spin.
- $[FeF_6]^{3-}$ is paramagnetic because it has unpaired electrons.

A19.3.2



Q19.3.3

Give the oxidation state of the metal, number of *d* electrons, and the number of unpaired electrons predicted for $[Co(NH_3)_6]Cl_3$.

S19.3.3

The oxidation state of the metal can be found by identifying the charge of one of each molecule in the coordinate compound, multiplying each molecule's charge by the respective number of molecules present, and adding the products. This final sum represents the charge of the overall coordination compound. You can then solve for the oxidation state of the metal algebraically. In this case, one chloride anion Cl^- has a charge of -1. So three chloride anions have a total charge of -3. One ammine ligand NH_3 has no charge so six ammine ligands have a total charge of zero. Finally, we are trying to solve for the oxidation state of a cobalt ion. Now we can write the equation that adds the total charges of each molecule or ion and is equal to the total charge of the overall coordinate compound.

$$(\text{oxidation state of Co})+(-3)+0=0 \tag{2.P.78}$$

$$\text{oxidation state of Co}=+3 \tag{2.P.79}$$

So the oxidation state of Co is +3. Now we need to identify the number of d-electrons in the Co^{3+} ion. The electron configuration for cobalt that has no charge is

$$[\text{Ar}]4\text{s}^2\text{3d}^7 \tag{2.P.80}$$

However, a Co^{3+} ion has 3 less electrons than its neutral counterpart and has an electron configuration of

$$[\text{Ar}]\text{3d}^6 \tag{2.P.81}$$

For transition metals, the s electrons are lost first. So cobalt loses its two 4s electrons first and then loses a single 3d electron meaning **Co^{3+} ion has 6 d electrons.** To predict the number of unpaired electrons, we must first determine if the complex is high spin or low spin. Whether the complex is high spin or low spin is determined by the ligand in the coordinate complex. Specifically, the ligand must be identified as either a weak-field ligand or a strong-field ligand based on the spectrochemical series. Weak-field ligands induce high spin while strong-field ligands induce low spin. We can then construct the energy diagram or crystal field diagram of the designated spin that has the proper electron placings. The geometric shape of the compound must also be identified to construct the correct diagram. Finally, from this crystal field diagram we can determine the number of unpaired electrons. The number of electrons in the diagram is equal to the number of d electrons of the metal. The ligand in this case is NH_3, which is a strong field ligand according to the spectrochemical series. This means that the complex is low spin. Additionally, six monodentate ligands means the ligand field is octahedral. The number of electrons that will be in the diagram is 6 since the metal ion Co^{3+} has 6 d electrons. Now the proper crystal field diagram can be constructed.



From the crystal field diagram, we can tell that **the complex has no unpaired electrons**.

A19.3.3

a) 3+

b) 6 d electrons

c) No unpaired electrons

Q19.3.4

The solid anhydrous solid $CoCl_2$ is blue in color. Because it readily absorbs water from the air, it is used as a humidity indicator to monitor if equipment (such as a cell phone) has been exposed to excessive levels of moisture. Predict what product is formed by this reaction, and how many unpaired electrons this complex will have.

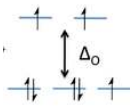
S19.3.4

From our knowledge of ligands and coordination compounds (or if you need a refresher Coordination Compounds), we can assume the product of $CoCl_2$ in water. H_2O is a common weak field ligand that forms six ligand bonds around the central Cobalt atom while the Chloride stays on the outer sphere. We can use this to determine the complex:

$[Co(H_2O)_6]Cl_2$

From this formation, we can use the Crystal Field Theory (CFT)(Crystal Field Theory) to determine the number of unpaired electrons. This coordination compound has six ligand bonds attached to the central atom which means the CFT model will follow the octahedral splitting. Keep in mind that we know H_2O is a weak field ligand and will produce a high spin. High spin is when the electrons pairing energy (P) is greater than the octahedral splitting energy. Thus, the electrons spread out and maximize spin.

In order to fill out our crystal field diagram, we need to determine the charge of cobalt. Because the H_2O ligand is neutral, and there are two chlorine ions, we can deduce the charge of cobalt is plus two in order to make the coordination complex neutral. From here, we can use the electron configuration of Co^{2+} is $[Ar]4s^23d^7$. The electrons that are taken away from the cobalt atom in order to form the plus two charge will from the 4s orbital and leave the 3d orbital untouched. Thus, there will be 7 electrons in the crystal field diagram and appear as:



We can see here that there are 3 unpaired electrons.

A19.3.4

$[Co(H_2O)_6]Cl_2$ with three unpaired electrons.

Q19.3.5

Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

A19.3.5

Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

It is not possible for a metal in the transition series to have six unpaired electrons. This is because transition metals have a general electron configuration of $(n-1)d^{1-10}\ ns^{1-2}$ where n is the quantum number. The last electron will go into the d orbital which has 5 orbitals that can each contain 2 electrons, yielding 10 electrons total. According to Hund's Rule, electrons prefer to fill each orbital singly before they pair up. This is more energetically favorable. Since there are only 5 orbitals and due to Hund's Rule, the maximum number of unpaired electrons a transition metal can have is 5. Therefore, there cannot be a complex of a transition metal that has 6 unpaired electrons.

https://chem.libretexts.org/@go/page/429159

For example, lets look at iron's electron configuration. Iron has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Now the most important orbital to look at is the d orbital which has 6 electrons in it, but there are only 4 unpaired electrons as you can see by this diagram:

3d: [↑ ↓] [ ] [ ] [ ] [ ]

Each [ ] represents an orbital within the d orbital. This diagram follows Hund's rule and shows why no transition metal can have 6 unpaired electrons.

Q19.3.6

How many unpaired electrons are present in each of the following?

a. $[CoF_6]^{3-}$ (high spin)
b. $[Mn(CN)_6]^{3-}$ (low spin)
c. $[Mn(CN)_6]^{4-}$ (low spin)
d. $[MnCl_6]^{4-}$ (high spin)
e. $[RhCl_6]^{3-}$ (low spin)

S19.3.6

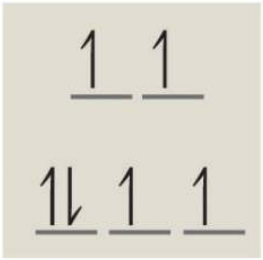
1. For $[CoF_6]^{3-}$, we first found the oxidation state of Co, which is 3+ since F has a 1- charge and since there is 6 F, Co's charge has to be 3+ for the overall charge to be 3-.

$$\text{charge of Co} + \text{-6} = \text{-6} \tag{2.P.82}$$

$$\text{charge of Co} = +3 \tag{2.P.83}$$

After finding the oxidation state, I then go to the periodic table to find its electron configuration: $[Ar]3d^6$

We distribute the 6 d-orbital electrons along the complex and since it is high spin, the electrons is distributed once in each energy level before it is paired. There is only one pair and the other 4 electrons are unpaired, making the answer 4.



2. The same process is repeated. We find the charge of Mn, which is 3+, making the electron configuration: $[Ar]3d^4$

$$\text{charge of Mn} + \text{-6} = \text{-3} \tag{2.P.84}$$

$$\text{charge of Mn} = +3 \tag{2.P.85}$$

There is a difference between this and number 1. This is low spin so instead of distributing one electron in each level before pairing it, I must distribute one electron on the bottom and then pair them all up before I'm able to move to the top portion. So since there is 4, there is only a pair at d_{yz} and the other two electrons are unpaired. Making the number of unpaired electrons 2.



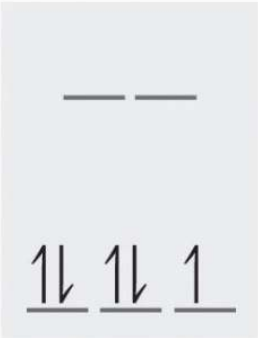
3.The same process as number 2 is applied. The only difference is that the charge of Mn is now 2+ so the electron configuration: $[Ar]3d^5$.

$$\text{charge of Mn} + \text{-6} = \text{-4} \tag{2.P.86}$$

https://chem.libretexts.org/@go/page/429159

$$\text{charge of Mn} = +2 \tag{2.P.87}$$

Since is it low spin like number 2, I only need to add an extra electron to the next level, making that 2 pairs of electron and only 1 electron unpaired.

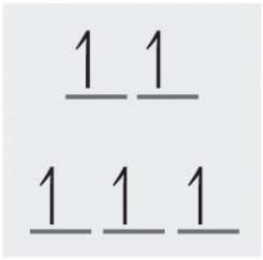


4. Since Cl has a -1 charge like CN, Mn's charge is also 2+ with the same electron configuration as number 3, which is 5.

$$\text{charge of Mn} + \text{-6} = \text{-4} \tag{2.P.88}$$

$$\text{charge of Mn} = +2 \tag{2.P.89}$$

With 5 electrons, this is high spin instead of low. So as stated in number 1, we pair distribute the electrons on all levels first. Since there are 5 electrons and 5 levels and they are al distributed, there are zero pairs, making that 5 unpaired electrons.



5. Using the same process as the problems above, Rh's charge is 3+, with the electron configuration: [Kr]$4d^6$.

$$\text{charge of Rh} + \text{-6} = \text{-3} \tag{2.P.90}$$

$$\text{charge of Mn} = +3 \tag{2.P.91}$$

With a low spin and 6 electrons, all electrons are paired up, making it 0 electrons that are unpaired.



A19.3.6

4; 2; 1; 5; 0

Q19.3.7

Explain how the diphosphate ion, $[O_3P{-}O{-}PO_3]^{4-}$, can function as a water softener that prevents the precipitation of Fe^{2+} as an insoluble iron salt.

S19.3.7

The diphosphate ion, $[O_3P{-}O{-}PO_3]^{4-}$ can function as a water softener keeping the iron in a water soluble form because of its more negative electrochemical potential than water's. This is similar to the way plating prevents metals from reacting with oxygen to corrode.

Mineral deposits are formed by ionic reactions. The Fe^{2+} will form an insoluble iron salt of iron(III) oxide-hydroxide when a salt of ferric iron hydrolyzes water. However, with the addition of $[O_3P{-}O{-}PO_3]^{4-}$, the Fe^{2+} cations are more attracted to the PO_3 group, forming a $Fe(PO_3)$ complex.

The excess minerals in this type of water is considered hard thus its name hard water.

Q19.3.8

For complexes of the same metal ion with no change in oxidation number, the stability increases as the number of electrons in the t_{2g} orbitals increases. Which complex in each of the following pairs of complexes is more stable?

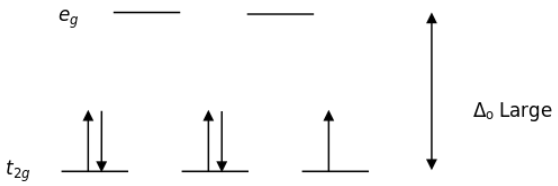
a. $[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$
b. $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3-}$
c. $[Mn(CN)_6]^{4-}$ or $[MnCl_6]^{4-}$

S19.3.8

The Spectrochemical Series is as follows

$$I^- < Br^- < SCN^- \approx Cl^- < F^- < OH^- < ONO^- < ox < H_2O < SCN^- < EDTA < NH_3 < en < NO_2^- < CN \qquad (2.P.92)$$

The strong field ligands (on the right) are low spin which fills in more electrons in the t_{2g} orbitals. The weak field ligands (on the left) are high spin so it can fill electrons in the t_{2g} orbitals and e_g orbitals. In conclusion, more electrons are filled up from the strong field ligands because the electrons don't move up to the e_g orbitals.



a. $[Fe(CN)_6]^{4-}$

CN is a stronger ligand than H_2O so it is low spin, which fills up the t_{2g} orbitals.

b. $[Co(NH_3)_6]^{3+}$

NH_3 is a stronger ligand than F.

c. $[Mn(CN)_6]^{4-}$

CN is a stronger ligand than Cl^-.

For more information regarding the shape of the complex and d-electron configuration, libretext provides more information on how to classify high and low spin complexes.

A19.3.8

$[Fe(CN)_6]^{4-}$; $[Co(NH_3)_6]^{3+}$; $[Mn(CN)_6]^{4-}$

Q19.3.9

Trimethylphosphine, $P(CH_3)_3$, can act as a ligand by donating the lone pair of electrons on the phosphorus atom. If trimethylphosphine is added to a solution of nickel(II) chloride in acetone, a blue compound that has a molecular mass of approximately 270 g and contains 21.5% Ni, 26.0% Cl, and 52.5% $P(CH_3)_3$ can be isolated. This blue compound does not have any isomeric forms. What are the geometry and molecular formula of the blue compound?

S19.3.9

1)Find the empirical formula. There is a total of 270 grams. To find out how many grams of each element/compound there are, multiply the percentage by the mass (270).

$$(270g)(0.215) = 58.05gNi \qquad (2.P.93)$$

$$(270g)(0.26) = 70.2gCl \tag{2.P.94}$$

$$(270g)(0.525) = 141.75gP(CH_3)_3 \tag{2.P.95}$$

Now that we have the grams of each element/compound, we can convert them to moles by using their molar mass.

$$(58.055gNi)(\frac{1mol.}{58.69gNi}) = 0.989mol.\,Ni \tag{2.P.96}$$

$$(70.2gCl)(\frac{1mol.}{35.45gCl}) = 1.98mol.\,Cl \tag{2.P.97}$$

$$(141.75gP(CH_3)_3)(\frac{1mol.}{76.07gP(CH_3)_3}) = 1.86mol.\,P(CH_3)_3 \tag{2.P.98}$$

Now that we have the moles of all elements/compounds, we can find the ratio of all them to each other. To do this, we take the element/compound with the least amount of moles and divide all element/compound moles by this amount. In this case, Ni has the least number of moles.

$$\frac{0.989mol.\,Ni}{0.989mol.\,Ni} = 1 \tag{2.P.99}$$

$$\frac{1.98mol.\,Cl}{0.989mol.\,Ni} = approx.2 \tag{2.P.100}$$

$$\frac{1.86mol.\,P(CH_3)_3}{0.989mol.\,Ni} = approx.2 \tag{2.P.101}$$

We now know the ratio of all element/compounds in the blue compound.

The empirical formula is: $NiCl(P(CH_3)_3)_2$

This formula shows us there are 4 ligands. There are 2 chlorine ligands and 2 trimethylphosphine ligands. This means that the blue compound has either a tetrahedral or square planar shape, where tetrahedral shapes are capable of different isomeric forms when all ligands are different (because if not, there is only 1 way for them to be arranged), and square planar shapes are capable of cis/trans forms. In the problem, it states this compound does not have any isomeric forms, therefore this has a tetrahedral shape.

A19.3.9

a) $NiCl(P(CH_3)_3)_2$

b) Tetrahedral

Q19.3.10

Would you expect the complex $[Co(en)_3]Cl_3$ to have any unpaired electrons? Any isomers?

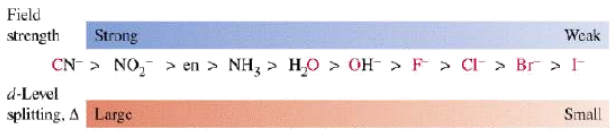
S19.3.10

Assign oxidation states to each element. Cl- has a -1 oxidation state. En is neutral, so 0. The entire complex is also neutral, so in order to balance the charges out, Co must be +3 because there are 3 chlorides, which gives a -3 charge.

STEP 2:

Write the electron configuration for Co^{3+}. $[Ar]3d^6$. There are 6 electrons.

STEP 3:



Check where en lies on the spectrochemical series. Does it have a strong field strength? It does, so these electrons will exist at the d-level with high splitting energy because the magnitude of the pairing energy is less than the crystal field splitting energy in the octahedral field.

You will the notice that there aren't any unpaired electrons when you draw the Crystal Field Theory (CFT) diagram.



This complex does not have any geometric isomers because cis-trans structures cannot be formed. The mirror image is nonsuperimpoasable, which means the enantiomers are chiral molecules; if the mirror image is placed on top on the original molecule, then they will never be perfectly aligned to give the same molecule.

A19.3.10

The complex does not have any unpaired electrons. The complex does not have any geometric isomers, but the mirror image is nonsuperimposable, so it has an optical isomer.

Q19.3.11

Would you expect the $Mg_3[Cr(CN)_6]_2$ to be diamagnetic or paramagnetic? Explain your reasoning.

S19.3.11

The first step to determine the magnetism of the complex is to calculate the oxidation state of the transition metal. In this case, the transition metal is Cr.

Before doing so, we need to find charge of the of the complex ion $[Cr(CN)_6]_2$ given that the oxidation state of Mg_3 is 2+. Using the subscripts of the Mg^{2+} ion and the $[Cr(CN)_6]_2$ complex, we find that the oxidation state of $[Cr(CN)_6]_2$, x, to be:

$3(+2) + 2(x) = 0$

$x = 3$

Now that we found the charge of the coordination complex, we are able to find the charge of the transition metal Cr given that the charge of CN is -1. Again, using the subscripts we find the oxidation state of Cr, y, to be:

$y + 6(-1) = -3$

$y = 3$

Therefore, the oxidation state of the transition metal Cr is Cr^{3+}

> Next, using the transition metal Cr^{3+} and the periodic table as reference, we can determine the electron configuration of Cr^{3+} to be $[Ar]d^3$. This means that Cr^{3+} has 3 unpaired electrons in the 3d sublevel. Therefore, we find that since at least one electron is unpaired(in this case all 3 electrons are unpaired), $Mg_3[Cr(CN)_6]_2$ is paramagnetic.

A19.3.11

a) Paramagnetic

Q19.3.12

Would you expect salts of the gold ion, Au^+, to be colored? Explain.

S19.3.12

No. **Colored ions have unpaired electrons in their outmost orbital**. A partially filled d orbital, for example, can yield various colors. After completing the noble gas configuration, we see that Au^+ has a configuration of [Xe] $4f^{14}$**$5d^{10}$**. Since Au^+ has a **completely filled d sublevel**, we are certain that any salts of the gold ion, Au^+ will be **colorless.**

*An example of a colored ion would be copper(II). Cu^{2+} has an electron configuration of [Ar]$3d^9$. It has one unpaired electron. Copper(II) appears blue.

A19.3.12

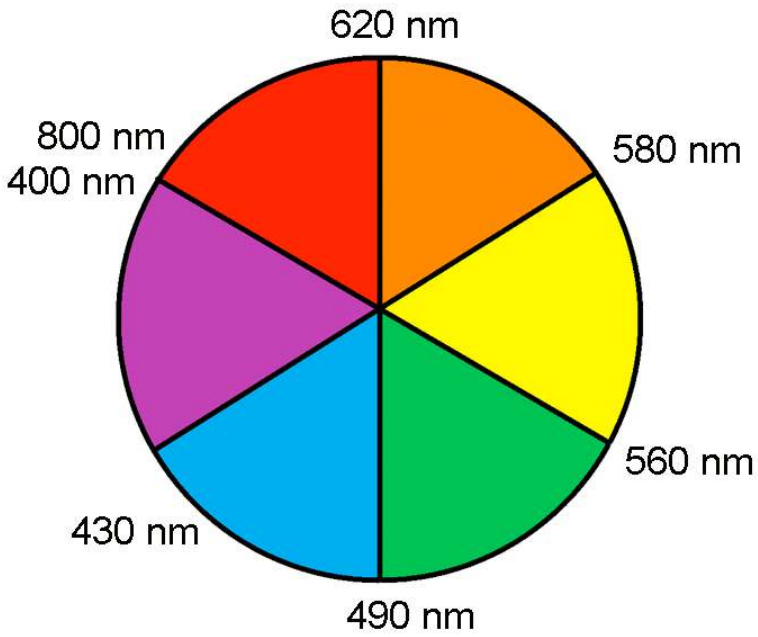
No. Au^+ has a complete 5*d* sublevel.

Q19.3.13

$[CuCl_4]^{2-}$ is green. $[Cu(H_2O)_6]^{2+}$is blue. Which absorbs higher-energy photons? Which is predicted to have a larger crystal field splitting?

S19.3.13

Although a color might appear a certain way, it actual absorbs a different color, opposite of it on the color wheel.



In this case;

$[CuCl_4]^{2-}$ appears green but is opposite of red on the color wheel which is absorbed and is characterized by wavelengths 620-800 nanometers.

$[Cu(H_2O)_6]^{2+}$ appears blue but is opposite of orange on the color wheel which is absorbed and is characterized by wavelengths 580-620 nanometers.

When determining which absorbs the higher energy photons, one must look at the complex itself. A higher energy indicates a high energy photon absorbed and a lower energy indicates a lower energy photon absorbed. How can we determine this? By looking at the complex and more specifically the ligand attached and its location in the spectrochemical series.

Merging to get spectrochemical series

$CO, CN^- > phen > en > NH_3 > NCS^- > H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$

Strong field, π acceptors, large Δ, low spin — σ only — Weak field, π donors, small Δ, high spin

$$E = \frac{hc}{\lambda}$$

The ligands attached are Water and Chlorine and since Water is a stronger ligand than Chlorine according to the series, it also has larger energy, indicating a higher energy. This means that the complex $[Cu(H_2O)_6]^{2+}$ absorbs a higher energy photon because of its a stronger ligand than chlorine.

Part 2 of this question also asks which complex is predicted to have a larger crystal field splitting. To determine this you also use the spectrochemical series and see which ligand is stronger. Since H_2O is stronger than Cl^- on the spectrochemical series, we can say $[Cu(H_2O)_6]^{2+}$ has a higher crystal field splitting.

A19.3.13

a) $[Cu(H_2O)_6]^{2+}$

b) $[Cu(H_2O)_6]^{2+}$ has a higher crystal field splitting

This page titled 2.P: Problems is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

3: d-Block Metal Chemistry- Coordination Complexes

- 3.1: Evidence for Electronic Structures
  - 3.1.1: Thermodynamic Data
  - 3.1.2: Magnetic Susceptibility
  - 3.1.3: Electronic Spectra
  - 3.1.4: Coordination Number and Molecular Shapes
- 3.2: Bonding Theories
  - 3.2.1: Crystal Field Theory
- 3.3: Ligand Field Theory
  - 3.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex
  - 3.3.2: Orbital Splitting and Electron Spin
  - 3.3.3: Ligand Field Stabilization Energy
  - 3.3.4: Tetrahedral Complexes
  - 3.3.5: Square-Planar Complexes
- 3.4: Angular Overlap
  - 3.4.1: Sigma Bonding in the Angular Overlap Model
  - 3.4.2: Pi Acceptors in the Angular Overlap Model
  - 3.4.3: Pi Donors in the Angular Overlap Model
  - 3.4.4: The Spectrochemical Series
  - 3.4.5: The Magnitude of Parameters $e\sigma$, $e\pi$ and Δ
  - 3.4.6: The Magnetochemical Series
- 3.5: The Jahn-Teller Effect
- 3.6: Four- and Six-Coordinate Preferences
- 3.7: Other Shapes
- 3.P: Problems

This page titled 3: d-Block Metal Chemistry- Coordination Complexes is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

SECTION OVERVIEW

3.1: Evidence for Electronic Structures

This section describes the types of experimental data that give us hints about the electronic structure of coordination complexes (ie the molecular orbitals, their energy levels, and electron configurations). The types of experimental observations discussed here have been used to generate the theories of bonding that are described later in this chapter.

Introduction

The frontier (valence) electrons and orbitals define the chemical and physical properties of any compound. In the transition metals and their coordination compounds, the d orbitals and d electrons are the ones of interest. Thus, the d orbitals and electrons will be the focus of this chapter.

One of the first things you might notice about valence d orbitals is the order of orbital energy levels of atoms and ions in the transition metals. For example, in the first row of transition metals, the 4s orbital fills before the $3d$ *in the atoms*. This indicates that $4s$ is lower in energy than $3d$ *in these atoms*. However, *in the ions* of the same elements, the $3d$ orbital is occupied while the $4s$ orbital is empty. This indicates the opposite, that the $3d$ orbital is lower in energy than $4s$ *in these ions*. The change in the relative energy levels of the $3d$ and $4s$ orbitals in atoms compared to ions is a result of the combined effects of shielding and penetration, as discussed in a previous chapter. The result is that the 3d and 4s orbital energy levels are close enough in energy that subtle changes in the environment can reverse the order.

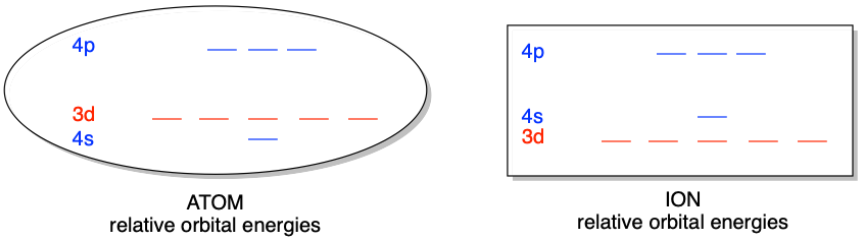


Figure 3.1.1: In early period 4 of the periodic table, the $4s$ orbital energy level is lower than $3d$ for atoms. However, in the ions of the same elements, the $3d$ is lower in energy than $4s$. (CC-BY-NC; Chris Schaller)

Furthermore, you are going to see that once the atom is surrounded by ligands, the five d orbitals are no longer degenerate. In a coordination compound, with ligands bound in a specific geometry, the d orbitals become split into slightly different energy levels. The splitting pattern depends on where the ligands are in space; in other words it depends on the coordination geometry. The patterns of splitting for tetrahedral and octahedral geometries are shown below. Notice that the splitting is reversed between metals in a tetrahedral coordination environment compared to an octahedral environment.

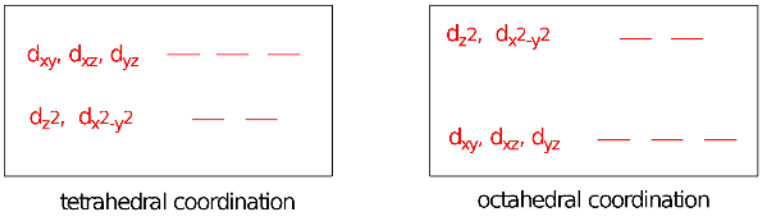


Figure 3.1.2: Splitting of d orbitals for (left) tetrahedral and (right) octahedral ligand geometries. (CC-BY-NC; Chris Schaller)

When the orbitals of a coordination compound are filled with electrons, the electron configuration depends on the energy difference between the lower and higher energy levels. For example, given five d electrons in an octahedral environment, there are two possible electron configurations. All five electrons may occupy the lower level of d orbitals (Fig. 3.1.3, left), so that some electrons are paired. Another possibility is that all the electrons will be unpaired if they populate both levels of the d orbitals (Fig. 3.1.3, right).

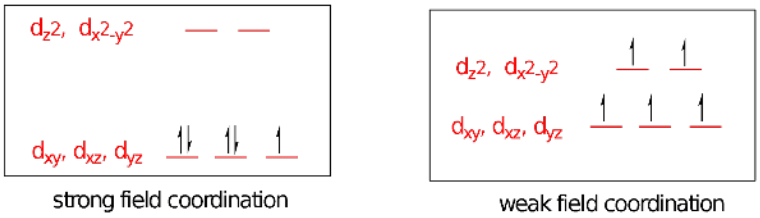


Figure 3.1.3: Two possible electron configurations for five electrons in an octahedral ligand field. (CC-BY-NC; Chris Schaller)

A number of factors determine which case results, including the identity of the metal ion and the nature of the ligands involved. These different filling orders have consequences, too. The magnetic properties of the complex, its propensity to undergo reactions, and its optical properties all depend on the configuration of these frontier electrons.

This chapter is an exploration of the nature of the metal-ligand bond and how both geometry and the mode of bonding influence the properties of coordination complexes.

3.1.1: Thermodynamic Data

3.1.2: Magnetic Susceptibility

3.1.3: Electronic Spectra

3.1.4: Coordination Number and Molecular Shapes

This page titled 3.1: Evidence for Electronic Structures is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.1.1: Thermodynamic Data

We can get some insight into the stability of coordination complexes by looking at their formation constants. The formation constant is the equilibrium constant for the reaction leading to the formation of a coordination complex. The greater the formation constant, the more thermodynamically stable the product complex compared to the reactant complex.

Many complexation reactions take place in aqueous solution by dissolving a metal ion in water to produce the "aqueous metal ion". An aqueous metal ion is one that is coordinated by a number of water molecules, and since it is charged, there must be counter ions to balance that charge. When an aqueous metal ion reacts to form a new complex, its formation constant indicates the stability of the product compared to the aqueous complex. Depending on the number of ligands that are replaced in the product compared to the reactant, the formation complex is defined as either a **stepwise formation constant** (K) or an **overall formation constant** (β).

For example, the formation of $[Cu(NH_3)(OH_2)_5]^{2+}$ complex ion from $Cu^{2+}_{(aq)}$ can be represented by the following *stepwise* reaction:[1]

$$[Cu(OH_2)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(OH_2)_5]^{2+} + H_2O \qquad K_1 = 1.9 \times 10^4$$

The formation constant, K_1, is a stepwise formation constant because it represents the substitution of a single aquo ligand (a coordinated water) by an ammine ligand. Another example is the reaction below that represents the substitution of four aquo ligands for four ammine ligands. The *overall* formation of the $[Cu(NH_3)_4(OH_2)_2]^{2+}$ complex ion from $Cu^{2+}_{(aq)}$ would be represented by this equation:

$$[Cu(OH_2)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(OH_2)_2]^{2+} + 4\,H_2O \qquad \beta_4 = 1.1 \times 10^{13}$$

This time, the formation constant represents the substitution of four ammine ligands for four aquo ligands. This transformation does not happen in one step, so the formation constant, β_4 is a composite of the equilibrium constants for four individual steps:

$$[Cu(OH_2)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(OH_2)_5]^{2+} + H_2O \qquad K_1 = \frac{[Cu(NH_3)(OH_2)_5^{2+}]}{[Cu(OH_2)_6^{2+}][NH_3]} = 1.9 \times 10^4$$

$$[Cu(NH_3)(OH_2)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(OH_2)_4]^{2+} + H_2O \qquad K_2 = \frac{[Cu(NH_3)_2(OH_2)_4^{2+}]}{[Cu(NH_3)(OH_2)_5^{2+}][NH_3]} = 3.9 \times 10^3$$

$$[Cu(NH_3)_2(OH_2)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(OH_2)_3]^{2+} + H_2O \qquad K_3 = \frac{[Cu(NH_3)_3(OH_2)_3^{2+}]}{[Cu(NH_3)_2(OH_2)_4^{2+}][NH_3]} = 1.0 \times 10^3$$

$$[Cu(NH_3)_3(OH_2)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(OH_2)_2]^{2+} + H_2O \qquad K_4 = \frac{[Cu(NH_3)_4(OH_2)_2^{2+}]}{[Cu(NH_3)_3(OH_2)_3^{2+}][NH_3]} = 1.5 \times 10^2$$

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 = (1.9 \times 10^4)(3.9 \times 10^3)(1.0 \times 10^3)(1.5 \times 10^2) = 1.1 \times 10^{13}$$

(\beta\) notation

The β notation is used to distinguish an overall formation constant from a stepwise formation constant. However, sometimes alternative notation will be used. You may see other texts, the literature, or your instructor using alternative ways to distinguish an overall formation constant like β_4 from the stepwise formation constant, like K_4. The important thing is to understand the conventions used for whatever source you are reading.

In both the examples above, the equilibrium lies to the right (in other words, the formation constant is >> 1). Another way to interpret this is that Cu(II) has a higher affinity for ammonia than for water, and thus the ammine complex is more stable than the aqueous metal ion. In the case of the copper tetraammine complex, replacement of each individual water by ammonia is favorable, so the aggregate formation constant β_4 becomes very large. The preference of Cu(II) for ammonia can be explained by the increased basicity of ammonia compared to water.

Formation constants can provide valuable insight into factors that contribute to the stability of coordination complexes, but we may need a more extensive set of data to build a more complete picture. If we look at formation constants in a series of complexes that have something in common, we may get an idea about additional factors that play a role in complex stability. Take a look at these examples:[2]

$$\begin{aligned} \mathrm{Cu^+(aq) + 2\,Cl^- \rightleftharpoons [CuCl_2]^-} \quad & K = 3.0 \times 10^5 \\ \mathrm{Cu^+(aq) + 2\,Br^- \rightleftharpoons [CuBr_2]^-} \quad & K = 8.0 \times 10^5 \\ \mathrm{Cu^+(aq) + 2\,I^- \rightleftharpoons [CuI_2]^-} \quad & K = 8.0 \times 10^8 \end{aligned}$$

The reactions above are simplified by abbreviating the aqueous metal ion, $\mathrm{[Cu(OH_2)n]^+}$ as $\mathrm{Cu^+(aq)}$. This time, we are dealing with Cu(I) rather than Cu(II). Note that basicity does not seem to play a role in this series. The pK_a's of the conjugate acids HCl, HBr, and HI are -6.7, -8.7, and -9.3, respectively. If basicity were important, chloride should bind most tightly, followed by bromide, and then iodide; that trend is reversed here. Instead, this case can be explained by an application of Pearson's hard-soft acid-base theory (HSAB). HSAB theory predicts that small, charge-dense bases will bind more tightly with small, charge-dense acids. Archetypically, hard bases have N, O, or F donor atoms. Conversely, larger, more polarizable bases bind more tightly with larger, more polarizable acids. Soft bases archetypically have P or S donor atoms. In this series of copper complexes, the iodide is the softest, most polarizable of the three halide ions shown, whereas the chloride is the hardest (although not as hard as fluoride). Cu(I) has a relatively low charge density, so it can be considered a soft acid. Soft acids and soft bases form strong bonds because of the pronounced covalency between the donor and acceptor. Of the three halides, iodide is the most capable of providing that soft-soft interaction with the Cu(I) ion.

Let's look at another major contributor to complex stability. In this case, aqueous nickel ion reacts with ammonia to produce the hexaammine complex, $\mathrm{[Ni(NH_3)_6]^{2+}}$. That's similar to the reaction of aqueous copper ion with ammonia; ammonia is a better donor in this case than water. However, ammine is easily displaced by ethylenediamine ($\mathrm{H_2NCH_2CH_2NH_2}$, abbreviated en) to provide an ethylenediamine complex, $\mathrm{[Ni(en)_3]_2^{+}}$.[2,3]

$$\begin{aligned} \mathrm{[Ni(OH_2)_6]^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}} \quad & K = 2.0 \times 10^8 \\ \mathrm{[Ni(NH_3)_6]^{2+} + 3\,en \rightleftharpoons [Ni(en)_3]^{2+} + 6\,NH_3} \quad & K = 4.7 \times 10^9 \end{aligned}$$

Once again, we see that an ammine ligand is a much more effective donor than an aquo ligand. The ethylenediamine ligand, however, binds exceptionally tightly, and can even displace ammine ligands. To gain insight into why a metal ion would have higher affinity toward $\mathrm{H_2NCH_2CH_2NH_2}$ (en) than $\mathrm{NH_3}$, despite the fact that the two ligands have similar donor atoms, we can look at the thermodynamic parameters (the entropy and enthalpy) of the reaction for the formation of $\mathrm{[Ni(en)_3]^{2+}}$ from $\mathrm{[Ni(NH_3)_6]^{2+}}$:

$$\begin{aligned} \Delta H^\circ &= -12.1\ \mathrm{kJ\ mol^{-1}} \\ \Delta S^\circ &= 184.9\ \mathrm{J\ mol^{-1}}K^{-1} \\ \text{and at 298 K, } -T\Delta S^\circ &= -55.1\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

That last term, $-T\Delta S^\circ$, is included for easier comparison to the enthalpy contribution, since these two factors are evaluated via the Gibbs free energy equation, $\Delta G = \Delta H - T\Delta S$. We see that the formation of $\mathrm{[Ni(en)_3]^{2+}}$ from $\mathrm{[Ni(NH_3)_6]^{2+}}$ is slightly favored enthalpically (by $\Delta H^\circ = -12.1\mathrm{kJ\ mol^{-1}}$), even though there are nitrogen atom donor ligands in both reactant and product complexes. However, this small preference is not likely the most important driving force for the large formation constant. The entropy factor is much larger in comparison ($T\Delta S^\circ = -55.1\ \mathrm{kJ\ mol^{-1}}$), indicating entropy is driving the huge formation constant for the ethylenediamine complex.

How do we interpret that large $T\Delta S^\circ$? The simplest approach to interpreting a change in entropy of a reaction is to evaluate the number of molecules in the reactants compared to the products. If there is an increase in the number of molecules, there is an increase in disorder (entropy).

In the replacement of aquo ligands with ammine ligands, there are seven species on either side of the equation:

$$\begin{array}{ccc} \mathrm{[Ni(OH_2)_6]^{2+} + 6\,NH_3} & \rightleftharpoons & \mathrm{[Ni(NH_3)_6]^{2+}} \\ 7\ \text{molecules} & & 7\ \text{molecules} \end{array}$$

We might not expect this reaction to have a large entropic driving force because the number of molecules is the same in the reactants and products.

On the other hand, in the replacement of ammine ligands with ethylenediamine ligands, there are four molecules on the reactant side, and seven on the products side.

$$\underset{}{[Ni(NH_3)_6]^{2+}} + 3\,en \quad \rightleftharpoons \quad \underset{}{[Ni(en)_3]^{2+}} + 6\,NH_3$$
$$\underset{4\text{ molecules}}{} \qquad\qquad \underset{7\text{ molecules}}{}$$

That means there is a net increase in the number of molecules in solution when the ethylenediamine replaces the ammines. An increase in the number of molecules represents an increase in the partitioning of energy, which is entropically favorable. The underlying reason for this difference is that each ethylenediamine ligand has two nitrogen donors, allowing one ethylenediamine to replace two ammines. The high formation constant for ligands that contain multiple donor atoms is called the **chelate effect**, from the Greek word for "crab" (which has two claws with which it can grab things). We call donors capable of binding through multiple atoms “polydentate” ligands (for “many-toothed”, indicating they can bite more strongly into the metal and hold on).

Formation constants of coordination complexes affect important processes ranging from industrial catalysis to biology. For example, most people are aware of carbon monoxide poisoning. Carbon monoxide leads to suffocation by displacing molecular oxygen from hemoglobin (Hb), the oxygen-carrying protein in blood cells. Hemoglobin has an Fe(II) ion bound in its active site which in turn coordinates molecular oxygen, increasing the oxygen-carrying capacity of a blood cell. The two relevant equilibria are:[4]

$$Hb + O_2 \rightleftharpoons HbO_2 \qquad K = 3.2\ \mu M^{-1}$$
$$Hb + CO \rightleftharpoons HbCO \qquad K = 750\ \mu M^{-1}$$

Here, Hb is just a shorthand for hemoglobin. The formation constants shown above indicate that carbon monoxide binds to hemoglobin hundreds of times more tightly than does oxygen. This difference can’t be caused by a chelate effect; both CO and O_2 are monodentate donors in this case. The origin for this difference comes from more subtle differences in metal-ligand binding that we will develop later in this chapter.

Problems

? Exercise 3.1.1.1

Show how we can combine the formation constants given above for $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ from $[Ni(HO_2)_6]^{2+}$ to determine the formation constant for the ethylenediamine complex from aqueous nickel ion.

$$[Ni(OH_2)_6]^{2+} + 3\,en \rightleftarrows [Ni(en)_3]^{2+} + 6\,H_2O \qquad K = ?$$

Answer

We know the formation constants of $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$. Let's call them "reactions i and j":

$$\text{Reaction } i: \qquad [Ni(OH_2)_6]^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} \qquad K_i = \frac{[Ni(NH_3)_6]}{[Ni(OH_2)_6][NH_3]} = 2.0 \times 10^8$$

$$\text{Reaction } j: \qquad [Ni(NH_3)_6]^{2+} + 3\,en \rightleftharpoons [Ni(en)_3]^{2+} + 6\,NH_3 \qquad K_j = \frac{[Ni(en)_3][NH_3]^6}{[Ni(NH_3)_6][en]^3} = 4.7 \times 10^9$$

and we want to find the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ from $[Ni(HO_2)_6]^{2+}$. We'll call this "reaction k".

$$\text{Reaction } k: \qquad [Ni(OH_2)_6]^{2+} + 3\,en \rightleftarrows [Ni(en)_3]^{2+} + 6\,H_2O \qquad K_k = ?$$

Reaction "k" is the sum of reaction "i" followed by reaction "j".

$$\begin{aligned} K_k &= K_i \times K_j \\ &= \frac{[Ni(NH_3)_6]}{[Ni(OH_2)_6][NH_3]} \times \frac{[Ni(en)_3][NH_3]^6}{[Ni(NH_3)_6][en]^3} = \frac{[Ni(en)_3]}{[Ni(OH_2)_6][en]^3} \\ &= (2.0 \times 10^8)(4.7 \times 10^9) = 9.4 \times 10^{17} \end{aligned}$$

Exercise 3.1.1.2

The formation constants shown below correspond to the substitution of one ligand on aqueous Cu(II) ion.[5] Propose a trend that explains the different stabilities of the complexes.

$$\begin{array}{ll} \mathrm{NH_3} & K = 2.0 \times 10^3 \\ \mathrm{F^-} & K = 8.0 \\ \mathrm{Cl^-} & K = 1.2 \\ \mathrm{Br^-} & K = 0.9 \end{array}$$

Answer

This trend could be explained by basicity, since ammonium ion is a weak base and the acidity of the hydrogen halides increase in the order HF < HCl < HBr. The ammine ligand is a better donor than any of the halides to the nickel ion, but fluoride is better than chloride and chloride is better than bromide. The reason for the acidity trend varies in the midst of this series. Among the halides, fluoride is the best donor because it is the least polarizable and least stable ion. However, in the second row of the periodic table, the nitrogen in ammonia is a better donor than fluoride because nitrogen is less electronegative than fluorine. This difference is enough to compensate for the fact that ammine is a neutral ligand, presumably with less Coulombic attraction to the copper ion than fluoride.

Note that this trend is very different for Cu(II) than for a similar series of ligands with Cu(I). Cu(II), with greater charge density, is harder in character than Cu(I). Thus, it doesn't necessarily bind more tightly to softer donors the way Cu(I) does.

Exercise 3.1.1.3

Ethylenediamine can be displaced from nickel by tren, (NH2CH2CH2)3N, another polydentate ligand.[3]

$$[\mathrm{Ni(en)_2(OH_2)_2}]^{2+} + \text{tren} \rightleftarrows [\mathrm{Ni(tren)(H_2O)_2}]^{2+} + 2\,\text{en} \qquad K = 76$$

a. What is the denticity of tren?
b. It is reported that ΔH° = +13.0 kJ mol^{-1} and ΔS° = 79.5 J mol^{-1} K^{-1}. Propose a reason for the moderately large formation constant.

Answer

a) Tren has a denticity of 4; it is sometimes described as a tetradentate ligand.

b) The enthalpy of reaction ΔH° = +13.0 kJ mol-1 and at 298 K, -TΔS° = -23.7 kJ mol-1. That means there are no arguments based on the donor-acceptor strength, such as HSAB or basicity, because the enthalpy of reaction is positive. The tightness of binding must result from the positive entropy, which comes from the net increase in the number of molecules as the reaction proceeds (the chelate effect).

The moderately positive enthalpy change is probably related to ring strain in the multidentate complex.

References

1. Complex-Ion Equilibria https://chem.libretexts.org/@go/page/516 (accessed Jun 25, 2021).
2. Complex Ion Formation Constants https://chem.libretexts.org/@go/page/6648 (accessed Jun 25, 2021).
3. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed. John Wiley & Sons: New York, 1980, pp 71-73.
4. Wilbur S, Williams M, Williams R, et al. Toxicological Profile for Carbon Monoxide. Atlanta (GA): Agency for Toxic Substances and Disease Registry (US); 2012 Jun. Table 3-12, Hemoglobin and Myoglobin Binding Kinetics and Equilibrium Constants for Oxygen and Carbon Monoxide. Available from: https://www.ncbi.nlm.nih.gov/books/NBK153687/table/T22/ (accessed Jun 26, 2021).
5. Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry*, 5th Ed. Pearson: Upper Saddle River, NJ, p. 358.

This page titled 3.1.1: Thermodynamic Data is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **10.1.1: Thermodynamic Data** by Chris Schaller is licensed CC BY-NC 4.0.

3.1.2: Magnetic Susceptibility

Electronic Structure

The electronic structure of coordination complexes can lead to several different properties that involve different responses to magnetic fields. These properties can vary between related compounds because of differences in electron counts, geometry, or donor strength. As a result, magnetic measurement of these materials can be used as a tool to provide insight into the structure of a coordination complex.

Diamagnetic and paramagnetic compounds are two common categories defined by interaction with a magnetic field. Diamagnetic compounds display a very slight repulsion from magnetic fields. The interaction is quite subtle and requires the proper instrumentation if it is to be observed; it's not something you would normally notice by waving a magnet in front of a vial of coordination complex. In contrast, paramagnetic compounds display a very slight attraction to magnetic fields. In terms of electronic structure, diamagnetic compounds have all of their electrons in pairs whereas paramagnetic compounds have one or more unpaired electrons. These definitions are not limited to coordination complexes. Atmospheric oxygen, O_2, is a common example of a paramagnetic compound. Atmospheric nitrogen, N_2, is a common example of a diamagnetic compound.

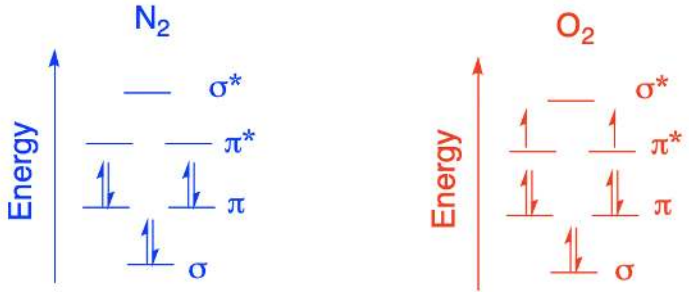


Figure 3.1.2.1: Valence molecular orbital diagrams of N_2 and O_2 show that N_2 is diamagnetic while O_2 is paramagnetic. (CC-BY-NC; Chris Schaller)

These differences arise because of a quantum mechanical property of electrons and other subatomic particles: spin. Spin does not have a direct macroscopic analogy; physical chemists often urge caution about equating it to a phenomenon on the level at which we observe the universe. However, we do know that spin is related to magnetic phenomena. We can think of an electron as having a magnetic moment. There are two allowed values of this magnetic moment ($+\frac{1}{2}$ and $-\frac{1}{2}$) that differ in orientation; spin is a vector quantity. Normally, there is no preference for one orientation over the other. If a coordination complex has one unpaired electron, and we have a million of those coordination complexes in a very tiny sample, about 500,000 of the unpaired electrons would have spin = $+\frac{1}{2}$ and about 500,000 of them would have spin = $-\frac{1}{2}$. The spin of each electron is randomly oriented. As a result, the material would have no net magnetic moment. In the presence of a magnetic field, however, there is a small energy difference between those two spin states. As a result, a majority of the spins adopt the energetically more favorable orientation. Although the material by itself has no net magnetic field, one has temporarily been induced by the influence of an external magnetic field. This is what we mean by magnetic susceptibility.

Measuring Magnetic Susceptibility

All diamagnetic compounds have a roughly similar response to a magnetic field; either their electrons are all paired or they are not. Paramagnetic compounds, however, can respond quite differently to a magnetic field, depending on the number of unpaired electrons. The more unpaired electrons there are, the stronger the magnetic susceptibility will be, and so the stronger the attraction between the compound and the magnetic field. For this reason, measuring the strength of attraction of a compound for a magnetic field can reveal the number of unpaired electrons in the compound. This relationship is most straightforward for complexes of first row transition metals ($3d$ metals), becoming a little more complicated for the $4d$ and $5d$ series.

A Guoy balance is probably the simplest example of a method for determining the presence of unpaired electrons in a coordination complex.[1] It uses a balance, a sample holder and a magnet. Essentially, the magnet is weighed in the presence and absence of the sample. The discrepancy between the two measurements arises because of the interaction of the sample with the magnetic field. Any diamagnetic sample causes slight downward repulsion, registering as a heavier weight. A paramagnetic sample suspended between the poles of the magnet causes a slight upward pull on the magnet, which registers as a lighter weight. The more unpaired electrons there are, the greater the induced magnetic moment, and so the lighter the weight becomes.

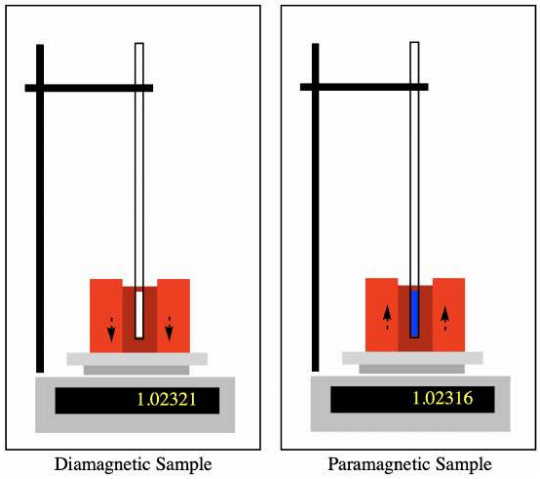


Figure 3.1.2.2: Diagram of a Guoy balance. A magnet (red) sits on a balance and a sample tube is placed in the center cavity of the magnet. (CC-BY-NC; Chris Schaller)

From that measurement, we can extract a parameter that we normally refer to as the effective magnetic moment of the material, μ_{eff}. The magnetic moment is expressed in units called Bohr magnetons. A Bohr magneton (BM or μ_B) is defined as:

$$1\text{BM} = \frac{eh}{4\pi mc}$$

in which e is the charge on an electron; h is Planck's constant; m is the mass of the electron; c is the speed of light.

This experimental quantity is fitted to a simple relationship that depends on the number of unpaired electrons. This mathematical model gives a prediction of the "spin-only" magnetic moment. If the magnetic moment arises purely from the number of unpaired electrons without additional complicating factors, the fit to the experimental data is pretty good.

$$\mu_{eff} \approx \mu_{so} = g\sqrt{S(S+1)}$$

Here, g is the gyromagnetic ratio, which is a proportionality constant between the angular momentum of the electron and the magnetic moment. It has a value of 2.00023, or approximately 2.0. The term $\sqrt{S(S+1)}$ is the value of the angular momentum, which depends on the number of unpaired electrons; S is the absolute value of the sum of the individual spins of the valence electrons. Of course, the spins would cancel out in electrons that were paired, because one would have $m_s = \frac{1}{2}$ and the other would have $m_s = -\frac{1}{2}$. For unpaired electrons, Hund's rule states that they would have parallel spins; for example, two unpaired electrons gives $S = 1$.

Number of unpaired electrons, n	Maximum total spin, S	Spin-only magnetic moment, $\mu_{so}(BM)$
1	$\frac{1}{2}$	1.73
2	1	2.83
3	$\frac{3}{2}$	3.87
4	2	4.90
5	$\frac{5}{2}$	5.92

The table above shows how the magnetic moment changes with the number of unpaired electrons. The maximum number of unpaired electrons given is five, because for a transition metal a sixth electron would have to pair up in a previously occupied orbital. In f-block elements, there could be seven unpaired electrons before pairing occurs because there are seven f orbitals rather than just five d orbitals.

Note that the expression for spin-only magnetic moment is sometimes written in an alternative way, based directly on the number of unpaired electrons, n, rather than S.

$$\mu_{eff} \approx \mu_{so} = \sqrt{n(n+2)}$$

There is an additional approximation in these cases, based on how the values of the spin-only magnetic moment correlate with the number of unpaired electrons. If we always round the value of μ_{so}, then it is one greater than the number of unpaired electrons. Thus, $\mu_{so} \approx n+1$, provided of course that there are any unpaired electrons at all; the relationship doesn't hold if n = 0 because then $\mu_{so} = 0$, not 1.

In reality, observed magnetic moments are slightly different than spin-only magnetic moments. In some cases, the observed magnetic moment is smaller than expected, but those cases are more complicated and we won't consider them here. Very often, the observed magnetic moments are larger than predicted because orbital angular momentum also plays a role in determining the magnitude of the overall magnetic moment. We may use a modified expression that takes this part into account.

$$\mu_{eff} \approx \mu_{s+L} = g\sqrt{S(S+1)+\frac{1}{4}L(L+1)}$$

Just as S is the absolute value of the sum of the spin quantum numbers in the ion, m_s, L is the absolute value of the sum of the orbital quantum numbers, m_l. There are five d orbitals, with $m_l = 2, 1, 0, -1, -2$, and the value of L has to be maximized according to Hund's rule. That means the value of L can be 3, 2, or 0.

As an example, suppose we have a Co^{2+} ion. Co^{2+} ion has a d^7 configuration. It has five d orbitals, so four of these electrons are paired, leaving only three unpaired electrons with parallel spins, so $S = 3/2$. In order to maximize the orbital quantum number, L, two electrons will be in an orbital with $m_l = 2$, two electrons will be in an orbital with $m_l = 1$, and one electron will be in each orbital with m_l = 0, -1, and -2. When we take the sum, we find $L = 2+2+1+1+0-1-2 = 3$. That gives us:

$$\mu_{s+L} = g\sqrt{3/2(3/2+1)+\frac{1}{4}3(3+1)} = 5.20$$

In comparison, $m_{so} = 3.87$ in this case. Observed values of μ_{eff} vary between different Co^{2+} complexes but are generally in the range 4.1 – 5.2 BM.[2] The orbital contribution is often smaller than expected, so magnetic susceptibilities frequently fall somewhere between μ_{so} and μ_{S+L}.

The use of a simple Guoy balance is an historically important method of determining magnetic susceptibility, and it is sometimes used in undergraduate laboratory experiments. Other methods are frequently used to measure magnetic susceptibility in the research laboratory. A magnetic susceptibility balance operates on a similar principle to the one behind the Guoy balance. A sample is placed within the poles of an electromagnet, causing the electromagnet to move very slightly. The current in the electromagnet is adjusted, changing its magnetic field, until the magnet comes back to its initial position. The magnitude of the current adjustment is proportional to the magnetic susceptibility of the sample.

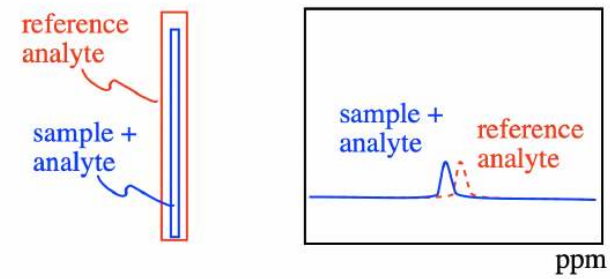


Figure 3.1.2.3: The Evans Method uses chemical shifts (from NMR) to measure magnetic susceptibility. Left: A capillary tube containing sample and a reference analyte is bathed in a larger tube containing reference analyte solution. Right: The NMR signal of a reference analyte (red) is shifted when that analyte is mixed with a paramagnetic sample (blue). (CC-BY-NC; Chris Schaller)

A superconducting quantum interference device (SQUID) uses a superconducting loop in an external magnetic field to measure magnetic susceptibility of a sample.[3] The sample is mechanically moved though the superconducting loop, inducing a change in current and magnetic field that are proportional to the magnetic susceptibility of the sample. Commercially produced SQUID magnetometers often have variable temperature controls, allowing magnetic susceptibility to be measured across a range of temperatures.

The Evans NMR method is quite common because of the widespread availability of high-field NMR spectrometers in research labs. A capillary containing the paramagnetic sample and a reference analyte is placed in an NMR tube containing the same reference analyte but without the paramagnetic sample. The analyte in the presence of the paramagnetic material will experience a local, induced magnetic field owing to the effect of the superconducting magnet of the NMR instrument on the paramagnetic

sample. Its NMR signals will shift as a result. The NMR signal of the analyte outside the capillary will undergo no such shift, and the difference in the two signals is an indicator of the magnetic susceptibility of the sample.

There are other types of magnetic behavior in addition to diamagnetism and paramagnetism. Ferromagnetic materials have long-range order with spins oriented parallel to each other, even in the absence of an external magnetic field. Common, permanent magnets are made from ferromagnetic materials. Antiferromagnetic materials also have long-range order, but the magnetic moments are arranged in opposing pairs. These three different magnetic behaviors are diagnosed by the temperature dependence of the magnetic susceptibility. Paramagnetic materials display magnetic susceptibility (χ_M, related to μ_{eff}) that increases with the inverse of temperature. Ferromagnetic materials have a critical temperature below which magnetic susceptibility rapidly rises. Antiferromagnetic materials have a critical temperature below which magnetic susceptibility rapidly falls. However, these behaviors are largely beyond the scope of the current discussion.

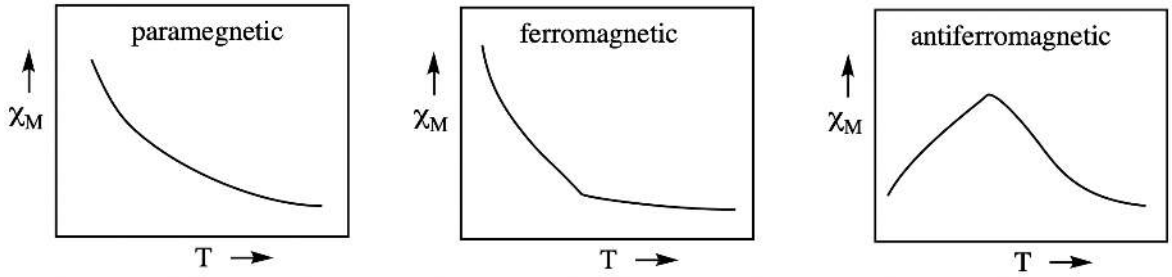


Figure 3.1.2.4: Magnetic behavior depends on temperature. Shown are plots of magnetic behaviour in terms of magnetic susceptibility χ_M versus temperature (T). (CC-BY-NC; Chris Schaller)

Problems

Exercise 3.1.2.1

Show that, given g = 2.0, then $g\sqrt{S(S+1)} = \sqrt{n(n+2)}$.

Answer

$$\begin{aligned}\mu_{so} &= g\sqrt{S(S+1)} \\ &= 2\sqrt{S(S+1)} \\ &= \sqrt{4S(S+1)} \\ &= \sqrt{2S(2S+2)}\end{aligned}$$

but $S = n(1/2)$ or $n = 2S$ then

$$\mu_{so} = \sqrt{n(n+2)}$$

Exercise 3.1.2.2

Calculate the value of μ_{so} in the following cases:

a) V^{4+} b) Cr^{2+} c) Ni^{2+} d) Co^{3+} e) Mn^{2+} f) Fe^{2+}

Answer

a) V^{4+} is d^1; $n = 1$; $\sqrt{n(n+2)} = 1.73$
b) Cr^{2+} is d^4; $n = 4$; $\sqrt{n(n+2)} = 4.90$
c) Ni^{2+} is d^8; $n = 2$; $\sqrt{n(n+2)} = 2.83$
d) Co^{3+} is d^6; $n = 0$; $\sqrt{n(n+2)} = 0$
e) Mn^{2+} is d^5; $n = 5$; $\sqrt{n(n+2)} = 5.92$
f) Fe^{2+} is d^6; $n = 4$; $\sqrt{n(n+2)} = 4.90$

g) Cr^{3+} is d^3; $n = 3$; $\sqrt{n(n+2)} = 3.87$
h) V^{3+} is d^2; $n = 2$; $\sqrt{n(n+2)} = 2.83$

Exercise 3.1.2.3

Calculate the value of μ_{eff} in the following cases:

a) V^{4+} b) Cr^{2+} c) Ni^{2+} d) Co^{3+} e) Mn^{2+} f) Fe^{2+}

g) Cr^{3+} h) V^{3+}

Answer

a) V^{4+} is d^1; $S = 1/2$; $L = 2$; $\mu_{s+L} = g\sqrt{1/2(1/2+1) + \frac{1}{4}2(2+1)} = 3.00$

b) Cr^{2+} is d^4; $S = 2$; $L = 2+1+0-1 = 2$; $\mu_{s+L} = g\sqrt{2(2+1) + \frac{1}{4}2(2+1)} = 5.48$

c) Ni^{2+} is d^8; $S = 1$; $L = 2+2+1+1+0+0-1-2 = 3$; $\mu_{s+L} = g\sqrt{1(1+1) + \frac{1}{4}3(3+1)} = 2.24$

d) Co^{3+} is d^6; $S = 2$; $L = 2+2+1+0-1-2 = 2$; $\mu_{s+L} = g\sqrt{(2+1) + \frac{1}{4}2(2+1)} = 5.48$

e) Mn^{2+} is d^5; $S = 5/2$; $L = 2+1+0-1-2 = 0$; $\mu_{s+L} = g\sqrt{5/2(5/2+1) + \frac{1}{4}0(0+1)} = 5.92$

f) Fe^{2+} is d^6; $S = 2$; $L = 2+2+1+0-1-2 = 2$; $\mu_{s+L} = g\sqrt{2(2+1) + \frac{1}{4}2(2+1)} = 5.48$

g) Cr^{3+} is d^3; $S = 3/2$; $L = 2+1+0 = 3$; $\mu_{s+L} = g\sqrt{3/2(3/2+1) + \frac{1}{4}3(3+1)} = 5.20$

h) V^{3+} is d^2; $S = 1$; $L = 2+1 = 3$; $\mu_{s+L} = g\sqrt{1(1+1) + \frac{1}{4}3(3+1)} = 2.24$

References

1. Lancashire, R. J. Magnetic Susceptibility https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/04%3A_Experimental_techniques/4.14%3A_Magnetism/Magnetic_Susceptibility_Measurements (accessed Jun 27, 2021).
2. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed. John Wiley & Sons: New York, 1980, p 628.
3. Raja, P. M. V.; Barron, A. R. Magnetism https://chem.libretexts.org/@go/page/55872 (accessed Jun 27, 2021).

This page titled 3.1.2: Magnetic Susceptibility is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **10.1.2: Magnetic Susceptibility** by Chris Schaller is licensed CC BY-NC 4.0.

3.1.3: Electronic Spectra

The interaction of different wavelengths of electromagnetic radiation with matter provides a vast amount of information about material structure. The absorption of UV-visible light is connected to the excitation of electrons to higher orbitals. Inherently, this spectroscopy reveals information about the electronic structure of compounds, including coordination complexes. This topic is important enough that it is the subject of a later chapter.

This page titled 3.1.3: Electronic Spectra is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **10.1.3: Electronic Spectra** by Chris Schaller is licensed CC BY-NC 4.0.

3.1.4: Coordination Number and Molecular Shapes

Examination of physical properties, such as electronic spectra or magnetic susceptibility, can often be used to distinguish between possible molecular geometries of coordination complexes. It can be difficult to predict the coordination number of a complex formed from a specific metal ion and a given set of ligands, to say nothing of its geometry. Steric crowding and valence electron count around the metal in the complex are just two of the factors that influence coordination number. Even for a given coordination number, there are sometimes different possible coordination geometries. For example, five-coordinate can adopt square pyramidal or trigonal bipyramidal geometry. In most cases, it is especially difficult to predict which geometry prevails. In fact, many complexes adopt a geometry somewhere between the two. Four-coordinate geometry offers a similar choice between square planar and tetrahedral geometry, although in this case it can be easier to predict which one is likely to occur. The energetic difference between these two possible geometries can often be explained based on the electronic structure of the complex.

This page titled 3.1.4: Coordination Number and Molecular Shapes is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **10.1.4: Coordination Number and Molecular Shapes** by Chris Schaller is licensed CC BY-NC 4.0.

3.2: Bonding Theories

Coordination complexes caused great fascination among chemists during the nineteenth century, although it wasn't until the century's end that Alfred Werner determined the fundamental principles of their structure. A fuller understanding of their structures was developed over the first half of the twentieth century. This understanding developed in stages, with newer theories and models building on previous ones rather than replacing them completely.

Crystal Field Theory

In the early 1930's, American physicists John Hasbrouck van Vleck and Hans Bethe developed a theoretical treatment of crystalline transition metal compounds that explained their magnetic and optical properties. This treatment did not consider bonding in any way, but it did concern itself with the geometry of ligands, or counterions, around a central metal ion. Electrostatic considerations formed the basis of the theory, with attention to repulsive forces between ligand electrons and d electrons on the metal ion. The model gave good predictions about the effect of ligand geometry on the electronic structure of the metal ion.

Ligand Field Theory

During the 1950's, British chemists John Stanley Griffith and Leslie Orgel combined some aspects of crystal field theory with molecular orbital theory to produce a bonding model for coordination complexes. Rather than just considering electrostatic interactions between metal and ligand, this approach used orbital interactions to model the role of covalency in determining the electronic structure of the complex.

Angular Overlap Model

This model is a specific approach to considering how ligand and metal orbitals combine to produce molecular orbitals in a coordination complex. It uses the symmetry and orientation of atomic orbitals to determine what combinations of these orbitals should be considered.

Computational Chemistry

The three "pencil-and-paper models" described above for bonding in coordination complexes have been greatly augmented by the power of modern computational chemistry. Although based on the same principles, computational methods offer a much higher level of quantitative information about electronic energy and allow relatively easy assessment of possible structural features such as coordination geometry. Pioneering methods included extended Hückel theory, originally developed by Roald Hoffman and Robert Burns Woodward to study pericyclic reactions. The method was later adapted by Hoffman and others to investigate inorganic and organometallic complexes. More recently, developments such as density functional theory have greatly facilitated computational work on transition metal systems because of their simplified treatment of many-electron systems. These approaches and others like them allow for the prediction of coordination complex properties through a computer interface.

This page titled 3.2: Bonding Theories is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **10.2: Bonding Theories** by Chris Schaller is licensed CC BY-NC 3.0.

3.2.1: Crystal Field Theory

As the name implies, crystal field theory was developed as a way of explaining phenomena in ionic crystalline solids. Bethe and van Vleck wished to provide a rationale for the magnetic properties of these materials, as well as their colors. The latter resulted from the wavelength of light absorbed, revealing something about differences in electronic energy levels in the ions of the crystalline solid. The magnetic properties also depended on electronic energy levels, because magnetism depended upon whether electrons were paired, and whether or not electrons are paired depends on the presence or absence of orbitals at the same energy level.

They first considered a transition metal ion in an octahedral hole formed between layers of counterions packed in a crystalline lattice. The metal ion would have six near neighbors: three above and three below. Of course, the ions would be held together by electrostatics: the negative charges on the counterions would be attracted to the positive charge on the metal ion.

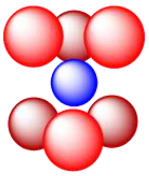


Figure 3.2.1.1: Illustration of a positively charged metal ion (blue) surrounded by six near neighbors with negative charges (red). (CC-BY-NC; Chris Schaller)

But in addition to that positive charge, the metal ion also has electrons of its own. How did the electrons of those neighboring counterions affect the energy of those metal electrons? "...If we're going to work this out carefully, we need to consider three different situations", thought the physicists. "We need to start by considering the energy of the metal valence orbitals in the absence of counterions. Since these are transition metal ions, we will pay close attention to the five d orbitals. What happens when those d orbitals are placed in a field of surrounding electrons, if the field is evenly distributed around them? In other words, what happens to them in a spherical field of negative charge? And then, what happens if those electrons are not evenly distributed? What happens if the surrounding electrons approach only along the Cartesian axes?"

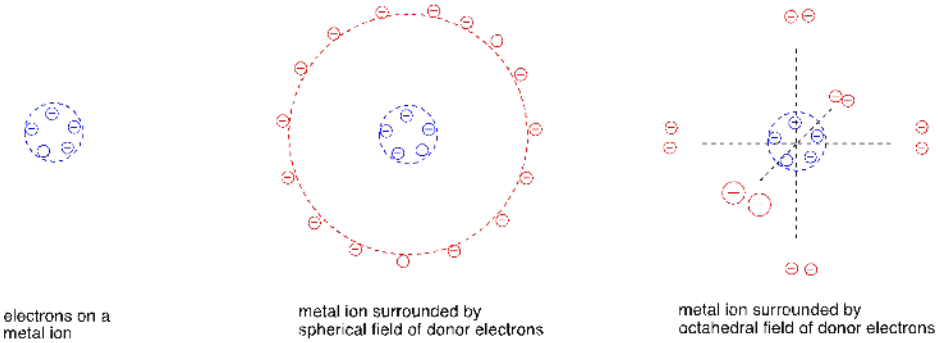


Figure 3.2.1.2: Illustration of the electrostatic charges to consider in idealized situations. (Left) imaginary situation of a "lone" metal ion with five d electrons in its valence shell. (Middle) Imaginary situation where a d^5 metal ion is surrounded by a spherical distribution of donor (Lewis base) electrons from a set of ligands. (Right) Imaginary situation where a d^5 metal ion is surrounded by a set of ligand donor electrons that are located along Cartesian coordinates (in an octahedral geometry). (CC-BY-NC; Chris Schaller)

The Cartesian axes are important here because, in an octahedron, the six ligands are ninety degrees (90°) apart from each other in space. We can think of two of those ligand electrons as lying in either direction from the metal ion along the z axis; two of them along the x axis; and the last two along the y axis.

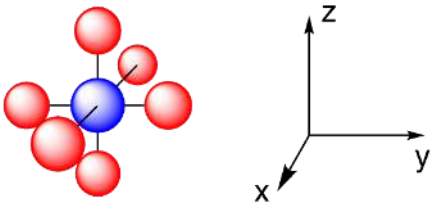


Figure 3.2.1.3: Illustration of a positively charged metal ion (blue) surrounded by six ligands (red) in an octahedral geometry where each ligand lies along the Cartesian axes. (CC-BY-NC; Chris Schaller)

Of course, when these metal electrons are placed in a field of negative charge, repulsion results, and the electrons on the metal go up in energy. They all increase in energy by the same amount.

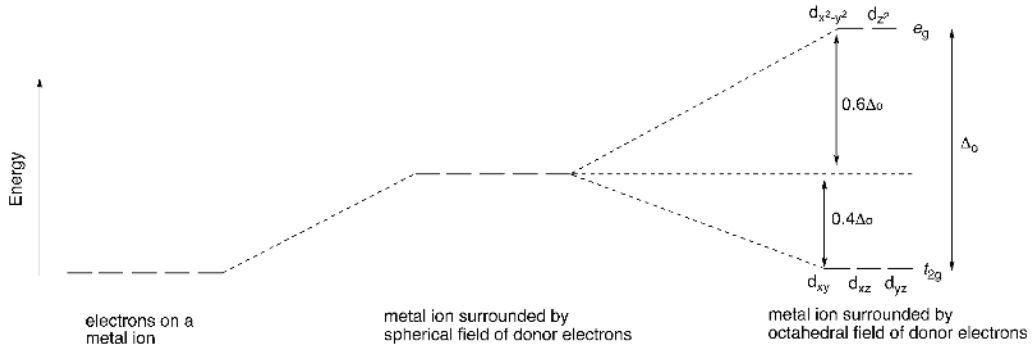


Figure 3.2.1.4: The relative energy levels of the valence d orbitals corresponding to the imaginary situations pictured in Figure 3.2.1.2 above. (Left) The five valence d orbitals of a "lone" metal ion are degenerate. (Middle) The electrons in the five valence d orbitals of a metal ion would be uniformly repelled by a spherical distribution of negative charge, and thus would be higher in energy than a "lone" metal ion. (Right) The electrons in each of the five valence d orbitals of a metal ion would interact to different extents with ligands located along each of the Cartesian coordinates, and thus their energies would be raised or lowered compared to the situation where charge was distributed in a uniform sphere. (CC-BY-NC; Chris Schaller)

The octahedral field is a different question, however, because the five d orbitals have different spatial distributions. Two of them (the d_{z^2} and $d_{x^2-y^2}$) lie along the axes. These orbitals are referred to as having e_g symmetry. The other three (the d_{xy}, d_{xz}, and d_{yz}) lie in between the axes. These three are referred to as having t_{2g} symmetry.

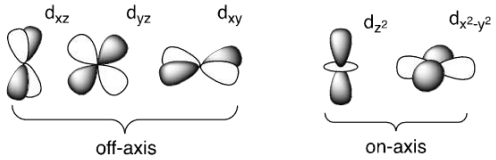


Figure 3.2.1.5: Illustration of the boundary surfaces of the five d orbitals. (CC-BY-NC; Chris Schaller)

Those two orbitals along the axes experience repulsion from the neighboring anions. Because all of the negative charge is focused in six positions rather than being uniformly distributed, the repulsion experienced by these orbitals is greater than it would be in a spherical field. On the other hand, the three orbitals between the axes experience very little repulsion; their energy is actually much lower than it would be in a spherical field of negative charge.

These two sets of orbitals are therefore found at two different energy levels. The energy difference between them is called the octahedral field splitting, Δ_o. Because the total amount of repulsion is the same in the octahedral field and the spherical field – it is just distributed differently – the average energy level of the orbitals should be the same in the two fields. This average energy of the orbitals is called the **barycenter**, a term borrowed from astronomy. Because two of the orbitals are raised above the barycenter in the octahedral field and three are lowered below the barycenter, then the e_g set must be $\frac{3}{5}\Delta_o$ $(= 0.6\Delta_o)$ above the barycenter and the t_{2g} set must be $\frac{2}{5}\Delta_o$ $(= 0.4\Delta_o)$ below the barycenter. That means the average energy lies at the barycenter.

A parameter called the crystal field stabilization energy (CFSE) was developed to assess the energy difference between the metal ion in an octahedral coordination geometry and a spherical field. To determine CFSE, we simply add up the energy of all the electrons relative to the energy level of electrons in the spherical field, in units of Δ_o. For an octahedral case:

$$\text{CFSE} = \left[\frac{2}{5}(\#\text{ of electrons in } t_{2g}) + \frac{3}{5}(\#\text{ of electrons in } e_g)\right] \times \Delta_o$$

Problems

? Exercise 3.2.1.1

Determine the crystal field stabilization energy (CFSE) in the following octahedral ions:

a) V^{3+} b) Ni^{2+} c) Cr^{3+} d) Zn^{2+}

Answer a

V^{3+} is d^2, with two electrons in the t_{2g} and zero electrons in e_g.

CFSE = $[2(-0.4)+0(0.6)] \times \Delta_o = -0.8\Delta_o$

Answer b

Ni^{2+} is d^8, with six electrons in t_{2g} and two electrons in e_g.

CFSE = $[6(-0.4)+2(0.6)] \times \Delta_o = -1.2\Delta_o$

Answer c

Cr^{3+} is d^3, with three electrons in t_{2g} and zero electrons in e_g.

CFSE = $[3(-0.4)+0(0.6)] \times \Delta_o = -1.2\Delta_o$

Answer d

Zn^{2+} is d^{10}, with six electrons in t_{2g} and four electrons in e_g.

CFSE = $[6(-0.4)+4(0.6)] \times \Delta_o = 0\Delta_o$.

This page titled 3.2.1: Crystal Field Theory is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

- **10.2.1: Crystal Field Theory** by Chris Schaller is licensed CC BY-NC 4.0.

SECTION OVERVIEW

3.3: Ligand Field Theory

3.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex

3.3.2: Orbital Splitting and Electron Spin

3.3.3: Ligand Field Stabilization Energy

3.3.4: Tetrahedral Complexes

3.3.5: Square-Planar Complexes

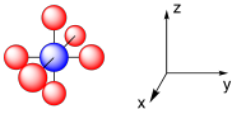
This page titled 3.3: Ligand Field Theory is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex

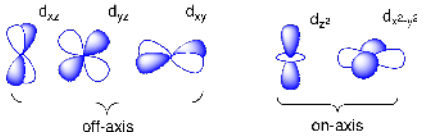
Crystal field theory is successful at providing some general insights into the differing energy levels of d orbitals in coordination complexes. That knowledge can help us to understand some of the magnetic properties of these compounds, which are determined by the number of unpaired electrons. It can also help us to understand some of the absorbed wavelengths of light in the UV-visible spectrum, which in some cases depends on the energy difference between different sets of d orbitals.

Ligand field theory picks up where crystal field theory left off by taking into consideration the importance of orbital overlap for covalent bonding. That factor adds another level of detail to our model of metal complex behavior, and it provides additional nuance to our understanding of why two related complexes may have very different properties.

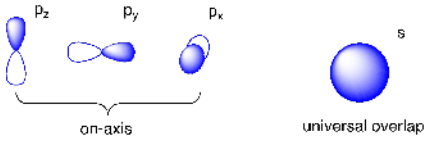
We can start by taking another look at octahedral coordination geometry. That's probably the most common coordination geometry. It's also the one we looked at when we considered crystal field theory. In this geometry, all six ligands are located along the x, y, or z axes.



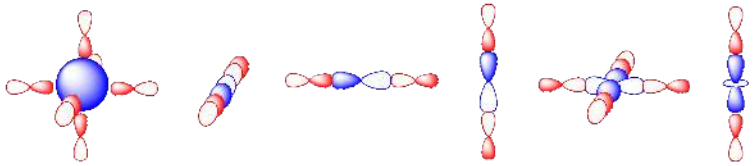
Once again, only two of the valence d orbitals are located along those axes. In crystal field theory, we considered that orientation as an opportunity for electron-electron repulsion between ligand lone pairs (or charges on neighboring anions) and the d electrons. This time, we'll think about the opportunity for covalent bonding that exists between ligand orbitals and the d orbitals along these axes.



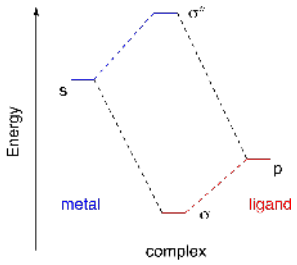
In addition to the d orbitals, we should also think about the potential for bonding with the metal's valence s and p orbitals. All three p orbitals are located along the axes where we find the ligands. They are ideally located for bonding with ligand orbitals along those axes. The s orbital is different: it is non-directional. No matter where a ligand is located, if it has sigma bonding, it will have the same overlap with that spherical s orbital. That means the s orbital is a good candidate for forming a covalent sigma bond with any ligand, no matter what the geometry.



That leaves us with six possible metal orbitals that could potentially overlap with the six ligands. Each metal orbital could potentially interact with any one of a number of these ligands. In the illustration below, we've made the assumption that the ligand orbitals are p orbitals. That's not a bad bet given that we are generally considering p-block elements as donor atoms in most ligands. The s orbital could presumably interact with up to six ligands. The metal p orbitals could interact with ligand orbitals in either direction along the axis. By inspection, it appears that the d orbitals could interact with two or four orbitals.



That ratio of six ligand orbitals to six ligand orbitals is coincidental. A one-to-one correspondence between metal orbitals and ligand orbitals isn't strictly required, but it's easier to think about that way. Let's begin by assuming that the s orbital interacts with just one donor orbital. Just like in MO construction for main group diatomics, if we start with two atomic orbitals and combine them, we get two molecular orbitals. One of them is the in-phase combination and the other one is the out-of-phase combination. The number of molecular orbitals we obtain is the same as the number of atomic orbitals we start with.



We can think of these two combinations as the addition of two orbitals together, with a positive coefficient if they are in phase and a negative coefficient if they are out of phase.

$$\psi M\text{-}L = a\psi M(s) + b\psi L(p)$$

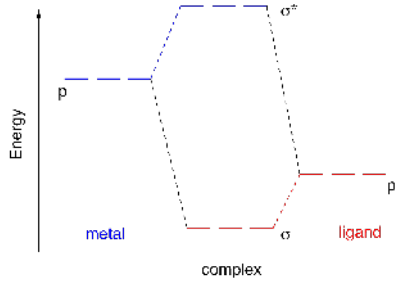
$$\psi^* M\text{-}L = c\psi M(s) - d\psi L(p)$$

Notice that the molecular orbital interaction diagram is asymmetric. The ligand orbital is at lower energy than the metal orbital. The donor atom is a p block element; it's to the right of the transition metals in the periodic table. The donor atom is more electronegative than the transition metal, so its electrons are at lower energy. In a case like that, the coefficients in the orbital combination follow a pattern. In the in-phase combination, the more electronegative element gets a larger coefficient than the less electronegative element ($b > a$). The opposite is true in the out-of-phase combination ($c > d$).

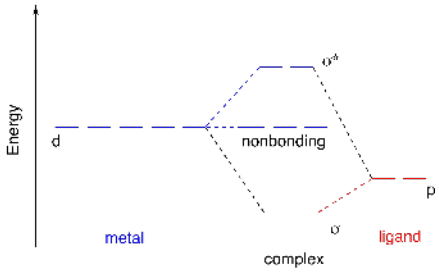


The molecular orbital more closely resembles the atomic orbital to which it is closest in energy, both spatially and energetically. Consequently, we often talk about the bonding orbital, σ, as though it is still a ligand p orbital, and the antibonding orbital, σ, as though it is still a metal s orbital. The bonding orbital is ligand-centered and the antibonding orbital is metal-centered.

If we consider the three metal p orbitals and their overlap with three of the ligand donor orbitals, we find a very similar outcome. The three σ* orbitals are metal-centered, whereas the three σ orbitals are ligand-centered.

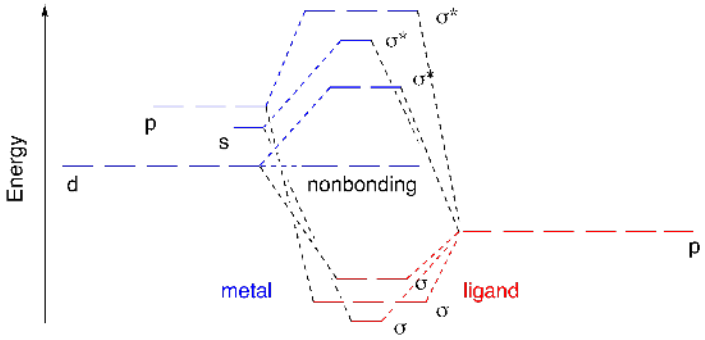


The d orbitals, on the other hand, present a significant variation. Only two of them appear to be capable of overlap with ligand p orbitals. If we pair those two d orbitals off with the remaining two ligand donor orbitals, we have three leftover metal d orbitals. Those three metal orbitals do not overlap with the ligand and so they are non-bonding.

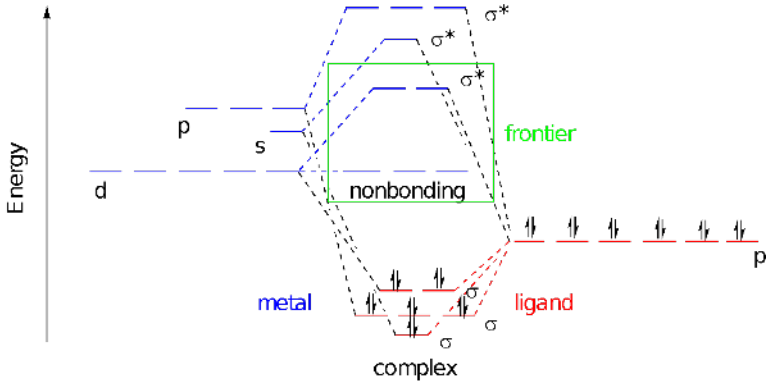


We can superimpose those three pictures to get a look at the full molecular orbital interaction diagram. It is still somewhat simplified. We are ignoring any core orbitals on the metal and we are also ignoring any ligand orbitals that aren't involved in sigma

bonding to the metal. Maybe we have ammine ligands but we are ignoring all of those N-H bonds and focusing solely on the M-N bonds.

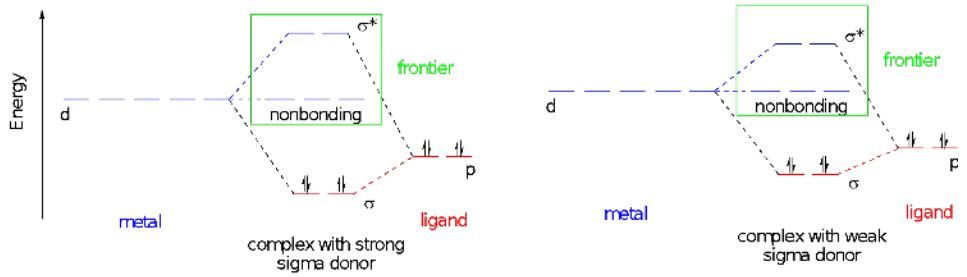


The six donor atoms are each donating a pair of electrons to the metal. Upon covalent bond formation, each of those lone pairs slides down into an energy well; they are stabilized by formation of the metal-ligand bond.

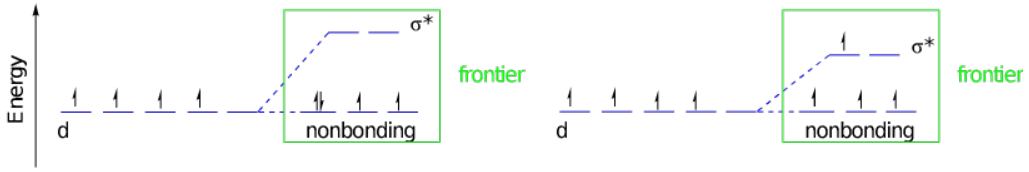


So far, we have ignored the electrons on the metal because we are looking at a general case. There could be anywhere from zero to ten electrons in the atomic d orbitals, depending on the metal and its oxidation state. These electrons will be crucial to many aspects of the behavior of the complex because they are found at the frontier. Frontier orbitals are often the key to understanding reactivity as well as physical properties such as magnetism and interaction with light.

We often consider only these frontier orbitals when we consider the properties of transition metal complexes. We ignore what seems like the most important part of the picture: the bonding orbitals. We do that because those bonding orbitals are not frontier orbitals. Furthermore, the stability of those bonding orbitals is reflected in the antibonding level. The lower the bonding electrons sink, the higher the antibonding levels rise. One immediate consequence of that connection is that the bond strength may control the gap between nonbonding and antibonding d orbitals. Strong sigma donors provide a large d-d gap, whereas weak sigma donors give a smaller d-d gap. Understanding donor strength can be a difficult task, but remember for example that more basic ligands are often stronger donors.



If we think about a specific case of metal ion, we can add some d electrons to the picture. Suppose we have a d^4 metal ion. Maybe it's a Cr^{2+} ion. This ion can take on two different electron configurations in an octahedral environment. With stronger donors, the d-d gap is potentially too large to promote a fourth electron into the next energy level, so the complex is left with two unpaired electrons. With weaker donors, the relatively small d-d gap may be smaller than the energy it takes to put two electrons into the same orbital, so there are four unpaired electrons. We'll return to the consequences of these situations on an upcoming page.



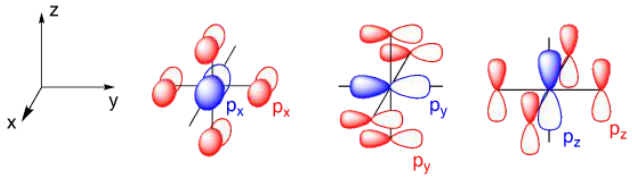
Pi Donor Ligands

The sigma donor strength of the ligand can have an appreciable effect on the d orbital splitting in the complex, and that might influence the properties of the complex. That's not something that we considered in crystal field theory, but thinking about bonding interactions has provided another layer of information. What other variations in ligand donation might play a role in the d orbital splitting?

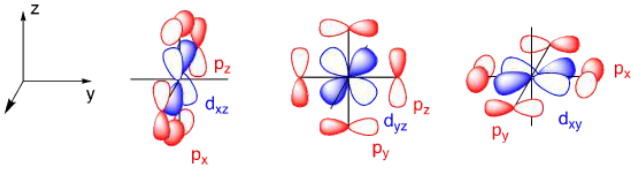
Suppose a donor atom had more than one lone pair. Could it donate a second? On paper, that makes another bond between the ligand and the metal. Bond formation is energy-releasing and stabilizing, although sometimes we get in trouble when we draw too many bonds, because we've run out of orbitals to interact with each other.



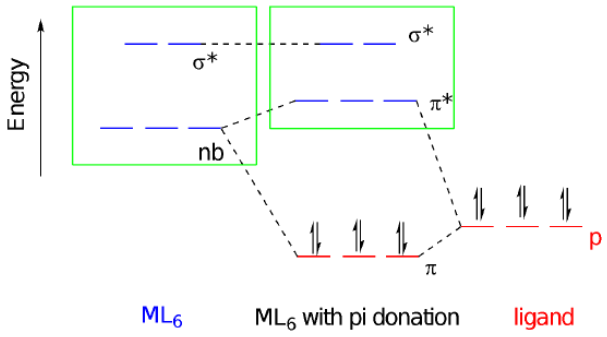
When we draw a pair of bonds between two atoms, we usually think of the first bond as a sigma bond and the second one as a pi bond. The question here is, can bromine form a pi bond with a transition metal? When we learn about pi bonds, we start by looking at two nitrogen atoms or two carbon atoms using parallel p orbitals to bond with each other. The resulting pi bond avoids the sigma bond because it is above and below the bond axis. We have already established that the metal can use its p orbitals for bonding. On paper, a metal p orbital in an octahedral complex could pi bond with four different ligands.



The trouble with that scheme is that we are already using these metal p orbitals for sigma bonding. We have other metal orbitals that could overlap with these ligand p orbitals, however, and we aren't using them for sigma bonding. These are the d_{xy}, d_{xz}, and d_{yz} orbitals. This set looks even more promising for pi bonding; the d orbitals reach out towards the ligand p orbitals, maximizing overlap. Once again, each d orbital could potentially form pi bonds with up to four ligands.



Let's consider the consequences of pi bond formation using the molecular orbital interaction diagram. This time we're just considering lone pairs on three ligands that could donate to the three different d orbitals of appropriate symmetry: the d_{xy}, d_{yz}, and d_{xz}. We get a bonding and an antibonding combination, but the three ligand pairs all go down in energy. As long as there are fewer than six d orbitals there is a net decrease in energy. Just like before, when these orbitals combine, the bonding combination has more ligand character whereas the antibonding combination has more metal character. The key change in terms of the frontier orbitals is that the d orbital splitting becomes smaller than in the case of the simple sigma bond donor.

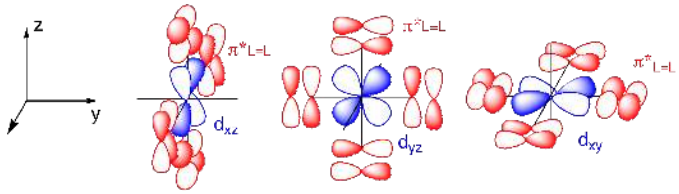


Ligand-to-metal donation is just one way to make a metal-ligand double bond. In those cases in which the metal has d electrons, the double bond could also be formed by donation from the metal to the ligand. The d electrons are most likely to occupy the d_{xy}, d_{xz}, and d_{yz}, as those orbitals are the lowest available ones. Those are the same orbitals that were involved in π bonding in ligand-to-metal donation. In addition to d electrons, there must also be an acceptor orbital on the ligand. That is to say, there must be an empty orbital on the ligand with π symmetry. Instead of a lone pair, this acceptor takes the form of a π* orbital on the ligand. That means there has to be a π bond between the donor atom and a second atom within the ligand. Carbon monoxide is the classic example of such a ligand.

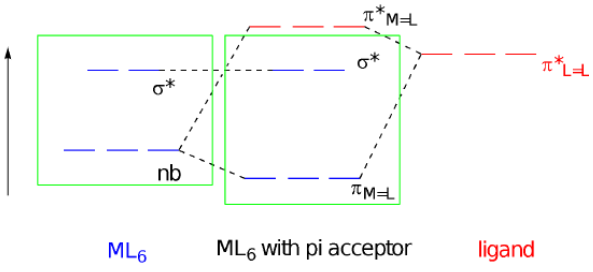


Metal-to-ligand π donation has the effect of breaking a π bond in the ligand because of the fact that electrons are donated into a ligand π* orbital. In terms of Lewis structures, this looks like an interaction that would strengthen the metal-ligand bond but weaken bonds within the ligand itself. When a metal π donates into a carbon monoxide, populating the CO π* orbital, the CO bond gets weaker.

Because we are still looking at π bond formation, the orbital pictures look somewhat similar to the ones for ligand-to-metal π donation, but with π* molecular orbitals instead of p atomic orbitals.



This time, the relevant ligand orbitals are higher in energy than the metal orbitals because they are antibonding. Antibonding orbitals are typically higher in energy than atomic orbitals. That means that when we construct orbital combinations from these pairs, the metal-ligand pi bonding orbital has more metal character. Conversely, the metal-ligand pi antibonding orbital has more ligand character. If there are any d electrons, they will drop into a lower energy well through formation of the pi bond. The ligand π* molecular orbitals are raised in energy, but that change has no energetic consequences since there aren't any electrons there.



In contrast to ligand-to-metal pi bond donation, metal-to-ligand pi bond formation has the effect of increasing the d orbital splitting. That gives us three different magnitudes of d orbital splitting for three different categories of ligand. The splitting follows the order pi donors < sigma donors < pi acceptors, at least as a rough trend; individual ligands may deviate from this trend for other reasons, such as the strength of sigma donation.

Group Theory as a Tool in Ligand Field Theory

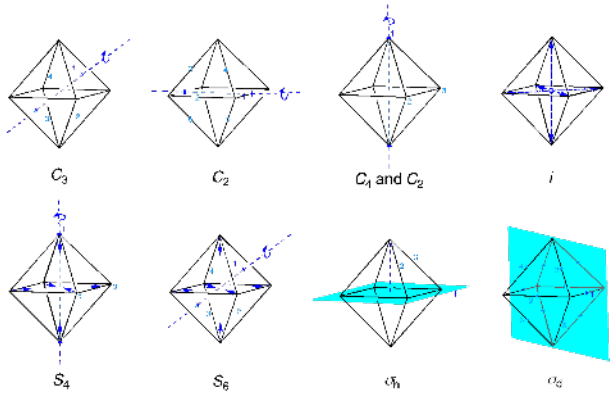
What if the orbital combinations are not obvious? What if you can't decide by inspection which ligand orbital would overlap with which metal orbital? There is a more general method of evaluating these things using group theory. We should use that approach for the octahedral geometry, because we already have a concrete example of what that should look like. We can use our knowledge of that outcome to build confidence in our results from group theory. Group theory may be a newer approach to us, and so it will be helpful to validate the results.

To get started, we are going to need a character table for an octahedral geometry, and we will need to consider how the bonding orbitals behave under the symmetry operations of this group. You can brush up on point groups and symmetry here.1

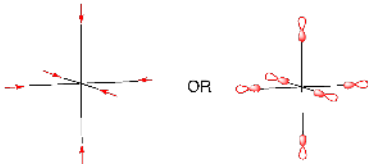
The top row of the character table for the octahedral point group organizes the symmetry operations and tells us how many of each operation we can find.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$

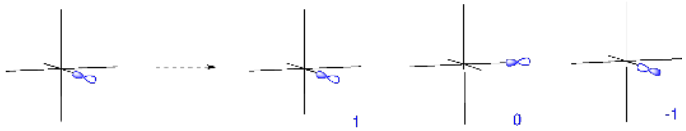
Apart from the identity element, there are ten additional symmetry elements in this point group. The C_3 axis passes through the four pairs of opposite faces of the octahedron. We can rotate by either 120 degrees or 240 degrees, making a total of eight operations. Six different C_2 axes pass through opposite edges of the octahedron. Additional C_2 axes are coincident with the C_4 axis passing through opposite corners of the octahedron (because $C_2 = C_4^2$, but not C_4^1 or C_4^3). There is an inversion center at the position of the metal ion. That inversion element makes possible an S_4 axis coincident with the C_4 axis and an S_6 axis coincident with the C_3 axis. Finally, there are two sets of mirror planes, one set in the equatorial planes and one set bisecting the faces of the octahedron.



We can use the character table to determine appropriate orbitals for bonding with the ligands. A set of vectors is often used for this purpose but p orbitals can be used just as well. We consider how each of the p orbitals will change under a particular symmetry element.



Has a p orbital remained in place, unchanged? That counts as 1. Has it moved into an entirely different position? That counts as 0. Has it remained in place, but with the opposite orientation? That counts as -1.



Looking at each of the symmetry elements gives us a reducible representation.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$

Γ	6	0	0	2	2	0	0	0	4	2	

If we look at the complete character table, we can find the irreducible representations that this reducible representation is composed of.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ (= C_4^2)	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 – x^2 – y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-1	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

We find that $\Gamma = A_{1g} + T_{1u} + E_g$. If we add together the characters for each of the symmetry elements in those three representations, we get the characters in our reducible representation for the ligand p orbitals.

The A_{1g} representation corresponds to the metal s orbital. The T_{1u} representation corresponds to the three metal p orbitals. The E_g representation corresponds to two of the d orbitals: $2z^2 – x^2 – y^2$ (usually abbreviated as z^2) and $x^2 – y^2$. The other three d orbitals (d_{xy}, d_{xz}, and d_{yz}) have T_{1u} symmetry and are not a match for the set of ligand orbitals that we examined. This is exactly the outcome that we established by looking at metal orbitals and ligand orbitals and deciding which ones would overlap. The match between the two approaches should provide some confidence about the use of character tables to make decisions about symmetry-appropriate bonding.

References

(1) Point Groups https://chem.libretexts.org/@go/page/269925 (accessed Jul 2, 2021).

Example 3.3.1.1

The formula for decomposing a reducible representation is based on taking the dot product and normalizing:

$$ai = 1hQN \bullet \chi(R) \bullet \chi(R)Q$$

in which ai is the number of times the irreducible representation appears in the reducible representation; h is the order of the point group (the total number of symmetry operations); N is the number of operations for a given symmetry element, Q; $\chi(R)$is the character of the reducible representation and $\chi(R)$is the character of the irreducible representation.

Use the formula to confirm the finding that, for sigma bonding in an octahedral geometry:

$$\Gamma = A_{1g} + T_{1u} + E_g.$$

Solution

ai = 1h QN· χ(R)·χ(R)Q

A_{1g}: ai = 148 [1·6·1+8·0·1+6·0·1+6·2·1+3·2·1+ 1·0·1+6·0·1 + 8·0·1+3·4·1+6·2·1] = 148 (6+12+ 6+12+12)= 148·48=1

A_{2g}: ai = 148 [1·6·1+8·0·1+6·0·(-1)+6·2·(-1)+3·2·1+ 1·0·1+6·0·(-1) + 8·0·1+3·4·1+6·2·(-1)] = 148 (6-12+ 6+12-12)= 148·0=0

E_g: ai = 148 [1·6·2+8·0·(-1)+6·0·0+6·2·0+3·2·2+ 1·0·2+6·0·0 + 8·0·(-1)+3·4·2+6·2·0] = 148 (12+12+ 24)= 148·48=1

T_{1g}: ai = 148 [1·6·3+8·0·0+6·0·(-1)+6·2·1+3·2·(-1)+ 1·0·3+6·0·1 + 8·0·0+3·4·(-1)+6·2·(-1)] = 148 (18+12- 6-12-12)= 148·0=0

T_{2g}: ai = 148 [1·6·3+8·0·0+6·0·1+6·2·(-1)+3·2·(-1)+ 1·0·3+6·0·(-1) + 8·0·0+3·4·(-1)+6·2·1] = 148 (18-12- 6-12+12)= 148·0=0

A_{1u}: ai = 148 [1·6·1+8·0·1+6·0·1+6·2·1+3·2·1+ 1·0·(-1)+6·0·(-1) + 8·0·(-1)+3·4·(-1)+6·2·(-1)] = 148 (6+12+ 6-12-12)= 148·0=0

A_{2u}: ai = 148 [1·6·1+8·0·1+6·0·(-1)+6·2·(-1)+3·2·1+ 1·0·(-1)+6·0·1 + 8·0·(-1)+3·4·(-1)+6·2·1] = 148 (6-12+ 6-12+12)= 148·0=0

E_u: ai = 148 [1·6·2+8·0·(-1)+6·0·0+6·2·0+3·2·2+ 1·0·(-2)+6·0·0 + 8·0·1+3·4·(-2)+6·2·0] = 148 (12+12- 24)= 148·0=0

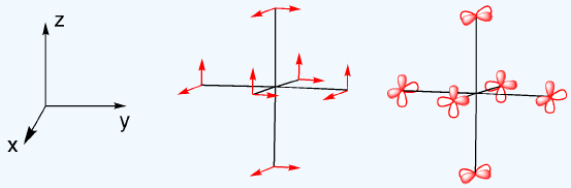
T_{1u}: ai = 148 [1·6·3+8·0·0+6·0·(-1)+6·2·1+3·2·(-1)+ 1·0·(-3)+6·0·(-1) + 8·0·0+3·4·1+6·2·1] = 148 (18+12- 6+12+12)= 148·48=1

T_{2u}: ai = 148 [1·6·3+8·0·0+6·0·1+6·2·(-1)+3·2·(-1)+ 1·0·(-3)+6·0·1 + 8·0·0+3·4·1+6·2·(-1)] = 148 (18-12- 6+12-12)= 148·0=0

$$\Gamma = A_{1g} + T_{1u} + E_g.$$

Example 3.3.1.1

Determine the reducible representation for the symmetry of the pi-bonding orbitals in an octahedral geometry. You can use simple vectors to represent the bias of the p orbitals.



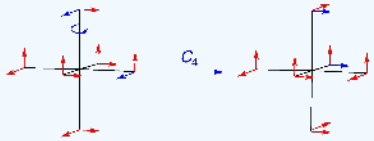
Solution

E: All 12 vectors remain in same place in same orientation. The character is 12.

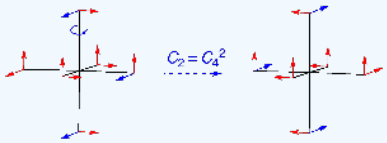
C_3: An off-axis rotation, so all vectors have moved. The character is 0.

C_2: An off-axis rotation, so all vectors have moved. The character is 0.

C_4: An on-axis rotation, but the vectors are off-axis. Note how the labeled vectors make the movement out of position clear. The character is 0.

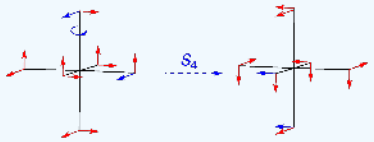


C_2 (= C_4^2): An on-axis rotation, but this time the four vectors located along the rotational axis just switch bias. The others move out of position. The character is -4.



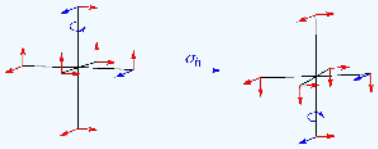
i: All 12 vectors move to the opposite side of the structure. The character is 0.

S_4: An on-axis rotation, followed by inversion. Note how the labeled vectors make the movement out of position clear. The character is 0.



S_6: An off-axis rotation, so all vectors have moved. The character is 0.

σ_h: Four vectors change position (character is 0); four vectors remain in position and keep original bias (character is 4); four vectors remain in position and switch bias (character is -4); net character is 0.



σ_d: An off-axis reflection, so all vectors have moved. The character is 0.

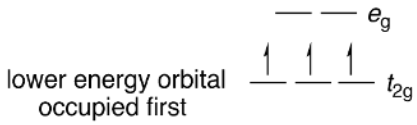
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ (= C_4^2)	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
Γ	12	0	0	0	-4	0	0	0	0	0

This page titled 3.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

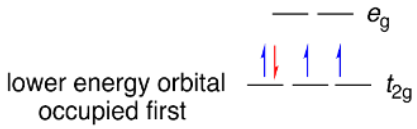
- **10.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex** by Chris Schaller is licensed CC BY-NC 4.0.

3.3.2: Orbital Splitting and Electron Spin

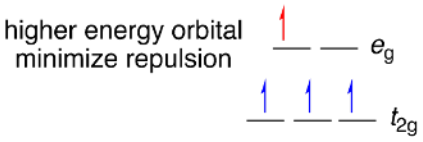
Once we have a d orbital splitting diagram for a particular geometry of a complex, we can populate the diagram with the known number of d electrons for a specific metal ion. If the complex is octahedral and the metal ion has 1, 2, or 3 d electrons, then the electrons will simply go in the lower level, the t_{2g} orbitals. For the d^3 case, one electron will occupy each orbital, with parallel spins.



What about a fourth electron? If the metal ion has a d^4 configuration, we could imagine two situations. The electron may also occupy one of the t_{2g} orbitals, which lie at lower energy. To do so, the fourth electron must be spin-paired with the other occupant of that orbital.



That's the low-spin configuration. The fourth electron has gone into the lower possible orbital rather than the higher possible one. Alternatively, the fourth electron could occupy one of the e_g orbitals. It would be at a higher energy level, but it would avoid that repulsive interaction with the other electron in the t_{2g} orbital. That would be the high-spin case. The fourth electron has gone into the higher possible orbital rather than the lower one.



The terms "high-spin" and "low-spin" really refer to the net spin of the atom. Each electron has a spin of a certain magnitude, but spin is a vector quantity. If two spins are pointing in the same direction, they add together, so the overall spin of the atom increases. If two spins are pointing in opposite directions, they cancel out, so the overall spin of the atom decreases. Having electrons paired in the same orbital leads to a lower spin for the atom.

The electron configuration of a d^4 metal ion in an octahedral complex depends broadly on two factors: the difference in energy between the t_{2g} and e_g levels (the octahedral field splitting, Δ_o) and the energy associated with pairing two electrons in the same orbital. We have already looked at some of the factors that influence the field splitting, so let's start by looking at that factor.

It is useful to be aware of some general trends in Δ_o. First, comparison between Δ_o measured for +3 cations and for +2 cations of the first-row transition metals manganese, iron, and cobalt shows that charge exerts a significant influence. The higher the charge on an ion, the larger Δ_o becomes. These examples are illustrated in Table 1.

Table 1. Comparison of Octahedral Field Splitting Between M(II) and M(III) Ions[1]

Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$Cr(OH_2)_6^{2+}$	14,000	$Cr(OH_2)_6^{3+}$	17,600
$Mn(OH_2)_6^{2+}$	7,500	$Mn(OH_2)_6^{3+}$	21,000
$Fe(OH_2)_6^{2+}$	10,000	$Fe(OH_2)_6^{3+}$	14,000

In each case, the M(III) ion has an octahedral field splitting that is significantly larger than the corresponding value in the M(II) case. However, comparisons of the field splitting between metals in different columns is complicated, with no simple trend.

Second, Δ_o is much larger for second-row than for first-row metals of the same group, as shown in Table 2. The value of Δ_o is even larger for third-row transition metals than second-row transition metals. As a result, transition metal ions from the second and third

rows are usually low-spin. First-row transition metal ions, with their smaller Δ_o values, are often high spin, but they can also be low spin, and charge is an important factor in determining which case will occur.

Table 2. Comparison of Octahedral Field Splitting Between Ions from Different Periods of the Periodic Table[2]

Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$CoCl_6^{3-}$	Not available	$Co(NH_3)_6^{3+}$	23,000
$RhCl_6^{3-}$	20,300	$Rh(NH_3)_6^{3+}$	33,900
$IrCl_6^{3-}$	24,900	$Ir(NH_3)_6^{3+}$	Not available

Although the available data is limited here, second-row rhodium has a larger octahedral field splitting than first-row cobalt, and third-row iridium displays a larger field splitting than second-row rhodium. Note that these examples are compared using complexes with identical ligands.

The configuration of first-row transition metals is also strongly influenced by the ligands in the complex, indicated in Table 3. For a given ion, we would expect π-acceptors to give relatively large values of Δ_o, whereas σ-donors would give a smaller Δ_o and π-donors would give a smaller value still. There may be some overlap between these groups, because there are stronger and weaker π-acceptors, for example, or stronger and weaker σ-donors, but that is the general trend that we would expect.

Table 3. Comparison of Octahedral Field Splitting Between Ions from Different Periods of the Periodic Table[2]

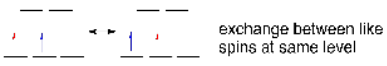
Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$CrBr_6^{3-}$	Not available	$NiBr_6^{2-}$	7,000
$CrCl_6^{3-}$	13,600	$NiCl_6^{2-}$	7,300
$Cr(OH_2)_6^{3+}$	17,400	$Ni(OH_2)_6^{2+}$	8,500
$Cr(NH_3)_6^{3+}$	21,600	$Ni(NH_3)_6^{2+}$	10,800
$Cr(CN)_6^{3-}$	26,300	$Ni(CN)_6^{2-}$	Not available

Among the chromium complexes, the π-accepting cyanide gives a much larger value of Δ_o than the π-donating chloride, as expected from molecular orbital considerations. In both the chromium and nickel cases, the ammine ligand, a simple σ-donor, provides a larger splitting that the aquo ligand, which is a π-donor. We may not be able to make predictions about electron configuration based solely on the type of ligand, but generally we would expect that a complex with π-accepting ligandswould be more likely to be low-spin than a complex with π-donating ligands.

In addition to comparing ligands of different classes, we may also want to look at differences between ligands of the same class. Frequently, among σ-donors and π-donors, basicity of the ligand plays a valuable predictive role. For example, when coordinated to Ni(II), chloride results in a larger field splitting than bromide. Chloride is more basic than bromide, as shown by the pKa of the conjugate acids (pK_a = -6 for HCl vs. -9 for HBr), leading to stronger coordination in the case of chloride; that means a lower energy for the donor electrons but a higher energy for the σ* orbital compared to bromide coordination.

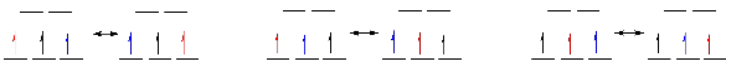
Let's take a look at the other factor that plays a role in determining the electron configuration: the pairing energy. We refer generally to the pairing energy as Π, but it actually has two components. Π_c is the coulombic portion of this energy. It arises from repulsion between two electrons that occupy the same region of space (the same orbital). Repulsion between the electrons causes energy to increase, so Π_c is a positive unit of energy.

The second component involves quantum mechanical exchange between like spins: Π_e is a stabilizing factor. When two electrons of like spin can exchange with each other, energy decreases: Π_e is a negative unit of energy. For example, in a d^2 octahedral metal, the two electrons are both at the t_{2g} level and have the same spin; that situation allows them to freely exchange with each other, which results in a decrease in energy.



In a d^3 system, the addition of just one more electron leads to a significant lowering of energy because the amount of exchange triples. Now, the electron in the first orbital can exchange with either the electron in the second or the third orbital. The electrons in

the second and third orbitals can also exchange with each other. That makes a total of three possible exchanges.



These two factors, repulsion and exchange, contribute to an overall or total pairing energy. Some values of total pairing energy are shown in Table 4.

Table 4. Comparison of Total Pairing Energies Between M(II) and M(III) Ions[3]

Complex	Π (cm^{-1})	Complex	Π (cm^{-1})
$Mn(OH_2)_6^{2+}$	25,500	$Mn(OH_2)_6^{3+}$	28,000
$Fe(OH_2)_6^{2+}$	17,600	$Fe(OH_2)_6^{3+}$	30,000
$Co(OH_2)_6^{2+}$	22,500	$Co(OH_2)_6^{3+}$	21,000

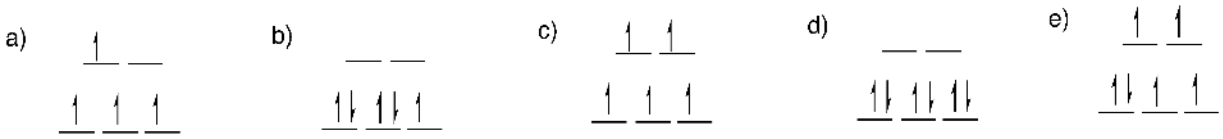
Like the field splitting, pairing energy is somewhat complex and is governed by more than one factor. However, it is worth pointing out that pairing energy is frequently (but not always) larger for more highly charged ions. For example, the pairing energy for both Mn(III) and Fe(III) are greater than the respective values for Mn(II) and Fe(II). That fact reflects the contraction of the more highly-charged ions. Confined to a smaller volume, repulsion between the electrons becomes greater.

In general, notice that the magnitudes of these pairing energies are pretty large compared to many of the octahedral field splitting values in the previous tables. In particular, they are larger than most of the values of Δ_o for first-row transition metals. That's why many first-row ions are high spin: the energy required to pair electrons in a low-spin configuration is often greater than the energy required to place an electron in the e_g level. The pairing energies are not that large compared to Δ_o for second- and third-row transition metals, so ions of those metals are more likely to be low spin.

So, if we are comparing the energy difference between two configurations, we need to take into account both the energy difference between the two orbital energy levels and the energy difference resulting from spin pairing. That could include both differences in electron-electron repulsion and differences in energy because of exchange.

Problems

1. Demonstrate the exchanges possible in the following configurations.



2. Determine the difference in Π_c between the high spin and low spin configuration in each of the following cases:

a) d^4 b) d^5 c) d^6

3. Determine the difference in Π_e between the high spin and low spin configuration in each of the following cases:

a) d^5 b) d^6 c) d^7

4. Given the value of Δ_o and Π in each case, predict whether the complex will be high spin or low spin.

a) $[Mn(OH_2)_6]^{2+}$

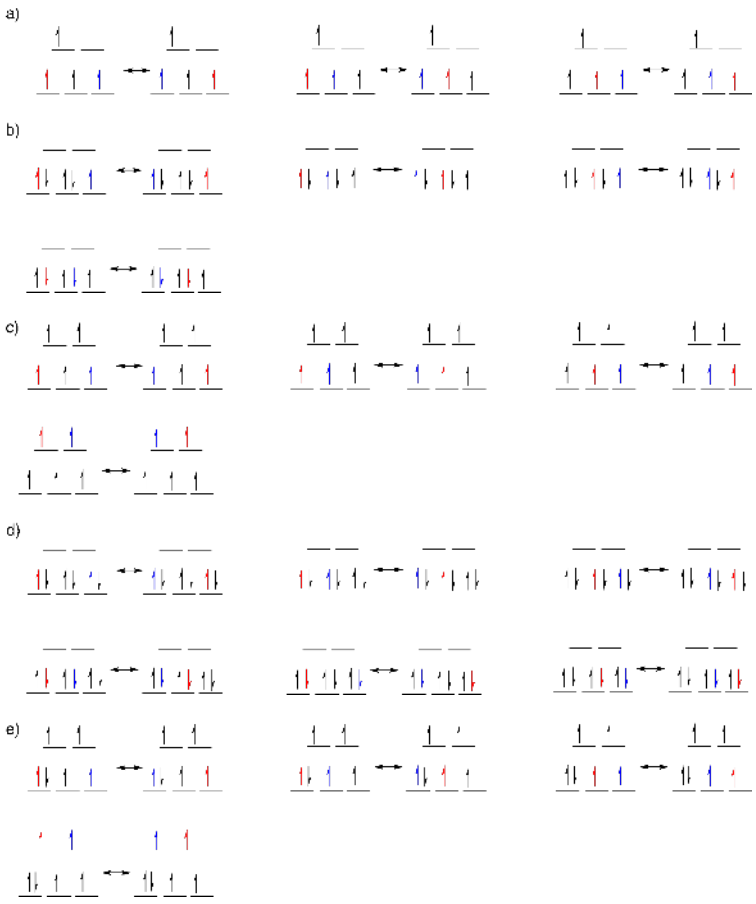
b) $[Mn(OH_2)_6]^{3+}$

c) $[Co(OH_2)_6]^{2+}$ (Δ_o = 14,000 cm^{-1})4

d) $[Co(OH_2)_6]^{3+}$ (Δ_o = 19,000 cm^{-1})4

Solutions

1.



2. Determine the difference in Π_c between the high spin and low spin configuration in each of the following cases:

a) d^4



The difference is: $\Delta E = ls - hs = \Pi_c - 0 = \Pi_c$.

b) d^5



The difference is: $\Delta E = ls - hs = 2\Pi_c - 0 = 2\Pi_c$.

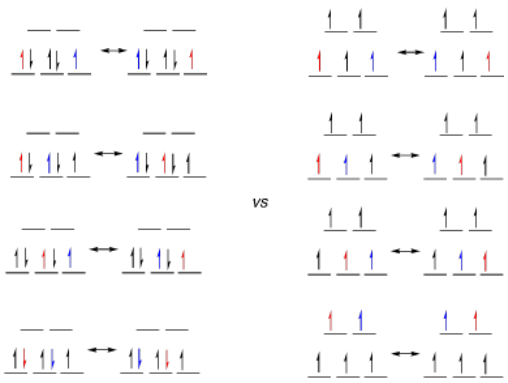
c) d^6



The difference is: $\Delta E = ls - hs = 2\Pi_c - 0 = 2\Pi_c$.

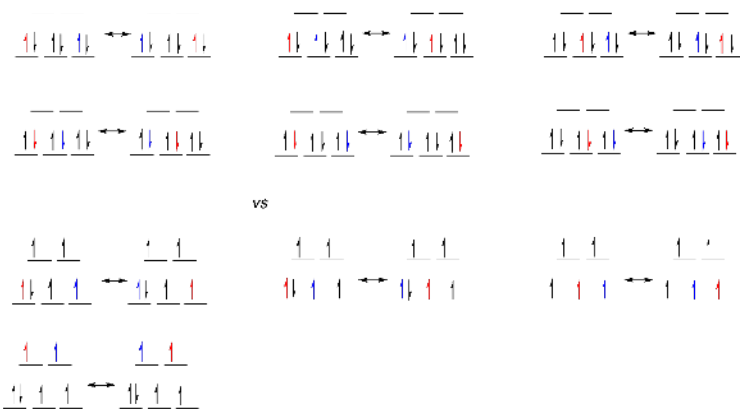
3. Determine the difference in Π_e between the high spin and low spin configuration in each of the following cases:

a) d^5



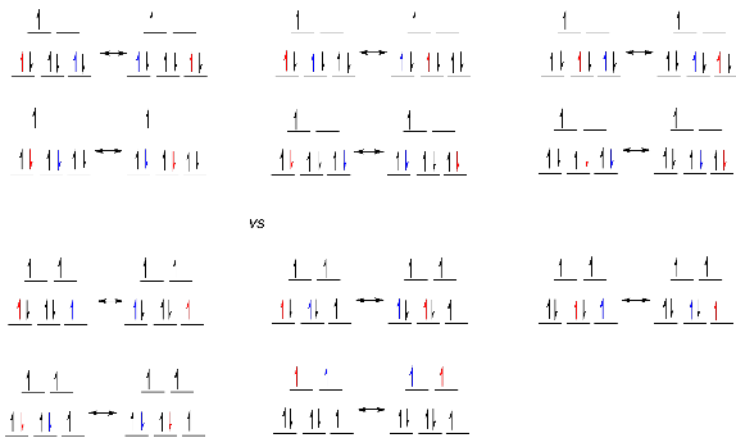
The difference is: ΔE = ls – hs = $4\Pi_e - 4\Pi_e = 0$

b) d_6



The difference is: ΔE = ls – hs = $6\Pi_e - 4\Pi_e = 2\Pi_e$

c) d^7



The difference is: ΔE = ls – hs = $6\Pi_e - 5\Pi_e = \Pi_e$

4. Given the value of Δ_o and Π in each case, predict whether the complex will be high spin or low spin.

a) $[Mn(OH_2)_6]^{2+}$

Δ_o = 7,500 cm^{-1} and Π = 25,500 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin.

b) $[Mn(OH_2)_6]^{3+}$

Δ_o = 21,000 cm^{-1} and Π = 28,000 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin.

c) $[Co(OH_2)_6]^{2+}$ (Δ_o = 10,000 cm^{-1})4

Δ_o = 10,000 cm^{-1} and Π = 22,500 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin.

d) $[Co(OH_2)_6]^{3+}$ (Δ_o = 19,000 cm^{-1})4

Δ_o = 19,000 cm^{-1} and Π = 21,000 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin, but note how similar the values are. Many Co(III) complexes are low spin.

References.

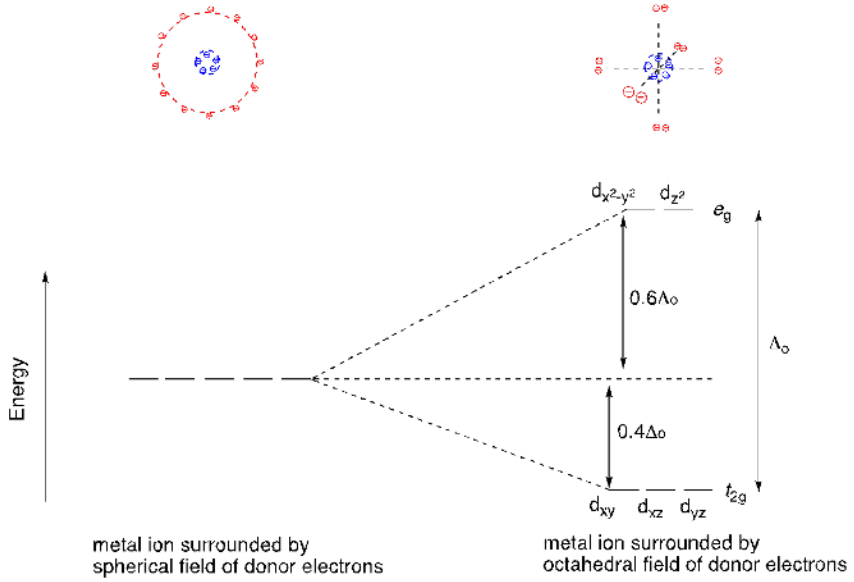
1. Dunn, T. M.; McClure, D. S.; Pearson, R. G. *Some Aspects of Crystal Field Theory*. Harper & Row: New York, 1965, p.82.
2. Sienko, M. A.; Plane, R. A. *Physical Inorganic Chemistry*. W. A. Benjamin: New York, 1963, p. 56.
3. Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed*. Pearson: Boston, 2014, p. 374.
4. Figgis, B. N.; Hitchman, M. A, *Ligand Field Theory and Its Applications*. Wiley-VCH: Brisbane, 2000, p. 215

This page titled 3.3.2: Orbital Splitting and Electron Spin is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

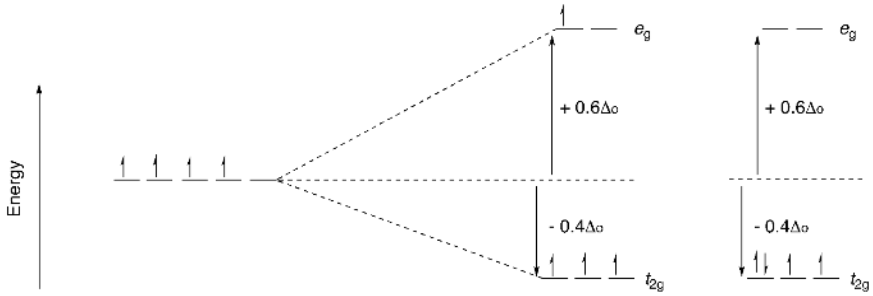
- **10.3.2: Orbital Splitting and Electron Spin** by Chris Schaller is licensed CC BY-NC 4.0.

3.3.3: Ligand Field Stabilization Energy

If we want to compare the stability of a particular electron configuration compared to the imaginary d electron configuration in a spherical electric field, we can calculate the ligand field stabilization energy. Remember, in crystal field theory, we compared the d electrons in a spherical field to the situation in which ligands approached in an octahedral geometry. The e_g level is destabilized by $0.6\Delta_o$ compared to undifferentiated d orbitals in a spherical field, whereas the t_{2g} level is $0.4\Delta_o$ lower in energy than the d orbitals in a spherical field.



Let's look at the case of a d^4 complex. That's an interesting case, because as we fill in the d electrons one by one, it is the first example in which there is the possibility of either a high spin or a low spin configuration. If we first consider the high-spin case, then we see that three of the electrons drop into the t_{2g} level and the last one goes into the e_g level.



The ligand field stabilization energy is the difference between energy in a spherical field and in an octahedral field. In the high spin d^4 case, that means three electrons are lower in energy and one is higher in an octahedral environment.

- High spin d^4:

$$\begin{aligned} \text{LFSE} &= [0.6(1) - 0.4(3)]\Delta_o \\ &= [0.6 - 1.2]\Delta_o \\ &= -0.6\Delta_o \end{aligned}$$

For comparison, in the low spin case, all four of the electrons are lower in energy in the presence of the octahedral field.

- Low spin d^4:

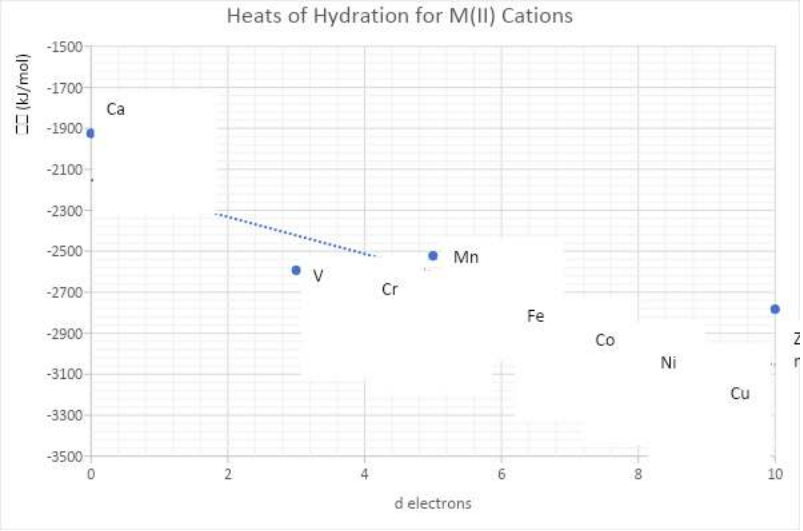
$$\begin{aligned} \text{LFSE} &= [0.6(0) - 0.4(4)]\Delta_o \\ &= -1.6\Delta_o \end{aligned}$$

Of course, the ligand field stabilization energy isn't the only contributor to energetic differences between possible electron configurations. Pairing energy will also play a role, including Coulombic or repulsive terms as well as exchange terms. The total energy difference between a high spin and low spin configuration will compare those energies as well. For the d^4 case:

$$\begin{aligned}\Delta E(\text{low spin} - \text{high spin}) &= (-1.6\Delta_o + \Pi_c + 3\Pi_e) - (-0.6\Delta_o + 3\Pi_e) \\ &= -\Delta_o + \Pi_c\end{aligned}$$

One application of ligand field stabilization energy is found in the hydration energies of metal ions. As a first approximation, we might expect that the energy released when a bond is formed between a ligand and a metal ion would be related to Coulomb's Law. If we look at values for the hydration of gas-phase ions, we expect the energies of reaction to become more negative as we move across the transition metals from left to right. That increase in magnitude of the exothermicity of hydration reflects the periodic trend in sizes of the ions. Ions of the same charge get smaller as we go to the right because of the increasing number of protons in the nucleus. As the radius of the atom decreases, the energy released upon binding a ligand increases.

The following graph illustrates this general phenomenon for a series of M^{2+} ions. There are gaps in the graph where data was unavailable. Some of the early transition metals are rarely observed as divalent ions.



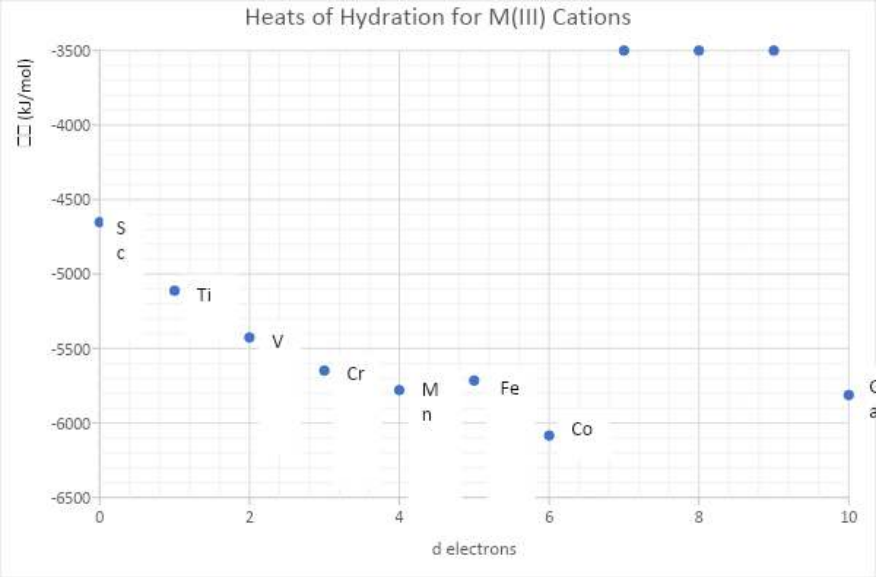
Overall, we can see a general progression towards more negative heats of hydration as we move across the series. That observation is consistent with Coulomb's Law. However, if we look carefully, we can see that some of the data points are a little higher compared to the rest (or a little lower, depending on your perspective). The higher data points occur at d^0, d^5 and d^{10} (Ca^{2+}, Mn^{2+} and Zn^{2+}). Assuming we are dealing with high spin configurations, which is often the case for the first row of transition metals, then these are exactly the cases in which we expect ligand field stabilization energy to be absent. The table below illustrates that point.

Table 3.3.1. Ligand Field Stabilization Energy for High Spin Configuration

Electron count (dn)	LFSE (Δo)
0	0
1	-0.2
2	-0.4
3	-0.6
4	-0.3
5	0
6	-0.2
7	-0.4

Electron count (dn)	LFSE (Δo)
8	-0.6
9	-0.3
10	0

We can confirm that what we are seeing is related to the d electron count, rather than some intrinsic property of individual metals, by looking at a similar series of M^{3+} ions. Once again, we observe the overall agreement with Coulomb's Law, and we see that the d^0 cases display a lower heat of hydration than the others because of a lack of ligand field stabilization energy.



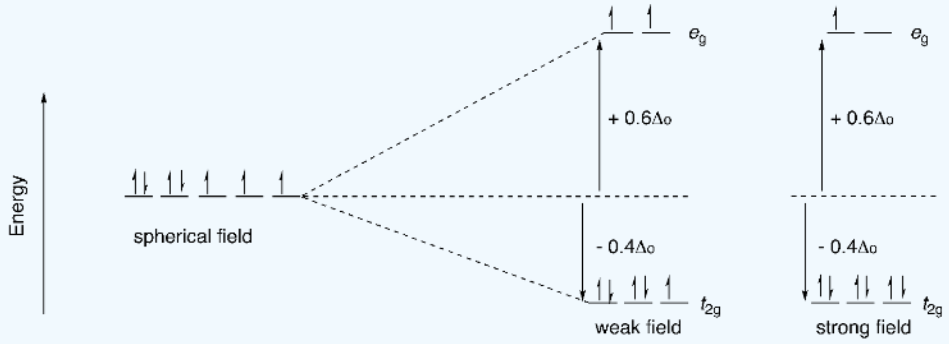
This time, Fe^{3+} is an outlier because it is d^5, rather than the d^4 Mn^{3+}. Again, some of the data is missing here because some of the later transition metals are rarely found as trivalent ions. Conversely, the ions that exhibit ligand field stabilization energies are depressed from the overall trend, displaying additional stabilization in an octahedral coordination environment.

Neither the hydration energies for the M^{2+} ions nor the hydration energies for the M^{3+} ions track perfectly with ligand field stabilization energies. There are a number of other factors that also impact these observed hydration energies, but they are beyond the scope of the current discussion. These factors include the nephelauxetic ("cloud-expanding") effect, in which interelectron repulsion in complexes can be lower than in free ions based on the degree of covalency in the complex.

Example 3.3.3.1

Draw a diagram showing the energetic differences between d^7 metal ions in a spherical field, a weak field octahedral environment, and a strong field octahedral environment.

Solution



Example 3.3.3.2

Show how you would calculate the ligand field stabilization energy in the following cases:

a. Low-spin d^5
b. High-spin d^5
c. Low-spin d^7
d. High-spin d^7

Solution

a. Low-spin d^5: LFSE = $[0.6\ (0) – 0.4\ (5)]\Delta_o = -2.0\Delta_o$
b. High-spin d^5: LFSE = $[0.6\ (2) – 0.4\ (3)]\Delta_o = [1.2 - 1.2]\Delta_o = 0\Delta_o$
c. Low-spin d^7: LFSE = $[0.6\ (1) – 0.4\ (6)]\Delta_o = [0.6 - 2.4]\Delta_o = -1.8\Delta_o$
d. High-spin d^7: LFSE = $[0.6\ (2) – 0.4\ (5)]\Delta_o = [1.2 - 2.0]\Delta_o = -0.8\Delta_o$

Example 3.3.3.3

Calculate the difference between low spin and high spin electronic configurations in the following cases:

a. d^5
b. d^7

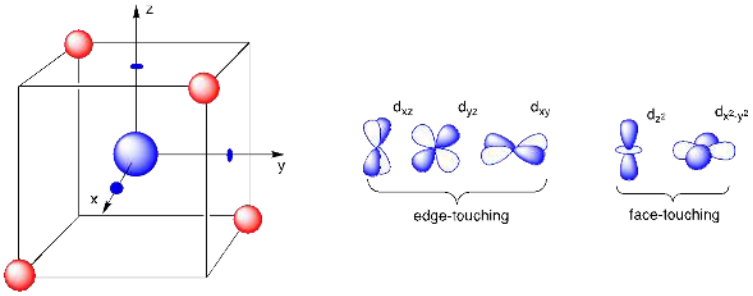
Solution

1. d^5: ΔE low spin – high spin = $(-2.0\Delta_o + 2\Pi_c + 4\Pi_e) - (0\Delta_o + 4\Pi_e) = -2\Delta_o$
2. d^7: ΔE low spin – high spin = $(-1.8\Delta_o + 3\Pi_c + 6\Pi_e) - (-0.8\Delta_o + 2\Pi_c + 5\Pi_e) = -\Delta_o + \Pi_c + \Pi_e$

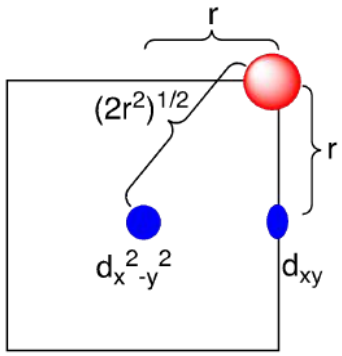
This page titled 3.3.3: Ligand Field Stabilization Energy is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.3.4: Tetrahedral Complexes

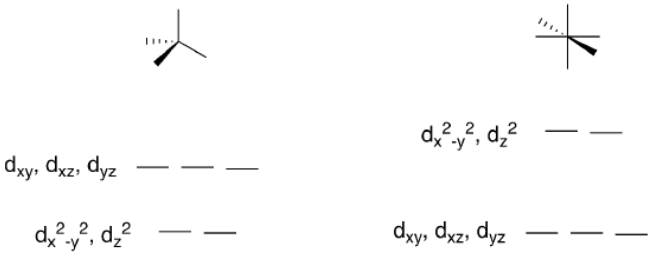
Tetrahedral geometry is even more common in chemistry than square planar geometry. Assessing the orbital interactions in tetrahedral geometry is somewhat more complicated, however, and it is common to proceed directly to a group theory approach. Nevertheless, let's take a look at this geometry and see what we can determine through simple observation before we see the results from a more rigorous approach. To begin, it helps to know that a tetrahedral geometry is defined as having four atoms arranged at alternating corners of a cube around a central atom.



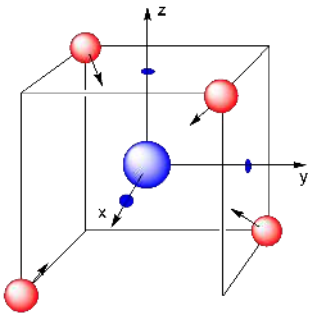
If we consider the orientation of the d orbitals, we find that they fall into two different groups. Although all five orbitals lie off-axis with respect to the ligands, some of them are pointed directly at the edges of the cube (d_{xy}, d_{xz}, d_{yz}) whereas the others point at the faces of the cube ($d_{x^2-y^2}$, d_{z^2}). The edge-touching orbitals lie a little closer to the ligands; we'll define this distance as *r*, which in this case is half the edge length of the cube. The face-touching orbitals are slightly farther away: based on the Pythagorean theorem, they are $r^2 + r^2 = 2\,r^2 = r^2$ away from the ligands.



Based on that simple observation, we might start to think about the dxy, dxz and dyz group as forming the antibonding orbitals upon interaction with the ligands. The dz2 and dx2-y2 would be left as non-bonding orbitals. This result would be exactly the opposite of the octahedral case. We would therefore expect an orbital splitting diagram that is exactly the inverse of the octahedral one. Maybe the splitting between orbital levels would be a little smaller, though, because of the lack of direct overlap between the ligands and the metal orbitals. After all, even the closest set of metal orbitals don't point directly at the ligands like in the octahedral case.

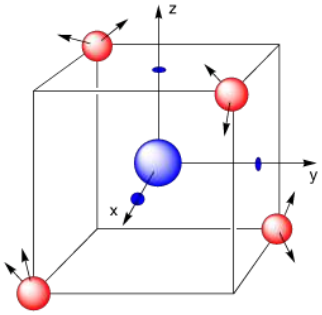


This supposition is confirmed through a group theory approach. We can use vectors pointing along the ligand-metal axes to examine sigma bonding, as shown below. We would subject these vectors to the symmetry transformations in the tetrahedral space group, T_d, shown in the table.



T_d	E	$8C_3$	$6C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ_σ	4	1	0	0	2		$A_1 + T_2$
Γ_π	8	-1	0	0	0		$E + T_1 + T_2$

That analysis leads to the reducible representation for sigma bonding, Γ_σ , shown in the table. This representation reduces to the irreducible representations, $A_1 + T_2$. The d orbitals represented here, the T_2 set, are indeed the d_{xy}, d_{xz} and d_{yz}. The non-bonding d orbitals are the E group, corresponding to d_{z^2} and $d_{x^2-y^2}$.



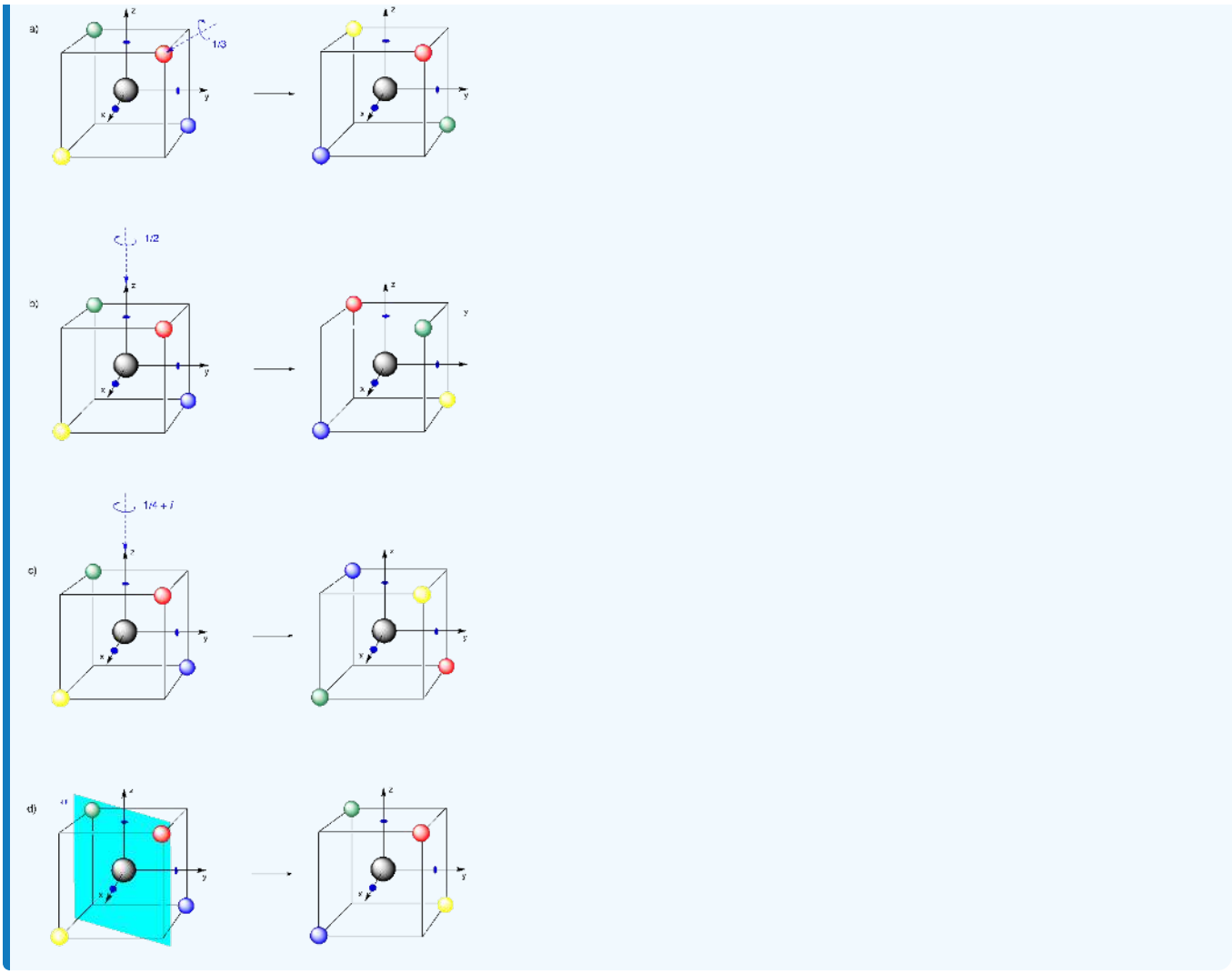
We can go further with the group theory approach and to determine the reducible representation for pi bonding, Γ_π , also shown in the table. Pi bonding is otherwise even more difficult to assess via simple inspection than was sigma bonding. The resulting representation reduces to $E + T_1 + T_2$. The d orbitals represented here include the expected d_{z^2} and $d_{x^2-y^2}$. Note, however, that they also include the d_{xy}, d_{xz}, and d_{yz} orbitals. That means that in the presence of a pi-donor ligand, the latter set are antibonding with respect to both sigma and pi bonding.

Example 3.3.4.1

Demonstrate these symmetry operations on the drawing of the tetrahedron within a cube shown above.

a. C_3
b. C_2
c. S_4
d. σ_d

Solution

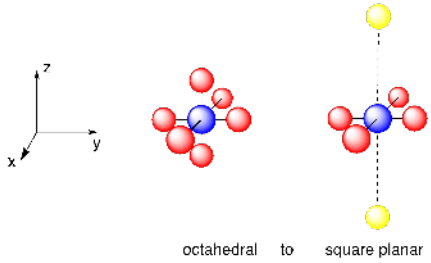


This page titled 3.3.4: Tetrahedral Complexes is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

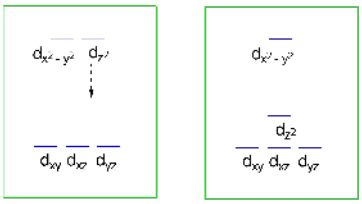
3.3.5: Square-Planar Complexes

Square planar geometry is much less common than octahedral, but square planar complexes assert their importance through their frequent appearance in key catalytic processes and other settings. Furthermore, having learned something about bonding in octahedral complexes, we can make some educated guesses about metal-orbital interactions in square planar complexes. Both geometries are nicely described by Cartesian coordinates and so it is relatively easy to draw comparisons between the two.

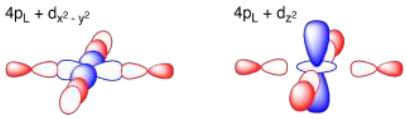
We can imagine how we might arrive at a square planar geometry simply by taking an octahedral geometry and removing two axial ligands. The four remaining equatorial ligands form a square planar complex.



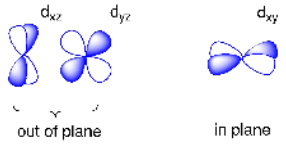
Since we already know something about the d orbital splitting diagram in an octahedral case, we can draw some rational conclusions about the consequence of this change. The axially-oriented d_{z^2} orbital drops in energy because it is no longer forming the antibonding combination with ligand orbitals along the z axis.



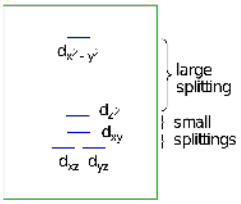
The d_{z^2} orbital does not drop all the way to the non-bonding level, however, because the toroid (the donut around the central node of the orbital) is still in plane with ligand orbitals along the x and y axes. Nevertheless, the d_{z^2} orbital overlaps with these ligand orbitals to a much lesser extent than the $d_{x^2-y^2}$ orbitals, so it drops to a level well below the $d_{x^2-y^2}$ orbital.



The d orbital splitting diagram shown above is not the one you will normally see for a square planar complex. The three non-bonding orbitals, d_{xy}, d_{xz} and d_{yz}, are degenerate in an octahedral geometry but not in a square planar one. The d_{xy} orbital is in the plane of the metal and ligands whereas the d_{xz} and d_{yz} are above and below that plane.



We therefore might not expect all three of these orbitals to be at the exact same energy level in the square planar coordination environment. We usually think of the d_{xy} orbital as lying at higher energy than the d_{xz}, d_{yz} pair because of the potential for interaction with the ligands that lie in the same plane as the d_{xy} orbital. The typical drawing of a d orbital splitting diagram reflects that subtle difference, showing the five metal d orbitals lying at four different energy levels with just one degenerate set (the d_{xz}, d_{yz} pair).



Note that there is a large splitting and two smaller splittings between the d orbitals, rather than the single splitting observed in an octahedral environment. As a result, when we talk about possible high spin and low spin electron population in the square planar environment, we are generally concerned with whether the electrons can surmount the large splitting and occupy the top orbital, the $d_{x^2-y^2}$.

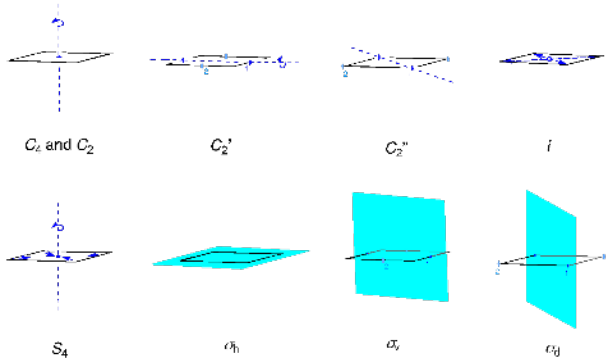
Sometimes, square planar d orbital splitting diagrams show the d_{xy} orbital above the d_{z^2} orbital and sometimes *vice versa*; the exact order varies with the ligands involved. The reasons for these differences are somewhat complicated. For example, this order can reflect the importance of pi bonding in a particular complex, as we will see later.

Group Theory Treatment of Square Planar Complexes

In octahedral coordination, we were able to use group theory to confirm the bonding picture we had arrived at through simple observation. We can do the same thing in the square planar case. This time, we need to use a character table for D_{4h} symmetry.

D_{4h}	E	$2C_4$	C_2	$2C_{2'}$	$2C_{2''}$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2$, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-1	0	2	0	0	(x, y)	

The ten symmetry elements listed in this table may be easier to grasp than the ones in the higher-symmetry octahedral point group. In this case, we see several two- or four-fold axes and some mirror planes. They are illustrated below.



If we consider only sigma bonding from the ligands, which was the initial consideration we thought about earlier, then we could look at how this picture operates when transformed by these symmetry elements:



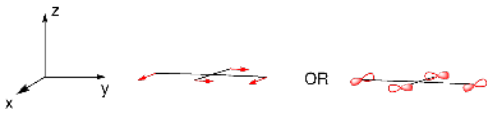
In that case, we obtain a reducible representation that can be reduced to the following:

$$\Gamma_{\sigma} = A_{1g} + B_{1g} + Eu$$

Returning to the character table, we find that the matching orbitals on the metal include the d_{z^2} and the $d_{x^2-y^2}$, as well as the s (represented by $x^2+ y^2$), the p_x and p_y. If we are just interested in the d orbital splitting diagram, that gives us the picture that we had obtained before. Two d orbitals display some antibonding character whereas the other three are non-bonding. Of course, this treatment does not take into account the subtly different interactions of the ligands with the d_{z^2} and the $d_{x^2-y^2}$ orbitals. Although they are of like symmetry, these orbitals overlap with the ligands to different extents.

Pi Bonding

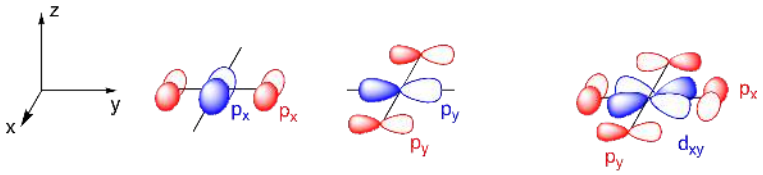
If we also want to include pi bonding in our understanding of these complexes, we have to think about two different orientations of the ligand p orbitals, which are not symmetrically equivalent in this case. The first orientation is parallel to the plane of the metal-ligand complex. It looks like this:



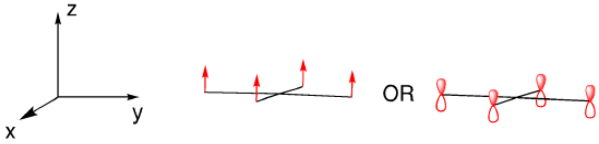
Treatment of those vectors with the symmetry elements leads to a reducible representation that can be represented by this one:

$$\Gamma_{\pi} \parallel = A_{2g} + B_{2g} + E_u$$

Consulting the character table, we find that the corresponding orbitals on the central atom are d_{xy}, p_x and p_y. In reality, the interaction with the d_{xy} is likely to be much more pronounced than with either the p_x or the p_y because of stronger overlap between the d_{xy} and the ligand p orbital.



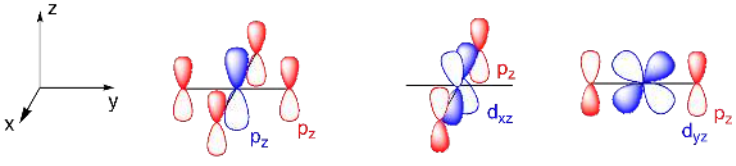
The second orientation is perpendicular to the plane of the complex.



This time, the irreducible representation is as follows:

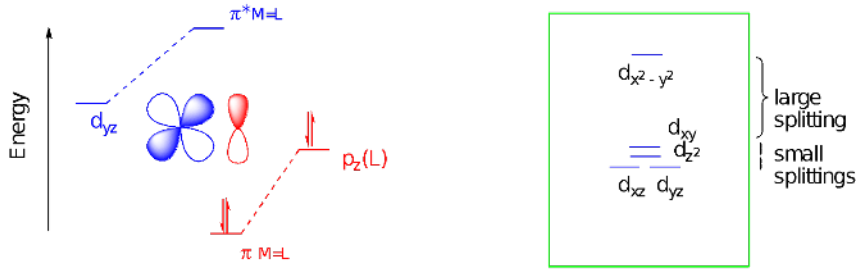
$$\Gamma_{\pi} \perp = A_{2g} + B_{2g} + E_u$$

According to the character table, this time the corresponding orbitals on the central atom are d_{xz}, d_{yz}, and p_z. Once again, because of stronger overlap between the d_{xy} or d_{yz} with the ligand p orbital compared to ligand overlap with the metal p_z, the former case is likely to be much more important than the latter.

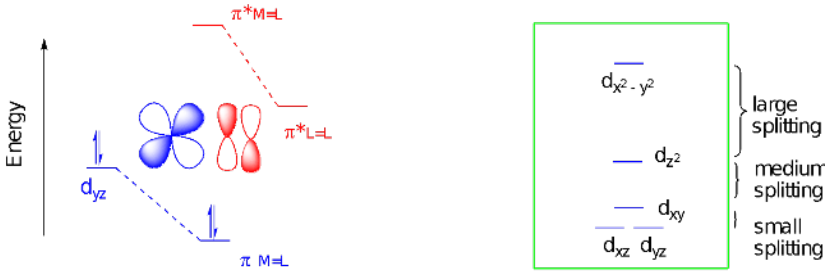


Thus, we see that the d orbitals that were not originally involved in sigma bonding have the potential to be involved in pi bonding. Which ones will actually be involved depends on the orientations of the ligands that are capable of pi bonding with these orbitals. That may be all of them in a more symmetric case (such as a homoleptic complex, in which all four ligands are the same as each other). It may be fewer in a complex with lower symmetry, in which the overall D_{4h} symmetry is broken by different ligands.

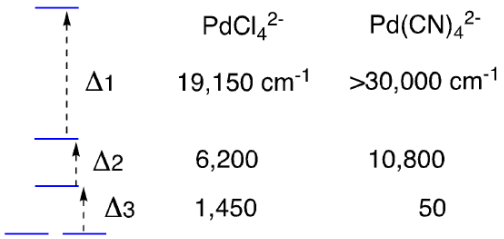
The nature of the ligands is probably of greater significance in terms of the magnitude of splittings in the d orbital diagram. If the metal forms a pi bond with the ligand via interaction with a p orbital on the ligand, then the resulting pi bond will be closer in both energy and character to the lower-energy ligand p orbital. We still think of that orbital as largely based on the more electronegative ligand. That means that the corresponding antibonding combination is more like the metal orbital in energy and character. It is still mostly a d orbital, for example. That results in a decrease in the splittings between d orbitals as the otherwise non-bonding set is pushed up in energy. We might even see the d_{xy} orbital at a higher energy level than the nominally sigma-antibonding d_{z^2} orbital, given a strong enough pi-bonding interaction.



On the other hand, if the metal orbital interacts with the empty π* orbital of a ligand such as cyanide or carbon monoxide, this situation will be reversed. Because of its antibonding nature, the ligand π* orbital lies above the metal d orbital in energy. When the two orbitals combine, the ligand π* orbital becomes the metal-ligand π* orbital. The metal d orbital drops in energy to form the metal-ligand bonding combination. Consequently, the metal orbitals involved in pi bonding to a pi acceptor drop in energy and splittings get larger. In particular, the gap between the pi bonding metal orbitals and the purely sigma bonding metal orbitals grows wider in this case.



The difference in overall splitting in these cases can be quite significant. For example, the differences between energy levels, denoted Δ1 and Δ2 below, are about 50% greater with the strongly pi-accepting cyanide ligand than with the pi-donating chloride in the corresponding homoleptic palladium complexes.[1]



In all of these cases, the splitting between the highest-lying $d_{x^2-y^2}$ orbital and the next highest is much larger than the other splittings. That factor leads to square planar complexes generally adopting a low-spin configuration, which in this case means the lower orbitals are all occupied before the $d_{x^2-y^2}$. Square planar complexes are most often observed with d^7 or d^8 metal ions, which avoids populating that highest-energy d orbital.

Problems

1. a) Demonstrate how to arrive at the reducible representation for sigma bonding under the D_{4h} symmetry of a square planar complex.

b) Determine the irreducible representation.

2. a) Demonstrate how to arrive at the reducible representation for pi bonding in the plane of the complex under the D_{4h} symmetry of a square planar complex.

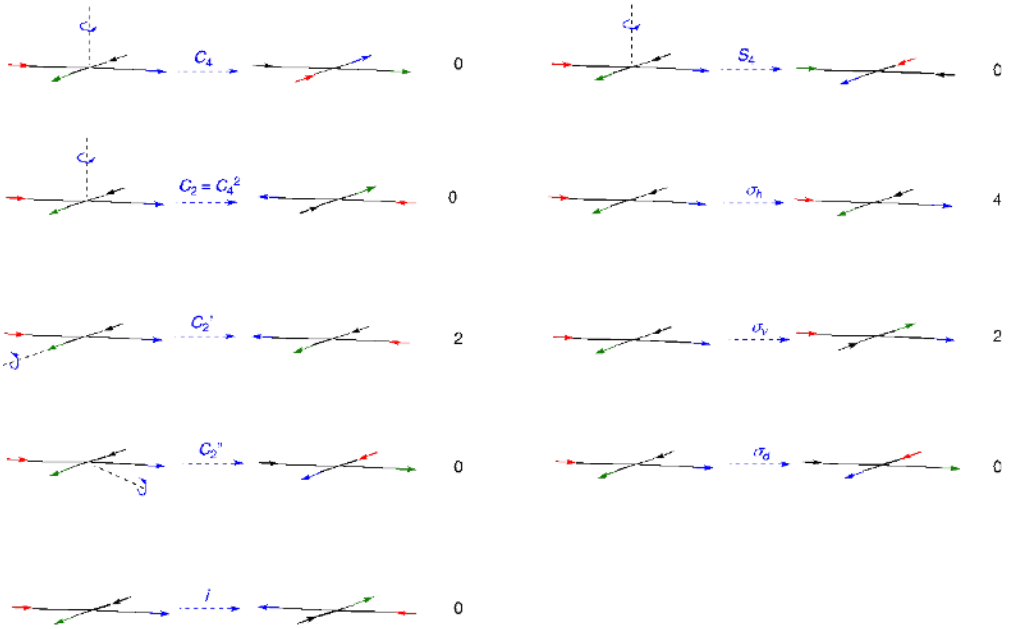
b) Determine the irreducible representation.

3. a) Demonstrate how to arrive at the reducible representation for pi bonding perpendicular to the plane of the complex under the D_{4h} symmetry of a square planar complex.

b) Determine the irreducible representation.

Solutions.

1. a) There are 4 unchanged vectors for *E*. For the others:



b) Γ_σ: Remember, ai = 1hQN·χ(R)·χ(R)Q

A_{1g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·1 + 2·0·1 + 1·0·1 + 2·0·1 + 1·4·1 + 2·2·1 + 2·0·1] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

A_{2g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·(-1) + 2·0·(-1) + 1·0·1 + 2·0·1 + 1·4·1 + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

B_{1g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·1 + 2·0·(-1) + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·2·1 + 2·0·(-1)] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

B_{2g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·(-1) + 2·0·1 + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·2·(-1) + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

E_g: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·2·0 + 2·0·0 + 1·0·2 + 2·0·0 + 1·4·(-2) + 2·2·0 + 2·0·0] = 1/16 [8 - 8] = 1/16(0) = 0

A_{1u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·1 + 2·0·1 + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

A_{2u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·(-1) + 2·0·(-1) + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·2·1 + 2·0·1] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

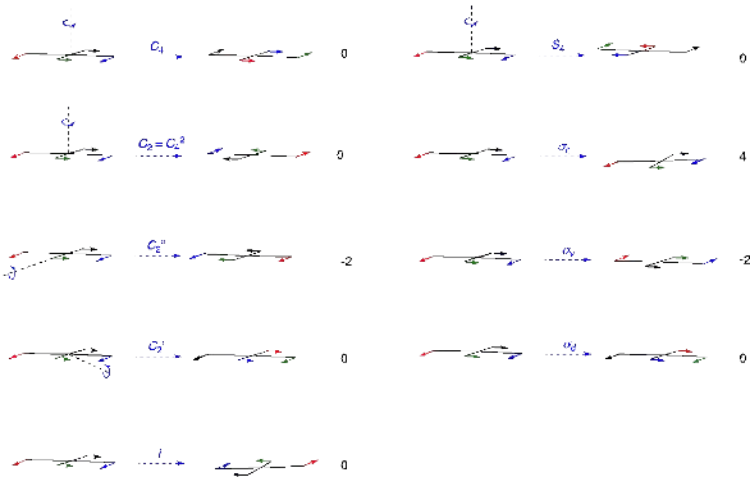
B_{1u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·1 + 2·0·(-1) + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·2·(-1) + 2·0·1] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

B_{2u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·(-1) + 2·0·1 + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·2·1 + 2·0·(-1)] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

E_u: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·2·0 + 2·0·0 + 1·0·(-2) + 2·0·0 + 1·4·2 + 2·2·0 + 2·0·0] = 1/16 [8 + 8] = 1/16(16) = 1

$\Gamma_\sigma = A_{1g} + B_{1g} + E_u$

2. a) There are 4 unchanged vectors for *E*. For the others:



b) $\Gamma_{\pi||}$:

A_{1g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·1 + 2·0·1 + 1·4·1 + 2·(-2)·1 + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

A_{2g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·1 + 2·0·1 + 1·4·1 + 2·(-2)·(-1) + 2·0·(-1)] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

B_{1g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·(-2)·1 + 2·0·(-1)] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

B_{2g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·(-2)·(-1) + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(16) = 1

E_g: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·2 + 2·0·0 + 1·4·(-2) + 2·(-2)·0 + 2·0·0] = 1/16 [8 - 8] = 1/16(0) = 0

A_{1u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·(-2)·(-1) + 2·0·(-1)] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

A_{2u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·(-2)·1 + 2·0·1] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

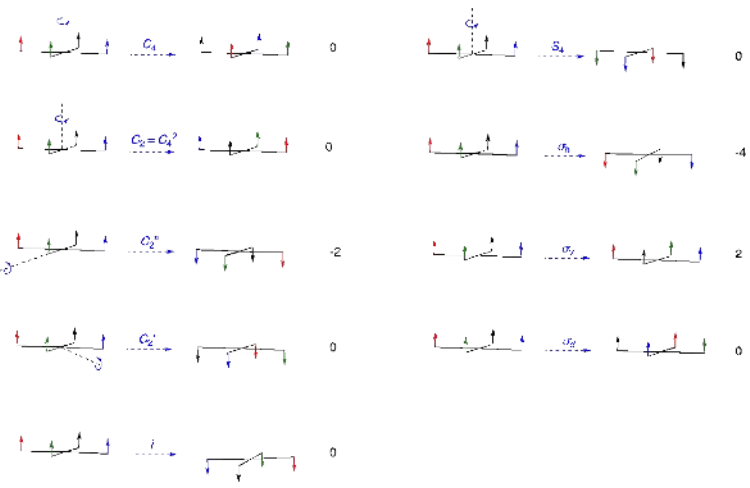
B_{1u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·(-2)·(-1) + 2·0·1] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

B_{2u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·(-2)·1 + 2·0·(-1)] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

E_u: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·(-2) + 2·0·0 + 1·4·2 + 2·(-2)·0 + 2·0·0] = 1/16 [8 + 8] = 1/16(16) = 1

$\Gamma_{\pi||} = A_{2g} + B_{2g} + E_u$

3. a) There are 4 unchanged vectors for *E*. For the others:



b) $\Gamma_{\pi}\perp$:

A_{1g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·1 + 2·0·1 + 1·(-4)·1 + 2·2·1 + 2·0·1] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

A_{2g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·1 + 2·0·1 + 1·(-4)·1 + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

B_{1g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·1 + 2·0·(-1) + 1·(-4)·1 + 2·2·1 + 2·0·(-1)] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

B_{2g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·1 + 2·0·(-1) + 1·(-4)·1 + 2·2·(-1) + 2·0·1] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

E_g: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·2 + 2·0·0 + 1·(-4)·(-2) + 2·2·0 + 2·0·0] = 1/16 [8 + 8] = 1/16(16) = 1

A_{1u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·(-1) + 2·0·(-1) + 1·(-4)·(-1) + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

A_{2u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·(-1) + 2·0·(-1) + 1·(-4)·(-1) + 2·2·1 + 2·0·1] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

B_{1u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·(-1) + 2·0·1 + 1·(-4)·(-1) + 2·2·(-1) + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

B_{2u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·(-1) + 2·0·1 + 1·(-4)·(-1) + 2·2·1 + 2·0·(-1)] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

E_u: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·(-2) + 2·0·0 + 1·(-4)·2 + 2·2·0 + 2·0·0] = 1/16 [8 - 8] = 1/16(0) = 0

$\Gamma_{\pi}\perp = A_{2u} + B_{2u} + E_g$

References

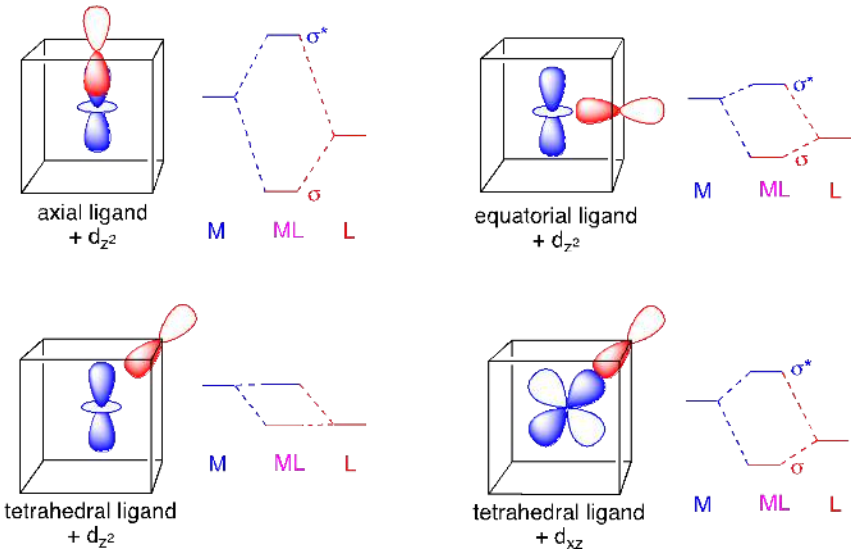
1. Gray, H. B.; Ballhausen, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 260-264.

This page titled 3.3.5: Square-Planar Complexes is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.4: Angular Overlap

The angular overlap model is an approach to quantifying the interaction between metal and ligand orbitals in different geometries, with a focus on the metal d orbitals. Although developed in the 1970's, this approach is still used as a starting point for theoretical calculations using advanced computational chemistry methods available today.1

The core concept of the angular overlap model is that different ligand orbitals will overlap with metal d orbitals to different extents because of the variety of angles at which these orbitals would approach each other. Stronger overlap leads to greater interaction. That means both greater stabilization of the ligand-centered bonding orbital and greater destabilization of the metal-centered antibonding orbital.



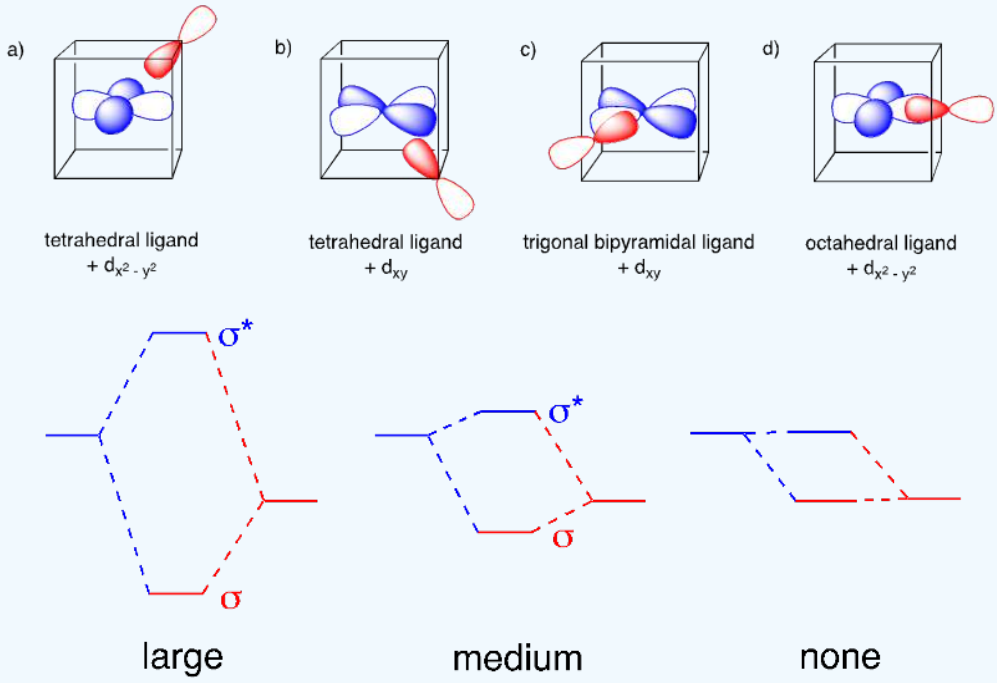
Let's look at some examples. Consider the overlap of the d_{z^2} orbital with an axial ligand in octahedral geometry, with the assumption that the d_{z^2} orbital lies in the axial direction. There should be considerable overlap between the metal and ligand orbitals, leading to both significant stabilization of the ligand donor electrons and similar destabilization of an electrons in the metal d_{z^2} orbital. By comparison, an equatorial ligand would have significantly less overlap with the d_{z^2} orbital. Instead of overlapping with the substantial lobe along the z axis, the ligand would be interacting with the minimal d_{z^2} toroid in the xy plane. The bonding orbital would be stabilized to a significantly lesser extent compared to the axial ligand. The antibonding orbital would be destabilized by a correspondingly smaller amount.

In the case of a tetrahedral ligand, there is essentially no overlap with the d_{z^2} orbital because its on-axis lobe is too far away from the cubic corner positions occupied by ligands in a tetrahedral array. There is really no bonding or antibonding in this case. On the other hand, the dxz orbital reaches a little closer to that corner position, allowing for some overlap with the ligand orbital. Consequently, there is some stabilization of the bonding electrons and destabilization of the antibonding d orbital. At first glance, the amount of overlap in this case, and the amount of stabilization or destabilization, appears much more similar to the case of the equatorial ligand with the d_{z^2} orbital than the axial ligand with the d_{z^2} orbital.

We will not go into the mathematics that explore the exact extent of overlap expected in each case. Instead, we will go straight to a summary of the results in the next section.

? Exercise 3.4.1

Estimate the degree of interaction between the ligand and metal orbital: large, medium, or none.



Answer

a) none b) medium c) medium (although it may appear greater than in (b), and it is) d) large

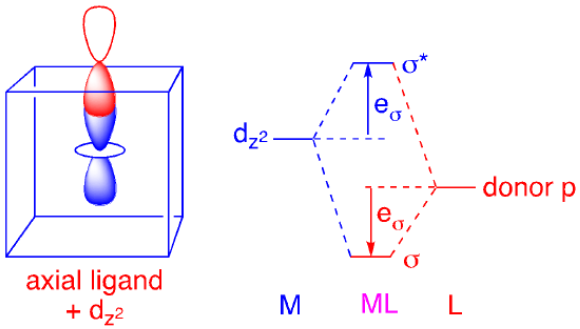
References

1. For example: Chilkuri, V. G.; DeBeer, S.; Neese, F. Ligand Field Theory and Angular Overlap Model Based Analysis of the Electronic Structure of Homovalent Iron–Sulfur Dimers. *Inorg. Chem.* **2020**, *59*(2), 984-995.

This page titled 3.4: Angular Overlap is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

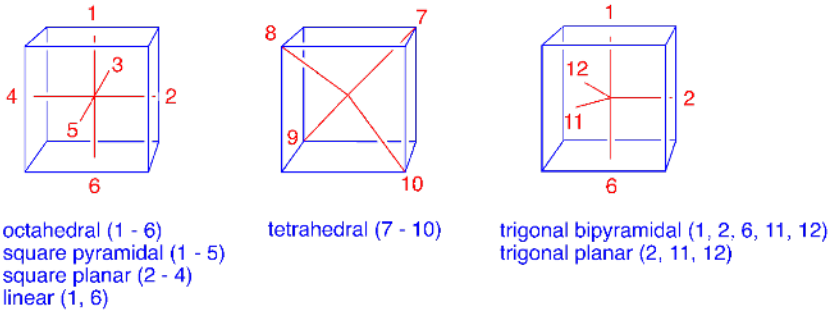
3.4.1: Sigma Bonding in the Angular Overlap Model

The pictures we considered previously explicitly addressed sigma overlap between the ligand donor orbital and the metal d acceptor orbital. The donor electrons drop in energy into the new sigma bonding combination and any electrons in the d orbital are raised into the new sigma antibonding combination. For example, when an axial ligand interacts with a metal dz2 orbital, the in-phase, bonding combination drops in energy by a quantity that we will call eσ. At the same time, the out-of-phase, antibonding combination is raised in energy by the same quantity, eσ. A real computational treatment would reveal that this is not exactly true; the amount of energy by which the bonding orbital is stabilized is slightly different from the amount by which the antibonding orbital is destabilized. However, the distinction is pretty minor for our purposes.



From the interactions we have already looked at, we know that this specific interaction is a strong one. Other metal-ligand interactions may involve less overlap than this one and will lead to smaller changes in energy. For this reason, other metal-ligand interactions are expressed as fractions of the quantity, eσ, found in the case of the dz2 orbital interacting with an axial ligand.

Our first task is to label the positions that will be occupied by ligands in a number of different geometries. To avoid a cluttered diagram of these positions, we can use three separate illustrations to illustrate the ligand positions in some common geometries. The first drawing below includes all the geometries in which ligands are found along Cartesian coordinates. The second drawing describes tetrahedral geometry, whereas the third one describes trigonal structures.



Given those ligand positions, we can assess the interactions that would occur if ligands were purely sigma donors. For reference, the dz2 orbital is assumed to lie along the axis between positions 1 and 6 and the magnitudes of the interactions are all scaled relative to the interaction of a ligand at position 1 or 6 with the dz2 orbital. We will not address the approach that was taken to arrive at these relative numbers; we will simply use the results tabulated here.

Sigma Interactions of Ligands with Metal d Orbitals (units of eσ)

Ligand Positions	dz2	dx2-y2	dxy	dxz	dyz
1	1	0	0	0	0
2	1/4	3/4	0	0	0
3	1/4	3/4	0	0	0
4	1/4	3/4	0	0	0
5	1/4	3/4	0	0	0

Ligand Positions	dz2	dx2-y2	dxy	dxz	dyz
6	1	0	0	0	0
7	0	0	1/3	1/3	1/3
8	0	0	1/3	1/3	1/3
9	0	0	1/3	1/3	1/3
10	0	0	1/3	1/3	1/3
11	1/4	3/16	9/16	0	0
12	1/4	3/16	9/16	0	0

In order to quantify the interactions between ligands and metal orbitals, we simply tally up the interactions for each orbital. For example, consider a complex like hexaamminecobalt(III) chloride, [Co(NH3)6]Cl3. It has six sigma donor ligands, forming an octahedral structure. The total interactions with each orbital in this geometry would be calculated by totaling the interactions at all the ligand positions for each orbital.

Looking under the dz2 column and totaling only the values for positions 1 through 6, we find:

dz2: (1 + 1/4 + 1/4 + 1/4 + 1/4 + 1) eσ = 3eσ

A similar approach using the dx2-y2 column leads to:

dx2-y2: (0 + 3/4 + 3/4 + 3/4 + 3/4 + 0) eσ = 3eσ

However, the remaining three d orbitals have no interactions with the ligands in these six positions:

dxy: 0; dxz: 0; dyz: 0

So, we find that the dz2 and dx2-y2 orbitals are both raised in energy by 3eσ. At the same time, we know that the ligand donor orbitals are stabilized by their interaction with the metal orbitals. To see how much, we can tally up the interaction for each ligand at its position. That is, for the ligand in position 1, we would add in its interaction with each of the five d orbitals to determine the amount by which it is stabilized by bonding. We simply add up the values across that row.

Ligand in position 1: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

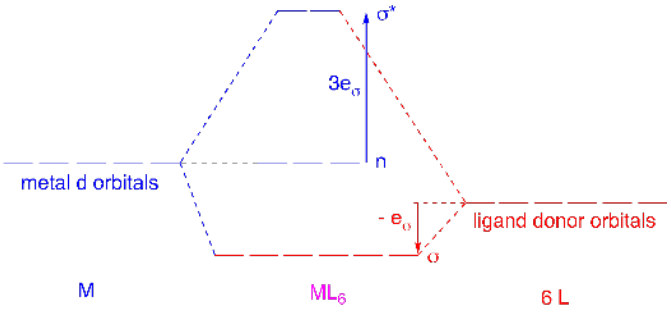
Ligand in position 3: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 4: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 5: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 6: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

We have now generated a diagram that looks very much like what we saw from ligand field theory. We see the familiar d orbital splitting diagram for octahedral geometry as well as stabilization of the ligand donor orbitals in sigma bonds.



The results from the angular overlap model are somewhat simplified compared to the results from ligand field theory. For example, they completely neglect any interaction between ligand orbitals and metal s or p orbitals. However, this model allows a very

straightforward calculation of the relative d orbital energy levels.

Problems

1. Use the results of the calculation for the octahedral geometry to calculate the net stabilization due to bonding (in units of eσ) for the following complexes.

a) [Co(NH3)6]Cl3 (assume low spin) b) [Fe(NH3)6](NO3)3 (assume high spin)

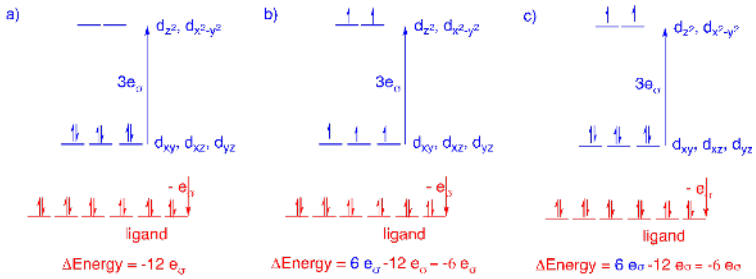
c) [Ni(NH3)6]Cl2

2. Use the table of sigma interactions to calculate orbital energy stabilization or destabilization for the following geometries.

a) trigonal planar ML3 b) square planar ML4 c) trigonal bipyramidal ML5

Solutions

1.



2. a) Positions 2, 11, 12.

dz2: (1/4 + 1/4 + 1/4) eσ = 3/4 eσ

dx2-y2: (3/4 + 3/16 + 3/16) eσ = 18/16 = 9/8 eσ

dxy: (0 + 9/16 + 9/16) eσ = 18/16 = 9/8 eσ

dxz: 0

dyz: 0

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 11: - (1/4 + 3/16 + 9/16 + 0 + 0) eσ = - eσ

Ligand in position 12: - (1/4 + 3/4 + 9/16 + 0 + 0) eσ = - eσ

b) Positions 2, 3, 4, 5.

dz2: (1/4 + 1/4 + 1/4 + 1/4) eσ = eσ

dx2-y2: (3/4 + 3/4 + 3/4 + 3/4) eσ = 3 eσ

dxy: 0

dxz: 0

dyz: 0

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 3: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 4: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 5: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

c) Positions 1, 2, 6, 11, 12.

dz2: (1 + 1/4 + 1+ 1/4 + 1/4) eσ = 11/4 eσ

dx2-y2: (0 + 3/4 + 0 + 3/16 + 3/16) eσ = 18/16 = 9/8 eσ

dxy: (0 + 0 + 0 + 9/16 + 9/16) eσ = 18/16 = 9/8 eσ

dxz: 0

dyz: 0

Ligand in position 1: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 6: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

Ligand in position 11: - (1/4 + 3/16 + 9/16 + 0 + 0) eσ = - eσ

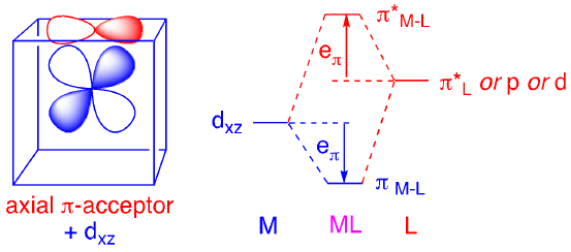
Ligand in position 12: - (1/4 + 3/4 + 9/16 + 0 + 0) eσ = - eσ

This page titled 3.4.1: Sigma Bonding in the Angular Overlap Model is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

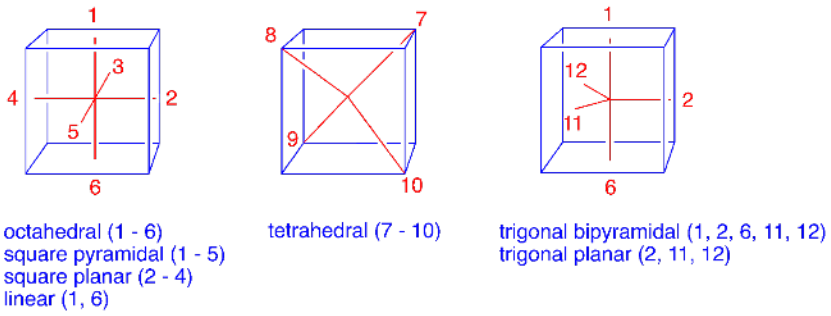
3.4.2: Pi Acceptors in the Angular Overlap Model

So far, we have considered only the effects of sigma donation on the d orbital splitting diagram using the angular overlap model. When we looked at ligand field theory, we saw that pi-donor and pi-acceptor effects produced significant changes in these diagrams. We generally see these effects in any ligands that have orbitals that can accept electron density from the metal (back-bonding). The paradigm of a pi acceptor is carbon monoxide, of course. Similar effects can be found in related ligands in which the donor atoms participate in pi bonding with another atom in the ligand, thus making a pi* orbital available for back-bonding. In addition, back-bonding is a feature of phosphine ligands and some N-heterocyclic carbenes.

We usually think about this interaction as illustrated below. The empty ligand orbital approaches so that it is perpendicular to the bond axis, allowing overlap with the filled metal d orbital. The interaction lowers the energy of the d electrons, which become bonding in nature, and raises the energy of the empty ligand orbital.



We can use the same ligand positions for pi acceptors that we already used for sigma donors. The orbitals will be oriented differently than the sigma donor orbitals but they will approach from the same directions..



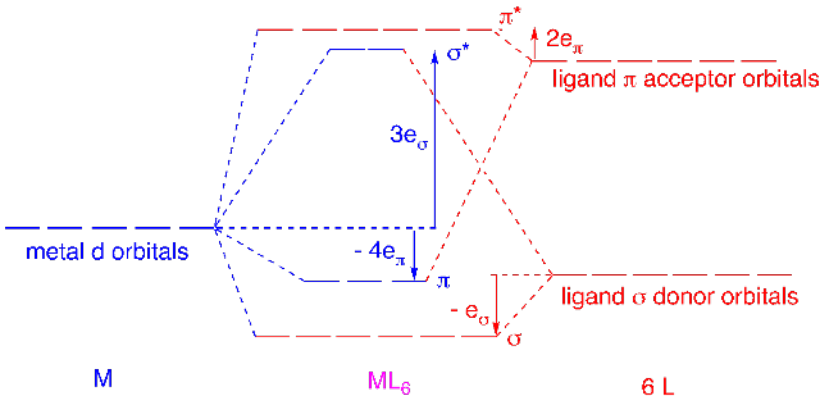
As before, we can use the results of calculations of the strengths of these interactions based on the amount of overlap; we don't need to know exactly how the numbers in the table below came about. This time, the maximum overlap occurs between a dxz orbital and a p orbital approaching in position 1, perpendicular to the bond axis. Several other combinations will be equally strong. This time, the stabilization is expressed in terms of eπ rather that eσ. The amount of energy in this case is somewhat smaller than in sigma donation because of a lesser degree of metal-ligand orbital overlap.

Sigma Interactions of Ligands with Metal d Orbitals (units of eπ)

Ligand Positions	dz2	dx2-y2	dxy	dxz	dyz
1	0	0	0	1	1
2	0	0	1	1	0
3	0	0	1	0	1
4	0	0	1	1	0
5	0	0	1	0	1
6	0	0	0	1	1
7	2/3	2/3	2/9	2/9	2/9
8	2/3	2/3	2/9	2/9	2/9

Ligand Positions	dz2	dx2-y2	dxy	dxz	dyz
9	2/3	2/3	2/9	2/9	2/9
10	2/3	2/3	2/9	2/9	2/9
11	0	3/4	1/4	1/4	3/4
12	0	3/4	1/4	1/4	3/4

These interactions modify the picture we built previously for simple sigma donors. In the new interaction diagram, a second set of ligand p orbitals is destabilized by the pi interaction. At the same time, some of the d orbitals are stabilized by the additional interaction. This modification is illustrated below for octahedral geometry.



Problems

1. Use the table of pi interactions to calculate orbital energy stabilization or destabilization for the following geometries.

a) trigonal planar ML3 b) square planar ML4 c) trigonal bipyramidal ML5

Solutions

1. a) Positions 2, 11, 12.

dz2: 0

dx2-y2: - (0 + 3/4 + 3/4) eπ = 6/4 = - 3/2 eπ

dxy: - (1 + 1/4 + 1/4) eσ = 6/4 = - 3/2 eπ

dxz: - (1 + 1/4 + 1/4) eσ = 6/4 = - 3/2 eπ

dyz: - (0 + 3/4 + 3/4) eσ = 6/4 = - 3/2 eπ

Ligand in position 2: (0 + 0 + 0 + 1 + 1) eπ = 2eπ

Ligand in position 11: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2eπ

Ligand in position 12: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2eπ

b) Positions 2, 3, 4, 5.

dz2: 0

dx2-y2: 0

dxy: - (1 + 1 + 1 + 1) = -4 eπ

dxz: - (1 + 0 + 1 + 0) = -2 eπ

dyz: - (0 + 1 + 0 + 1) = -2 eπ

Ligand in position 2: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ

Ligand in position 3: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ

Ligand in position 4: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ

Ligand in position 5: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ

c) Positions 1, 2, 6, 11, 12.

dz2: 0

dx2-y2: - (0 + 0 + 0 + 3/4 + 3/4) eπ = -3/2 eπ

dxy: - (0 + 1 + 0 + 1/4 + 1/4) eπ = -3/2 eπ

dxz: - (1 + 1 + 1 + 1/4 + 1/4) eπ = -7/2 eπ

dyz: - (1 + 0 + 1 + 3/4 + 4/4) eπ = -7/2 eπ

Ligand in position 1: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ

Ligand in position 2: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ

Ligand in position 6: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ

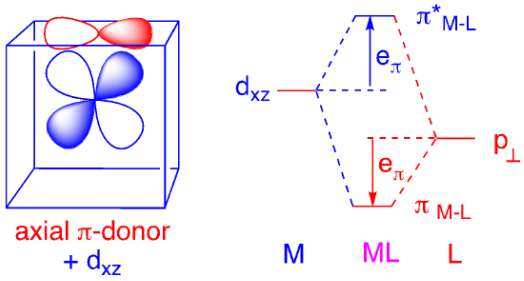
Ligand in position 11: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2 eπ

Ligand in position 12: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2 eπ

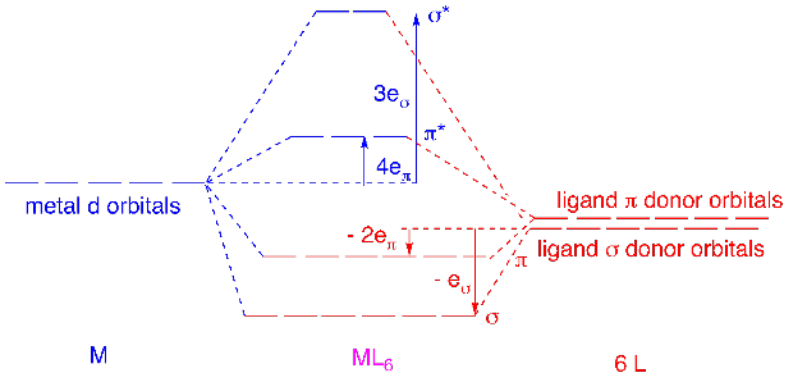
This page titled 3.4.2: Pi Acceptors in the Angular Overlap Model is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.4.3: Pi Donors in the Angular Overlap Model

Ligands in which the donor atom has more than one lone pair are capable of pi donation to the metal. Common examples include halide and alkoxide ligands. The overlap question in this case is exactly the same as in the case of pi acceptors; the same table of interactions applies here. However, since the ligand electrons are forming the pi bond in this case, the ligand electrons are stabilized and the d orbitals with which they overlap are destabilized.



In octahedral geometry, for example, we see the off-axis d orbitals raised modestly in energy in the presence of pi donor ligands. The angular overlap model allows us to quantify the relative changes in energy because of these ligand interactions.



Example 3.4.3.1

Confirm the stabilization and destabilization of orbitals due to pi donation in the octahedral interaction diagram shown above.

Solution

Positions 1, 2, 3, 4, 5, 6.

- dz2: 0
- dx2-y2: 0
- dxy: (0 + 1 + 1 + 1 + 1 + 0) = 4 eπ
- dxz: (1 + 1 + 0 + 1 + 0 + 1) = 4 eπ
- dyz: (1 + 0 + 1 + 0 + 1 + 1) = 4 eπ

- Ligand in position 1: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ
- Ligand in position 2: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ
- Ligand in position 3: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ
- Ligand in position 4: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ
- Ligand in position 5: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ
- Ligand in position 6: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ

This page titled 3.4.3: Pi Donors in the Angular Overlap Model is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.4.4: The Spectrochemical Series

The spectrochemical series was determined through an examination of the absorption spectra of a series of octahedral $\mathrm{Co(III)}$ complexes by Tsuchida in the 1930's. The position of the d-d absorption band is influenced by the field strength of the ligand, which leads to greater or lesser values of Δ_o. That interaction depends on both the relative energies of the metal and ligand orbitals and the degree of overlap between these orbitals. The closer in energy the two orbitals are to each other, the greater the interaction. Also, the greater the overlap between the two orbitals, the greater the interaction.

Recall that sigma donors simply donate a lone pair to the metal but do not have additional metal-ligand interactions. The classic example is ammonia. The nitrogen in ammonia has only one lone pair to donate and is a simple sigma donor. Ethylenediamine, $\mathrm{NH_2CH_2CH_2NH_2}$ (en), is also a sigma donor because it has a single lone pair on each nitrogen atom. The en ligand is a slightly stronger sigma donor than ammonia. The difference is explained by the slightly stronger basicity of en compared to ammonia; the nitrogen lone pairs in en are better donors to both protons and metal ions.

en > NH3 (basicity)

The common pi donors include the halides and some oxygen donors. In these cases, the donor atom has an additional lone pair (or more) which may engage in formation of a pi bond by donation to a metal d orbital. Among the halides, fluoride produces the largest field splitting and iodide the smallest. This trend is also explained in terms of the relative basicity of these halides; fluoride is more basic than bromide. In addition, there is also understood to be better overlap between fluorine's p orbital and the d acceptor of a positively charged metal ion, compared to larger halides such as iodine.

F- > Cl- > Br- > I- (basicity)

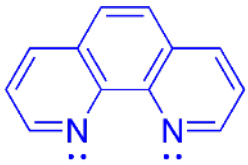
Oxygen donors do not follow this basicity trend. Hydroxide is thought to act as a better pi donor than water, partly because of its negative charge. A carboxylate ligand is not quite as strong a pi donor as hydroxide, probably because its lone pair is delocalized into the carbonyl group.

H20 > RCO2- > HO- (pi donation anion vs neutral)

The pi acceptors include familiar examples such as carbon monoxide (carbonyl ligand) as well as the aromatic phenanthroline.

CO > -CN > phenanthroline > NO2- > SCN-

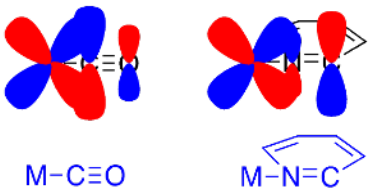
The phenanthroline may be an unfamiliar ligand. It is an aromatic amine, like pyridine. Other aromatic ligands, if they donate through a lone pair such as a phenyl, $\mathrm{C_6H_5^-}$, can also be considered pi acceptors. These compounds feature a pi bond that includes the donor atom, so there is a pi* orbital at that position capable of undergoing back-donation from the metal.



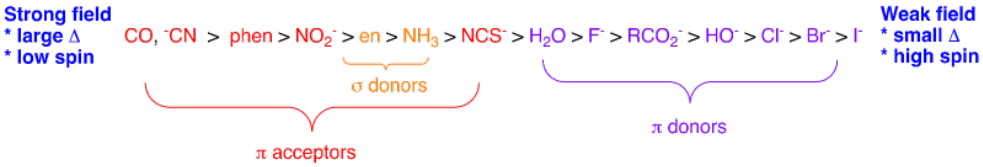
phenanthroline (phen)

Again, there are subtle variations among the field strengths exhibited by these pi acceptors, and there may be several factors contributing to those differences. For example, the cyanide is only slightly weaker field than the isoelectronic carbon monoxide. That small difference may be due to the negative charge on the cyanide rendering it a weaker electron acceptor. On the other hand, phenanthroline is neutral, but it is still a weaker donor than carbon monoxide. That weaker field may be due to the smaller lobe on the nitrogen atom in the pi* orbital in phenanthroline. Because nitrogen is more electronegative than carbon, it makes a greater contribution to the C=N pi bonding orbital than carbon; the opposite is true in the antibonding orbital. Carbon monoxide, in contrast, features a larger lobe on carbon in its pi* orbital. The result is better metal-ligand pi overlap with carbon monoxide than with phenanthroline.

Phosphines are also commonly considered to be pi acceptors, for subtle reasons that have been subject to some debate.1

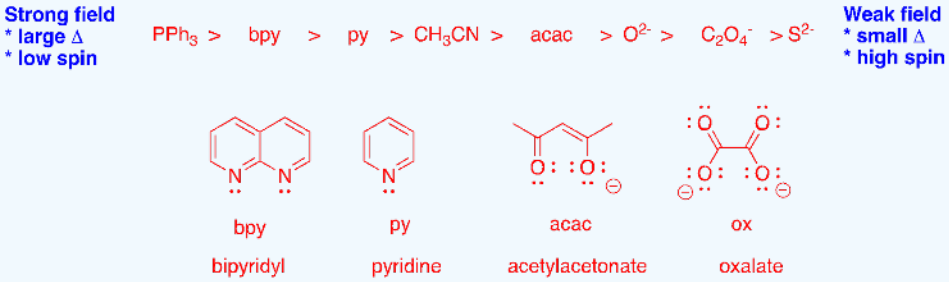


All three of these series can be collated to arrive at a combined list, which is a more complete spectrochemical series. Note that there may be some overlap between the different types of donors. Nevertheless, the overall trend holds: pi acceptors lead to the greatest field splitting on average, whereas di donors lead to the smallest.



Example 3.4.4.1

Some additional common ligands are displayed according to field strength, below. Classify these ligands as pi donors, sigma donors, or pi acceptors.



Solution

Ph3, based on its structure, appears to be a sigma donor only because it has just one lone pair on the donor atom. However, phosphines tend to behave as pi acceptors; that is, they appear to withdraw some electron density from the metal as indicated by the response of reporter ligands such as CO.

Bpy, py and CH3CN (acetonitrile) all appear to be pi acceptors. Like phen, they behave as weak pi acceptors.

Acac, oxide, oxalate and sulfide are all pi donors. The donor atom in each case has a lone pair in addition to the sigma donor pair.

References

1. Wolczanski, P. T. "Flipping the Oxidation State Formalism: Charge Distribution in Organometallic Complexes as Reported by Carbon Monoxide". *Organometallics* **2017**, *36*, 622-631.

This page titled 3.4.4: The Spectrochemical Series is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

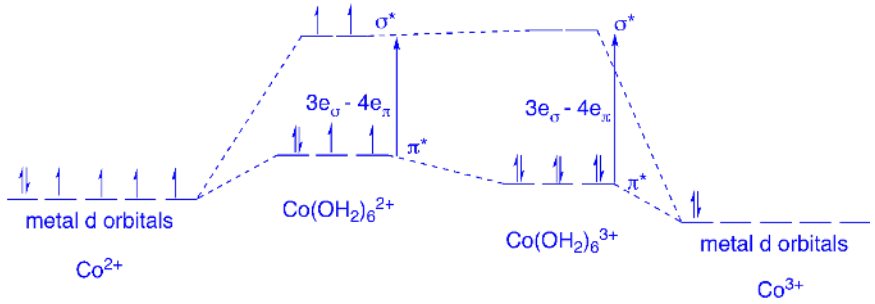
3.4.5: The Magnitude of Parameters eσ, eπ and Δ

In the angular overlap model (AOM), the field splitting, Δ, can be shown to result from a combination of the interaction parameters eσ and eπ. For example, in octahedral geometry,

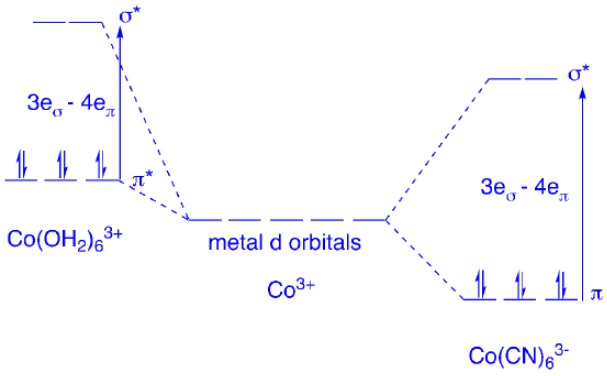
$$\Delta = 3e\sigma - 4e\pi \tag{3.4.5.1}$$

in which the value of eπ is positive for a pi donor but negative for a pi acceptor.

The magnitude of these parameters varies from one complex to another. As we have seen previously in examination of ligand field theory, both the metal ion and the identity of the ligand play a role in determining the magnitude of the field splitting. As outlined in the previous section on ligand field theory, the identity of the metal influences the d orbital splitting. Even for the same element, an increase in charge translates into a significant increase in the splitting parameter. For this reason, aqueous $\mathrm{Co(II)}$ ion is high spin, whereas the aqueous $\mathrm{Co(III)}$ ion is low spin.



The spectrochemical series tells us that the ligands also play a major role in determining the magnitude of the field splitting, with pi donors producing a smaller splitting than pi acceptors. The splitting produced by an aquo ligand is much smaller than the produced by a cyano ligand, for example.



Spectroscopic data can be used to determine the parameters eσ and eπ. A series of examples for different ligands coordinated to the Cr^{3+} ion are outlines in Table 3.4.5.1.

Table 3.4.5.1: Angular Overlap Parameters in Octahedral Cr(III) Complexes[1]

Ligand	eσ	eπ	Δ (cm-1)
π acceptors			
-CN	7,530	-930	26,310
pyridine	6,150	-330	19,770
σ donors			
en	7,260	assumed 0	21,780
NH3	7,180	assumed 0	21,540
π donors			

Ligand	eσ	eπ	Δ (cm-1)
HO-	8,600	2,150	17,200
H2O	7,550	1,850	15,250
F-	8,200	2,000	16,600
Cl-	5,700	980	13,180
Br-	5,380	950	12,430
I-	4,100	670	9,620

It is worth noting that the parameters observed for Cr(III), although mostly consistent with the spectrochemical series, are not identical to those seen in Co(III). In particular, the places of water and hydroxide are switched in the series. Once again, the identity of the metal plays a role in the strength of interaction with the ligand, and certain ligands may be observed to interact more strongly with some metals than with others.

Example 3.4.5.1

Calculate Δ for tetrahedral Ni^{2+} when coordinated with the following ligands, given the parameters eσ and eπ.[1]

a. PPh_3 with $e\sigma = 5,000\ cm^{-1}$ and $e\pi = -1,750\ cm^{-1}$
b. Cl^- with $e\sigma = 3,900\ cm^{-1}$ and $e\pi = 1,500\ cm^{-1}$
c. Br^- with $e\sigma = 3,600\ cm^{-1}$ and $e\pi = -1,000\ cm^{-1}$

Solution

This question is a direct application of Equation 3.4.5.1:

a. PPh_3:

$$\begin{aligned}\Delta &= 3e\sigma - 4e\pi \\ &= 3(5,000) - 4(-1,750)cm^{-1} \\ &= 22,000\ cm^{-1}.\end{aligned}$$

b. Cl^-:

$$\begin{aligned}\Delta &= 3(3,900) - 4(1,500) \\ &= 5,700\ cm^{-1}.\end{aligned}$$

c. Br^-:

$$\begin{aligned}\Delta &= 3(3,600) - 4(1,000) \\ &= 6,800\ cm^{-1}.\end{aligned}$$

Example 3.4.5.2

AOM parameters eσ were calculated from spectroscopic data for a series of bidentate nickel complexes with octahedral geometry, $Ni(en')_2(NCS)_2$.[2]

- en' = $H_2NCH_2CH_2NH_2$ with eσ = 4,010 cm-1
- en' = $(CH_3)_2NCH_2CH_2N(CH_3)_2$ with eσ = 3,165 cm-1
- en' = $(CH_3CH_2)_2NCH_2CH_2NH_2$ with eσ = 2,485 cm-1 ($-NEt_2$); eσ = 4,650 cm-1 ($-NH_2$)

Explain the reasons for the differences in the eσ values.

Solution

Greater steric hindrance appears to decrease the interaction between the sigma donor and the metal. Thus, the magnitude of eσ decreases from the least hindered $-NH_2$ group to the most hindered NEt_2 group.

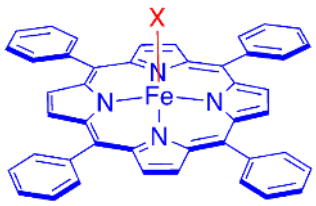
References

1. Figgis, B. N.; Hitchman, M. A. *Ligand Field Theory and Its Applications*. Wiley-VCH: New York, 2000, p. 71.
2. Lever, A. B. P.; Walker, I. M.; McCarthy, P. J.; Mertes, K. B.; Jircitano, A.; Sheldon, R. "Crystallographic and Spectroscopic Studies of Low-Symmetry Nickel(II) Complexes Possessing Ling Nickel-Nitrogen Bonds", *Inorg. Chem.* **1983**, *22*, 2252-8.

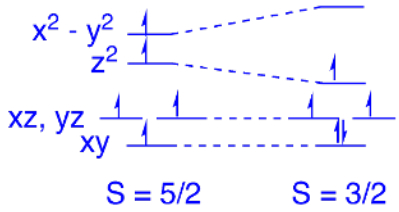
This page titled 3.4.5: The Magnitude of Parameters eσ, eπ and Δ is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.4.6: The Magnetochemical Series

The relative strengths of metal-ligand binding interactions distilled into the spectrochemical series depend on an inference drawn from the difference between the ground and excited states. In contrast, the **magnetochemical series** offers similar information based solely on observation of the ground state. These observations are possible in iron(III) porphyrin complexes because of a subtle change in spin state that occurs upon substitution of the axial position with different ligands. The result is a series analogous to the spectrochemical series that is called the magnetochemical series. This series was developed chiefly by the lab of Christopher Reed at University of Southern California and University of California, Riverside.1



There are two unusual things that happen with these porphyrin complexes that allow measurement of metal-ligand interactions in this way. A distortion that occurs in the weak field case of these square pyramidal complexes results in spin pairing in the weak field configuration rather than the high field case. Also, in these porphyrin complexes, a quantum mechanical admixture occurs in which the 5/2 and 3/2 states exist in superposition with each other. As a result, the spin state in these complexes is often intermediate between these two cases.



One additional feature makes these porphyrin complexes quite useful in measuring a magnetochemical series. Paramagnetic complexes produce dramatic shifts in nuclear magnetic resonance spectroscopy. In this case, the hydrogen atoms of the 5-membered pyrrole rings in the porphyrin system shift from about -60 ppm in the S = 3/2 case to about +80 ppm in the S = 5/2 case. In the case of a quantum admixture, the shift ranges in between these two limiting values. This NMR shift can be used to compare the field strength of the axial ligand.

An array of experiments eventually lead to a magnetochemical series. Example ligands from this series are shown in order here, from strong field to weak field:

$$NO^+ = CO > R_3Sn^- > -CH_3 > RS^- > F^- > -OPh > N_3^- = -OAc > NCS^- > Cl^- = -OH > Br^- > I^-$$

In addition, this method has allowed the inclusion of several very weakly bound ligands. These can be appended to the series as follows:

$$I^- > ReO_4^- > BF_4^- > CF_3SO_3^- > ClO_4^- > H_2O > SbF_6^- > CB_{11}H_{12}^-$$

Note the unusual position of water, which shows up as a much lower field ligand than in the Co(III) based spectrochemcial series for octahedral complexes. The difference is thought to come from the low spin Co(III) vs. the usually high spin Fe(III). Pi bonding is less favourable in the latter case and so the order in the iron porphyrin complexes is more strongly reflective of sigma donating effects. The anionic hydroxide is a better sigma donor than water because of greater electrostatic attraction to the metal.

Example 3.4.6.1

Organometallic ligands such as $-CH_3$ are not typically included in the spectrochemical series.

a. Characterize $-CH_3$ in terms of ligand type (pi donor, sigma donor, pi acceptor).
b. Explain why it appears so high in the magnetochemical series compared to other anions such as F-.

Solution

a. -CH3 is a sigma donor.
b. The -CH3 anion would be extraordinarily basic. The pKa of CH4 is estimated to be approximately 50, compared to a pKa of approximately 4 for HF. The -CH3 anion is a very strong sigma donor.

References

1. Reed, C.; Guiset, F. "Reversal of H2O and OH- Ligand Field Strength on the Magnetochemical Series Relative to the Spectrochemical Series. Novel 1-equiv Water Chemistry of Iron(III) Tetraphenylporphyrin Complexes." *J. Am. Chem. Soc.*, **2000**, *122*, 3281-2.

This page titled 3.4.6: The Magnetochemical Series is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.5: The Jahn-Teller Effect

Certain metal ions frequently display distortions from ideal geometry, such that the symmetry of the compound is lowered. In tetragonal distortions of octahedral complexes, for example, the metal-ligand bond distances of two axial ligands may be significantly longer than the distances of the equatorial ligands. Alternatively, two of the metal-ligand distances may be compressed compared to others.

Sometimes, these distortions can be experimentally observed. For example, EXAFS (X-ray absorption fine structure) data for [Cu(OH2)6](BrO3)2, an octahedral complex in which all six Cu-O bonds ought to be the same length, show two different Cu-O distances of 1.96(1) and 2.32(2) Å (the digit in parentheses is used to convey the degree of uncertainty in X-ray measurements).1 That's an approximately 20% difference between the same kind of metal-ligand bond distances within the same complex.

These distortions, often called **Jahn-Teller distortions**, are observed in complexes of transition metals with specific electron configurations: high spin d4, low spin d7, and d9 (for which there is neither a low nor high spin case). These configurations give rise to unequally occupied degenerate orbitals. Degenerate orbitals are multiple orbitals at the same energy. The three p orbitals in an atomic shell are degenerate, for example. In contrast, non-degenerate orbitals occur at different energy levels. These two cases are illustrated below with the simplest conceivable case, a pair of orbitals.

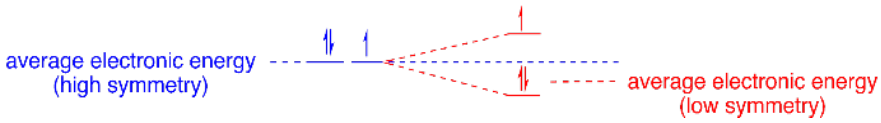


A set of degenerate orbitals might be equally or unequally occupied depending on the number of available electrons. For example, in the simple case of two degenerate orbitals, equal occupancy would occur if there were two electrons or four electrons because those even numbers of electrons could be divided evenly between the two orbitals. Either one or three electrons would lead to unequally occupied orbitals; there is no way to put the same number of electrons in each orbital in this case.

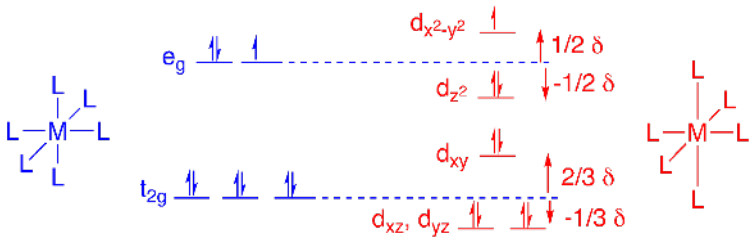




These cases of unequally occupied degenerate orbitals can lead to opportunities for distortion. When the symmetry of a complex drops, two otherwise degenerate orbitals might no longer exist at the same energy as each other. That means, for example, that instead of having three electrons at the same energy, we would have two electrons at lower energy and one at higher. There would be a net decrease in energy in the non-symmetric, distorted case.

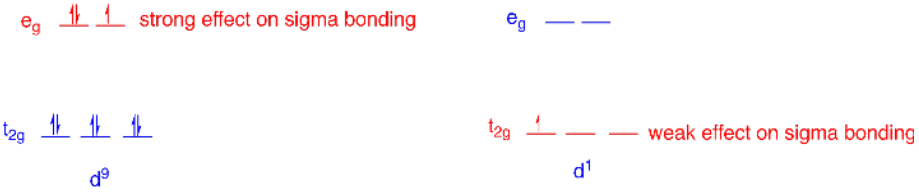


In the context of an octahedral d9 complex, elongation of the bonds to the axial ligands leads to a very slight lowering of the d orbitals that interact with ligands along the z axis: the dz2 and the dxz and dyz. The other orbitals are shown increasing slightly according to the principle that the average energy of the orbitals is preserved at the orbital barycenter (as opposed to the energy of the electrons, which decreases in this case).



Not all cases of unequally occupied degenerate orbitals produce measurable Jahn Teller distortions. In octahedral geometry, examples of strong Jahn Teller effects are seen when the unequally occupied orbitals are in the eg set rather than the t2g set. The eg

set is the one that is linked to sigma bonding, after all, so the orbitals in that level are strongly influenced by the strength of that sigma bonding interaction, and hence the bond length.



Changes in bond length are not the only observable result of the Jahn Teller effect. The absorption spectra of some octahedral complexes show two distinct d-d bands rather than the one band absorbed for pure octahedral symmetry. This observation is a consequence of having additional orbital levels giving rise to distinct electronic transitions. This phenomenon is also seen if the excited state, rather than the ground state, experiences Jahn Teller distortion.

The Jahn Teller effect also plays a role in reactivity. For example, it is thought to promote the lability of octahedral Cu(II) complexes by weakening the bonds to axial ligands via the tetragonal distortion.

References

1. Persson, I.; Persson, P.; Sandstrom, M.; Ullström, A.-S. "Structure of Jahn–Teller distorted solvated copper(ii) ions in solution, and in solids with apparently regular octahedral coordination geometry." *J. Chem. Soc. Dalton* **2002**, 1256-1265.

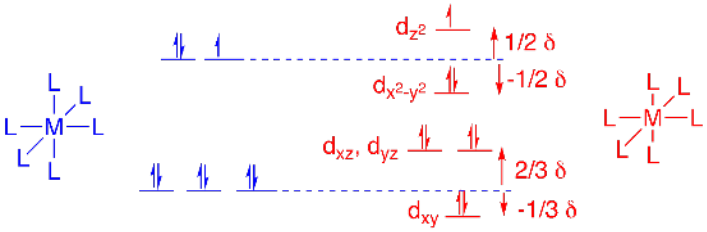
Problems

1. Given the effect of axial bond elongation on the d orbital energy levels in an octahedral complex, show the corresponding effects that would result from shortening of the axial metal ligand bonds.

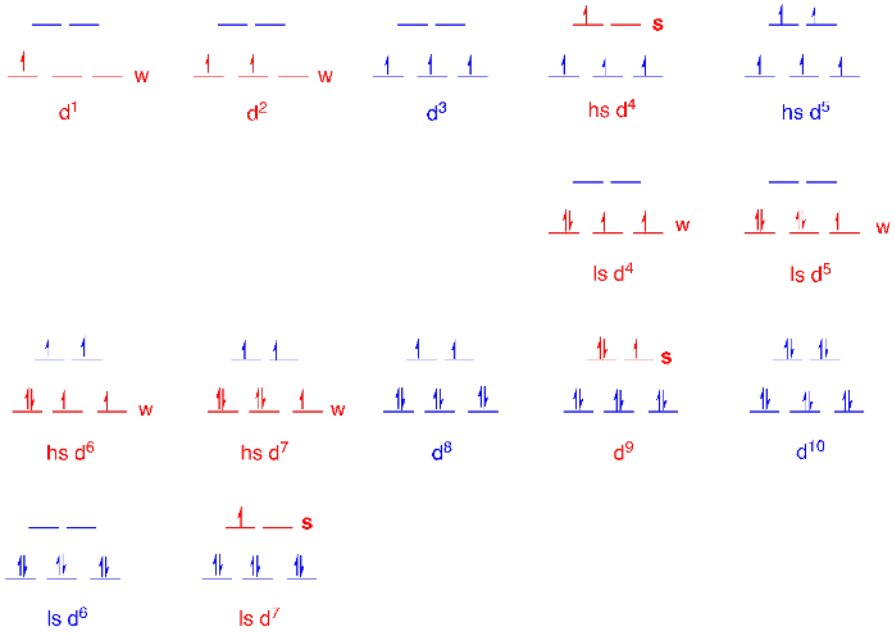
2. Fill in octahedral d orbital splitting diagrams for d1 to d10 configurations to show why only high spin d4, low spin d7 and d9 configurations exhibit strong Jahn Teller distortions.

Solutions

1. This time, dz2 is elevated, along with the dxz and dyx.



2. The w indicates a weak Jahn Teller effect. The s indicates a strong Jahn Teller effect.



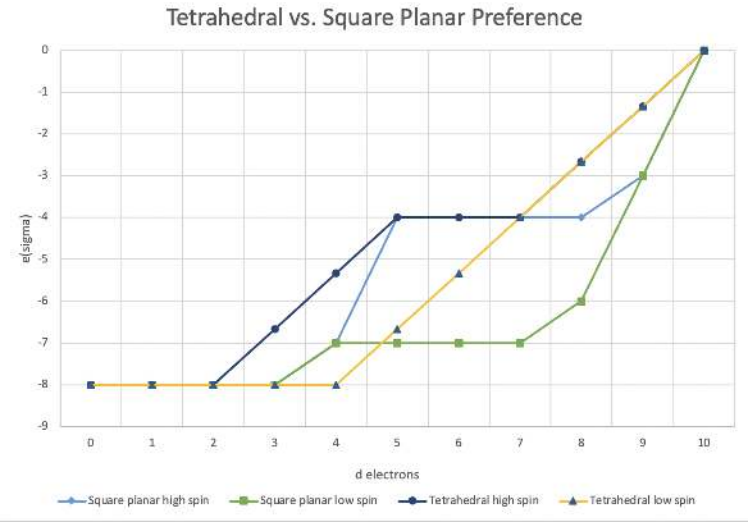
This page titled 3.5: The Jahn-Teller Effect is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.6: Four- and Six-Coordinate Preferences

Students sometimes want to be able to predict the coordination geometry that will be adopted by a particular combination of metal ion and ligands. In reality, there are enough variables involved in both the ligand and the metal that such predictions are not possible with any certainty.

Nevertheless, there are some broad trends that can be highlighted by looking at what the angular overlap model says about geometric preferences. One of the most common questions is whether a four coordinate complex will adopt a tetrahedral or square planar geometry. Probably the most important factor in this case is the steric bulk of the ligands. The ligand-metal-ligand bond angles in tetrahedral geometry are ideally 109 degrees, compared to 90 degrees in square planar geometry. As a result, ligands are spaced further apart in tetrahedral geometry than in square planar geometry, so bulkier ligands favor tetrahedral complexes.

On the other hand, the angular overlap model (as well as other approaches) suggests some advantages of square planar geometry. A comparison of eσ at a range of d electron configurations for both high spin and low spin cases is plotted below.

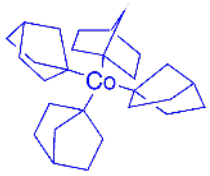


From the outset, we should note that low spin tetrahedral complexes are almost unheard of, so we should really compare square planar to the high spin tetrahedral case. In the comparison between high spin tetrahedral and high spin square planar geometry, square planar is favored only for d3, d4, d8 and d9 configuration. However, as we will see shortly, square planar complexes of d3 and d4 metals are not very common because metals with those electron configurations are more likely to adopt higher coordination geometries, such as five or six coordination. All of the other cases are more likely to adopt a tetrahedral geometry because if electronic stabilization factors are equal then steric factors (relief of ligand crowding) will prevail.

If we are comparing low spin square planar to high spin tetrahedral cases, there is an increased preference for the square planar geometry for all but the d1, d2 and d10 configurations. That suggests square planar geometry is usually favored unless there are steric factors that push the geometry to tetrahedral. Of course, the comparison we have used ignores eπ. Because the magnitude of eσ and eπ vary with different ligands and metals, we can't easily include both factors in one graph. However, we do know that π donors will make it more likely that we are dealing with a high spin square planar case, whereas π acceptors will lead to a low spin square planar case. These two cases have a dramatic effect on the d orbital splitting diagram. The angular overlap model suggests a dramatic reordering of the square planar d orbital splitting diagram in these cases.

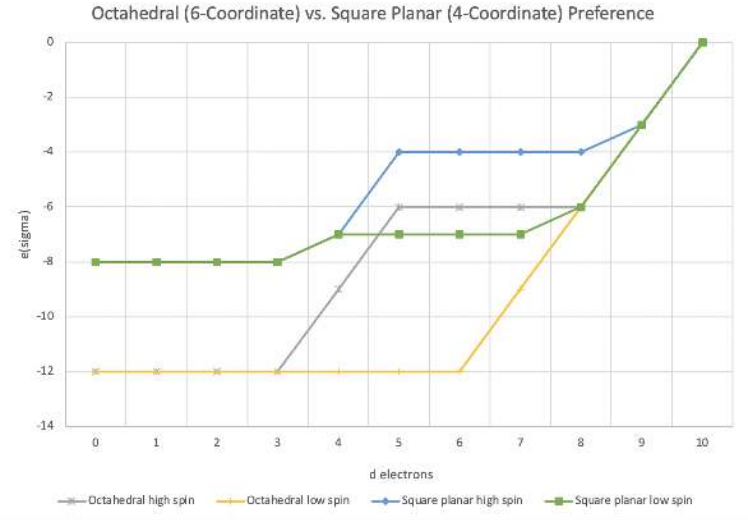
Consequently, square planar geometry is expected to be much more common in cases with π acceptor ligands, whereas tetrahedral geometry should be more common in cases with π donor ligands.

It is worth noting that the first reported group of low spin tetrahedral complexes, the crystallographically characterized tetrakis(norbornyl)cobalt(IV), (nor)4Co, as well as the cationic and anionic (nor)4Co+ and (nor)4Co-, are d5, d4 and d6 complexes, respectively.1 AOM predicts very similar stabilization in low spin square planar and low spin tetrahedral geometries in these cases. However, the tetrahedral geometry is largely enforced by the bulky norbornyl ligands.



$(nor)_4Co$

As mentioned above, there is a general preference for six coordination over four coordination, especially at lower d electron counts. A simple AOM comparison indicates octahedral geometry is favored for the low spin case between d0 and d7. Even high spin octahedral geometry is favored electronically over low spin square planar up to d4, with only a modest preference for square planar between d5 and d7. It isn't surprising that octahedral geometry is so common. In very simple terms, this preference comes from the energetically favored formation of six metal-ligand bonds rather than only four metal-ligand bonds.



Example 3.6.1

Confirm the stabilization values from the angular overlap model for (a) high spin and (b) low spin tetrahedral geometry.

Solution

Stabilization (σ only) ΔE = 0(# *e* electrons) - 43(# *t2* electrons) - 4(2 electrons per ligand) eσ

a) For high spin:

- d0: ΔE = 0(0) + 43(0) - 8 eσ = -8 eσ
- d1: ΔE = 0(1) + 43 (0) - 8 eσ = -8 eσ
- d2: ΔE = 0(2) + 43 (0) - 8 eσ = -8 eσ
- d3: ΔE = 0(2) + 43 (1) - 8 eσ = -623 eσ
- d4: ΔE = 0(2) - 43(2) - 8 eσ = -513 eσ
- d5: ΔE = 0(2) - 43 (3) - 8 eσ = -4 eσ
- d6: ΔE = 0(3) - 43 (3) - 8 eσ = -4 eσ
- d7: ΔE = 0(4) - 43 (3) - 8 eσ = -4 eσ
- d8: ΔE = 0(4) - 43 (4) - 8 eσ = -223 eσ
- d9: ΔE = 0(4) - 43 (5) - 8 eσ = -113 eσ
- d10: ΔE = 0(4) - 43 (6) - 8 eσ = 0 eσ

b) For low spin:

- d0: ΔE = 0(0) + 43 (0) - 8 eσ = -8 eσ
- d1: ΔE = 0(1) + 43 (0) - 8 eσ = -8 eσ
- d2: ΔE = 0(2) + 43 (0) - 8 eσ = -8 eσ

- d3: ΔE = 0(3) + 43 (0) - 8 eσ = -8 eσ
- d4: ΔE = 0(4) -43 (0) - 8 eσ = -8 eσ
- d5: ΔE = 0(4) - 43 (1) - 8 eσ = -623 eσ
- d6: ΔE = 0(4) - 43 (2) - 8 eσ = -513 eσ
- d7: ΔE = 0(4) - 43 (3) - 8 eσ = -4 eσ
- d8: ΔE = 0(4) - 43 (4) - 8 eσ = -223 eσ
- d9: ΔE = 0(4) - 43 (5) - 8 eσ = -113 eσ
- d10: ΔE = 0(4) - 43 (6) - 8 eσ = 0 eσ

Example 3.6.2

Calculate the preference for square planar geometry for each d electron count in (a) the case of high spin square planar vs. high spin tetrahedral, and (b) the case of low spin square planar vs. high spin tetrahedral.

Solution

Preference = ΔΔE = ΔE(square planar) - ΔE(tetrahedral)

a) For high spin:

- d0: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d1: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d2: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d3: ΔΔE = - 8 - (-623)eσ = -113eσ
- d4: ΔΔE = -7 - (-513) eσ = -123eσ
- d5: ΔΔE = -4 - (4) eσ = 0 eσ
- d6: ΔΔE = -4 - (4) eσ = 0 eσ
- d7: ΔΔE = -4 - (4) eσ = 0 eσ
- d8: ΔΔE = -4 - (223) eσ = -113 eσ
- d9: ΔE = -3 - (113) eσ = -123 eσ
- d10: ΔE = 0 - (0) eσ = 0 eσ

b) For low spin:

- d0: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d1: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d2: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d3: ΔΔE = - 8 - (-623)eσ = -113eσ
- d4: ΔΔE = -7 - (-513) eσ = -123eσ
- d5: ΔΔE = -7 - (4) eσ = -3 eσ
- d6: ΔΔE = -7 - (4) eσ = -3 eσ
- d7: ΔΔE = -7 - (4) eσ = -3 eσ
- d8: ΔΔE = -6 - (223) eσ = -313 eσ
- d9: ΔE = -3 - (113) eσ = -123 eσ
- d10: ΔE = 0 - (0) eσ = 0 eσ

References

1. Byrne, E. K.; Theopold, K. H. "Synthesis, Characterization, and Electron-Transfer Reactivity of Norbornyl Complexes of Cobalt in Unusually High Oxidation States." *J. Am. Chem. Soc.* **1989**, *111*, 3887-3896.

This page titled 3.6: Four- and Six-Coordinate Preferences is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.7: Other Shapes

Although four- and six-coordinate geometries are probably the most commonly observed in inorganic chemistry, a range of other shapes have also been reported.1 The other most common coordination number is five. Geometries for five-coordination include both trigonal bipyramidal and square pyramidal. Both are common, and distorted geometries in between these two limiting cases are even more commonly observed. The fractional parameter, τ (tau), is usually reported with structural analyses of five-coordinate compounds to convey where the structure falls on this continuum. A value of τ = 1 corresponds to perfect trigonal bipyramidal and a value of τ = 0 corresponds to perfect square pyramidal. Most reported complexes have values solidly in between these extremes. However, there are some ligands, such as porphyrins, in which a rigid ring of four basal donors enforces square pyramidal geometry more closely.

Lower coordination numbers are less common but are reported in certain cases. Two-coordinate compounds are sometimes observed in complexes of the coinage metals. They include a range of ligands, including σ donors in [Ag(NH3)2]+ ion, π donors in [CuCl2]- ion and π acceptors in [Au(CN)2]- ion, for example. Three coordinate complexes have been reported from across the periodic table, especially with sterically demanding ligands such as Bradley and Chisholm's [(Me3Si)2N]3M (Sc, Ti, V, Cr, Fe) or Wolczanski's (t-Bu3SiO)3Ta.2,3

Coordination numbers higher than six are sometimes observed. These cases often involve early transition metals in high oxidation states that are less electronically saturated. Examples are also seen in the lanthanides and actinides owing to their large size. There is even a reported sixteen-coordinate complex, although it is of an alkali metal ion and not a transition metal ion.

References

1. Gispert, J. R. *Coordination Chemistry*, Wiley-VCH: Weinheim, Germany, **2008**, pp. 59-80.

2. Bradley, D. C.; Copperthwaite, R. G.; Extine, M. W.; Reichert, W. W.; Chisholm, M. H. (1978). "Transition Metal Complexes of Bis(Trimethyl-silyl)Amine (1,1,1,3,3,3-Hexamethyldisilazane)" *Inorganic Syntheses.* **1978**, *18*. p. 112.

3. Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. "Carbon monoxide cleavage by (silox)3Ta (silox = tert-Bu3SiO-): physical, theoretical, and mechanistic investigations", *J. Am. Chem. Soc.* **1989**, *111*, 25, 9056-9072.

4. Pollak, D.; Goddard, R.; Pörschke, K.-R. "Cs[H2NB2(C6F5)6] Featuring an Unequivocal 16-Coordinate Cation". *J. Am. Chem. Soc.* **2016**, *138*, 30, 9444-9451.

Problems

1. Use the angular overlap model to

i) calculate d orbital energy destabilization and

ii) construct d orbital splitting diagrams for linear (two-coordinate) geometry with the following ligand types.

a) sigma donor b) pi acceptor c) pi donor

2. Use the angular overlap model with sigma-only interactions to calculate d orbital energy destabilization in square pyramidal geometry.

3. Use the angular overlap model with sigma-only interactions to construct d orbital splitting diagrams for the following geometries.

a) trigonal planar b) trigonal pyramidal c) square bipyramidal

Solutions

1. i) a) Positions 1, 6.

dz2: (1 + 1) eσ = 2 eσ

dx2-y2: (0 + 0) eσ = 0

dxy: (0 + 0) eσ = 0

dxz: 0

dyz: 0

b) Positions 1, 6.

dz2: 0

dx2-y2: - (0 + 0) eπ = 0

dxy: - (0 + 0) eπ = 0

dxz: - (1 + 1) eπ = -2 eπ

dyz: - (1 + 1) eπ = -2 eπ

c) Positions 1, 6.

dz2: 0

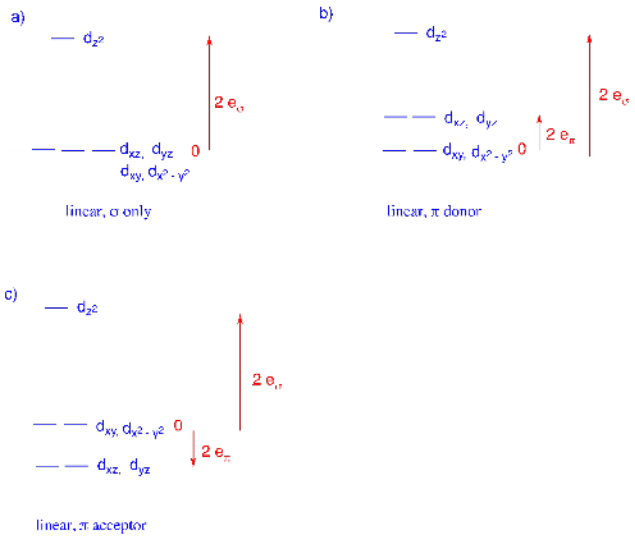
dx2-y2: (0 + 0) eπ = 0

dxy: (0 + 0) eπ = 0

dxz: (1 + 1) eπ = 2 eπ

dyz: (1 + 1) eπ = 2 eπ

ii)



2. Positions 1, 2, 3, 4, 5:

dz2: (1 + 1/4 + 1/4 + 1/4 + 1/4) eσ = 2eσ

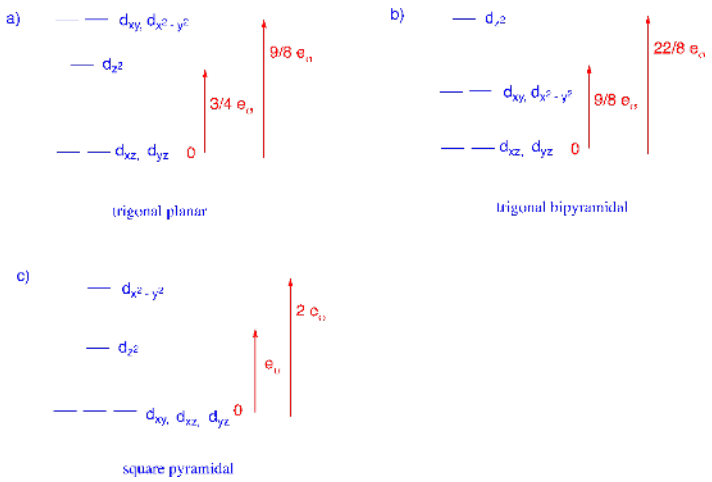
dx2-y2: (0 + 3/4 + 3/4 + 3/4 + 3/4) eσ = 3eσ

dxy: 0

dxz: 0

dyz: 0

3.



This page titled 3.7: Other Shapes is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

3.P: Problems

This page titled 3.P: Problems is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller.

SECTION OVERVIEW

4: d-Block Metal Chemistry

The d-block elements are found in groups 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 of the periodic table; d-block elements are also known as the transition metals. The d orbital is filled with the electronic shell “n-1.”

4.1: Properties of Transition Metals

- 4.1.1: A Brief Survey of Transition-Metal Chemistry
- 4.1.2: Electron Configuration of Transition Metals
- 4.1.3: General Trends among the Transition Metals
- 4.1.4: Introduction to Transition Metals I
- 4.1.5: Introduction to Transition Metals II
- 4.1.6: Metallurgy
  - 4.1.6.1: An Introduction to the Chemistry of Metal Extraction
  - 4.1.6.2: The Extraction of Copper
  - 4.1.6.3: The Extraction of Iron
    - 4.1.6.3.1: Iron Production
  - 4.1.6.4: The Extraction of Silver
    - 4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate
- 4.1.7: Oxidation States of Transition Metals
- 4.1.8: Transition Metals in Biology

4.2: Transition Metals

- 4.2.1: Chemistry of Actinium
- 4.2.2: Chemistry of Lanthanum
- 4.2.3: Chemistry of Scandium
- 4.2.4: Chemistry of Yttrium
- 4.2.5: Group 3 Elemental Properties

4.3: Transition Metals

- 4.3.1: Group 4 Elemental Properties
- 4.3.2: Chemistry of Hafnium
- 4.3.3: Chemistry of Rutherfordium
- 4.3.4: Chemistry of Titanium
- 4.3.5: Chemistry of Zirconium

4.4: Transition Metals

- 4.4.1: Chemistry of Dubnium
- 4.4.2: Chemistry of Niobium
- 4.4.3: Chemistry of Tantalum
- 4.4.4: Chemistry of Vanadium
- 4.4.5: Group 5 Elemental Properties

4.5: Transition Metals

4.5.1: Chemistry of Chromium

4.5.1.1: Chemistry of Chromium

4.5.1.2: Potassium Chromium Sulfate

4.5.2: Chemistry of Molybdenum

4.5.2.1: Molybdenum Disulfide

4.5.3: Chemistry of Seaborgium

4.5.4: Chemistry of Tungsten

4.6: Transition Metals

4.6.1: Chemistry of Bohrium

4.6.2: Chemistry of Manganese

4.6.2.1: Chemistry of Manganese

4.6.3: Chemistry of Rhenium

4.6.4: Chemistry of Technetium

4.7: Transition Metals

4.7.1: Chemistry of Hassium

4.7.2: Chemistry of Iron

4.7.2.1: Iron in Humans

4.7.3: Chemistry of Osmium

4.7.4: Chemistry of Ruthenium

4.8: Transition Metals

4.8.1: Chemistry of Cobalt

4.8.2: Chemistry of Iridium

4.8.3: Chemistry of Meitnerium

4.8.4: Chemistry of Rhodium

4.9: Transition Metals

4.9.1: Chemistry of Darmstadtium

4.9.2: Chemistry of Nickel

4.9.3: Chemistry of Palladium

4.9.4: Chemistry of Platinum

4.10: Transition Metals

4.10.1: Chemistry of Copper

4.10.2: Chemistry of Gold

4.10.3: Chemistry of Roentgenium

4.10.4: Chemistry of Silver

4.10.4.1: Silver Chloride

4.10.4.2: Silver Nitrate

4.11: Transition Metals

4.11.1: Chemistry of Cadmium

4.11.1.1: Cadmium Sulfide

4.11.2: Chemistry of Copernicium

4.11.3: Chemistry of Mercury

4.11.4: Chemistry of Zinc

4: d-Block Metal Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

4.1: Properties of Transition Metals

The transition metals, groups 3–12 in the periodic table, are generally characterized by partially filled d subshells in the free elements or their cations. (Although the metals of group 12 do not have partially filled d shells, their chemistry is similar in many ways to that of the preceding groups, and we therefore include them in our discussion.) Unlike the s-block and p-block elements, the transition metals exhibit significant horizontal similarities in chemistry in addition to their vertical similarities.

- 4.1.1: A Brief Survey of Transition-Metal Chemistry
- 4.1.2: Electron Configuration of Transition Metals
- 4.1.3: General Trends among the Transition Metals
- 4.1.4: Introduction to Transition Metals I
- 4.1.5: Introduction to Transition Metals II
- 4.1.6: Metallurgy
  - 4.1.6.1: An Introduction to the Chemistry of Metal Extraction
  - 4.1.6.2: The Extraction of Copper
  - 4.1.6.3: The Extraction of Iron
    - 4.1.6.3.1: Iron Production
  - 4.1.6.4: The Extraction of Silver
    - 4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate
- 4.1.7: Oxidation States of Transition Metals
- 4.1.8: Transition Metals in Biology

4.1: Properties of Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.1.1: A Brief Survey of Transition-Metal Chemistry

Learning Objectives

- To use periodic trends to understand the chemistry of the transition metals.

As we shall see, the two heaviest members of each group usually exhibit substantial similarities in chemical behavior and are quite different from the lightest member.

Group 3 (Sc, Y, La, and Ac)

As shown in Table 4.1.1.1, the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n-1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

$$2M_{(s)} + 6H_2O_{(l)} \rightarrow 2M(OH)_{3(s)} + 3H_{2(g)} \tag{4.1.1.1}$$

> *The chemistry of the group 3 metals is almost exclusively that of the M^{3+} ion; the elements are powerful reductants.*

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated metal ion: $M^{3+}(aq)$.

Table 4.1.1.1: Some Properties of the Elements of Groups 3, 4, and 5

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
3	Sc	21	$4s^23d^1$	1.36	162	1541	2.99
	Y	39	$5s^24d^1$	1.22	180	1522	4.47
	La	57	$6s^25d^1$	1.10	183	918	6.15
	Ac	89	$7s^26d^1$	1.10	188	1051	10.07
4	Ti	22	$4s^23d^2$	1.54	147	1668	4.51
	Zr	40	$5s^24d^2$	1.33	160	1855	6.52
	Hf	72	$6s^25d^24f^{14}$	1.30	159	2233	13.31
5	V	23	$4s^23d^3$	1.63	134	1910	6.00
	Nb	41	$5s^24d^3$	1.60	146	2477	8.57
	Ta	73	$6s^25d^34f^{14}$	1.50	146	3017	16.65

The group 3 metals react with nonmetals to form compounds that are primarily ionic in character. For example, reacting group 3 metals with the halogens produces the corresponding trihalides: MX_3. The trifluorides are insoluble in water because of their high lattice energies, but the other trihalides are very soluble in water and behave like typical ionic metal halides. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called sesquioxides (M_2O_3), which react with H_2O or CO_2 to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but "mischmetal," a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

$$2FeTiO_{3(s)} + 6C_{(s)} + 7Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + 2FeCl_{3(g)} + 6CO_{(g)} \tag{4.1.1.2}$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

> *The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.*

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Figure 23.2, the group 4 metals become denser, higher melting, and more electropositive down the column (Table 4.1.1.1). Unexpectedly, however, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

$$TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)} \tag{4.1.1.3}$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure 4.1.1.1). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

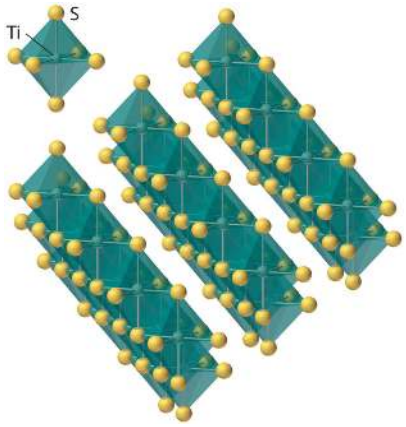


Figure 4.1.1.1: The Layered Structure of TiS_2. Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

Group 5 (V, Nb, and Ta)

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of V_4C_3, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of SO_2 to SO_3 in the contact process for the production of sulfuric acid. In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as Nb_3Zr and Nb_3Ge, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

> *The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.*

As indicated in Table 4.1.1.1, the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state (M_2O_5), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 4.1.1.2). Consistent with its covalent character, V_2O_5 is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Because vanadium ions with different oxidation states have different numbers of d electrons, aqueous solutions of the ions have different colors: in acid V(V) forms the pale yellow $[VO_2]^+$ ion; V(IV) is the blue vanadyl ion $[VO]^{2+}$; and V(III) and V(II) exist as the hydrated V^{3+} (blue-green) and V^{2+} (violet) ions, respectively.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

Group 6 (Cr, Mo, and W)

As an illustration of the trend toward increasing polarizability as we go from left to right across the d block, in group 6 we first encounter a metal (Mo) that occurs naturally as a sulfide ore rather than as an oxide. Molybdenite (MoS_2) is a soft black mineral that can be used for writing, like PbS and graphite. Because of this similarity, people long assumed that these substances were all the same. In fact, the name molybdenum is derived from the Greek molybdos, meaning “lead.” More than 90% of the molybdenum produced annually is used to make steels for cutting tools, which retain their sharp edge even when red hot. In addition, molybdenum is the only second- or third-row transition element that is essential for humans. The major chromium ore is chromite ($FeCr_2O_4$), which is oxidized to the soluble $[CrO_4]^{2-}$ ion under basic conditions and reduced successively to Cr_2O_3 and Cr with carbon and aluminum, respectively. Pure chromium can be obtained by dissolving Cr_2O_3 in sulfuric acid followed by electrolytic reduction; a similar process is used for electroplating metal objects to give them a bright, shiny, protective surface layer. Pure tungsten is obtained by first converting tungsten ores to WO_3, which is then reduced with hydrogen to give the metal.

> *The metals become increasing polarizable across the d block.*

Consistent with periodic trends, the group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 4.1.1.2). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to extensive polarization of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from Cr^{2+}, which is a powerful reductant, to CrO_3, a red solid that is a powerful oxidant. For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

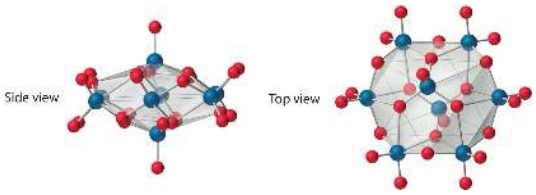
Table 4.1.1.2: Some Properties of the Elements of Groups 6 and 7

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
6	Cr	24	$4s^1 3d^5$	1.66	128	1907	7.15
	Mo	42	$5s^1 4d^5$	2.16	139	2623	10.20
	W	74	$6s^2 5d^4 4f^{14}$	1.70	139	3422	19.30
7	Mn	25	$4s^2 3d^5$	1.55	127	1246	7.30
	Tc	43	$5s^2 4d^5$	2.10	136	2157	11.50
	Re	75	$6s^2 5d^5 4f^{14}$	1.90	137	3186	20.80

> The chemistry of the two heaviest group 6 metals (Mo and W) is dominated by the +6 oxidation state. The chemistry of the lightest element (Cr) is dominated by lower oxidation states.

As observed in previous groups, the group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases, and their melting points decrease. Recall that as the electronegativity of the halogens decreases from F to I, they are less able to stabilize high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but CrF_6 is unstable at temperatures above −100°C, whereas MoF_6 and WF_6 are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-row elements, the other halogens can oxidize chromium to only the trihalides, CrX_3 (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and MoI_3, and tungsten gives WCl_6, WBr_5, and WI_4.

Both Mo and W react with oxygen to form the covalent trioxides (MoO_3 and WO_3), but Cr reacts to form only the so-called sesquioxide (Cr_2O_3). Chromium will form CrO_3, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in base to form the corresponding oxoanions ($[MO_4]^{2-}$). Consistent with periodic trends, the sesquioxide of the lightest element in the group (Cr_2O_3) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH they form a series of polymeric anions called isopolymetallates, such as the $[Mo_8O_{26}]^{4-}$ ion, whose structure is as follows:



An isopolymolybdate cluster. The $[Mo_8O_{26}]^{4-}$ ion, shown here in both side and top views, is typical of the oxygen-bridged clusters formed by Mo(VI) and W(VI) in aqueous solution.

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is MoS_2; it has a layered structure similar to that of TiS_2 (Figure 4.1.1.1), in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both MoS_2 and WS_2 are used as lubricants in a variety of applications, including automobile engines. Because tungsten itself has an extraordinarily high melting point (3380°C), lubricants described as containing “liquid tungsten” actually contain a suspension of very small WS_2 particles.

As in groups 4 and 5, the elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

Group 7 (Mn, Tc, and Re)

Continuing across the periodic table, we encounter the group 7 elements (Table 4.1.1.2). One group 7 metal (Mn) is usually combined with iron in an alloy called ferromanganese, which has been used since 1856 to improve the mechanical properties of steel by scavenging sulfur and oxygen impurities to form MnS and MnO. Technetium is named after the Greek technikos, meaning "artificial," because all its isotopes are radioactive. One isotope, ^{99m}Tc (m for metastable), has become an important biomedical tool for imaging internal organs. Because of its scarcity, Re is one of the most expensive elements, and its applications are limited. It is, however, used in a bimetallic Pt/Re catalyst for refining high-octane gasoline.

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from −3 to +7 are known, with the most common being +2 and +4 (Figure 4.1.1.3). In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive. In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configuration, the aqueous Mn^{3+} ion, with a $3d^4$ valence electron configuration, is a potent oxidant that is able to oxidize water. It is difficult to generalize about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Like vanadium, compounds of manganese in different oxidation states have different numbers of d electrons, which leads to compounds with different colors: the $Mn^{2+}(aq)$ ion is pale pink; $Mn(OH)_3$, which contains Mn(III), is a dark brown solid; MnO_2, which contains Mn(IV), is a black solid; and aqueous solutions of Mn(VI) and Mn(VII) contain the green manganate ion $[MnO_4]^{2-}$ and the purple permanganate ion $[MnO_4]^-$, respectively.

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with F_2 gives only MnF_3, a high-melting, red-purple solid, whereas Re reacts with F_2 to give ReF_7, a volatile, low-melting, yellow solid. Again, reaction with the less oxidizing, heavier halogens produces halides in lower oxidation states. Thus reaction with Cl_2, a weaker oxidant than F_2, gives $MnCl_2$ and $ReCl_6$. Reaction of Mn with oxygen forms only Mn_3O_4, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite (Fe_3O_4). In contrast, Tc and Re form high-valent oxides, the so-called heptoxides (M_2O_7), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Under forced conditions, manganese will form Mn_2O_7, an unstable, explosive, green liquid. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of MoS_2, as well as more complex heptasulfides (M_2S_7). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

> *The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.*

Groups 8, 9, and 10

In many older versions of the periodic table, groups 8, 9, and 10 were combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry, in addition to the similarities within each column. In part, these horizontal similarities are due to the fact that the ionization potentials of the elements, which increase slowly but steadily across the d block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10). As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3 for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called precious metals because they are rather rare in nature and mostly chemically inert.

> *The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.*

Group 8 (Fe, Ru, and Os)

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

Group 9 (Co, Rh, and Ir)

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as "cobalt blue," and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

Group 10 (Ni, Pd, and Pt)

Nickel silicates are easily processed; consequently, nickel has been known and used since antiquity. In fact, a 75:25 Cu:Ni alloy was used for more than 2000 years to mint "silver" coins, and the modern US nickel uses the same alloy. In contrast to nickel, palladium and platinum are rare (their terrestrial abundance is about 10–15 ppb), but they are at least an order of magnitude more abundant than the heavier elements of groups 8 and 9. Platinum and palladium are used in jewelry, the former as the pure element and the latter as the Pd/Au alloy known as white gold.



Over 2000 years ago, the Bactrian civilization in Western Asia used a 75:25 alloy of copper and nickel for its coins. A modern US nickel has the same composition, but a modern Canadian nickel is nickel-plated steel and contains only 2.5% nickel by mass.

Trends in Group 8, 9, and 10

Some properties of the elements in groups 8–10 are summarized in Table 4.1.1.3 As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. We are now at the point in the d block where there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation state formed by losing the ns2 valence electrons. In addition, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 4.1.1.3: Some Properties of the Elements of Groups 8, 9, and 10

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
8	Fe	26	$4s^2 3d^6$	1.83	126	1538	7.87
	Ru	44	$5s^1 4d^7$	2.20	134	2334	12.10
	Os	76	$6s^2 5d^6 4f^{14}$	2.20	135	3033	22.59
9	Co	27	$4s^2 3d^7$	1.88	125	1495	8.86

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
	Rh	45	$5s^1 4d^8$	2.28	134	1964	12.40
	Ir	77	$6s^2 5d^7 4f^{14}$	2.20	136	2446	22.50
10	Ni	28	$4s^2 3d^8$	1.91	124	1455	8.90
	Pd	46	$4d^{10}$	2.20	137	1555	12.00
	Pt	78	$6s^2 5d^8 4f^{14}$	2.20	139	1768	21.50

We stated that higher oxidation states become less stable as we go across the d-block elements and more stable as we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride NiF_2. In contrast to Fe, Ru and Os form a series of fluorides up to RuF_6 and OsF_7. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, Fe_2O_3, and the mixed-valent Fe_3O_4 (magnetite), all of which are nonstoichiometric. In contrast, Ru and Os form the dioxides (MO_2) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases rapidly as we go farther across the d block.

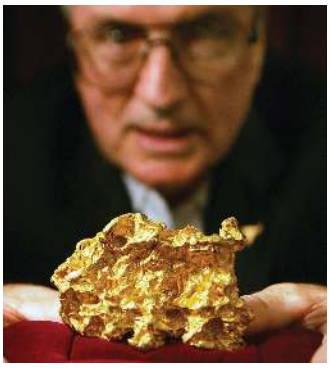
> *Higher oxidation states become less stable across the d-block, but more stable down a group.*

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion (S_2^{2-}), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions (S^{2-}). This combination of highly charged cations and easily polarized anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far the most important of these is cementite (Fe_3C), which is used to strengthen steel. At high temperatures, Fe_3C is soluble in iron, but slow cooling causes the phases to separate and form particles of cementite, which gives a metal that retains much of its strength but is significantly less brittle than pure iron. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to H_2 but essentially impermeable to all other gases, including He. Consequently, diffusion of H_2 through Pd is an effective method for separating hydrogen from other gases.

Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.



This 1 kg gold nugget was found in Australia; in 2005, it was for sale in Hong Kong at an asking price of more than US$64,000.

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.



The Chuquicamata copper mine in northern Chile, the world's largest open-pit copper mine, is 4.3 km long, 3 km wide, and 825 m deep. Each gigantic truck in the foreground (and barely visible in the lower right center) can hold 330 metric tn (330,000 kg) of copper ore.

Some properties of the coinage metals are listed in Table 4.1.1.4 The electronegativity of gold (χ = 2.40) is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single ns electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled ns orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold anion Au^- with a $6s^25d^{10}$ valence electron configuration.

Table 4.1.1.4: Some Properties of the Elements of Groups 11 and 12

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
11	Cu	29	$4s^13d^{10}$	1.90	128	1085	8.96

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
	Ag	47	$5s^14d^{10}$	1.93	144	962	10.50
	Au	79	$6s^15d^{10}4f^{14}$	2.40	144	1064	19.30
12	Zn	30	$4s^23d^{10}$	1.65	134	420	7.13
	Cd	48	$5s^24d^{10}$	1.69	149	321	8.69
	Hg	80	$6s^25d^{10}4f^{14}$	1.90	151	−38.8	13.53

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. Hence they are noble metals that are particularly well suited for use in coins and jewelry. Copper reacts with O_2 at high temperatures to produce Cu_2O and with sulfur to form Cu_2S. Neither silver nor gold reacts directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black Ag_2S coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidizing acids. Thus both Cu and Ag dissolve in HNO_3 and in hot concentrated H_2SO_4, while Au dissolves in the 3:1 $HCl:HNO_3$ mixture known as aqua regia. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stable $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores.

> *Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.*

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilize the higher oxidation states (Au^{3+} and Cu^{2+}). Thus all the copper(II) halides except the iodide are known, but the only dihalide of silver is AgF_2. In contrast, all the gold trihalides (AuX_3) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

Group 12 (Zn, Cd, and Hg)

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled (n − 1)d subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. Cadmium is used as the cathode in rechargeable NiCad batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries.

As shown in Table 4.1.1.4, the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two ns electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion Hg_2^{2+}.

> *The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.*

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO,

whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

Example 4.1.1.1

For each reaction, explain why the indicated products form.

a. $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$
b. $WO_3(s) + 3C(s) + 3Cl_2(g) \xrightarrow{\Delta} WCl_6(s) + 3CO(g)$
c. $Sc_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Sc(OH)_4]^-(aq)$
d. $2KMnO_4(aq) + 2H_2SO_4(l) \rightarrow Mn_2O_7(l) + 2KHSO_4(soln) + H_2O(soln)$
e. $4CrCl_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 8Cl^-(aq) + 2H_2O(l)$

Given: balanced chemical equation

Asked for: why the indicated products form

Strategy:

Refer to the periodic trends in this section.

Solution:

a. The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid–base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyze in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.
b. This reaction involves the oxide of a group 6 metal in its highest oxidation state (WO_3) and two elements, one of which is a reductant (C) and the other an oxidant (Cl_2). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form CCl_4, and WO_3 is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and chlorine. The most likely combination is WCl_6 (leaving the oxidation state of the metal unchanged).
c. One of the reactants is a strong base (OH^-), so an acid–base reaction is likely if the other reactant is acidic. Because oxides like Sc_2O_3, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect Sc_2O_3 to dissolve in base to form a soluble hydroxide complex.
d. Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidized further. A redox reaction is impossible, which leaves an acid–base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.
e. Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidized. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which Cr^{2+} ions are oxidized and O_2 is reduced. In the presence of protons, the reduction product of O_2 is water, so we need to determine only the identity of the oxidation product of Cr^{2+}. Chromium forms compounds in two common higher oxidation states: the Cr^{3+} ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than O_2. We therefore predict that the reaction will form $Cr^{3+}(aq)$ and water.

Exercise 4.1.1.1

Predict the products of each reactions and then balance each chemical equation.

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+}$
b. $Na_2Cr_2O_7(aq) + H_2SO_4(l) \rightarrow$
c. $FeBr_2(aq) + O_2(g) \xrightarrow{H^+}$
d. $VBr_4(l) + H_2O(l) \rightarrow$

e. $ZrO_2(s) + C(s) + Cl_2(g) \xrightarrow{\Delta}$

Answer

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+} Cr^{3+}(aq) + Fe^{2+}(aq)$
b. $Na_2Cr_2O_7(aq) + 2H_2SO_4(l) \rightarrow 2NaHSO_4(soln) + H_2O(soln) + 2CrO_3(s)$
c. $4FeBr_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 8Br^-(aq)$
d. $VBr_4(l) + H_2O(l) \rightarrow VO^{2+}(aq) + 4Br^-(aq) + 2H^+(aq)$
e. $ZrO_2(s) + 2C(s) + 2Cl_2(g) \xrightarrow{\Delta} ZrCl_4(s) + 2CO(g)$

Summary

The elements tend to become more polarizable going across the d block and higher oxidation states become less stable; higher oxidation states become more stable going down a group. The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form compounds that are largely ionic and with oxygen to form sesquioxides (M_2O_3). The group 4 metals also have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-radius ratio causes extensive polarization of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity. The group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states lower than +5. The oxides are sufficiently polarized to make them covalent in character. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarizable across the row, their affinity for oxygen decreases. The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidizing strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but Cr_2O_3 is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups. The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits an extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidizing halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. The group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties. In groups 8, 9, and 10, the ionization potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of group 8 metals in their highest oxidation state are powerful oxidants. The reaction of metals in groups 8, 9, and 10 with the chalcogens is complex, and these elements form a range of binary nitrides, carbides, and borides. The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides. The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

Contributors and Attributions

- Anonymous

4.1.1: A Brief Survey of Transition-Metal Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **A Brief Survey of Transition-Metal Chemistry** is licensed CC BY-NC-SA 4.0.

4.1.2: Electron Configuration of Transition Metals

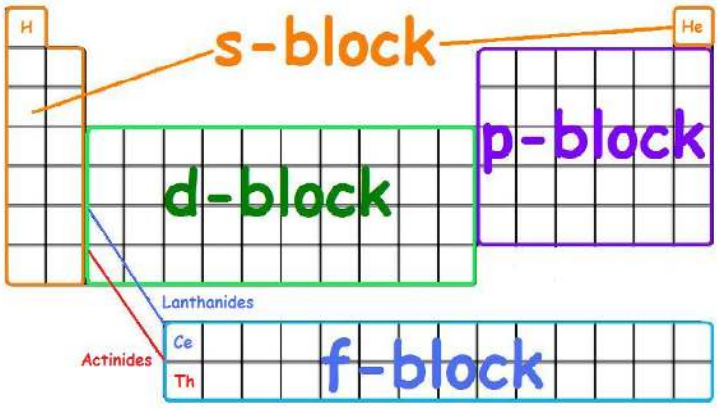
Electron configuration describes the distribution of electrons among different orbitals (including shells and subshells) within atoms and molecules.

Introduction

There are four principle orbitals (s, p, d, and f) which are filled according to the energy level and valence electrons of the element. All four orbitals can hold different number of electrons. The s-orbital can hold 2 electrons, and the other three orbitals can hold up to 6, 10, and 14 electrons, respectively. The s-orbital primarily denotes group 1 or group 2 elements, the p-orbital denotes group 13, 14, 15, 16, 17, or 18 elements, and the f-orbital denotes the Lanthanides and Actinides group. The main focus of this module however will be on the electron configuration of transition metals, which are found in the d-orbitals (d-block).

The electron configuration of transition metals is special in the sense that they can be found in numerous oxidation states. Although the elements can display many different oxidation states, they usually exhibit a common oxidation state depending on what makes that element most stable. For this module, we will work only with the first row of transition metals; however the other rows of transition metals generally follow the same patterns as the first row.

The s, p, d, and f-orbitals are identified on the periodic table below:



First Row Transition Metals

In the first row of the transition metals, the ten elements that can be found are: **Scandium (Sc), Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), and Zinc (Zn).**

Below is a table of the oxidation states that the transition metals can or cannot form. As stated in the boxes, the “No” indicates that the elements are not found with that oxidation state. The “Rare” signifies the oxidation states that the elements are rarely found in. Lastly, the “**Common**” identifies the oxidation states that the elements readily found in.

Oxidation States vs. First Row Transition Metals

First Row Transition Metals		Oxidation States						
Element Symbol	Atomic Number	+1	+2	+3	+4	+5	+6	+7
Sc	21	No	Rare	**Common**	No	No	No	No
Ti	22	No	Rare	Rare	**Common**	No	No	No
V	23	Rare	**Common (lilac)**	**Common (green)**	**Common (blue)**	**Common (yellow)**	No	No

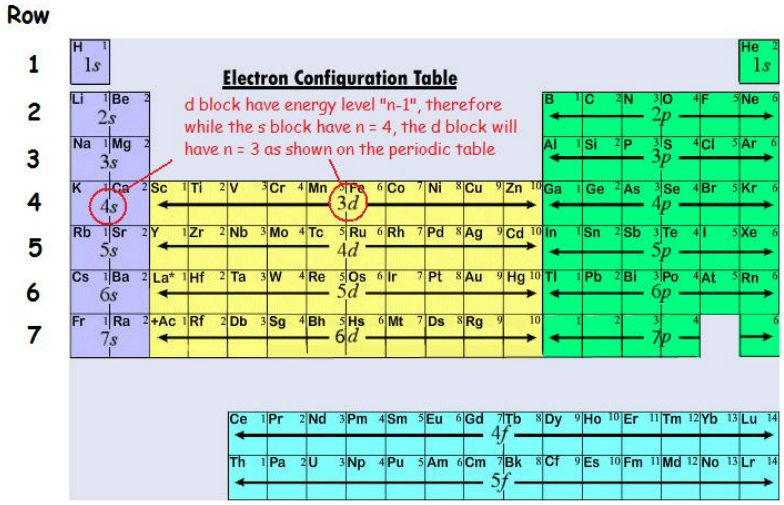
Cr	24	Rare	**Common**	**Common (Most stable)**	Rare	Rare	**Common**	No
Mn	25	Rare	**Common (Most stable) (pink/red)**	**Common (purple/red)**	**Common**	Rare **(blue)**	**Common (green)**	**Common (purple)**
Fe	26	Rare	**Common (ferrous)**	**Common (ferric)**	Rare	Rare	Rare	No
Co	27	Rare	**Common**	**Common**	Rare	Rare	Rare	No
Ni	28	Rare	**Common**	Rare	Rare	No	No	No
Cu	29	Rare	**Common (blue/green)**	No	No	No	No	No
Zn	30	No	**Common**	No	No	No	No	No

Filling Transition Metal Orbitals

The electron configuration for the **first row transition metals** consists of 4s and 3d subshells with an argon (noble gas) core. This only applies to the first row transition metals, adjustments will be necessary when writing the electron configuration for the other rows of transition metals. The noble gas before the first row of transition metals would be the core written with brackets around the element symbol (i.e. [Ar] would be used for the **first row** transition metals), and the electron configuration would follow a [Ar] $ns^x nd^x$ format. In the case of first row transition metals, the electron configuration would simply be [Ar] $4s^x 3d^x$. The energy level, "n", can be determined based on the periodic table, simply by looking at the row number in which the element is in. However, there is an exception for the d-block and f-block, in which the energy level, "n" for the d block is "n-1" ("n" minus 1) and for the f block is "n-2" (See following periodic table for clarification). In this case, the "x" in ns^x and nd^x is the number of electrons in a specific orbital (i.e. s-orbitals can hold up to a maximum of 2 electrons, p-orbitals can hold up to 6 electrons, d-orbitals can hold up to 10 electrons, and f-orbitals can hold up to 14 electrons). To determine what "x" is, simply count the number of boxes that you come across before reaching the element you are attempting to determine the electron configuration for.

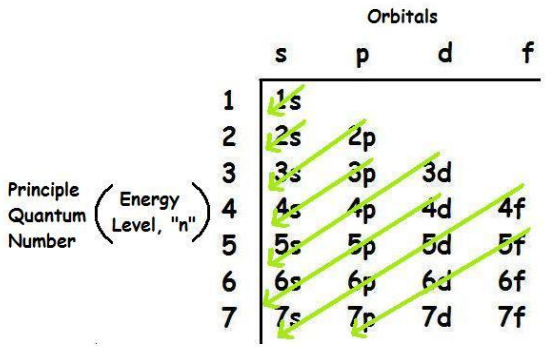
Example of Determining Energy Levels (n)

For example, if we want to determine the electron configuration for Cobalt (Co) at ground state, we would first look at the row number, which is 4 according to the periodic table below; meaning **n = 4 for the s-orbital**. In addition, since we know that the energy level for the d orbital is "n-1", therefore **n = 3 for the d-orbital** in this case. Thus, the electron configuration for Cobalt at ground state would simply be Co: [Ar] $4s^2 3d^7$. The reason why it is $3d^7$ can be explained using the periodic table. As stated, you could simply count the boxes on the periodic table, and since Cobalt is the 7th element of the first row transition metals, we get Co: [Ar] $4s^2 3d^7$.



Order of Filling the Subshells

The following image shows the order for filling the subshells:



Order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

Transition Metals with an Oxidation State

In the ground state, the electron configuration of the transition metals follows the format, ns^2nd^x. As for the electron configuration for transition metals that are charged (i.e. Cu^+), the electrons from the s orbital will be moved to the d-orbital to form either ns^0nd^x or ns^1nd^x.

It is helpful to first write down the electron configuration of an element at its ground state before attempting to determine the electron configuration of an element with an oxidation state. See examples below.

Example 1: Vanadium
Vanadium at Ground State (Neutral): V: 5 **d**-electrons = [Ar] $4s^23d^3$ Vanadium with an Oxidation State of +4: V^{4+}: [Ar] $4s^03d^1$ Or you can also write it as V^{4+}: [Ar] $3d^1$

Example 2: Nickel



Above is a video showing how to write the electron configuration for Nickel (Ni) and Zirconium (Zr) from the d-block.
Nickel at Ground State:
Ni: 8 **d**-electrons = [Ar] $4s^2 3d^8$
Nickel with an Oxidation State of +2:
Ni^{2+}: [Ar] $4s^0 3d^8$
Or simply Ni^{2+}: [Ar] $3d^8$
In this example, the electron configuration for Ni^{2+} still kept its $3d^8$, but lost the $4s^2$ (became $4s^0$) because the s-orbital has the highest energy level of n = 4 in this case. Therefore, the s-orbital will lose its electrons first, before the d-orbital, and so Ni^{2+} can be written as [Ar] $4s^0 3d^8$ OR [Ar] $3d^8$.

Electron Configuration of a Second Row Transition Metal (Rhodium)

Rhodium at Ground State:

Rh: 7 **d**-electrons = [Kr] $5s^2 4d^7$

Rhodium with an Oxidation State of +3:

Rh^{3+}: [Kr] $5s^0 4d^6$

Or simply Rh^{3+}: [Kr] $4d^6$

Example 3: Osmium

Note: Osmium is stable with oxidation states of +2, +3, +4, as well as +8.
Osmium at Ground State:
Os: 6 **d**-electrons = [Xe] $6s^2 4f^{14} 5d^6$
Osmium with an Oxidation State of +2:
Os: [Xe] $4f^{14} 5d^6$
Osmium with an Oxidation State of +3:
Os: [Xe] $4f^{14} 5d^5$
For fourth row transition metals, the electron configuration is very similar to the electron configuration of the third row transition metals. However, for a fourth row transition metal, you would follow the format of [Rn] 7sx5fx6dx rather than the third row transition metal formating of [Xe] 6sx4fx5dx.

References

1. Petrucci, Ralph. Harwood, William. Herring, Geoffrey. Madura, Jeffery. *General Chemistry: Principles and Modern Applications, 9th Edition.* Pearson Education, Inc. New Jersey, 2007.
2. Hein, et al. Introduction to General, Organic, and Biochemistry. 9th ed. Hoboken, NJ 2009.

Problems

1. What is the maximum number of electrons each orbital (s, p, d, f) can hold, respectively?
2. Write the electron configuration for Sc^{3+}.
3. Write the electron configuration for Ti^{2+}.
4. Which first row transition metal is the only element that forms an oxidation state of +7?
5. For additional practice, try to write the electron configuration of all the first row transition metals with their common oxidation states:

To see an example of an element from the second row or third row transition metals, see "Electron Configuration of a Second Row Transition Metal (Rhodium)" and "Electron Configuration of a Third Row Transition Metal (Osmium)".)

A) V^{2+} B) V^{3+} C) V^{5+} D) Cr^{2+} E) Cr^{3+} F) Cr^{6+} G) Mn^{2+} H) Mn^{3+}

I) Mn^{4+} J) Mn^{6+} K) Mn^{7+} L) Fe^{2+} M) Fe^{3+} N) Co^{2+} O) Co^{3+} P) Cu^{2+} Q) Zn^{2+}

Solutions

See File Attachment for Solutions. (You will probably need Adobe Reader to open the PDF file.)

Contributors

- Liza Chu (UCD)

4.1.2: Electron Configuration of Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Electron Configuration of Transition Metals** is licensed CC BY-NC-SA 4.0.

4.1.3: General Trends among the Transition Metals

Learning Objectives

- To understand the trends in properties and reactivity of the d-block elements.

The transition metals, groups 3–12 in the periodic table, are generally characterized by partially filled d subshells in the free elements or their cations. (Although the metals of group 12 do not have partially filled d shells, their chemistry is similar in many ways to that of the preceding groups, and we therefore include them in our discussion.) Unlike the s-block and p-block elements, the transition metals exhibit significant horizontal similarities in chemistry in addition to their vertical similarities.

Electronic Structure and Reactivity of the Transition Metals

The valence electron configurations of the first-row transition metals are given in Table 4.1.3.1. As we go across the row from left to right, electrons are added to the 3d subshell to neutralize the increase in the positive charge of the nucleus as the atomic number increases. With two important exceptions, the 3d subshell is filled as expected based on the aufbau principle and Hund's rule. Unexpectedly, however, chromium has a $4s^1 3d^5$ electron configuration rather than the $4s^2 3d^4$ configuration predicted by the aufbau principle, and copper is $4s^1 3d^{10}$ rather than $4s^2 3d^9$. In Chapter 7, we attributed these anomalies to the extra stability associated with half-filled subshells. Because the ns and (n − 1)d subshells in these elements are similar in energy, even relatively small effects are enough to produce apparently anomalous electron configurations.

Table 4.1.3.1: Valence Electron Configurations of the First-Row Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$

In the second-row transition metals, electron–electron repulsions within the 4d subshell cause additional irregularities in electron configurations that are not easily predicted. For example, Nb and Tc, with atomic numbers 41 and 43, both have a half-filled 5s subshell, with $5s^1 4d^4$ and $5s^1 4d^6$ valence electron configurations, respectively. Further complications occur among the third-row transition metals, in which the 4f, 5d, and 6s orbitals are extremely close in energy. Although La has a $6s^2 5d^1$ valence electron configuration, the valence electron configuration of the next element—Ce—is $6s^2 5d^0 4f^2$. From this point through element 71, added electrons enter the 4f subshell, giving rise to the 14 elements known as the lanthanides. After the 4f subshell is filled, the 5d subshell is populated, producing the third row of the transition metals. Next comes the seventh period, where the actinides have three subshells (7s, 6d, and 5f) that are so similar in energy that their electron configurations are even more unpredictable.

As we saw in the s-block and p-block elements, the size of neutral atoms of the d-block elements gradually decreases from left to right across a row, due to an increase in the effective nuclear charge (Z_{eff}) with increasing atomic number. In addition, the atomic radius increases down a group, just as it does in the s and p blocks. Because of the lanthanide contraction, however, the increase in size between the 3d and 4d metals is much greater than between the 4d and 5d metals (Figure 23.1).The effects of the lanthanide contraction are also observed in ionic radii, which explains why, for example, there is only a slight increase in radius from Mo^{3+} to W^{3+}.

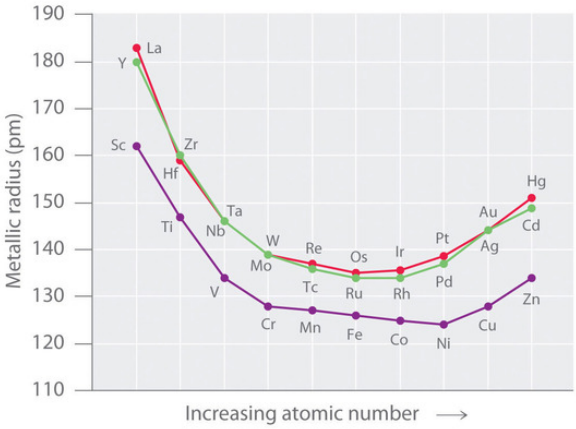


Figure 4.1.3.1: The Metallic Radii of the First-, Second-, and Third-Row Transition Metals. Because of the lanthanide contraction, the second- and third-row transition metals are very similar in size.

As you learned previously, electrons in (n − 1)d and (n − 2)f subshells are only moderately effective at shielding the nuclear charge; as a result, the effective nuclear charge experienced by valence electrons in the d-block and f-block elements does not change greatly as the nuclear charge increases across a row. Consequently, the ionization energies of these elements increase very slowly across a given row (Figure 4.1.3.2). In addition, as we go from the top left to the bottom right corner of the d block, electronegativities generally increase, densities and electrical and thermal conductivities increase, and enthalpies of hydration of the metal cations decrease in magnitude, as summarized in Figure 4.1.3.2 Consistent with this trend, the transition metals become steadily less reactive and more “noble” in character from left to right across a row. The relatively high ionization energies and electronegativities and relatively low enthalpies of hydration are all major factors in the noble character of metals such as Pt and Au.

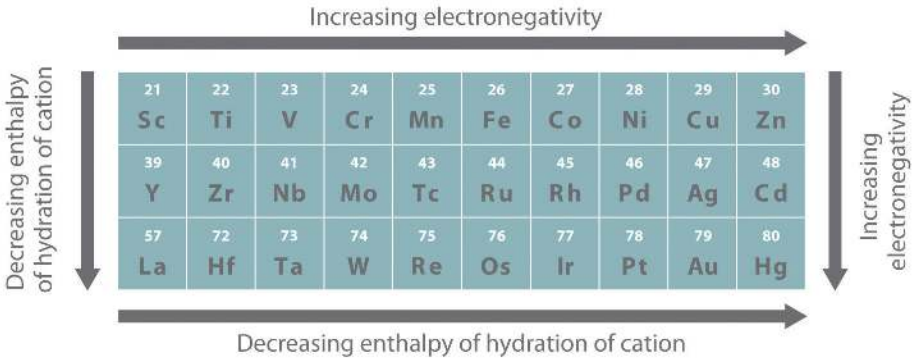


Figure 4.1.3.2: Some Trends in Properties of the Transition Metals. The electronegativity of the elements increases, and the hydration energies of the metal cations decrease in magnitude from left to right and from top to bottom of the d block. As a result, the metals in the lower right corner of the d block are so unreactive that they are often called the “noble metals.”

Trends in Transition Metal Oxidation States

The similarity in ionization energies and the relatively small increase in successive ionization energies lead to the formation of metal ions with the same charge for many of the transition metals. This in turn results in extensive horizontal similarities in chemistry, which are most noticeable for the first-row transition metals and for the lanthanides and actinides. Thus all the first-row transition metals except Sc form stable compounds that contain the 2+ ion, and, due to the small difference between the second and third ionization energies for these elements, all except Zn also form stable compounds that contain the 3+ ion. The relatively small increase in successive ionization energies causes most of the transition metals to exhibit multiple oxidation states separated by a single electron. Manganese, for example, forms compounds in every oxidation state between −3 and +7. Because of the slow but steady increase in ionization potentials across a row, high oxidation states become progressively less stable for the elements on the right side of the d block. The occurrence of multiple oxidation states separated by a single electron causes many, if not most, compounds of the transition metals to be paramagnetic, with one to five unpaired electrons. This behavior is in sharp contrast to that of the p-block elements, where the occurrence of two oxidation states separated by two electrons is common, which makes virtually all compounds of the p-block elements diamagnetic.

> *Due to a small increase in successive ionization energies, most of the transition metals have multiple oxidation states separated by a single electron.*

Most compounds of transition metals are paramagnetic, whereas virtually all compounds of the p-block elements are diamagnetic.

The electronegativities of the first-row transition metals increase smoothly from Sc (χ = 1.4) to Cu (χ = 1.9). Thus Sc is a rather active metal, whereas Cu is much less reactive. The steady increase in electronegativity is also reflected in the standard reduction potentials: thus E° for the reaction $M^{2+}(aq) + 2e^- \rightarrow M^0(s)$ becomes progressively less negative from Ti (E° = −1.63 V) to Cu (E° = +0.34 V). Exceptions to the overall trends are rather common, however, and in many cases, they are attributable to the stability associated with filled and half-filled subshells. For example, the $4s^23d^{10}$ electron configuration of zinc results in its strong tendency to form the stable Zn^{2+} ion, with a $3d^{10}$ electron configuration, whereas Cu^+, which also has a $3d^{10}$ electron configuration, is the only stable monocation formed by a first-row transition metal. Similarly, with a half-filled subshell, Mn^{2+} ($3d^5$) is much more difficult to oxidize than Fe^{2+} ($3d^6$). The chemistry of manganese is therefore primarily that of the Mn^{2+} ion, whereas both the Fe^{2+} and Fe^{3+} ions are important in the chemistry of iron.

The transition metals form cations by the initial loss of the ns electrons of the metal, even though the ns orbital is lower in energy than the (n − 1)d subshell in the neutral atoms. This apparent contradiction is due to the small difference in energy between the ns and (n − 1)d orbitals, together with screening effects. The loss of one or more electrons reverses the relative energies of the ns and (n − 1)d subshells, making the latter lower in energy. Consequently, all transition-metal cations possess d^n valence electron configurations, as shown in Table 23.2 for the 2+ ions of the first-row transition metals.

> *All transition-metal cations have d^n electron configurations; the ns electrons are always lost before the (n − 1)d electrons.*

Table 4.1.3.1: d-Electron Configurations of the Dications of the First-Row Transition Metals

Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}

The most common oxidation states of the first-row transition metals are shown in Table 4.1.3.3 The second- and third-row transition metals behave similarly but with three important differences:

1. The maximum oxidation states observed for the second- and third-row transition metals in groups 3–8 increase from +3 for Y and La to +8 for Ru and Os, corresponding to the formal loss of all ns and (n − 1)d valence electrons. As we go farther to the right, the maximum oxidation state decreases steadily, reaching +2 for the elements of group 12 (Zn, Cd, and Hg), which corresponds to a filled (n − 1)d subshell.
2. Within a group, higher oxidation states become more stable down the group. For example, the chromate ion ($[CrO_4]^{2-}$) is a powerful oxidant, whereas the tungstate ion ($[WO_4]^{2-}$) is extremely stable and has essentially no tendency to act as an oxidant.
3. Cations of the second- and third-row transition metals in lower oxidation states (+2 and +3) are much more easily oxidized than the corresponding ions of the first-row transition metals. For example, the most stable compounds of chromium are those of Cr(III), but the corresponding Mo(III) and W(III) compounds are highly reactive. In fact, they are often pyrophoric, bursting into flames on contact with atmospheric oxygen. As we shall see, the heavier elements in each group form stable compounds in higher oxidation states that have no analogues with the lightest member of the group.

> *The highest possible oxidation state, corresponding to the formal loss of all valence electrons, becomes increasingly less stable as we go from group 3 to group 8, and it is never observed in later groups.*

In the transition metals, the stability of higher oxidation states increases down a column.

Table 4.1.3.3: Common Oxidation States of the First-Row Transition Metals*

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

*The convention of using roman numerals to indicate the oxidation states of a metal is used here.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
electronic structure	s^2d^1	s^2d^2	$s^2\ d^3$	s^1d^5	s^2d^5	s^2d^6	s^2d^7	s^2d^8	s^1d^{10}	s^2d^{10}
oxidation states				I					I	
		II	II	II	II	II	II	II	II	II
	III	III	III	III	III	III	III	III	III	
		IV	IV	IV	IV	IV	IV	IV		
			V	V	V	V	V			
				VI	VI	VI				
					VII					

*The convention of using roman numerals to indicate the oxidation states of a metal is used here.

Binary transition-metal compounds, such as the oxides and sulfides, are usually written with idealized stoichiometries, such as FeO or FeS, but these compounds are usually cation deficient and almost never contain a 1:1 cation:anion ratio. Thus a substance such as ferrous oxide is actually a nonstoichiometric compound with a range of compositions.

The acid–base character of transition-metal oxides depends strongly on the oxidation state of the metal and its ionic radius. Oxides of metals in lower oxidation states (less than or equal to +3) have significant ionic character and tend to be basic. Conversely, oxides of metals in higher oxidation states are more covalent and tend to be acidic, often dissolving in strong base to form oxoanions.

Example 4.1.3.1

Two of the group 8 metals (Fe, Ru, and Os) form stable oxides in the +8 oxidation state. Identify these metals; predict the stoichiometry of the oxides; describe the general physical and chemical properties, type of bonding, and physical state of the oxides; and decide whether they are acidic or basic oxides.

Given: group 8 metals

Asked for: identity of metals and expected properties of oxides in +8 oxidation state

Strategy:

Refer to the trends outlined in Figure 23.1, Figure 23.2, Table 23.1, Table 23.2, and Table 23.3 to identify the metals. Decide whether their oxides are covalent or ionic in character, and, based on this, predict the general physical and chemical properties of the oxides.

Solution:

The +8 oxidation state corresponds to a stoichiometry of MO_4. Because the heavier transition metals tend to be stable in higher oxidation states, we expect Ru and Os to form the most stable tetroxides. Because oxides of metals in high oxidation states are generally covalent compounds, RuO_4 and OsO_4 should be volatile solids or liquids that consist of discrete MO_4 molecules, which the valence-shell electron-pair repulsion (VSEPR) model predicts to be tetrahedral. Finally, because oxides of transition metals in high oxidation states are usually acidic, RuO_4 and OsO_4 should dissolve in strong aqueous base to form oxoanions

Exercise 4.1.3.1

Predict the identity and stoichiometry of the stable group 9 bromide in which the metal has the lowest oxidation state and describe its chemical and physical properties.

Answer

Because the lightest element in the group is most likely to form stable compounds in lower oxidation states, the bromide will be $CoBr_2$. We predict that $CoBr_2$ will be an ionic solid with a relatively high melting point and that it will dissolve in water to give the $Co^{2+}(aq)$ ion.

Summary

The transition metals are characterized by partially filled d subshells in the free elements and cations. The ns and (n − 1)d subshells have similar energies, so small influences can produce electron configurations that do not conform to the general order in which the subshells are filled. In the second- and third-row transition metals, such irregularities can be difficult to predict, particularly for the third row, which has 4f, 5d, and 6s orbitals that are very close in energy. The increase in atomic radius is greater between the 3d and 4d metals than between the 4d and 5d metals because of the lanthanide contraction. Ionization energies and electronegativities increase slowly across a row, as do densities and electrical and thermal conductivities, whereas enthalpies of hydration decrease. Anomalies can be explained by the increased stabilization of half-filled and filled subshells. Transition-metal cations are formed by the initial loss of ns electrons, and many metals can form cations in several oxidation states. Higher oxidation states become progressively less stable across a row and more stable down a column. Oxides of small, highly charged metal ions tend to be acidic, whereas oxides of metals with a low charge-to-radius ratio are basic.

Key Takeaways

- Transition metals are characterized by the existence of multiple oxidation states separated by a single electron.
- Most transition-metal compounds are paramagnetic, whereas virtually all compounds of the p-block elements are diamagnetic.

Conceptual Problems

1. The transition metals show significant horizontal similarities in chemistry in addition to their vertical similarities, whereas the same cannot be said of the s-block and p-block elements. Explain why this is so.
2. The energy of the d subshell does not change appreciably in a given period. Why? What effect does this have on the ionization potentials of the transition metals? on their electronegativities?
3. Standard reduction potentials vary across the first-row transition metals. What effect does this have on the chemical reactivity of the first-row transition metals? Which two elements in this period are more active than would be expected? Why?
4. Many transition metals are paramagnetic (have unpaired electrons). How does this affect electrical and thermal conductivities across the rows?
5. What is the lanthanide contraction? What effect does it have on the radii of the transition metals of a given group? What effect does it have on the chemistry of the elements in a group?
6. Why are the atomic volumes of the transition elements low compared with the elements of groups 1 and 2? Ir has the highest density of any element in the periodic table (22.65 g/cm^3). Why?
7. Of the elements Ti, Ni, Cu, and Cd, which do you predict has the highest electrical conductivity? Why?
8. The chemistry of As is most similar to the chemistry of which transition metal? Where in the periodic table do you find elements with chemistry similar to that of Ge? Explain your answers.
9. The coinage metals (group 11) have significant noble character. In fact, they are less reactive than the elements of group 12. Explain why this is so, referring specifically to their reactivity with mineral acids, electronegativity, and ionization energies. Why are the group 12 elements more reactive?

Structure and Reactivity

1. Give the valence electron configurations of the 2+ ion for each first-row transition element. Which two ions do you expect to have the most negative E° value? Why?
2. Arrange Ru^{3+}, Cu^{2+}, Zn, Ti^{4+}, Cr^{3+}, and Ni^{2+} in order of increasing radius.
3. Arrange Pt^{4+}, Hg^{2+}, Fe^{2+}, Zr^{4+}, and Fe^{3+} in order of decreasing radius.
4. Of Ti^{2+}, V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, which divalent ion has the smallest ionic radius? Explain your reasoning.

Answers

1. Ti^{2+}, $3d^2$; V^{2+}, $3d^3$; Cr^{2+}, $3d^4$; Mn^{2+}, $3d^5$; Fe^{2+}, $3d^6$; Co^{2+}, $3d^7$; Ni^{2+}, $3d^8$; Cu^{2+}, $3d^9$; Zn^{2+}, $3d^{10}$. Because Z_{eff} increases from left to right, Ti^{2+} and V^{2+} will have the most negative reduction potentials (be most difficult to reduce).

3. $Hg^{2+} > Fe^{2+} > Zr^{4+} > Fe^{3+} > Pt^{4+}$

4.1.3: General Trends among the Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **General Trends among the Transition Metals** is licensed CC BY-NC-SA 4.0.

4.1.4: Introduction to Transition Metals I

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electronegativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

Physical Properties

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block) such as Calcium. Transition elements:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form compounds which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and compounds;
- form compounds with profound catalytic activity;
- form stable complexes.

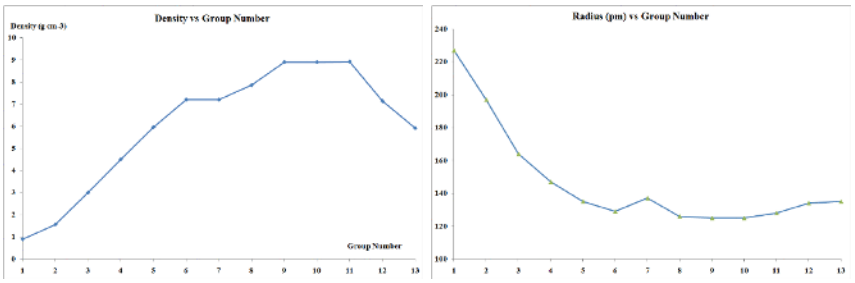
Table 1: Summary of select physical properties of transition elements:

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Sc	3	2.99	1541	2831	164	[Ar] $3d^1 4s^2$	631	
Ti	4	4.50	1660	3287	147	[Ar]$3d^2 4s^2$	658	-engines/aircraft industry-density is 60% of iron
V	5	5.96	1890	3380	135	[Ar]$3d^3 4s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr	6	7.20	1857	2670	129	[Ar]$3d^5 4s^1$	653	-alloys eg with C steel, the most significant use
Mn	7	7.20	1244	1962	137	[Ar]$3d^5 4s^2$	717	-alloys eg with Cu

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Fe	8	7.86	1535	2750	126	[Ar]3d^{6}4s^2	759	-alloys eg with C steel, the most significant use
Co	9	8.90	1495	2870	125	[Ar]3d^{7}4s^2	758	-alloys eg with Cr and W for hardened drill bits
Ni	10	8.90	1455	2730	125	[Ar]3d^{8}4s^2	737	-alloys Fe/Ni armor plating, resists corrosion
Cu	11	8.92	1083	2567	128	[Ar]3d^{10}4s^1	746	-high electrical conductivity (2nd to Ag), wiring
Zn	12	7.14	420	907	137	[Ar]3d^{10}4s^2	906	

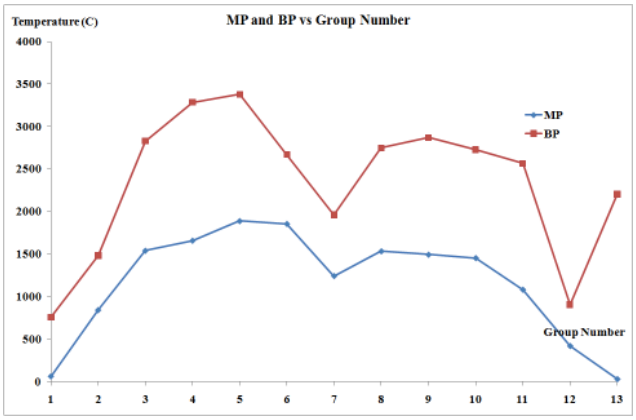
Densities and metallic radii

The transition elements are much denser than the s-block elements and show a gradual increase in density from scandium to copper. This trend in density can be explained by the small and irregular decrease in metallic radii coupled with the relative increase in atomic mass.



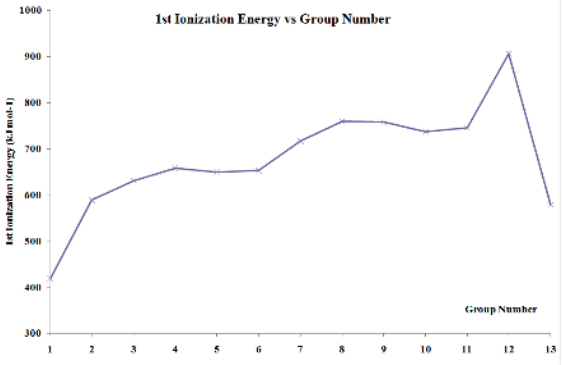
Melting and boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.



Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by 580 kJ mol^{-1}.



Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

In the case of copper, the 3d level is full, but only one electron occupies the 4s orbital. This suggests that in copper the 3d orbital energy is lower than the 4s orbital. Thus the 3d orbital energy has passed from higher to lower as we move across the period from potassium to zinc. However, the whole question of preference of an atom to adopt a particular electronic configuration is not determined by orbital energy alone. In chromium it can be shown that the 4s orbital energy is still below the 3d which suggests a configuration [Ar] $3d^4 4s^2$. However due to the effect of electronic repulsion between the outer electrons the actual configuration becomes [Ar]$3d^5 4s^1$ where all the electrons in the outer orbitals are unpaired. It should be remembered that the factors that determine electronic configuration in this period are indeed delicately balanced.

Redox Couple	E°/V

$Mn^{2+}(aq.)/Mn(s)$	-1.18
$H^{+}(aq.)/H_2(g)$	0.00

This shows that elemental Mn is a stronger reductant than molecular hydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

4.1.4: Introduction to Transition Metals I is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Introduction to Transition Metals I** is licensed CC BY-NC-SA 4.0.

4.1.5: Introduction to Transition Metals II

This page explains what a transition metal is in terms of its electronic structure, and then goes on to look at the general features of transition metal chemistry. These include variable oxidation state (oxidation number), complex ion formation, colored ions, and catalytic activity.

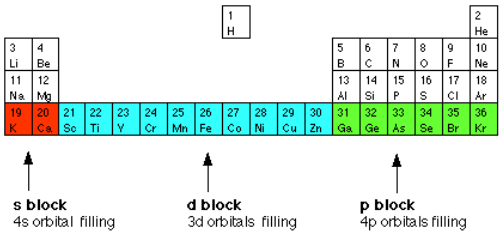
What is a transition metal?

The terms transition metal (or element) and d block element are sometimes used as if they mean the same thing. They don't - there's a subtle difference between the two terms. We'll explore d block elements first:

d-block elements

You will remember that when you are building the Periodic Table and working out where to put the electrons using the Aufbau Principle, something odd happens after argon.

At argon, the 3s and 3p levels are full, but rather than fill up the 3d levels next, the 4s level fills instead to give potassium and then calcium. Only after that do the 3d levels fill. The elements in the Periodic Table which correspond to the d levels filling are called **d block elements**. The first row of these is shown in the shortened form of the Periodic Table below.



The electronic structures of the d block elements shown are:

Sc	[Ar] $\mathbf{3d^1}4s^2$
Ti	[Ar] $\mathbf{3d^2}4s^2$
V	[Ar] $\mathbf{3d^3}4s^2$
Cr	[Ar] $\mathbf{3d^5 4s^1}$
Mn	[Ar] $\mathbf{3d^5 4s^2}$
Fe	[Ar] $\mathbf{3d^6}4s^2$
Co	[Ar] $\mathbf{3d^7}4s^2$
Ni	[Ar] $\mathbf{3d^8}4s^2$
Cu	[Ar] $\mathbf{3d^{10} 4s^1}$
Zn	[Ar] $\mathbf{3d^{10} 4s^2}$

You will notice that the pattern of filling is not entirely tidy! It is broken at both chromium and copper.

Transition metals

Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:

The official IUPAC definition:

A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.

The older definition:

> **A transition metal is one which forms one or more stable ions which have *incompletely* filled d orbitals.**

Notice how similar these two definitions are. The only difference is that the IUPAC definition allows for the atom itself having incompletely filled d levels as well as the ions.

The problem lies only at the extreme left-hand end of the d block with, for example, scandium: Scandium has the electronic structure [Ar] $3d^1 4s^2$. When it forms ions, it always loses the 3 outer electrons and ends up with an argon structure. The Sc^{3+} ion has **no d electrons** and so does not meet the second (older) definition.

Zinc has the electronic structure [Ar] $3d^{10} 4s^2$. When it forms ions, it always loses the two 4s electrons to give a 2+ ion with the electronic structure [Ar] $3d^{10}$. The zinc ion has **full d levels** and does not meet either definition.

By contrast, copper, [Ar] $3d^{10} 4s^1$, forms two ions. In the Cu^+ ion the electronic structure is [Ar] $3d^{10}$. However, the more common Cu^{2+} ion has the structure [Ar] $3d^9$. Copper is definitely a transition metal because the Cu^{2+} ion has an incomplete d level.

Transition metal ions

Here you are faced with one of the most irritating facts in chemistry at this level! When you work out the electronic structures of the first transition series (from scandium to zinc) using the Aufbau Principle, you do it on the basis that the 3d orbitals have higher energies than the 4s orbitals.

That means that you work on the assumption that the 3d electrons are added after the 4s ones. However, in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.

> It is important to note that when d block elements form ions, the 4s electrons are always lost first.

To write the electronic structure for Co^{2+}:

Co		[Ar] $3d^7 4s^2$
Co^{2+}		[Ar] $3d^7$

The 2+ ion is formed by the loss of the two 4s electrons.

To write the electronic structure for V^{3+}:

V		[Ar] $3d^3 4s^2$
V^{3+}		[Ar] $3d^2$

The 4s electrons are lost first followed by one of the 3d electrons.

Variable oxidation state (number)

One of the key features of transition metal chemistry is the wide range of oxidation states (oxidation numbers) that the metals can show. It would be wrong, though, to give the impression that only transition metals can have variable oxidation states. For example, elements like Sulfur or nitrogen or chlorine have a very wide range of oxidation states in their compounds - and these obviously aren't transition metals. However, this variability is less common in metals apart from the transition elements. Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.

Examples of variable oxidation states in the transition metals

- **Iron:** Iron has two common oxidation states (+2 and +3) in, for example, Fe^{2+} and Fe^{3+}. It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-}.
- **Manganese:** Manganese has a very wide range of oxidation states in its compounds. For example:

+2	in Mn^{2+}

+3	in Mn_2O_3
+4	in MnO_2
+6	in MnO_4^{2-}
+7	in MnO_4^-

You will find the above examples and others looked at in detail if you explore the chemistry of individual metals from the transition metal menu. There is a link to this menu at the bottom of the page.

Explaining the variable oxidation states in the transition metals

We'll look at the formation of simple ions like Fe^{2+} and Fe^{3+}. When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process. On the whole, the compound formed is the one in which most energy is released. The more energy released, the more stable the compound. There are several energy terms to think about, but the key ones are:

- The amount of energy needed to ionize the metal (the sum of the various ionization energies)
- The amount of energy released when the compound forms. This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

The more highly charged the ion, the more electrons you have to remove and the more ionization energy you will have to provide. But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

Thinking about a typical non-transition metal (calcium)

The formula for Calcium chloride is $CaCl_2$. Why is that? If you tried to make CaCl, (containing a Ca^+ ion), the overall process is slightly exothermic. By making a Ca^{2+} ion instead, you have to supply more ionization energy, but you get out lots more lattice energy. There is much more attraction between chloride ions and Ca^{2+} ions than there is if you only have a 1+ ion. The overall process is very exothermic. Because the formation of $CaCl_2$ releases much more energy than making CaCl, then $CaCl_2$ is more stable - and so forms instead.

What about $CaCl_3$? This time you have to remove yet another electron from calcium. The first two come from the 4s level. The third one comes from the 3p. That is much closer to the nucleus and therefore much more difficult to remove. There is a large jump in ionization energy between the second and third electron removed. Although there will be a gain in lattice enthalpy, it is not anything like enough to compensate for the extra ionization energy, and the overall process is very endothermic. It definitely is not energetically sensible to make $CaCl_3$!

Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the 2+ or the 3+ ion.

Fe		[Ar] $3d^6 4s^2$
Fe^{2+}		[Ar] $3d^6$
Fe^{3+}		[Ar] $3d^5$

The 4s orbital and the 3d orbitals have very similar energies. There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second. The figures for the first three ionization energies (in kJ mol^{-1}) for iron compared with those of calcium are:

metal	1st IE	2nd IE	3rd IE
Ca	590	1150	4940
Fe	762	1560	2960

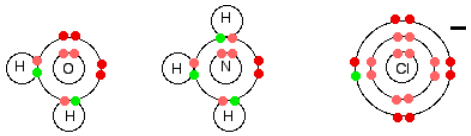
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

In the iron case, the extra ionization energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made. The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say, $FeCl_2$ or $FeCl_3$. That means that it is not too difficult to convert between the two compounds.

The formation of complex ions

What is a complex ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion.

Some examples of complex ions formed by transition metals

$[Fe(H_2O)_6]^{2+}$

$[Co(NH_3)_6]^{2+}$

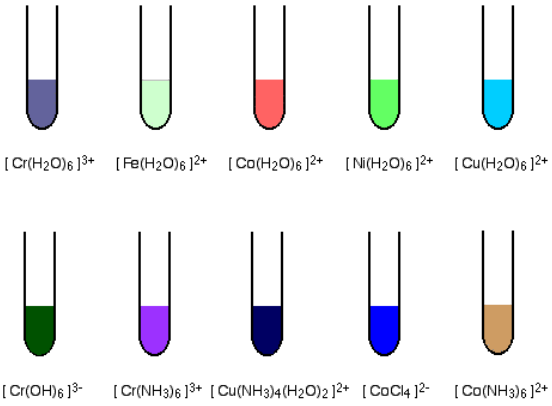
$[Cr(OH)_6]^{3-}$

$[CuCl_4]^{2-}$

Other metals also form complex ions - it is not something that only transition metals do. Transition metals do, however, form a very wide range of complex ions.

The formation of colored compounds

The diagrams show approximate colors for some common transition metal complex ions.



You will find these and others discussed if you follow links to individual metals from the transition metal menu (link at the bottom of the page). Alternatively, you could explore the complex ions menu (follow the link in the help box which has just disappeared off the top of the screen).

The origin of color in the transition metal ions

When white light passes through a solution of one of these ions, or is reflected off it, some colors in the light are absorbed. The color you see is how your eye perceives what is left. Attaching ligands to a metal ion has an effect on the energies of the d orbitals.

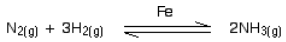
Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

Catalytic Activity

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

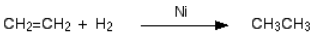
Iron in the Haber Process

The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst.



Nickel in the hydrogenation of C=C bonds

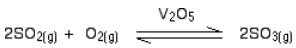
This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.



Transition metal compounds as catalysts

Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.



Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 4.1.5: Introduction to Transition Metals II is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Introduction to Transition Metals II** by Jim Clark is licensed CC BY-NC 4.0.

SECTION OVERVIEW

4.1.6: Metallurgy

Topic hierarchy

4.1.6.1: An Introduction to the Chemistry of Metal Extraction

4.1.6.2: The Extraction of Copper

4.1.6.3: The Extraction of Iron

4.1.6.3.1: Iron Production

4.1.6.4: The Extraction of Silver

4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate

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

4.1.6.1: An Introduction to the Chemistry of Metal Extraction

This page looks at the various factors which influence the choice of method for extracting metals from their ores, including reduction by carbon, reduction by a reactive metal (like sodium or magnesium), and by electrolysis. Details for the extraction of aluminum, copper, iron and titanium are given in separate pages in this section.

What are "ores"?

An ore is any naturally-occurring source of a metal that you can economically extract the metal from. Aluminum, for example, is the most common metal in the Earth's crust, occurring in all sorts of minerals. However, it isn't economically worthwhile to extract it from most of these minerals. Instead, the usual ore of aluminum is bauxite - which contains from 50 - 70% of aluminum oxide.

Copper is much rarer, but fortunately can be found in high-grade ores (ones containing a high percentage of copper) in particular places. Because copper is a valuable metal, it is also worth extracting it from low-grade ores as well. Ores are commonly oxides, for example:

- bauxite (Al_2O_3)
- haematite (Fe_2O_3)
- rutile (TiO_2)

. . . or sulfides, for example:

- pyrite (FeS_2)
- chalcopyrite ($CuFeS_2$)

Concentrating the ore

This simply means getting rid of as much of the unwanted rocky material as possible before the ore is converted into the metal. In some cases this is done chemically. For example, pure aluminum oxide is obtained from bauxite by a process involving a reaction with sodium hydroxide solution. This is described in detail on the aluminum page in this section. Some copper ores can be converted into copper(II) sulfate solution by leaving the crushed ore in contact with dilute sulphuric acid for a long time. Copper can then be extracted from the copper(II) sulfate solution. But, in many cases, it is possible to separate the metal compound from unwanted rocky material by physical means. A common example of this involves froth flotation.

Froth flotation

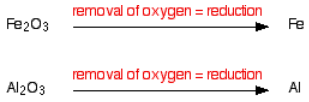
The ore is first crushed and then treated with something which will bind to the particles of the metal compound that you want and make those particles hydrophobic. "Hydrophobic" literally means "water fearing". In concentrating copper ores, for example, pine oil is often used. The pine oil binds to the copper compounds, but not to the unwanted rocky material.

The treated ore is then put in a large bath of water containing a foaming agent (a soap or detergent of some kind), and air is blown through the mixture to make a lot of bubbles. Because they are water-repellent, the coated particles of the metal compound tend to be picked up by the air bubbles, float to the top of the bath, and are allowed to flow out over the sides. The rest of the rocky material stays in the bath.

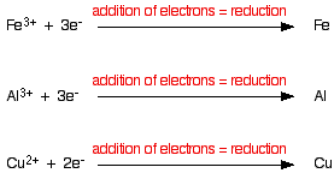
Reducing the metal compound to the metal

Why is this reduction?

At its simplest, where you are starting from metal oxides, the ore is being reduced because oxygen is being removed.



However, if you are starting with a sulfide ore, for example, that's not a lot of help! It is much more helpful to use the definition of reduction in terms of addition of electrons. To a reasonable approximation, you can think of these ores as containing positive metal ions. To convert them to the metal, you need to add electrons - reduction.



Choosing a method of reduction

There are various economic factors you need to think about in choosing a method of reduction for a particular ore. These are all covered in detail on other pages in this section under the extractions of particular metals. What follows is a quick summary.

You need to consider:

- the cost of the reducing agent;
- energy costs;
- the desired purity of the metal.

There may be various environmental considerations as well - some of which will have economic costs.

Chemical Reduction

Carbon (as coke or charcoal) is cheap. It not only acts as a reducing agent, but it also acts as the fuel to provide heat for the process. However, in some cases (for example with aluminum) the temperature needed for carbon reduction is too high to be economic - so a different method has to be used. Carbon may also be left in the metal as an impurity. Sometimes this can be removed afterwards (for example, in the extraction of iron); sometimes it can't (for example in producing titanium), and a different method would have to be used in cases like this.

Other more reactive metals can be used to reduce the ore. Titanium is produced by reducing titanium(IV) chloride using a more reactive metal such as sodium or magnesium. As you will see if you read the page about titanium extraction, this is the only way of producing high purity metal.

$$TiCl_4 + 4Na \rightarrow Ti + 4NaCl$$

The more reactive metal sodium releases electrons easily as it forms its ions:

$$4Na \rightarrow 4Na^+ + 4e^-$$

These electrons are used to reduce the titanium(IV) chloride:

$$TiCl_4 + 4e^- \rightarrow Ti + 4Cl^-$$

The downside of this is expense. You have first to extract (or to buy) the sodium or magnesium. The more reactive the metal is, the more difficult and expensive the extraction becomes. That means that you are having to use a very expensive reducing agent to extract the titanium. As you will see if you read the page about titanium extraction, there are other problems in its extraction which also add to the cost.

Reduction by electrolysis

This is a common extraction process for the more reactive metals - for example, for aluminum and metals above it in the electrochemical series. You may also come across it in other cases such as one method of extracting copper and in the purification of copper. During electrolysis, electrons are being added directly to the metal ions at the cathode (the negative electrode). The downside (particularly in the aluminum case) is the cost of the electricity. An advantage is that it can produce very pure metals.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 4.1.6.1: An Introduction to the Chemistry of Metal Extraction is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **An Introduction to the Chemistry of Metal Extraction** by Jim Clark is licensed CC BY-NC 4.0.

4.1.6.2: The Extraction of Copper

Learning Objectives

- To understand the basic principles of copper extraction from ores
- To understand the basis of it s purification by electrolysis
- To identify some common uses of copper

Extracting copper from its ores

The method used to extract copper from its ores depends on the nature of the ore. Sulfide ores such as chalcopyrite ($CuFeS_2$) are converted to copper by a different method from silicate, carbonate or sulfate ores. Chalcopyrite (also known as copper pyrites) and similar sulfide ores are the commonest ores of copper. The ores typically contain low percentages of copper and have to be concentrated before refining (e.g., via froth flotation).



Figure 1: Chalcopyrite extracted from Zacatecas, Mexico. from Rob Lavinsky (iRocks.com) under a CC-BY-SA-3.0 license.

The Process

The concentrated ore is heated strongly with silicon dioxide (silica) and air or oxygen in a furnace or series of furnaces.

- The copper(II) ions in the chalcopyrite are reduced to copper(I) sulfide (which is reduced further to copper metal in the final stage).
- The iron in the chalcopyrite ends up converted into an iron(II) silicate slag which is removed.
- Most of the sulfur in the chalcopyrite turns into sulfur dioxide gas. This is used to make sulfuric acid via the Contact Process.

An overall equation for this series of steps is:

$$2CuFeS_2 + 2SiO_2 + 4O_2 \rightarrow Cu_2S + 2FeSiO_3 + 3SO_2 \tag{4.1.6.2.1}$$

The copper(I) sulfide produced is converted to copper with a final blast of air.

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2 \tag{4.1.6.2.2}$$

The end product of this is called *blister copper* - a porous brittle form of copper, about 98 - 99.5% pure.

Exploring the redox processes in this reaction

It is worthwhile spending some time sorting out what the reducing agent is in these reactions, because at first sight there does not appear to be one! Or, if you look superficially, it seems as if it might be oxygen! But that's silly! We'll start by looking at the second reaction because it is much easier to see what is happening.

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2 \tag{4.1.6.2.3}$$

Let's look at the oxidation states of everything.

- In the copper(I) sulfide, the copper is +1 and the sulfur -2.
- The oxidation states of the elements oxygen (in the gas) and copper (in the metal) are 0.
- In sulfur dioxide, the oxygen has an oxidation state of -2 and the sulfur +4.

That means that both the copper and the oxygen have been reduced (decrease in oxidation state). The sulfur has been oxidized (increase in oxidation state). The reducing agent is therefore the sulfide ion in the copper(I) sulfide.

The other reaction is more difficult to deal with, because you can't work out all of the oxidation states by following the simple rules - there are too many variables in some of the substances. You have to use some chemical knowledge as well.

$$2CuFeS_2 + 2SiO_2 + 4O_2 \rightarrow Cu_2S + 2FeSiO_3 + 3SO_2 \quad (4.1.6.2.4)$$

In the $CuFeS_2$, you would have to know that the copper and iron are both in oxidation state +2, for example. You would also have to know that the oxidation state of the silicon remains unchanged at +4. So use that information to work out what has been oxidized and what reduced in this case!

You should find that copper has been reduced from +2 to +1; oxygen (in the gas) has been reduced from 0 to -2 (oxygen in the SiO_2 is unchanged); and three of the four sulfurs on the left-hand side have been oxidized from -2 to +4 (the other is unchanged). Once again, the sulfide ions are acting as the reducing agent.

Extracting of Copper from Other Ores

Copper can be extracted from non-sulfide ores by a different process involving three separate stages:

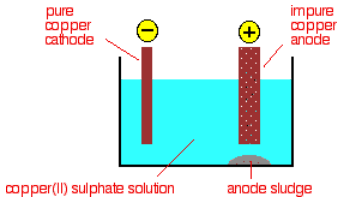
1. Reaction of the ore (over quite a long time and on a huge scale) with a dilute acid such as dilute sulfuric acid to produce a very dilute copper(II) sulfate solution.
2. Concentration of the copper(II) sulfate solution by solvent extraction. The very dilute solution is brought into contact with a relatively small amount of an organic solvent containing something which will bind with copper(II) ions so that they are removed from the dilute solution. The solvent must not mix with the water. The copper(II) ions are removed again from the organic solvent by reaction with fresh sulfuric acid, producing a much more concentrated copper(II) sulfate solution than before.
3. Electrolysis of the new solution. Copper(II) ions are deposited as copper on the cathode (for the electrode equation, see under the purification of copper below). The anodes for this process were traditionally lead-based alloys, but newer methods use titanium or stainless steel. The cathode is either a strip of very pure copper which the new copper plates on to, or stainless steel which it has to be removed from later.

Purification of copper

When copper is made from sulfide ores by the first method above, it is impure. The blister copper is first treated to remove any remaining sulfur (trapped as bubbles of sulfur dioxide in the copper - hence "blister copper") and then cast into anodes for refining using electrolysis.

Electrolytic Refining

The purification uses an electrolyte of copper(II) sulfate solution, impure copper anodes, and strips of high purity copper for the cathodes. The diagram shows a very simplified view of a cell.



At the cathode, copper(II) ions are deposited as copper.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad (4.1.6.2.5)$$

At the anode, copper goes into solution as copper(II) ions.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \quad (4.1.6.2.6)$$

For every copper ion that is deposited at the cathode, in principle another one goes into solution at the anode. The concentration of the solution should stay the same. All that happens is that there is a transfer of copper from the anode to the cathode. The cathode gets bigger as more and more pure copper is deposited; the anode gradually disappears. In practice, it isn't quite as simple as that because of the impurities involved.

What happens to the impurities?

Any metal in the impure anode which is below copper in the electrochemical series (reactivity series) does not go into solution as ions. It stays as a metal and falls to the bottom of the cell as an "anode sludge" together with any unreactive material left over from the ore. The anode sludge will contain valuable metals such as silver and gold.

Metals above copper in the electrochemical series (like zinc) will form ions at the anode and go into solution. However, they won't get discharged at the cathode provided their concentration does not get too high. The concentration of ions like zinc will increase with time, and the concentration of the copper(II) ions in the solution will fall. For every zinc ion going into solution there will obviously be one fewer copper ion formed. (See the next note if you aren't sure about this.) The copper(II) sulfate solution has to be continuously purified to make up for this.

Uses of copper

Amongst other things copper is used for:

- electrical wiring. It is a very good conductor of electricity and is easily drawn out into wires.
- domestic plumbing. It does not react with water, and is easily bent into shape.
- boilers and heat exchangers. It is a good conductor of heat and does not react with water.
- making brass. Brass is a copper-zinc alloy. Alloying produces a metal harder than either copper or zinc individually. Bronze is another copper alloy, but with tin.
- coinage. In many countries, as well as the more obvious copper-colored coins, "silver" coins are also copper alloys - this time with nickel; these are known as cupronickel alloys. UK pound coins and the gold-colored bits of euro coins are copper-zinc-nickel alloys.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 4.1.6.2: The Extraction of Copper is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **The Extraction of Copper** by Jim Clark is licensed CC BY-NC 4.0.

4.1.6.3: The Extraction of Iron

This page looks at the use of the Blast Furnace in the extraction of iron from iron ore, and the conversion of the raw iron from the furnace into various kinds of steel.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

This page titled 4.1.6.3: The Extraction of Iron is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **The Extraction of Iron** by Jim Clark is licensed CC BY-NC 4.0.

4.1.6.3.1: Iron Production

The production of iron from its ore involves an oxidation-reduction reaction carried out in a blast furnace. Iron ore is usually a mixture of iron and vast quantities of impurities such as sand and clay referred to as gangue. The iron found in iron ores are found in the form of iron oxides. As a result of these impurities, iron must be first separated from the gangue and then converted to pure iron. This is accomplished by the method of *pyrometallurgy*, a high temperature process. The high temperatures are needed for the reduction of iron and the oxidation of the limestone which will be seen below.

Introduction

The production of iron from its ore involves a redox reaction carried out in a blast furnace. The furnace is filled at the top with the iron ore oxide most commonly hematite (Fe_2O_3) but can also magnetite (Fe_3O_4), carbon called coke and limestone ($CaCO_3$). For the purpose of this discussion the iron ore oxide hematite (Fe_2O_3) will be shown. On a side note, Hematite gets its name from the Greek word meaning blood like because of the color of one form of its powder. The Ancient Greeks believed that large deposits of hematite were formed from battles that were fought and the blood from these battles flowed into the ground.

To begin the process a blast of hot air is forced in at the bottom of the furnace that helps create a large temperature variation with the bottom being 2273 K and the top 473 K. The amount of oxygen is strictly controlled so that carbon monoxide is the main product as shown:

$$2C(s) + O_2\ (g) \longrightarrow 2CO(g) + \text{heat}$$

Similarly carbon and carbon monoxide both contribute in the reduction of the iron (III) oxide to give the impure metal as shown:

$$Fe_2O_3\ (s) + 3C\ (s) \longrightarrow 2Fe(l) + 3CO_2(g)$$

$$Fe_2O_3\ (s) + 3CO(g) \longrightarrow 2Fe(l) + 3CO_2\ (g)$$

One of the most interesting part of this redox reaction is that the majority of the carbon dioxide formed is itself reduced when it comes to contact with the unburned coke and produce more reducing agent. As the process continue the molten iron flow down through the furnace and collects at the bottom, where it is removed through an opening in the side. When it cools the impure iron is brittle and some cases soft due to the presence of the small impurities, such as sulfur and phosphorus.

Thus the impure iron coming from the bottom of the furnace is further purified. The most common method is the basic oxygen furnace. In the furnace, oxygen is blown into the impure iron. This is vital because the oxygen oxidizes the phosphorus and sulfur shown in the following redox reactions:

$$P_4(s) + 5O_2\ (g) \longrightarrow P_4O_{10}\ (g)$$

$$S_8(s) + 8O_2\ (g) \longrightarrow 8SO_2\ (g)$$

The oxides either escapes as gases or react with basic oxides that are added or used to line the furnace. This final purification step removes much of the impurities and the result is ordinary carbon steel. Thus iron is obtained through the process of oxidation-reduction.

Outside links

- A video showing the production of steel: http://www.youtube.com/watch?v=Yov7Z0rMyHI&feature=related
- A Video showing the chemistry of iron: video.google.com/videoplay?do...ron+production

References

1. Kotz, John C. Treichel, Paul Jr. *Chemistry & Chemical Reactivity: Fourth Edition.* Saunders College Publishing, 1999.
2. Housecroft, Catherine E. Sharpe, Alan G. *Inorganic Chemistry: Second Edition.* Pearson Prentice Hall, 2005.

4.1.6.3.1: Iron Production is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Iron Production** is licensed CC BY-NC-SA 4.0.

4.1.6.4: The Extraction of Silver

Contributors and Attributions

4.1.6.4: The Extraction of Silver is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **The Extraction of Silver** is licensed CC BY-NC-SA 4.0.

4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate

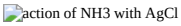
Silver Chloride

AgNO3 combines with chloride ions and forms AgCl precipitate.



Properties

- AgCl is obtained as a white precipitate
- AgCl is insoluble in water.
- It is soluble in aqueous ammonia



Silver Nitrate

In the preparation of silver nitrate dilute nitric acid is used. Silver combines with HNO3 and forms silver nitrate.



Contributors and Attributions

4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Preparation and uses of Silver chloride and Silver nitrate** is licensed CC BY-NC-SA 4.0.

4.1.7: Oxidation States of Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple oxidation states experimentally observed.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

Table 4.1.7.1

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x, p_y, p_z; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number n+1

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.

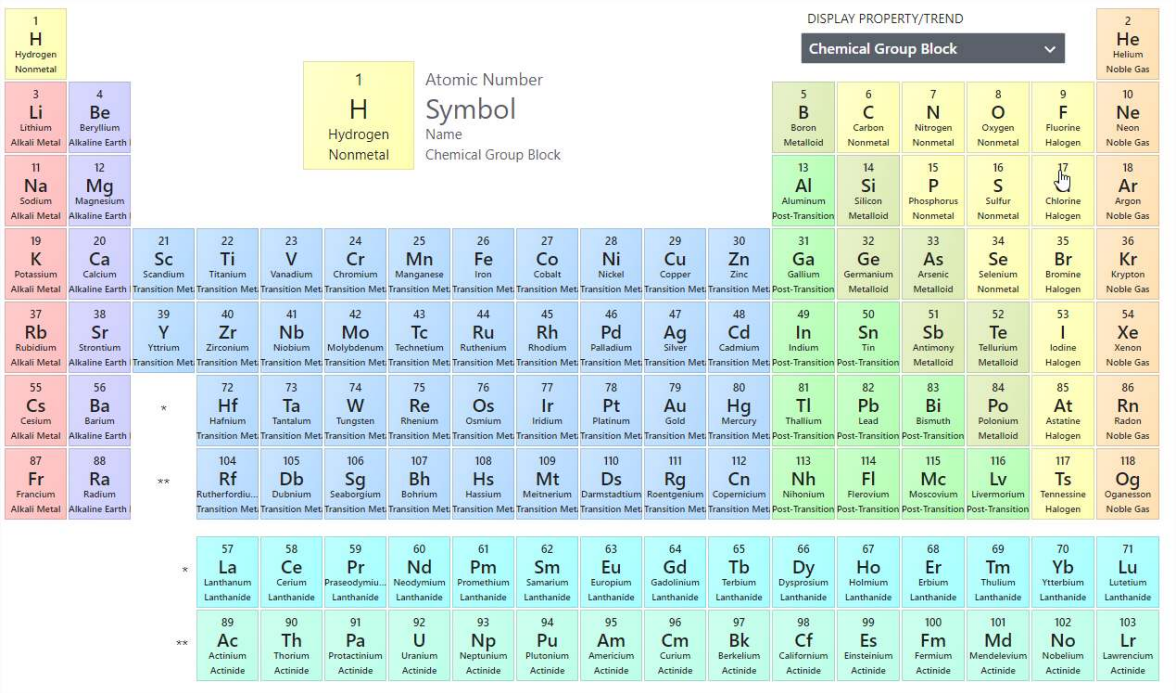


Figure 4.1.7.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$$

or

$$[Ar]\ 4s^2\ 3d^3.$$

The neutral atom configurations of the fourth period transition metals are in Table 4.1.7.2

Table 4.1.7.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] $4s^2 3d^1$	[Ar] $4s^2 3d^2$	[Ar] $4s^2 3d^3$	[Ar] ~~$4s^2 3d^4$~~	[Ar] $4s^2 3d^5$	[Ar] $4s^2 3d^6$	[Ar] $4s^2 3d^7$	[Ar] $4s^2 3d^8$	[Ar] ~~$4s^2 3d^9$~~	[Ar] $4s^2 3d^{10}$
			[Ar] $4s^1 3d^5$					[Ar] $4s^1 3d^{10}$	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 4.1.7.1). The electronic configuration for chromium is not [Ar] $4s^2 3d^4$ but instead it is [Ar] $4s^1 3d^5$. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 4.1.7.2that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose it's s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see formation of coordination complexes.

Example 4.1.7.1

Write the electronic configurations of:

a. neutral iron,
b. iron(II) ion, and
c. iron(III) ion.

Answer

The atomic number of iron is 26 so there are 26 protons in the species.

a. Fe: [Ar] $4s^2$ $3d^6$
b. Fe^{2+}: [Ar] $3d^6$
c. Fe^{3+}: [Ar] $3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

Example 4.1.7.2

Determine the more stable configuration between the following pair:

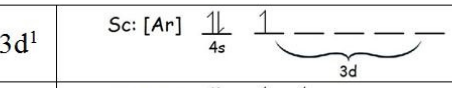
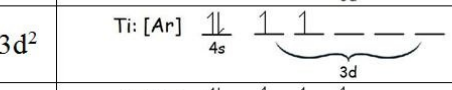
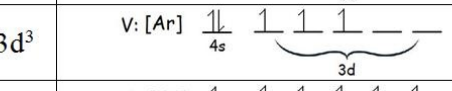
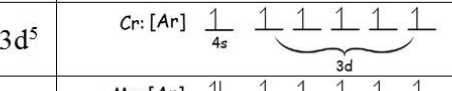
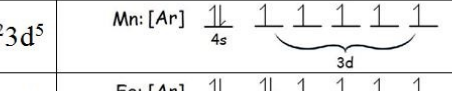
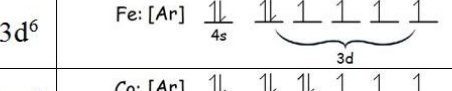
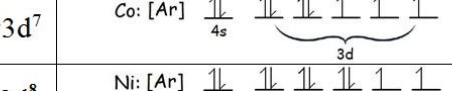
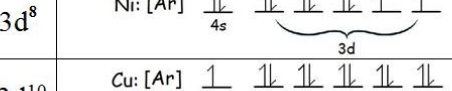
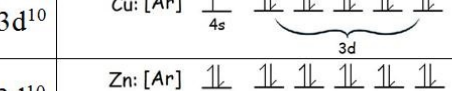
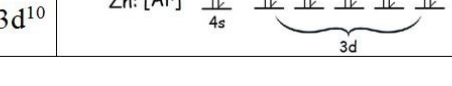
a. [Kr] $5s^2$ $4d^6$ vs. [Kr] $5s^1$ $4d^7$
b. Ag^{1+} vs. Ag^{2+}

Answer

a. This describes Ruthenium. There is only one 5s electron.
b. Once-oxidized silver ([Kr] $4d^{10}$) is more stable than twice- ([Kr] $4d^9$).

Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^7$	
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^8$	
Copper (Cu)	29	+1,+2	Cu: [Ar] $4s^1 3d^{10}$	
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

Example 4.1.7.3

What makes zinc stable as Zn^{2+}? What makes scandium stable as Sc^{3+}?

Answer

Zinc has the neutral configuration $[Ar]4s^2 3d^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as $[Ar]4s^2 3d^1$. Losing 3 electrons brings the configuration to the noble state with valence $3p^6$.

Example 4.1.7.4

Why is iron almost always Fe^{2+} or Fe^{3+}?

Answer

Iron is written as $[Ar]4s^2 3d^6$. Losing 2 electrons from the s-orbital ($3d^6$) or 2 s- and 1 d-orbital ($3d^5$) electron are fairly stable oxidation states.

Example 4.1.7.5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

Answer

Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $Mn_{(s)}$, Mn(II) as MnO, Mn(II,III) as Mn_3O_4, Mn(IV) as MnO_2, or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^-, and so on.

Oxidation State of Transition Metals in Compounds

When given an ionic compound such as $AgCl$, you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the halogen group of the periodic table, we then know that it has a charge of -1, or simply Cl^-. In addition, by seeing that there is no overall charge for $AgCl$, (which is determined by looking at the top right of the compound, i.e., $AgCl^{\#}$, where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us Ag^+ and Cl^-, in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

Example 4.1.7.6

Determine the oxidation state of cobalt in $CoBr_2$.

Answer

Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 (Br^-). Since there are two bromines each with a charge of -1. In addition, we know that $CoBr_2$ has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

Example 4.1.7.7

What is the oxidation state of zinc in $ZnCO_3$. (Note: the CO_3 anion has a charge state of -2)

Answer

Knowing that CO_3 has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us Zn^{2+} and CO_3^{-2}, in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate (MnO_4^-) ion. Since oxygen has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us Mn^{7+} and $4\ O^{2-}$, which will result as MnO_4^-.

> *This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.*

Manganese: A Case Study

Manganese is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.



Figure 4.1.7.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

Mn_2O_3 is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.

$$[\mathrm{Ar}]4s^0 3d^4$$

MnO_2 is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than Mn^{3+}.

$$[\mathrm{Ar}]4s^0 3d^3$$

$KMnO_4$ is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.

$$[\mathrm{Ar}]4s^0 3d^0$$

Since the 3p orbitals are all paired, this complex is diamagnetic.

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) Copper(I) Chloride: CuCl	(B) Copper(II) Nitrate: $Cu(NO_3)_2$	(C) Gold(V) Fluoride: AuF_5
(D) Iron(II) Oxide: FeO	(E) Iron(III) Oxide: Fe_2O_3	(F) Lead(II) Chloride: $PbCl_2$
(G) Lead(II) Nitrate: $Pb(NO_3)_2$	(H) Manganese(II) Chloride: $MnCl_2$	(I) Molybdenum trioxide: MoO_3
(J) Nickel(II) Hydroxide: $Ni(OH)_2$	(K) Platinum(IV) Chloride: $PtCl_4$	(L) Silver Sulfide: Ag_2S
(M) Tungsten(VI) Fluoride: WF_6	(N) Vanadium(III) Nitride: VN	(O) Zirconium Hydroxide: $Zr(OH)_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate (MnO_4^{2-})
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?
4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

References

1. Oxtoby D, Gillis H P, Campion, A. *Principles of Modern Chemistry, 6th ed.* Thomson Brooks/Cole, Belmont. 2008; 313-318.
2. Audi A, Sherwood, P. *Valence-band x-ray photoelectron spectroscopic studies of manganese and its oxides interpreted by cluster and band structure calculations*; Surf. Interface Anal.; 2002; 33; 274-282.
3. Reaney S, Kwik-Uribe C, Smith D. *Manganese Oxidation State and Its Implications for Toxicity.* Chem. Res. Toxicol.; 2002; 15; 1119-1126.
4. *CRC Handbook, 88th ed. Sct. 1, Prt. 1 Electron Configuration and Ionization Energy of Neutral Atoms in the Ground State*; 13-14.
5. *CRC Handbook, 88th ed. Sct. 4, Prt. 1 Melting, Boiling, Triple, and Critical Point Temperatures of the Elements*; 133-134.

Contributors and Attributions

- Margaux Kreitman (UCD), Joslyn Wood, Liza Chu (UCD)

4.1.7: Oxidation States of Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Oxidation States of Transition Metals** is licensed CC BY-NC-SA 4.0.

4.1.8: Transition Metals in Biology

Learning Objectives

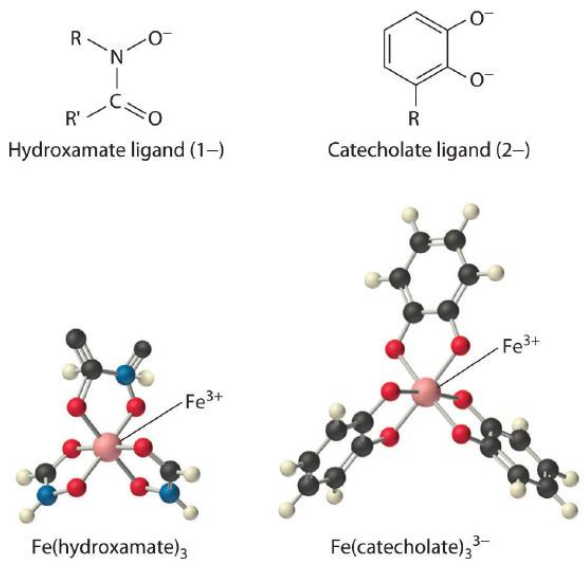
- To become familiar with some of the roles of transition-metal complexes in biological systems.

In this section, we describe several systems that illustrate the roles transition metals play in biological systems. Our goal is for you to understand why the chemical properties of these elements make them essential for life. We begin with a discussion of the strategies organisms use to extract transition metals from their environment. The section continues with a brief discussion of the use of transition metals in reactions that involve the transfer of electrons, reactions of small molecules such as O_2, Lewis-acid catalysis, and the generation of reactive organic radicals.

Uptake and Storage of Transition Metals

There are three possible dietary levels for any essential element: deficient, optimal, and toxic, in order of increasing concentration in the diet. If the concentration of an essential element in the diet is too low, an organism must be able to extract the element from the environment and concentrate it. If the concentration of an essential element in the diet is too high, an organism must be able to limit its intake to avoid toxic effects. Moreover, organisms must be able to switch off the uptake process rapidly if dietary levels rise suddenly, and they must be able to store essential elements for future use.

Three distinct steps are involved in transition metal uptake. First, the metal must be "mobilized" from the environment and brought into contact with a cell in a form that can be absorbed. Second, the metal must be transported across the cell membrane into the cell. Third, the element must be transported to its point of utilization within a cell or to other cells within the organism. In our discussion, we focus on the uptake, transport, and storage of iron, which illustrates the most important points. Because iron deficiency (anemia) is the most widespread nutritional deficiency known in humans, the uptake of iron is especially well understood.



Iron complexes in biological systems. Iron(III) forms very stable octahedral complexes with hydroxamate and catecholate ligands.

The solubility of metal ions such as Fe^{3+}, which form highly insoluble hydroxides, depends on the pH and the presence of complexing agents. In an oxygen-containing atmosphere, iron exists as Fe(III) because of the positive reduction potential of Fe^{3+} ($Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E° = +0.77$ V). Because ferric hydroxide [$Fe(OH)_3$] is highly insoluble ($K_{sp} \approx 1 \times 10^{-39}$), the equilibrium concentration of $Fe^{3+}(aq)$ at pH 7.0 is very low, about 10^{-18} M. You would have to drink 2×10^{13} L of iron-saturated water per day (roughly 5 mi^3) to consume the recommended daily intake of Fe for humans, which is about 1 mg/day. Animals such as humans can overcome this problem by consuming concentrated sources of iron, such as red meat, but microorganisms cannot.

Consequently, most microorganisms synthesize and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Siderophores are generally cyclic compounds that use bidentate ligands,

such as the hydroxamate and catecholate groups shown here, to bind Fe^{3+} in an octahedral arrangement. Typical siderophores are ferrichrome, a cyclic peptide produced by fungi, and enterobactin, a cyclic ester produced by bacteria (Figure 4.1.8.1). Attaching the three iron ligands to a cyclic framework greatly increases the stability of the resulting Fe^{3+} complex due to the chelate effect described in Section 23.4. The formation constants for the Fe^{3+} complexes of ferrichrome and enterobactin are about 10^{32} and 10^{40}, respectively, which are high enough to allow them to dissolve almost any Fe(III) compound.

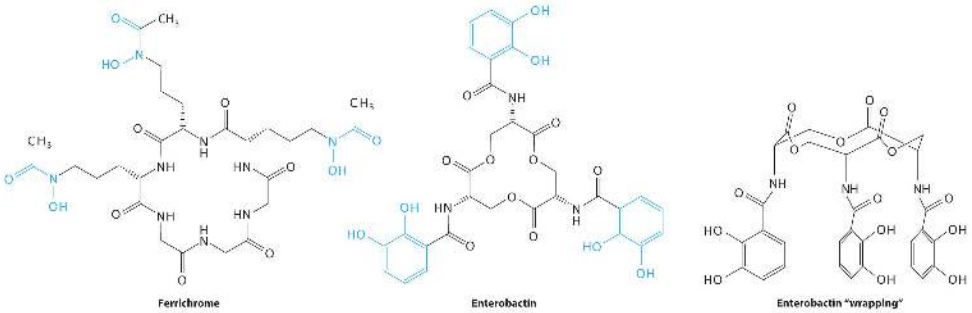


Figure 4.1.8.1: Siderophores. Ferrichrome (a) and enterobactin (b) are siderophores that use hydroxamate and catecholate ligands, respectively, to bind Fe^{3+}. The "wrapped" drawing of enterobactin (c) shows how the cyclic ester framework places the three catecholate ligands in the correct orientation to bind to a single Fe^{3+} ion, which is an application of the chelate effect. The actual structure of ferrichrome is similar to that of enterobactin, with the three hydroxamate ligands adjacent to one another for optimal binding of Fe^{3+}. Note: For clarity, most or all hydrogen atoms have been omitted in this and the following structures.

Siderophores increase the $[Fe^{3+}]$ in solution, providing the bacterium that synthesized them (as well as any competitors) with a supply of iron. In addition, siderophores neutralize the positive charge on the metal ion and provide a hydrophobic "wrapping" that enables the Fe^{3+}–siderophore complex to be recognized by a specific protein that transports it into the interior of a cell. Once it is inside a cell, the iron is reduced to Fe^{2+}, which has a much lower affinity for the siderophore and spontaneously dissociates.

In contrast, multicellular organisms can increase the concentration of iron in their diet by lowering the pH in the gastrointestinal tract. At pH 1.0 (the approximate pH of the stomach), most Fe(III) salts dissolve to form $Fe^{3+}(aq)$, which is absorbed by specific proteins in the intestinal wall. A protein called transferrin forms a complex with iron(III), allowing it to be transported to other cells. Proteins that bind tightly to Fe(III) can also be used as antibacterial agents because iron is absolutely essential for bacterial growth. For example, milk, tears, and egg white all contain proteins similar to transferrin, and their high affinity for Fe^{3+} allows them to sequester iron, thereby preventing bacteria from growing in these nutrient-rich media.

Iron is released from transferrin by reduction to Fe^{2+}, and then it is either used immediately (e.g., for the synthesis of hemoglobin) or stored in a very large protein called ferritin for future use (Figure 4.1.8.2). Ferritin uses oxygen to oxidize Fe^{2+} to Fe^{3+}, which at neutral pH precipitates in the central cavity of the protein as a polymeric mixture of $Fe(OH)_3$ and $FePO_4$. Because a fully loaded ferritin molecule can contain as many as 4500 Fe atoms, which corresponds to about 25% Fe by mass, ferritin is an effective way to store iron in a highly concentrated form. When iron is needed by a cell, the Fe^{3+} is reduced to the much more soluble Fe^{2+} by a reductant such as ascorbic acid (vitamin C). The structure of ferritin contains channels at the junctions of the subunits, which provide pathways for iron to enter and leave the interior of a molecule.

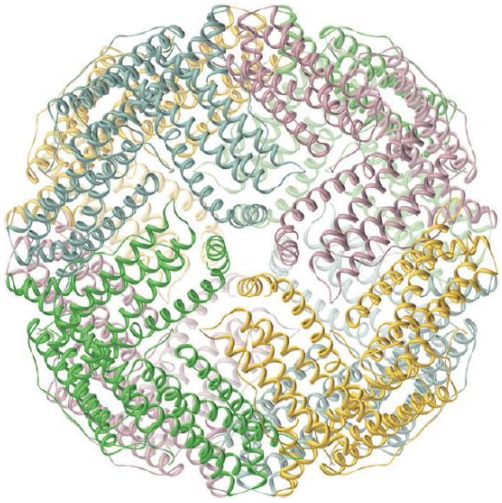


Figure 4.1.8.2: Ferritin, an Iron Storage Protein. A schematic drawing of the structure of iron-loaded ferritin, showing the almost spherical protein shell inside which the iron hydroxide/phosphate core is formed.

Metalloproteins and Metalloenzymes

A protein that contains one or more metal ions tightly bound to amino acid side chains is called a metalloprotein; some of the most common ligands provided by amino acids are shown here. A metalloprotein that catalyzes a chemical reaction is a metalloenzyme. Thus all metalloenzymes are metalloproteins, but the converse is not true. Recent estimates suggest that more than 40% of all known enzymes require at least one metal ion for activity, including almost all the enzymes responsible for the synthesis, duplication, and repair of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).

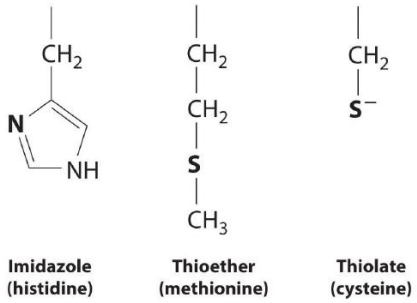


Figure 4.1.8.2*b*: Ligands used in biological systems. These metal ligands are commonly found in metalloproteins.

Electron-Transfer Proteins

Proteins whose function is to transfer electrons from one place to another are called electron-transfer proteins. Because they do not catalyze a chemical reaction, electron-transfer proteins are not enzymes; they are biochemical reductants or oxidants consumed in an enzymatic reaction. The general reaction for an electron-transfer protein is as follows:

$$M^{n+} + e^- \rightleftharpoons M^{(n-1)+} \tag{4.1.8.1}$$

Because many transition metals can exist in more than one oxidation state, electron-transfer proteins usually contain one or more metal ions that can undergo a redox reaction. Incorporating a metal ion into a protein has three important biological consequences:

1. The protein environment can adjust the redox potential ($E^{0\prime}$), of the metal ion over a rather large potential range, whereas the redox potential of the simple hydrated metal ion [M_n^+(aq)], is essentially fixed.
2. The protein can adjust the structure of the metal complex to ensure that electron transfer is rapid.
3. The protein environment provides specificity, ensuring that the electron is transferred to only the desired site.

Three important classes of metalloproteins transfer electrons: blue copper proteins, cytochromes, and iron–sulfur proteins, which generally transfer electrons at high (> 0.20 V), intermediate (±0 V), and low (−0.20 to −0.50 V) potentials, respectively (Table 23.12). Although these electron-transfer proteins contain different metals with different structures, they are all designed to ensure rapid electron transfer to and from the metal. Thus when the protein collides with its physiological oxidant or reductant, electron

transfer can occur before the two proteins diffuse apart. For electron transfer to be rapid, the metal sites in the oxidized and reduced forms of the protein must have similar structures.

Table 4.1.8.1: Some Properties of the Most Common Electron-Transfer Proteins

Protein	Metal Center	M/e− Transferred	Reduction Potential (V)
iron–sulfur proteins*	$[Fe(SR)_4]^{2-}$	1 Fe	−0.1 to +0.1
	$[(RS)_2FeS_2Fe(SR)_2]^{2-}$	2 Fe	−0.2 to −0.4
	$[Fe_3S_4(SR)_3]^{3-}$	3 Fe	−0.1 to −0.2
	$[Fe_4S_4(SR)_4]^{2-}$	4 Fe	−0.3 to −0.5
cytochromes	Fe-heme (low spin)	1 Fe	~0
blue copper proteins†	$[Cu(Im)_2(SR)(SR_2)]^{-}$	1 Cu	≥ +0.20

* A sulfur bound to an organic group is represented as SR.

† See Figure 4.1.8.2*b* for the structure of imidazole (Im).

Blue Copper Proteins

Blue copper proteins were first isolated from bacteria in the 1950s and from plant tissues in the early 1960s. The intense blue color of these proteins is due to a strong absorption band at a wavelength of about 600 nm. Although simple Cu^{2+} complexes, such as $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, are also blue due to an absorption band at 600 nm, the intensity of the absorption band is about 100 times less than that of a blue copper protein. Moreover, the reduction potential for the Cu^{2+}/Cu^{+} couple in a blue copper protein is usually +0.3 to +0.5 V, considerably more positive than that of the aqueous Cu^{2+}/Cu^{+} couple (+0.15 V).

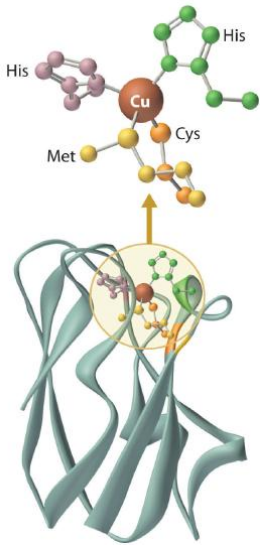


Figure 4.1.8.3: A Blue Copper Protein. In both the oxidized and reduced forms of a blue copper protein, the copper is coordinated by four ligands (two histidine imidazole nitrogen atoms, a cysteine thiolate sulfur, and a thioether sulfur of a methionine) in a roughly tetrahedral arrangement.

The copper center in blue copper proteins has a distorted tetrahedral structure, in which the copper is bound to four amino acid side chains (Figure 4.1.8.3). Although the most common structures for four-coordinate Cu^{2+} and Cu^{+} complexes are square planar and tetrahedral, respectively, the structures of the oxidized (Cu^{2+}) and reduced (Cu^{+}) forms of the protein are essentially identical. Thus the protein forces the Cu^{2+} ion to adopt a higher-energy structure that is more suitable for Cu^{+}, which makes the Cu^{2+} form easier to reduce and raises its reduction potential.

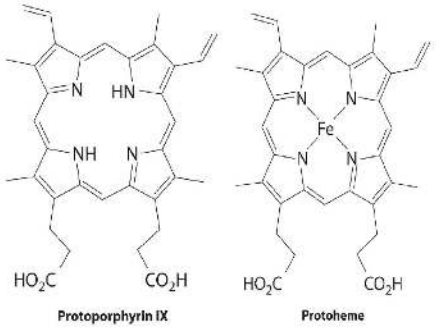
Moreover, by forcing the oxidized and reduced forms of the metal complex to have essentially the same structure, the protein ensures that electron transfer to and from the copper site is rapid because only minimal structural reorganization of the metal center is required. Kinetics studies on simple metal complexes have shown that electron-transfer reactions tend to be slow when the structures of the oxidized and reduced forms of a metal complex are very different, and fast when they are similar. You will see that

other metal centers used for biological electron-transfer reactions are also set up for minimal structural reorganization after electron transfer, which ensures the rapid transfer of electrons.

Cytochromes

The cytochromes (from the Greek cytos, meaning “cell”, and chroma, meaning “color”) were first identified in the 1920s by spectroscopic studies of cell extracts. Based on the wavelength of the maximum absorption in the visible spectrum, they were classified as cytochromes a (with the longest wavelength), cytochromes b (intermediate wavelength), and cytochromes c (shortest wavelength). It quickly became apparent that there was a correlation between their spectroscopic properties and other physical properties. For examples, cytochromes c are generally small, soluble proteins with a reduction potential of about +0.25 V, whereas cytochromes b are larger, less-soluble proteins with reduction potentials of about 0 V.

All cytochromes contain iron, and the iron atom in all cytochromes is coordinated by a planar array of four nitrogen atoms provided by a cyclic tetradentate ligand called a porphyrin. The iron–porphyrin unit is called a heme group. The structures of a typical porphyrin (protoporphyrin IX) and its iron complex (protoheme) are shown here. In addition to the four nitrogen atoms of the porphyrin, the iron in a cytochrome is usually bonded to two additional ligands provided by the protein, as shown in Figure 4.1.8.4



A cytochrome. Shown here is protoporphyrin IX and its iron complex, protoheme.

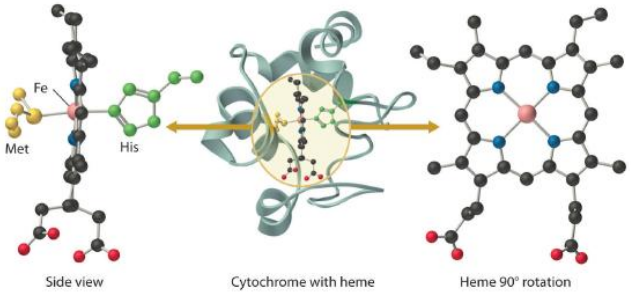


Figure 4.1.8.4: A Cytochrome c. In a cytochrome c, the heme iron is coordinated to the nitrogen atom of a histidine imidazole and the sulfur atom of a methionine thioether, in addition to the four nitrogen atoms provided by the porphyrin.

In contrast to the blue copper proteins, two electron configurations are possible for both the oxidized and reduced forms of a cytochrome, and this has significant structural consequences. Thus Fe^{2+} is d^6 and can be either high spin (with four unpaired electrons) or low spin (with no unpaired electrons). Similarly, Fe^{3+} is d^5 and can also be high spin (with five unpaired electrons) or low spin (with one unpaired electron). In low-spin heme complexes, both the Fe^{2+} and the Fe^{3+} ions are small enough to fit into the “hole” in the center of the porphyrin; hence the iron atom lies almost exactly in the plane of the four porphyrin nitrogen atoms in both cases. Because cytochromes b and c are low spin in both their oxidized and reduced forms, the structures of the oxidized and reduced cytochromes are essentially identical. Hence minimal structural changes occur after oxidation or reduction, which makes electron transfer to or from the heme very rapid.

> *Electron transfer reactions occur most rapidly when minimal structural changes occur during oxidation or reduction.*

Iron–Sulfur Proteins

Although all known bacteria, plants, and animals use iron–sulfur proteins to transfer electrons, the existence of these proteins was not recognized until the late 1950s. Iron–sulfur proteins transfer electrons over a wide range of reduction potentials, and their iron content can range from 1 to more than 12 Fe atoms per protein molecule. In addition, most iron–sulfur proteins contain stoichiometric amounts of sulfide (S^{2-}).

These properties are due to the presence of four different kinds of iron–sulfur units, which contain one, two, three, or four iron atoms per Fe–S complex (Figure 4.1.8.5). In all cases, the Fe^{2+} and Fe^{3+} ions are coordinated to four sulfur ligands in a tetrahedral environment. Due to tetrahedral coordination by weak-field sulfur ligands, the iron is high spin in both the Fe^{3+} and Fe^{2+} oxidation states, which results in similar structures for the oxidized and reduced forms of the Fe–S complexes. Consequently, only small structural changes occur after oxidation or reduction of the Fe–S center, which results in rapid electron transfer.

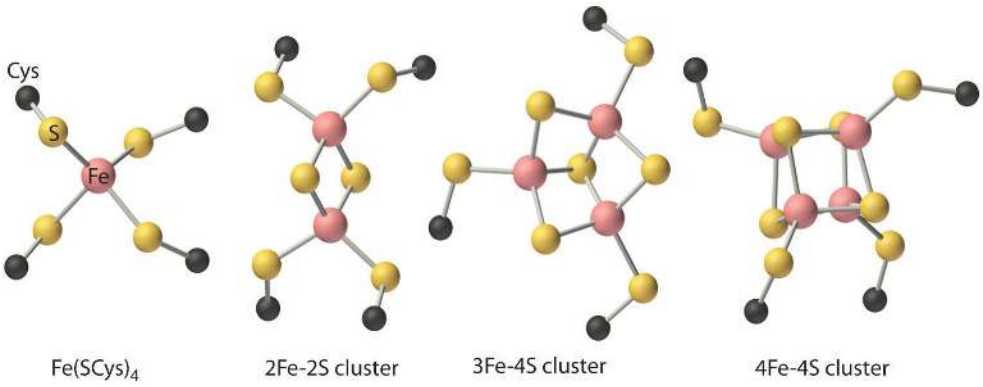


Figure 4.1.8.5: Fe–S Centers in Proteins: Four kinds of iron–sulfur centers, containing one, two, three, and four iron atoms, respectively, are known in electron-transfer proteins. Although they differ in the number of sulfur atoms provided by cysteine thiolates versus sulfide, in all cases the iron is coordinated to four sulfur ligands in a roughly tetrahedral environment.

Reactions of Small Molecules

Although small molecules, such as O_2, N_2, and H_2, do not react with organic compounds under ambient conditions, they do react with many transition-metal complexes. Consequently, virtually all organisms use metalloproteins to bind, transport, and catalyze the reactions of these molecules. Probably the best-known example is hemoglobin, which is used to transport O_2 in many multicellular organisms.

> *Under ambient conditions, small molecules, such as O_2, N_2, and H_2, react with transition-metal complexes but not with organic compounds.*

Oxygen Transport

Many microorganisms and most animals obtain energy by respiration, the oxidation of organic or inorganic molecules by O_2. At 25°C, however, the concentration of dissolved oxygen in water in contact with air is only about 0.25 mM. Because of their high surface area-to-volume ratio, aerobic microorganisms can obtain enough oxygen for respiration by passive diffusion of O_2 through the cell membrane. As the size of an organism increases, however, its volume increases much more rapidly than its surface area, and the need for oxygen depends on its volume. Consequently, as a multicellular organism grows larger, its need for O_2 rapidly outstrips the supply available through diffusion. Unless a transport system is available to provide an adequate supply of oxygen for the interior cells, organisms that contain more than a few cells cannot exist. In addition, O_2 is such a powerful oxidant that the oxidation reactions used to obtain metabolic energy must be carefully controlled to avoid releasing so much heat that the water in the cell boils. Consequently, in higher-level organisms, the respiratory apparatus is located in internal compartments called mitochondria, which are the power plants of a cell. Oxygen must therefore be transported not only to a cell but also to the proper compartment within a cell.

Three different chemical solutions to the problem of oxygen transport have developed independently in the course of evolution, as indicated in Table 4.1.8.2 Mammals, birds, reptiles, fish, and some insects use a heme protein called hemoglobin to transport oxygen from the lungs to the cells, and they use a related protein called myoglobin to temporarily store oxygen in the tissues. Several classes of invertebrates, including marine worms, use an iron-containing protein called hemerythrin to transport oxygen,

whereas other classes of invertebrates (arthropods and mollusks) use a copper-containing protein called hemocyanin. Despite the presence of the hem- prefix, hemerythrin and hemocyanin do not contain a metal–porphyrin complex.

Table 4.1.8.2: Some Properties of the Three Classes of Oxygen-Transport Proteins

Protein	Source	M per Subunit	M per O_2 Bound	Color (deoxy form)	Color (oxy form)
hemoglobin	mammals, birds, fish, reptiles, some insects	1 Fe	1 Fe	red-purple	red
hemerythrin	marine worms	2 Fe	2 Fe	colorless	red
hemocyanin	mollusks, crustaceans, spiders	2 Cu	2 Cu	colorless	blue

Myoglobin and Hemoglobin

Myoglobin is a relatively small protein that contains 150 amino acids. The functional unit of myoglobin is an iron–porphyrin complex that is embedded in the protein (Figure 26.8.1). In myoglobin, the heme iron is five-coordinate, with only a single histidine imidazole ligand from the protein (called the proximal histidine because it is near the iron) in addition to the four nitrogen atoms of the porphyrin. A second histidine imidazole (the distal histidine because it is more distant from the iron) is located on the other side of the heme group, too far from the iron to be bonded to it. Consequently, the iron atom has a vacant coordination site, which is where O_2 binds.

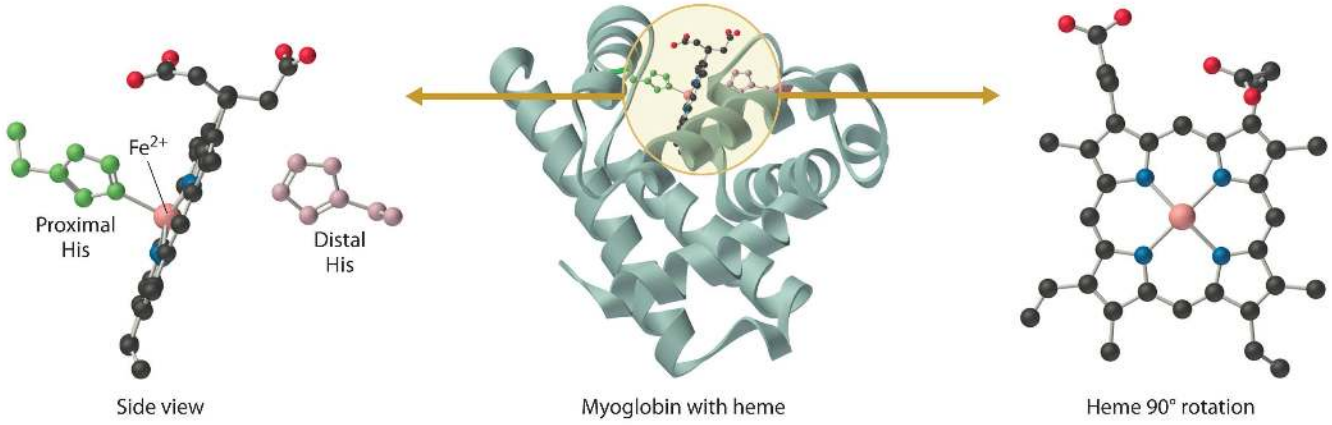


Figure 4.1.8.6: The Structure of Deoxymyoglobin, Showing the Heme Group. The iron in deoxymyoglobin is five-coordinate, with one histidine imidazole ligand from the protein. Oxygen binds at the vacant site on iron.

In the ferrous form (deoxymyoglobin), the iron is five-coordinate and high spin. Because high-spin Fe^{2+} is too large to fit into the "hole" in the center of the porphyrin, it is about 60 pm above the plane of the porphyrin. When O_2 binds to deoxymyoglobin to form oxymyoglobin, the iron is converted from five-coordinate (high spin) to six-coordinate (low spin; Figure 26.8.2). Because low-spin Fe^{2+} and Fe^{3+} are smaller than high-spin Fe^{2+}, the iron atom moves into the plane of the porphyrin ring to form an octahedral complex. The O_2 pressure at which half of the molecules in a solution of myoglobin are bound to O_2 ($P_{1/2}$) is about 1 mm Hg (1.3×10^{-3} atm).

> *A vacant coordination site at a metal center in a protein usually indicates that a small molecule will bind to the metal ion, whereas a coordinatively saturated metal center is usually involved in electron transfer.*

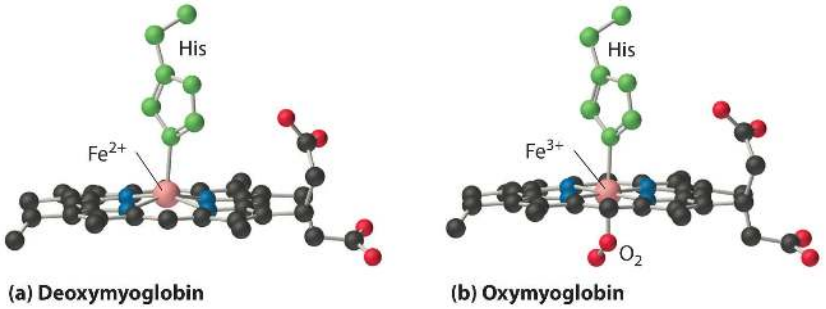


Figure 4.1.8.7: Oxygen Binding to Myoglobin and Hemoglobin. (a) The Fe^{2+} ion in deoxymyoglobin is high spin, which makes it too large to fit into the "hole" in the center of the porphyrin. (b) When O_2 binds to deoxymyoglobin, the iron is converted to low-spin Fe^{3+}, which is smaller, allowing the iron to move into the plane of the four nitrogen atoms of the porphyrin to form an octahedral complex.

Hemoglobin consists of two subunits of 141 amino acids and two subunits of 146 amino acids, both similar to myoglobin; it is called a tetramer because of its four subunits. Because hemoglobin has very different O_2-binding properties, however, it is not simply a "super myoglobin" that can carry four O_2 molecules simultaneously (one per heme group). The shape of the O_2-binding curve of myoglobin (Mb; Figure 4.1.8.7) can be described mathematically by the following equilibrium:

$$MbO_2 \rightleftharpoons Mb + O_2 \tag{4.1.8.2}$$

$$K_{diss} = \frac{[Mb][O_2]}{[MbO_2]} \tag{4.1.8.3}$$

In contrast, the O_2-binding curve of hemoglobin is S shaped (Figure 4.1.8.8). As shown in the curves, at low oxygen pressures, the affinity of deoxyhemoglobin for O_2 is substantially lower than that of myoglobin, whereas at high O_2 pressures the two proteins have comparable O_2 affinities. The physiological consequences of the unusual S-shaped O_2-binding curve of hemoglobin are enormous. In the lungs, where O_2 pressure is highest, the high oxygen affinity of deoxyhemoglobin allows it to be completely loaded with O_2, giving four O_2 molecules per hemoglobin. In the tissues, however, where the oxygen pressure is much lower, the decreased oxygen affinity of hemoglobin allows it to release O_2, resulting in a net transfer of oxygen to myoglobin.

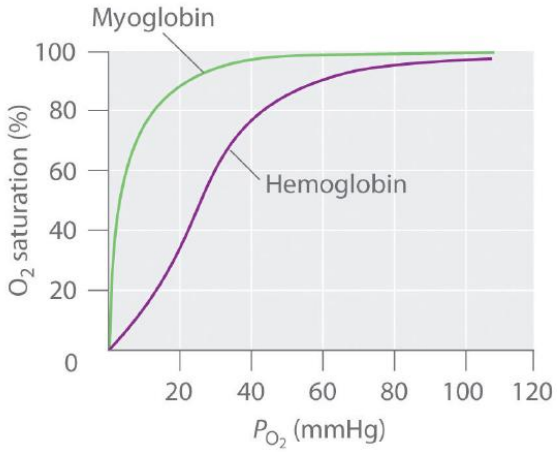


Figure 4.1.8.8: The O_2-Binding Curves of Myoglobin and Hemoglobin. The curve for myoglobin can be described by a simple equilibrium between deoxy- and oxymyoglobin, but the S-shaped curve for hemoglobin can be described only in terms of a cooperative interaction between the four hemes.

The S-shaped O_2-binding curve of hemoglobin is due to a phenomenon called cooperativity, in which the affinity of one heme for O_2 depends on whether the other hemes are already bound to O_2. Cooperativity in hemoglobin requires an interaction between the four heme groups in the hemoglobin tetramer, even though they are more than 3000 pm apart, and depends on the change in structure of the heme group that occurs with oxygen binding. The structures of deoxyhemoglobin and oxyhemoglobin are slightly different, and as a result, deoxyhemoglobin has a much lower O_2 affinity than myoglobin, whereas the O_2 affinity of oxyhemoglobin is essentially identical to that of oxymyoglobin. Binding of the first two O_2 molecules to deoxyhemoglobin causes

the overall structure of the protein to change to that of oxyhemoglobin; consequently, the last two heme groups have a much higher affinity for O_2 than the first two.

Oxygen is not unique in its ability to bind to a ferrous heme complex; small molecules such as CO and NO bind to deoxymyoglobin even more tightly than does O_2. The interaction of the heme iron with oxygen and other diatomic molecules involves the transfer of electron density from the filled t_{2g} orbitals of the low-spin d^6 Fe^{2+} ion to the empty π* orbitals of the ligand. In the case of the Fe^{2+}–O_2 interaction, the transfer of electron density is so great that the Fe–O_2 unit can be described as containing low-spin Fe^{3+} (d^5) and O_2^-. We can therefore represent the binding of O_2 to deoxyhemoglobin and its release as a reversible redox reaction:

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{3+} - O_2 - \tag{4.1.8.4}$$

As shown in Figure 4.1.8.9, the Fe–O_2 unit is bent, with an Fe–O–O angle of about 130°. Because the π* orbitals in CO are empty and those in NO are singly occupied, these ligands interact more strongly with Fe^{2+} than does O_2, in which the π* orbitals of the neutral ligand are doubly occupied.

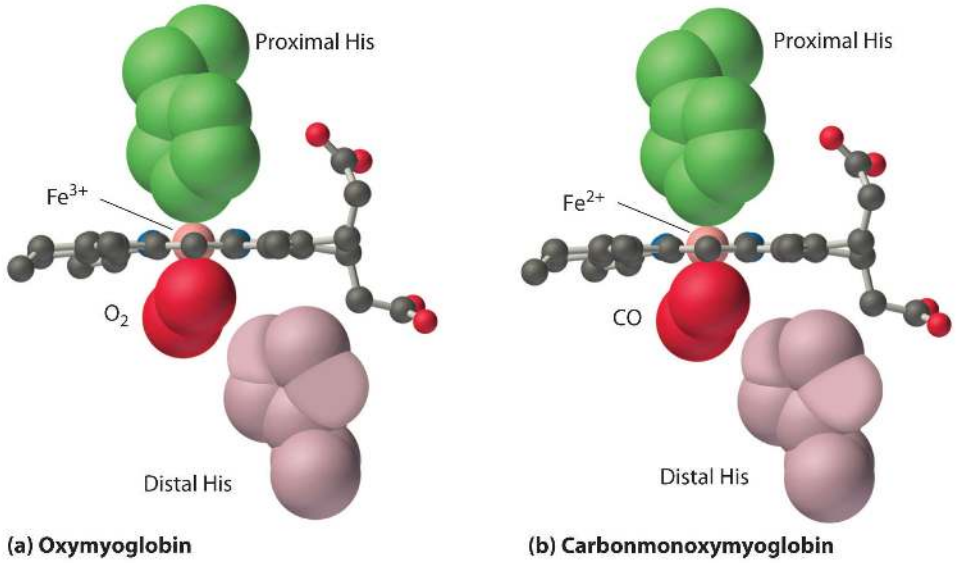


Figure 4.1.8.9: Binding of O_2 and CO to the Iron of Myoglobin. Because the Fe–O–O unit is bent, while the Fe–C–O unit is linear, the imidazole group of the distal histidine in hemoglobin interferes with CO binding and decreases the affinity of hemoglobin for CO.

Although CO has a much greater affinity for a ferrous heme than does O_2 (by a factor of about 25,000), the affinity of CO for deoxyhemoglobin is only about 200 times greater than that of O_2, which suggests that something in the protein is decreasing its affinity for CO by a factor of about 100. Both CO and NO bind to ferrous hemes in a linear fashion, with an Fe–C(N)–O angle of about 180°, and the difference in the preferred geometry of O_2 and CO provides a plausible explanation for the difference in affinities. As shown in Figure 4.1.8.9, the imidazole group of the distal histidine is located precisely where the oxygen atom of bound CO would be if the Fe–C–O unit were linear. Consequently, CO cannot bind to the heme in a linear fashion; instead, it is forced to bind in a bent mode that is similar to the preferred structure for the Fe–O_2 unit. This results in a significant decrease in the affinity of the heme for CO, while leaving the O_2 affinity unchanged, which is important because carbon monoxide is produced continuously in the body by degradation of the porphyrin ligand (even in nonsmokers). Under normal conditions, CO occupies approximately 1% of the heme sites in hemoglobin and myoglobin. If the affinity of hemoglobin and myoglobin for CO were 100 times greater (due to the absence of the distal histidine), essentially 100% of the heme sites would be occupied by CO, and no oxygen could be transported to the tissues. Severe carbon-monoxide poisoning, which is frequently fatal, has exactly the same effect. Thus the primary function of the distal histidine appears to be to decrease the CO affinity of hemoglobin and myoglobin to avoid self-poisoning by CO.

Hemerythrin

Hemerythrin is used to transport O_2 in a variety of marine invertebrates. It is an octamer (eight subunits), with each subunit containing two iron atoms and binding one molecule of O_2. Deoxyhemerythrin contains two Fe^{2+} ions per subunit and is colorless,

whereas oxyhemerythrin contains two Fe^{3+} ions and is bright reddish violet. These invertebrates also contain a monomeric form of hemerythrin that is located in the tissues, analogous to myoglobin. The binding of oxygen to hemerythrin and its release can be described by the following reaction, where the HO_2^- ligand is the hydroperoxide anion derived by the deprotonation of hydrogen peroxide (H_2O_2):

$$2\,Fe^{2+} + O_2 + H^+ \rightleftharpoons 2\,Fe^{3+}\text{–}O_2H \tag{4.1.8.5}$$

Thus O_2 binding is accompanied by the transfer of two electrons (one from each Fe^{2+}) and a proton to O_2.

Hemocyanin

Hemocyanin is used for oxygen transport in many arthropods (spiders, crabs, lobsters, and centipedes) and in mollusks (shellfish, octopi, and squid); it is responsible for the bluish-green color of their blood. The protein is a polymer of subunits that each contain two copper atoms (rather than iron), with an aggregate molecular mass of greater than 1,000,000 amu. Deoxyhemocyanin contains two Cu^+ ions per subunit and is colorless, whereas oxyhemocyanin contains two Cu^{2+} ions and is bright blue. As with hemerythrin, the binding and release of O_2 correspond to a two-electron reaction:

$$2\,Cu^+ + O_2 \rightleftharpoons Cu^{2+}\text{–}O_2^{2-}\text{–}Cu^{2+} \tag{4.1.8.6}$$

Although hemocyanin and hemerythrin perform the same basic function as hemoglobin, these proteins are not interchangeable. In fact, hemocyanin is so foreign to humans that it is one of the major factors responsible for the common allergies to shellfish.

> *Myoglobin, hemoglobin, hemerythrin, and hemocyanin all use a transition-metal complex to transport oxygen.*

Enzymes Involved in Oxygen Activation

Many of the enzymes involved in the biological reactions of oxygen contain metal centers with structures that are similar to those used for O_2 transport. Many of these enzymes also contain metal centers that are used for electron transfer, which have structures similar to those of the electron-transfer proteins discussed previously. In this section, we briefly describe two of the most important examples: dioxygenases and methane monooxygenase.

Dioxygenases are enzymes that insert both atoms of O_2 into an organic molecule. In humans, dioxygenases are responsible for cross-linking collagen in connective tissue and for synthesizing complex organic molecules called prostaglandins, which trigger inflammation and immune reactions. Iron is by far the most common metal in dioxygenases; and the target of the most commonly used drug in the world, aspirin, is an iron enzyme that synthesizes a specific prostaglandin. Aspirin inhibits this enzyme by binding to the iron atom at the active site, which prevents oxygen from binding.

Methane monooxygenase catalyzes the conversion of methane to methanol. The enzyme is a monooxygenase because only one atom of O_2 is inserted into an organic molecule, while the other is reduced to water:

$$CH_4 + O_2 + 2\,e^- + 2\,H^+ \rightarrow CH_3OH + H_2O \tag{4.1.8.7}$$

Because methane is the major component of natural gas, there is enormous interest in using this reaction to convert methane to a liquid fuel (methanol) that is much more convenient to ship and store. Because the C–H bond in methane is one of the strongest C–H bonds known, however, an extraordinarily powerful oxidant is needed for this reaction. The active site of methane monooxygenase contains two Fe atoms that bind O_2, but the details of how the bound O_2 is converted to such a potent oxidant remain unclear.

Metal Ions as Lewis Acids

Reactions catalyzed by metal ions that do not change their oxidation states during the reaction are usually group transfer reactions, in which a group such as the phosphoryl group ($-PO_3^{2-}$) is transferred. These enzymes usually use metal ions such as Zn^{2+}, Mg^{2+}, and Mn^{2+}, and they range from true metalloenzymes, in which the metal ion is tightly bound, to metal-activated enzymes, which require the addition of metal ions for activity. Because tight binding is usually the result of specific metal–ligand interactions, metalloenzymes tend to be rather specific for a particular metal ion. In contrast, the binding of metal ions to metal-activated enzymes is largely electrostatic in nature; consequently, several different metal ions with similar charges and sizes can often be used to give an active enzyme.

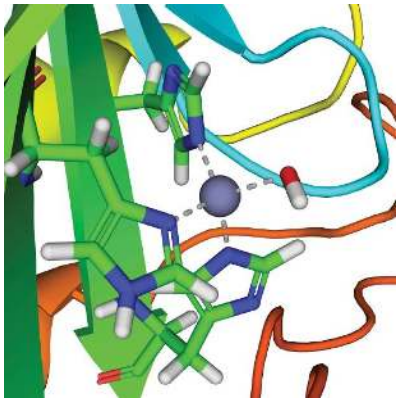
> *Metalloenzymes generally contain a specific metal ion, whereas metal-activated enzymes can use any of several metal ions of similar size and charge.*

A metal ion that acts as a Lewis acid can catalyze a group transfer reaction in many different ways, but we will focus on only one of these, using a zinc enzyme as an example. Carbonic anhydrase is found in red blood cells and catalyzes the reaction of CO_2 with water to give carbonic acid.

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{4.1.8.8}$$

Although this reaction occurs spontaneously in the absence of a catalyst, it is too slow to absorb all the CO_2 generated during respiration. Without a catalyst, tissues would explode due to the buildup of excess CO_2 pressure. Carbonic anhydrase contains a single Zn^{2+} ion per molecule, which is coordinated by three histidine imidazole ligands and a molecule of water. Because Zn^{2+} is a Lewis acid, the pK_a of the Zn^{2+}–OH_2 unit is about 8 versus 14 for pure water. Thus at pH 7–8, a significant fraction of the enzyme molecules contain the Zn^{2+}–OH^- group, which is much more reactive than bulk water. When carbon dioxide binds in a nonpolar site next to the Zn^{2+}–OH^- unit, it reacts rapidly to give a coordinated bicarbonate ion that dissociates from the enzyme:

$$Zn^{2+}\text{–}OH^- + CO_2 \rightleftharpoons Zn^{2+}\text{–}OCO_2H^- \rightleftharpoons Zn^{2+} + HCO_3^- \tag{4.1.8.9}$$



The active site of carbonic anhydrase.

Thus the function of zinc in carbonic anhydrase is to generate the hydroxide ion at pH 7.0, far less than the pH required in the absence of the metal ion.

Enzymes That Use Metals to Generate Organic Radicals

An organic radical is an organic species that contains one or more unpaired electrons. Chemists often consider organic radicals to be highly reactive species that produce undesirable reactions. For example, they have been implicated in some of the irreversible chemical changes that accompany aging. It is surprising, however, that organic radicals are also essential components of many important enzymes, almost all of which use a metal ion to generate the organic radical within the enzyme. These enzymes are involved in the synthesis of hemoglobin and DNA, among other important biological molecules, and they are the targets of pharmaceuticals for the treatment of diseases such as anemia, sickle-cell anemia, and cancer. In this section, we discuss one class of radical enzymes that use vitamin B_{12}.

Vitamin B_{12} was discovered in the 1940s as the active agent in the cure of pernicious anemia, which does not respond to increased iron in the diet. Humans need only tiny amounts of vitamin B_{12}, and the average blood concentration in a healthy adult is only about 3.5×10^{-8} M. The structure of vitamin B_{12}, shown in Figure 4.1.8.10, is similar to that of a heme, but it contains cobalt instead of iron, and its structure is much more complex. In fact, vitamin B_{12} has been called the most complex nonpolymeric biological molecule known and was the first naturally occurring organometallic compound to be isolated. When vitamin B_{12} (the form present in vitamin tablets) is ingested, the axial cyanide ligand is replaced by a complex organic group.

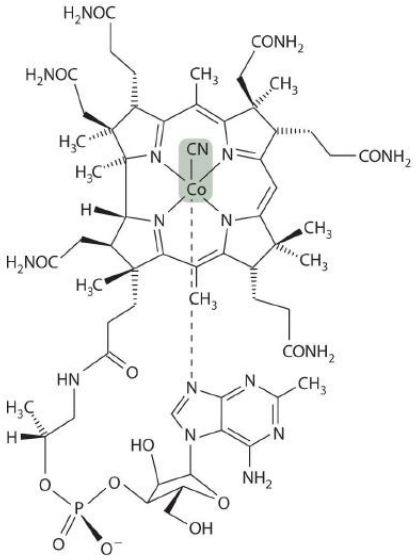
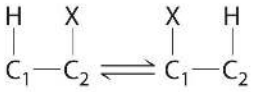


Figure 4.1.8.10: Vitamin B_{12} In the body, the axial cyanide ligand found in the vitamin is replaced by a complex organic unit. Heterolytic cleavage of the Co–C bond in the resulting organometallic complex generates an organic radical for the catalysis of rearrangement reactions.

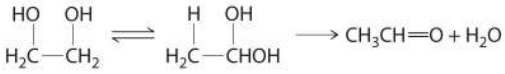
The cobalt–carbon bond in the enzyme-bound form of vitamin B_{12} and related compounds is unusually weak, and it is particularly susceptible to homolytic cleavage:

$$\mathrm{CoCH_2R} \rightleftharpoons \mathrm{Co^{2+}} + \cdot\mathrm{CH_2R} \tag{4.1.8.10}$$

Homolytic cleavage of the Co^{3+}–CH_2R bond produces two species, each of which has an unpaired electron: a d^7 Co^{2+} derivative and an organic radical, $\cdot CH_2R$, which is used by vitamin B_{12}-dependent enzymes to catalyze a wide variety of reactions. Virtually all vitamin B_{12}-catalyzed reactions are rearrangements in which an H atom and an adjacent substituent exchange positions:



In the conversion of ethylene glycol to acetaldehyde, the initial product is the hydrated form of acetaldehyde, which rapidly loses water:



The enzyme uses the $\cdot CH_2R$ radical to temporarily remove a hydrogen atom from the organic substrate, which then rearranges to give a new radical. Transferring the hydrogen atom back to the rearranged radical gives the product and regenerates the $\cdot CH_2R$ radical.

The metal is not involved in the actual catalytic reaction; it provides the enzyme with a convenient mechanism for generating an organic radical, which does the actual work. Many examples of similar reactions are now known that use metals other than cobalt to generate an enzyme-bound organic radical.

> *Nearly all vitamin B_{12}-catalyzed reactions are rearrangements that occur via a radical reaction.*

Summary

Three separate steps are required for organisms to obtain essential transition metals from their environment: mobilization of the metal, transport of the metal into the cell, and transfer of the metal to where it is needed within a cell or an organism. The process of iron uptake is best understood. To overcome the insolubility of $Fe(OH)_3$, many bacteria use organic ligands called siderophores, which have high affinity for Fe(III) and are secreted into the surrounding medium to increase the total concentration of dissolved

iron. The iron–siderophore complex is absorbed by a cell, and the iron is released by reduction to Fe(II). Mammals use the low pH of the stomach to increase the concentration of dissolved iron. Iron is absorbed in the intestine, where it forms an Fe(III) complex with a protein called transferrin that is transferred to other cells for immediate use or storage in the form of ferritin.

Proteins that contain one or more tightly bound metal ions are called metalloproteins, and metalloproteins that catalyze biochemical reactions are called metalloenzymes. Proteins that transfer electrons from one place to another are called electron-transfer proteins. Most electron-transfer proteins are metalloproteins, such as iron–sulfur proteins, cytochromes, and blue copper proteins that accept and donate electrons. The oxidized and reduced centers in all electron-transfer proteins have similar structures to ensure that electron transfer to and from the metal occurs rapidly. Metalloproteins also use the ability of transition metals to bind small molecules, such as O_2, N_2, and H_2, to transport or catalyze the reactions of these small molecules. For example, hemoglobin, hemerythrin, and hemocyanin, which contain heme iron, nonheme iron, and copper, respectively, are used by different kinds of organisms to bind and transfer O_2. Other metalloenzymes use transition-metal ions as Lewis acids to catalyze group transfer reactions. Finally, some metalloenzymes use homolytic cleavage of the cobalt–carbon bond in derivatives of vitamin B_{12} to generate an organic radical that can abstract a hydrogen atom and thus cause molecular rearrangements to occur.

Key Takeaway

- Organisms have developed strategies to extract transition metals from the environment and use the metals in electron-transfer reactions, reactions of small molecules, Lewis-acid catalysis, and the generation of reactive organic radicals.

Conceptual Problems

1. What are the advantages of having a metal ion at the active site of an enzyme?
2. Why does the structure of the metal center in a metalloprotein that transfers electrons show so little change after oxidation or reduction?

Structure and Reactivity

1. In enzymes, explain how metal ions are particularly suitable for generating organic radicals.
2. A common method for treating carbon-monoxide poisoning is to have the patient inhale pure oxygen. Explain why this treatment is effective.

4.1.8: Transition Metals in Biology is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Transition Metals in Biology** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.2: Transition Metals

The observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n-1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive.

Topic hierarchy

4.2.1: Chemistry of Actinium
4.2.2: Chemistry of Lanthanum
4.2.3: Chemistry of Scandium
4.2.4: Chemistry of Yttrium
4.2.5: Group 3 Elemental Properties

4.2: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.2.1: Chemistry of Actinium

Actinium, named from the Greek aktinos (ray) is a rare, extremely radioactive metal that glows in the dark (the photo shown above is of Ac_2O_3). It was discovered by Debierne in 1899 and again in 1902 by Giesel. Eventual priority was given to Debierne's work.

Samples of actinium quickly decay to thorium and francium. The longest-lived isotope (Ac-227) has a half-life of 21.8 years. The element is obtained as an impurity in pitchblende, an ore mined for its uranium content. One-tenth of one gram of actinium can be recovered from 1 ton of pitchblende!

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Actinium** is licensed CC BY-NC-SA 4.0.

4.2.2: Chemistry of Lanthanum

Discovered in 1893 by Mosander, lanthanum is named from the Greek lanthanein, "to lie hidden". That is an apt description since lanthanum generally occurs along with other so-called rare earth elements and is very difficult to separate. The abundance of the metal is similar to that of zinc or nickel.

Lanthanum is used in the electrodes for high-intensity carbon-arc lamps and also in the production of high-purity europium metal (element 63). The pure metal is silvery white and malleable. It is soft enough to cut with a knife and will oxidize readily in the air as well as react with moisture. For that reason the metal is usually stored under oil or kerosene. Most lanthanum is extracted from monazite sands.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Lanthanum** is licensed CC BY-NC-SA 4.0.

4.2.3: Chemistry of Scandium

This module was designed to give general information about Scandium, a transition metal element. Having some knowledge of the properties of Scandium provides for a better understanding of the production of items such as spacecraft and sports equipment, as well as providing for a better general understanding of Earth's elements.

Contributors and Attributions

- Kevin Fan (UCD)
- Katherine Cubbon

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

- **Chemistry of Scandium** is licensed CC BY-NC-SA 4.0.

4.2.4: Chemistry of Yttrium

The current claim-to-fame for yttrium (named from a Swedish village, Ytterby) is its use in the so-called 1-2-3 oxide superconductors (along with barium and copper). These were the first superconducting materials to function at liquid nitrogen temperatures. The element was discovered in 1789 by Gadolin and finally isolated in 1828 by Wöhler. More than 15 tons of the oxide are now produced each year. In addition to its use in the research of superconductivity, it is also used in phosphors (red) for color television tubes.

Yttrium metal is ductile and silvery. Powdered samples and turnings from machining can burst into flame. Most commercial yttrium is produced from monazite sands which are also the source for most of the rare earth elements.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Yttrium** is licensed CC BY-NC-SA 4.0.

4.2.5: Group 3 Elemental Properties

As shown in Table 1.1.1, the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n-1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

$$2M_{(s)} + 6H_2O_{(l)} \rightarrow 2M(OH)_{3(s)} + 3H_{2(g)} \tag{1.1.1}$$

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated M^{3+}(aq) ion.

Commercial uses of the group 3 metals are limited, but “mischmetal,” a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

4.2.5: Group 3 Elemental Properties is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Group 3 Elemental Properties** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.3: Transition Metals

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons.

4.3.1: Group 4 Elemental Properties
4.3.2: Chemistry of Hafnium
4.3.3: Chemistry of Rutherfordium
4.3.4: Chemistry of Titanium
4.3.5: Chemistry of Zirconium

4.3: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.3.1: Group 4 Elemental Properties

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

$$2\,FeTiO_3(s) + 6\,C(s) + 7\,Cl_2(g) \rightarrow 2\,TiCl_4(g) + 2\,FeCl_3(g) + 6\,CO(g) \tag{4.3.1.1}$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

> The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Table 4.3.1.1: Some Properties of the Elements of Groups 4

Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm3)
Ti	22	$4s^23d^2$	1.54	147	1668	4.51
Zr	40	$5s^24d^2$	1.33	160	1855	6.52
Hf	72	$6s^25d^24f^{14}$	1.30	159	2233	13.31

Consistent with the periodic trends, the group 4 metals become denser, higher melting, and more electropositive down the column (Table 4.3.1.1). Unexpectedly, however, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2\,Cl_2(g) \tag{4.3.1.2}$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure 4.3.1.1). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

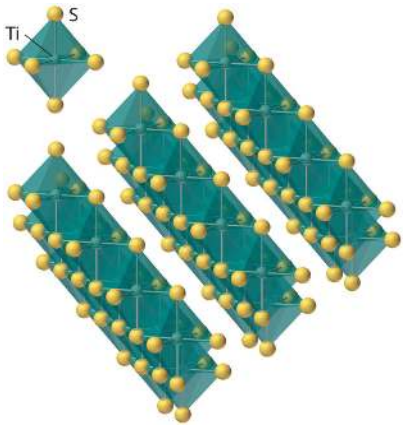


Figure 4.3.1.1: The Layered Structure of TiS_2. Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

4.3.1: Group 4 Elemental Properties is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Group 4 Elemental Properties** is licensed CC BY-NC-SA 4.0.

4.3.2: Chemistry of Hafnium

More abundant than better known metals such as silver and gold, hafnium (from the Latin Hafnia, a name for Copenhagen) was not discovered until 1923 by Coster and de Hevesy. The reason is the similarity of hafnium to zirconium. Mendeleev had predicted the existence of element 72 but had wrongly suggested it might be found along with titanium ores. Instead it lay hidden with "pure" samples of zirconium. Later Niels Bohr predicted the arrangement of outer electrons for element 72 and it was using X-ray techniques to study this very thing that led to the identification of hafnium as a separate element (thus the connection to Copenhagen in the name for the metal: Bohr's hometown).

Hafnium metal is used in the manufacture of control rods for nuclear reactors because of its ability to absorb neutrons.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Hafnium** is licensed CC BY-NC-SA 4.0.

4.3.3: Chemistry of Rutherfordium

In 1964 researchers in the Soviet Union at Dubna announced their discovery of element 104. A similar claim was made by researchers at the University of California at Berkeley. The Soviet scientists claimed to have bombarded a target of Pu-242 with Ne-22, resulting in a nucleus with 104 protons and a mass number of 260.

$$^{22}_{10}\mathrm{Ne} + ^{242}_{94}\mathrm{Pu} \rightarrow ^{260}_{104}Rf$$

The Berkeley team used a Cf-249 target and isotopes of carbon for projectiles, resulting in isotopes of 104 with mass numbers of 257 and 259. Several other isotopes were also prepared by the American team.

$$^{12}_{6}\mathrm{C} + ^{249}_{98}\mathrm{Cf} \rightarrow ^{257}_{104}\mathrm{Rf} + 4\,^{1}_{0}\mathrm{n}$$

The naming and priority of discovery controversy has raged ever since and Rutherfordium is the approved name selected by the IUPAC in August 1997.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Rutherfordium** is licensed CC BY-NC-SA 4.0.

4.3.4: Chemistry of Titanium

Discovered independently by William Gregor and Martin Klaproth in 1795, titanium (named for the mythological Greek Titans) was first isolated in 1910. Gregor, a Cornish vicar and amateur chemist isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4.Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction because of its:

- Excellent Corrosion Resistance
- High Heat Transfer Efficiency
- Superior Strength-To-Weight Ratio

For example, when it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.



Uses of titanium

Titanium is a highly corrosion-resistant metal with great tensile strength. It is ninth in abundance for elements in the earth's crust. It has a relatively low density (about 60% that of iron). It is also the tenth most commonly occurring element in the Earth's crust. That all means that titanium should be a really important metal for all sorts of engineering applications. In fact, it is very expensive and only used for rather specialized purposes. Titanium is used, for example:

- in the aerospace industry - for example in aircraft engines and air frames;
- for replacement hip joints;
- for pipes, etc, in the nuclear, oil and chemical industries where corrosion is likely to occur.

Titanium is very expensive because it is awkward to extract from its ores - for example, from rutile, TiO_2. Whilst a biological function in man is not known, it has excellent biocompatibility--that is the ability to be ignored by the human body's immune system--and an extreme resistance to corrosion. Titanium is now the metal of choice for hip and knee replacements.



Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)

Titanium Extraction

Titanium cannot be extracted by reducing the ore using carbon as a cheap reducing agent, like with iron. The problem is that titanium forms a carbide, TiC, if it is heated with carbon, so you don't get the pure metal that you need. The presence of the

carbide makes the metal very brittle. That means that you have to use an alternative reducing agent. In the case of titanium, the reducing agent is either sodium or magnesium. Both of these would, of course, first have to be extracted from their ores by expensive processes.

The titanium is produced by reacting titanium(IV) chloride, $TiCl_4$ - NOT the oxide - with either sodium or magnesium. That means that you first have to convert the oxide into the chloride. That in turn means that you have the expense of the chlorine as well as the energy costs of the conversion. High temperatures are needed in both stages of the reaction.

Titanium is made by a batch process. In the production of iron, for example, there is a continuous flow through the Blast Furnace. Iron ore and coke and limestone are added to the top, and iron and slag removed from the bottom. This is a very efficient way of making something. With titanium, however, you make it one batch at a time. Titanium(IV) chloride is heated with sodium or magnesium to produce titanium. The titanium is then separated from the waste products, and an entirely new reaction is set up in the same reactor. This is a slow and inefficient way of doing things. Traces of oxygen or nitrogen in the titanium tend to make the metal brittle. The reduction has to be carried out in an inert argon atmosphere rather than in air; that also adds to costs.

Wilhelm J. Kroll developed the process in Luxemburg around the mid 1930's and then after moving to the USA extended it to enable the extraction of Zirconium as well. Titanium ores, mainly rutile (TiO_2) and ilmentite ($FeTiO_3$), are treated with carbon and chlorine gas to produce titanium tetrachloride.

$$TiO_2 + Cl_2 \rightarrow TiCl_4 + CO_2$$

Fractionation

Titanium tetrachloride is purified by distillation (Boiling point of 136.4) to remove iron chloride.

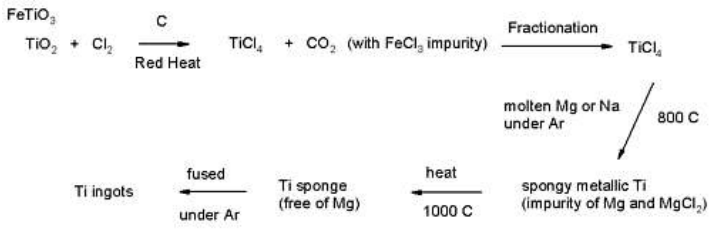
Reduction

Purified titanium tetrachloride is reacted with molten magnesium under argon to produce a porous “titanium sponge”.

$$TiCl_4 + 2\,Mg \rightarrow Ti + 2\,MgCl_2$$

Melting

Titanium sponge is melted under argon to produce ingots.



Kroll process

Titanium Halides

Titanium(IV) Halides

Formula	Color	MP	BP	Structure
TiF_4	white	-	284	fluoride bridged
$TiCl_4$	Colorless	-24	136.4	-
$TiBr_4$	yellow	38	233.5	hcp I- but essentially monomeric cf. SnI_4
TiI_4	violet-black	155	377	hcp I- but essentially monomeric cf. SnI_4

Preparations

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolyzed. They are all expected to be diamagnetic.

Titanium(III) halides

Formula	Color	MP	BP	m (BM)	Structure
TiF_3	blue	950d	-	1.75	-
$TiCl_3$	violet	450d	-	-	BiI_3
$TiBr_3$	violet	-	-	-	BiI_3
TiI_3	violet-black	-	-	-	-

Preparations:

They can be prepared by reduction of TiX_4 with H_2.

Titanium Oxides and Aqueous Chemistry

Titanium oxides

Formula	Color	MP	m (BM)	Structure
TiO_2	white	1892	diam.	rutile - Refractive Index 2.61-2.90 cf. Diamond 2.42

Preparations

obtained from hydrolysis of TiX_4 or Ti(III) salts.

TiO_2 reacts with acids and bases.

In Acid: $TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)

In Base: $MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$) M_2TiO_4 orthotitanates.

Peroxides are highly colored and can be used for Colorimetric analysis.

pH <1 $[TiO_2(OH)(H_2O)x]+$

pH 1-2 $[(O_2)Ti\text{-}O\text{-}Ti(O_2)](OH)_x^{2-x}$; x=1-6

$[Ti(H_2O)_6]^{3+}$ -> $[Ti(OH)(H_2O)_5]^{2+}$ + [H+] pK=1.4

$TiO^{2+} + 2H^+ + e^-$ -> $Ti^{3+} + H_2O$ E=0.1V

Representative complexes

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases such as;

$2PEt_3$ -> $TiCl_4(PEt_3)_2$
$2MeCN$ -> $TiCl_4(MeCN)_2$
bipy -> $TiCl_4$(bipy)

Solvolysis can occur if ionisable protons are present in the ligand;

$2NH_3$ -> $TiCl_2(NH_2)_2$ + 2HCl
$4H_2O$ -> TiO_2.aq + 4HCl
2EtOH -> $TiCl_2(OEt)_2$ + 2HCl

$TiCl_3$ has less Lewis acid strength but can form adducts also;

3pyr -> $TiCl_3pyr_3$

Conversion of titanium oxide into titanium chloride

The ore rutile (impure titanium(IV) oxide) is heated with chlorine and coke at a temperature of about 900°C.

$$TiO_2 + 2Cl_2 + 2C \longrightarrow TCl_4 + 2CO$$

Other metal chlorides are formed as well because of other metal compounds in the ore. Very pure liquid titanium(IV) chloride can be separated from the other chlorides by fractional distillation under an argon or nitrogen atmosphere. Titanium(IV) chloride reacts violently with water. Handling it therefore needs care and is stored in totally dry tanks.

Reduction of the titanium chloride

Reduction by sodium: The titanium(IV) chloride is added to a reactor in which very pure sodium has been heated to about 550°C - everything being under an inert argon atmosphere. During the reaction, the temperature increases to about 1000°C.

$$\mathrm{TiCl_4 + 4\,Na \longrightarrow Ti + 4\,NaCl}$$

After the reaction is complete, and everything has cooled (several days in total - an obvious inefficiency of the batch process), the mixture is crushed and washed with dilute hydrochloric acid to remove the sodium chloride.

Reduction by magnesium

This is the method used in the rest of the world. The method is similar to using sodium, but this time the reaction is:

$$\mathrm{TiCl_4 + 4\,Mg \longrightarrow Ti + 2\,MgCl_2}$$

The magnesium chloride is removed from the titanium by distillation under very low pressure at a high temperature.

Outside Links

- Beattie, James K. "A New Perspective on Rutile." *J. Chem. Educ.* **1998** *75* 641.
- Gisser, Kathleen R. C.; Geselbracht, Margaret; Cappellari, Ann; Hunsberger, Lynn; Ellis, Arthur B.; Perepezko, John; Lisensky, George C. "Nickel-Titanium Memory Metal: A "Smart" Material Exhibiting a Solid-State Phase Change and Superelasticity." *J. Chem. Educ.* **1994**, *71*, 334.
- "Complexes and First-Row Transition Elements", D. Nicholls
- "Basic Inorganic Chemistry", F.A. Cotton, G. Wilkinson and P.L. Gaus
- "Advanced Inorganic Chemistry", F.A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann
- "Chemistry of the Elements", Greenwood and Earnshaw

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)
- {{template.ContribLancashire()}}

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

- **Chemistry of Titanium** is licensed CC BY-NC-SA 4.0.

4.3.5: Chemistry of Zirconium

Named for the mineral zircon in which it can be found, zirconium was discovered in 1789 by Klaproth and eventually isolated in 1824 by Berzelius. The metal reacts with oxygen and nitrogen in the atmosphere to form a protective coating that inhibits further corrosion. It is resistant to weak acids and even forms a low-temperature superconductor when alloyed with niobium.

Zirconium finds applications in industry which suit its high corrosion resistance and strength. It is very similar to the less plentiful Hafnium (see below) and the two are very difficult to separate. Most samples of either are contaminated with small amounts of the other element.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Zirconium** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.4: Transition Metals

All group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

4.4.1: Chemistry of Dubnium
4.4.2: Chemistry of Niobium
4.4.3: Chemistry of Tantalum
4.4.4: Chemistry of Vanadium
4.4.5: Group 5 Elemental Properties

4.4: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.4.1: Chemistry of Dubnium

The synthesis of element 105 was reported by Soviet scientists at the research station in Dubna as early as 1967 and by scientists at U.C. Berkeley in 1970. The Soviet scientists reported synthesis by bombarding Am-243 with Ne-22. At Berkeley, Cf-249 was bombarded with N-15.

At the purported time of discovery the Soviets suggested the name Nielsbohrium (Ns) for the element while the American group suggested Hahnium (Ha). But the ensuing controversy over the discovery of this and other 6d-elements led the IUPAC to adopt its numerical system for naming elements beyond 103 until some agreements could be reached (hence Unp or Unnilpentium for 105).

The longest lived isotope has a half-life of 34 seconds. Dubnium is the name approved by the IUPAC in August 1997.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Dubnium** is licensed CC BY-NC-SA 4.0.

4.4.2: Chemistry of Niobium

Discovered in a museum in 1801, niobium was named after Niobe, the mythological daughter of Tantalus (the metal is chemically related to Tantalum). Occurring in the earth's crust in proportions of about 20 parts-per-million, niobium is used as an alloying agent with iron and nickel. It has commercial uses in atomic reactors and has superconductive properties when alloyed with tin or aluminum.

In many places niobium is known as columbium since it was originally "discovered" in a mineral named columbite. However, careful subsequent analysis indicated that the "new" element was actually Tantalum. The rediscovery of the element we know now as niobium was not even associated with columbium until after the official statistics were in.

Pure niobium looks much like steel but resists corrosion better due to a thin coating of oxide that forms on all exposed surfaces. The only acid that attacks Nb at room temperature is HF. Above 200° the metal becomes more reactive.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Niobium** is licensed CC BY-NC-SA 4.0.

4.4.3: Chemistry of Tantalum

Named for the mythological character Tantalus by Anders Ekenberg who discovered it in 1802, tantalum is a heavy, gray metal that resembles the more expensive platinum in many respects and is sometimes used as an economical substitute for that element. The metal comprises only 0.0002% of the earth's crust and most deposits lie outside the U.S. which is the chief consumer.

Tantalum alloys are corrosion and wear resistant and find use in dental and surgical tools. Tantalum oxide is used in some electronic components and a composite of tantalum carbide (TaC) and graphite is one of the hardest materials ever produced.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Tantalum** is licensed CC BY-NC-SA 4.0.

4.4.4: Chemistry of Vanadium

Vanadium takes its name from the Scandinavian goddess Vanadis and was discovered in 1801 by Andrés Manuel del Rio. It was isolated in 1867 by Henry Roscoe as a silvery-white metal that is somewhat heavier than aluminum but lighter than iron. It has excellent corrosion resistance at room temperature.

The history of its discovery is an interesting tale. del Rio sent his brown ore samples, containing what he thought was a new element to Paris for analysis and confirmation, along with a brief explanation that was ambiguous. The complete analysis and description of his work were lost in a shipwreck so the Paris lab saw nothing but brown powder and a brief confusing note. A second sample sent to Berlin was mislabeled lead chromate when it arrived. del Rio gave up, losing confidence in his discovery. The element was rediscovered in 1867 by Nils Sefstrôm.

Vanadium has an unusually large number of stable oxidation states (+2, +3, +4, +5)each of which is characterized by a unique color in solution. The metal is used as an alloying agent for steel. It combines with nearly all non-metals in compounds.

Vanadium(V) oxide as a Catalyst

During the *Contact Process* for manufacturing sulfuric acid, sulfur dioxide has to be converted into sulfur trioxide, which is done by passing sulfur dioxide and oxygen over a solid vanadium(V) oxide catalyst.

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$$

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number). The sulfur dioxide is oxidized to sulfur trioxide by the vanadium(V) oxide. In the process, the vanadium(V) oxide is reduced to vanadium(IV) oxide.

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$$

The vanadium(IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

Vanadium's oxidation states

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. This section looks at ways of changing between them. It starts with a bit of description, and then goes on to look at the reactions in terms of standard redox potentials (standard electrode potentials).



Figure 4.4.4.1: Oxidation states of vanadium in acidic solution. From left to right the oxidation state goes from +5 to +2. (CC BY-SA 3.0; W. Oelen)

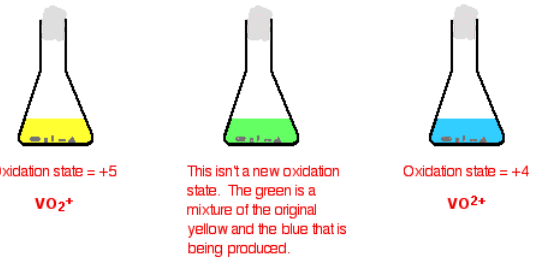
Reducing vanadium(V) in stages to vanadium(II)

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate, NH_4VO_3. This isn't very soluble in water and is usually first dissolved in sodium hydroxide solution. The solution can be reduced using zinc and an acid - either hydrochloric acid or sulfuric acid, usually using moderately concentrated acid. The exact vanadium ion present in the solution is very

complicated, and varies with the pH of the solution. The reaction is done under acidic conditions when the main ion present is $\mathbf{VO_2^+}$ - called the dioxovanadium(V) ion.

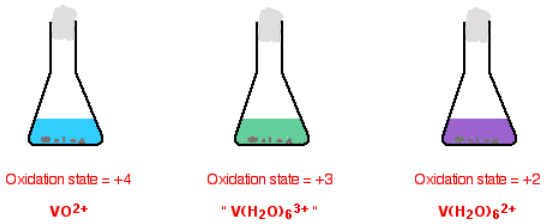
If you do the reaction in a small flask, it is normally stoppered with some cotton wool. This allows hydrogen (produced from a side reaction between the zinc and acid) to escape. At the same time it stops much air from entering. This prevents re-oxidation of the lower oxidation states of vanadium (particularly the +2 state) by oxygen in the air. The reaction is usually warmed so that the changes happen in a reasonable time. The reduction is shown in two stages. Some individual important colors are shown, but the process is one continuous change from start to finish.

The reduction from +5 to +4



It is important to notice that the green color you see isn't actually another oxidation state. it is just a mixture of the original yellow of the +5 state and the blue of the +4. Be very careful with the formulae of the two vanadium ions - they are very easy to confuse!

The reduction from +4 to +2. The color changes just continue.



The reason for the inverted commas around the vanadium(III) ion is that this is almost certainly a simplification. The exact nature of the complex ion will depend on which acid you use in the reduction process. The simplification is probably reasonable at this level.

Re-oxidation of the vanadium(II)

The vanadium(II) ion is very easily oxidized. If you remove the cotton wool from the flask and pour some solution into a test tube, it turns green because of its contact with oxygen in the air. It is oxidized back to vanadium(III). If it is allowed to stand for a long time, the solution eventually turns blue as the air oxidizes it back to the vanadium(IV) state - VO^{2+} ions. Adding nitric acid (a reasonably powerful oxidizing agent) to the original vanadium(II) solution also produces blue VO^{2+} ions. The vanadium(II) is again oxidized back to vanadium(IV).

Using Zinc as the reducing agent

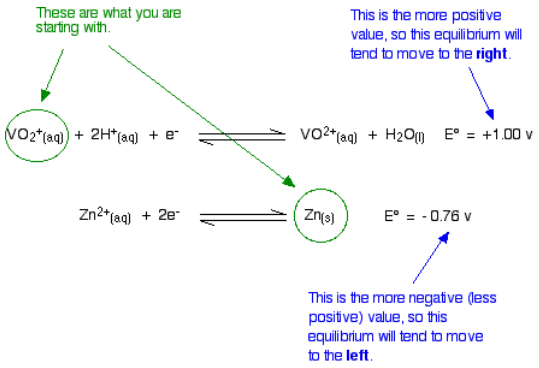
Let's look at the first stage of the reduction - from VO_2^+ to VO^{2+}. The redox potential for the vanadium half-reaction is given by:

$$VO_2^+{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightleftharpoons VO^{2+}{}_{(aq)} + H_2O_{(l)} \quad E^\circ = +1.00\ v$$

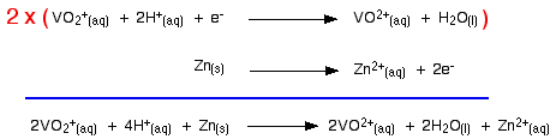
The corresponding equilibrium for the zinc is:

$$Zn^{2+}{}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^\circ = -0.76\ v$$

The simple principle is that if you couple two of these half-reactions together, the one with the more positive E° value will move to the right; the one with the more negative (or less positive) E° moves to the left. If you mix together zinc and VO_2^+ ions in the presence of acid to provide the H^+ ions:

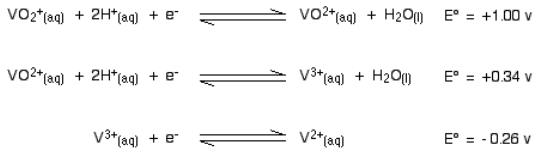


That converts the two equilibria into two one-way reactions. You can write these down and combine them to give the ionic equation for the reaction if you want to.



The other stages of the reaction

Here are the E° values for all the steps of the reduction from vanadium(V) to vanadium(II):



. . . and here is the zinc value again:

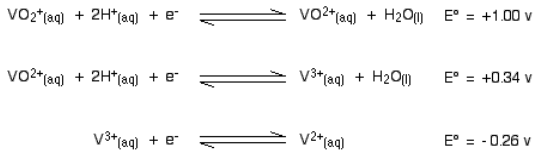


Remember that for the vanadium reactions to move to the right (which is what we want), their E° values must be more positive than whatever you are reacting them with. In other words, for the reactions to work, zinc must always have the more negative value - and that's the case. Zinc can reduce the vanadium through each of these steps to give the vanadium(II) ion.

Using other reducing agents

Suppose you replaced zinc as the reducing agent by tin. How far would the set of reductions go this time?

Here are the E° values again:



. . . and here is the tin value:



For each reduction to happen, the vanadium reaction has to have the more positive E° value because we want it to go to the right. That means that the tin must have the more negative value.

- In the first vanadium equation (from +5 to +4), the tin value is more negative. That works OK.
- In the second vanadium equation (from +4 to +3), the tin value is again the more negative. That works as well.
- But in the final vanadium reaction (from +3 to +2), tin no longer has the more negative E° value. Tin won't reduce vanadium(III) to vanadium(II).

Re-oxidation of the vanadium(II)

The vanadium(II) oxidation state is easily oxidized back to vanadium(III) - or even higher.

Oxidation by hydrogen ions

You will remember that the original reduction we talked about was carried out using zinc and an acid in a flask stoppered with a piece of cotton wool to keep the air out. Air will rapidly oxidize the vanadium(II) ions - but so also will the hydrogen ions present in the solution!

The vanadium(II) solution is only stable as long as you keep the air out, and in the presence of the zinc. The zinc is necessary to keep the vanadium reduced. What happens if the zinc isn't there? Look at these E° values:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0\ v$$

The reaction with the more negative E° value goes to the left; the reaction with the more positive (or less negative) one to the right. That means that the vanadium(II) ions will be oxidized to vanadium(III) ions, and the hydrogen ions reduced to hydrogen.

Will the oxidation go any further - for example, to the vanadium(IV) state? Have a look at the E° values and decide:

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0\ v$$

In order for the vanadium equilibrium to move to the left, it would have to have the more negative E° value. It hasn't got the more negative E° value and so the reaction does not happen.

Oxidation by nitric acid

In a similar sort of way, you can work out how far nitric acid will oxidize the vanadium(II). Here's the first step:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

The vanadium reaction has the more negative E° value and so will move to the left; the nitric acid reaction moves to the right.

Nitric acid will oxidize vanadium(II) to vanadium(III). The second stage involves these E° values:

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

The nitric acid again has the more positive E° value and so moves to the right. The more negative (less positive) vanadium reaction moves to the left. Nitric acid will certainly oxidize vanadium(III) to vanadium(IV). Will it go all the way to vanadium(V)?

$$VO_2^+{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +1.00\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

No, it won't! For the vanadium reaction to move to the left to form the dioxovanadium(V) ion, it would have to have the more negative (less positive) E° value. It hasn't got a less positive value, and so the reaction does not happen.

You can work out the effect of any other oxidizing agent on the lower oxidation states of vanadium in exactly the same way. But don't assume that because the E° values show that a reaction is possible, it will necessarily happen.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)
- Stephen R. Marsden

This page titled 4.4.4: Chemistry of Vanadium is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Chemistry of Vanadium** by Jim Clark is licensed CC BY-NC 4.0.

4.4.5: Group 5 Elemental Properties

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of V_4C_3, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of SO_2 to SO_3 in the contact process for the production of sulfuric acid. In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as Nb_3Zr and Nb_3Ge, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

> The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.

Table 1.1.1: Some Properties of the Elements of Group 5

Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
Zr	40	$5s^24d^2$	1.33	160	1855	6.52
Hf	72	$6s^25d^24f^{14}$	1.30	159	2233	13.31
V	23	$4s^23d^3$	1.63	134	1910	6.00
Nb	41	$5s^24d^3$	1.60	146	2477	8.57
Ta	73	$6s^25d^34f^{14}$	1.50	146	3017	16.65

As indicated in Table 1.1.1, the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state (M_2O_5), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 1.1.2). Consistent with its covalent character, V_2O_5 is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Because vanadium ions with different oxidation states have different numbers of d electrons, aqueous solutions of the ions have different colors: in acid V(V) forms the pale yellow $[VO_2]^+$ ion; V(IV) is the blue vanadyl ion $[VO]^{2+}$; and V(III) and V(II) exist as the hydrated V^{3+} (blue-green) and V^{2+} (violet) ions, respectively.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

4.4.5: Group 5 Elemental Properties is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Group 5 Elemental Properties** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.5: Transition Metals

The group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction.

Topic hierarchy

4.5.1: Chemistry of Chromium

4.5.1.1: Chemistry of Chromium

4.5.1.2: Potassium Chromium Sulfate

4.5.2: Chemistry of Molybdenum

4.5.2.1: Molybdenum Disulfide

4.5.3: Chemistry of Seaborgium

4.5.4: Chemistry of Tungsten

4.5: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.5.1: Chemistry of Chromium

Chromium is the 24th element in the periodic table and it is found in about 0.0122% of the Earth's crust. It is named after the Greek word "c*hroma*," meaning color. This element produces many beautifully colored compounds, as well as a wide array of colored solutions. Chromium is also a very useful industrial metal.

Contributors and Attributions

- Kaitlyn Kortright (UCD)
- Stephen R. Marsden

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

- **Chemistry of Chromium** is licensed CC BY-NC-SA 4.0.

4.5.1.1: Chemistry of Chromium

This page looks at some aspects of chromium chemistry. It includes: reactions of chromium(III) ions in solution (summarised from elsewhere on the site); the interconversion of the various oxidation states of chromium; the chromate(VI)-dichromate(VI) equilibrium; and the use of dichromate(VI) ions as an oxidizing agent (including titrations).

Reactions of chromium(III) ions in solution

The simplest ion that chromium forms in solution is the hexaaquachromium(III) ion - $[Cr(H_2O)_6]^{3+}$.

The acidity of the hexaaqua ions

In common with the other 3+ ions, the hexaaquachromium(III) ion is fairly acidic - with a pH for typical solutions in the 2 - 3 range.

The ion reacts with water molecules in the solution. A hydrogen ion is lost from one of the ligand water molecules:

$$Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5(OH)^{2+} + H_3O^+$$

The complex ion is acting as an acid by donating a hydrogen ion to water molecules in the solution. The water is, of course, acting as a 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 this:

$$Cr(H_2O)_6^{3+} \rightleftharpoons Cr(H_2O)_5(OH)^{2+} + H^+(aq)$$

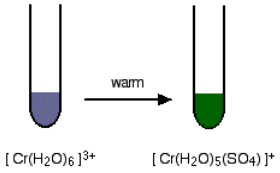
However, if you write it like this, remember that the hydrogen ion isn't just falling off the complex ion. It is being pulled off by a water molecule in the solution. Whenever you write "$H^+_{(aq)}$" what you really mean is a hydroxonium ion, H_3O^+.

Ligand exchange reactions involving chloride or sulfate ions

The hexaaquachromium(III) ion is a "difficult to describe" violet-blue-grey color. However, when it is produced during a reaction in a test tube, it is often green. 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.

Reactions of hexaaquachromium(III) ions with hydroxide ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the chromium ion.

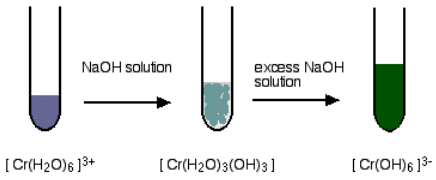
Once a hydrogen ion has been removed from three of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

$$Cr(H_2O)_6^{3+} + 3\,OH^- \longrightarrow [Cr(H_2O)_3(OH)_3](s) + 3\,H_2O$$

But the process doesn't stop there. More hydrogen ions are removed to give ions like $[Cr(H_2O)_2(OH)_4]^-$ and $[Cr(OH)_6]^{3-}$. For example:

$$[Cr(H_2O)_3(OH)_3](s) + 3\,OH^- \longrightarrow [Cr(OH)_6]^{3-}(aq) + 3\,H_2O$$

The precipitate *redissolves* because these ions are soluble in water. In the test-tube, the color changes are:



Reactions of hexaaquachromium(III) ions with ammonia solution

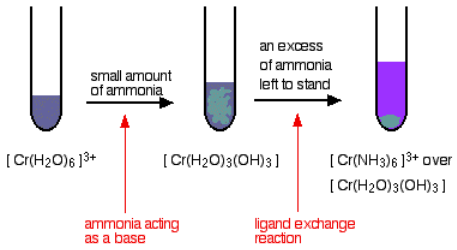
The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

$$[Cr(H_2O)_6]^{3+}(aq) + 3\,NH_3(aq) \longrightarrow [Cr(H_2O)_3(OH)_3](s) + 3\,NH_4^+(aq)$$

That precipitate dissolves to some extent if you add an excess of ammonia (especially if it is concentrated). The ammonia replaces water as a ligand to give hexaamminechromium(III) ions (this is an example of a ligand exchange reaction).

$$[Cr(H_2O)_6]^{3+}(aq) + 6\,NH_3(aq) \longrightarrow [Cr(NH_3)_6]^{3+}(aq) + 6\,H_2O(l)$$

The color changes are:



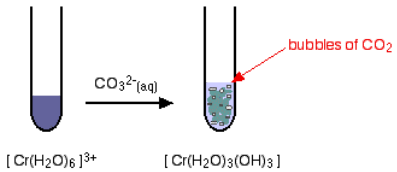
Reactions of hexaaquachromium(III) ions with carbonate ions

If you add sodium carbonate solution to a solution of hexaaquachromium(III) ions, you get exactly the same precipitate as if you added sodium hydroxide solution or ammonia solution. This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex.

Depending on the proportions of carbonate ions to hexaaqua ions, you will get either hydrogencarbonate ions formed or carbon dioxide gas from the reaction between the hydrogen ions and carbonate ions. The more usually quoted equation shows the formation of carbon dioxide.

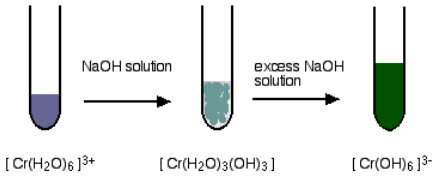
$$2\,[Cr(H_2O)_6]^{3+}(aq) + 3\,CO_3^{2-}(aq) \longrightarrow 2\,[Cr(H_2O)_3(OH)_3](s) + 3\,CO_2(g) + 3\,H_2O(l)$$

Apart from the carbon dioxide, there is nothing new in this reaction:

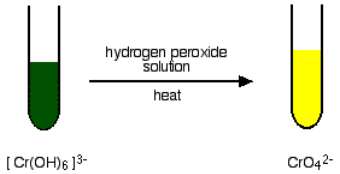


The oxidation of chromium(III) to chromium(VI)

An excess of sodium hydroxide solution is added to a solution of the hexaaquachromium(III) ions to produce a solution of green hexahydroxochromate(III) ions.



This is then oxidised by warming it with hydrogen peroxide solution. You eventually get a bright yellow solution containing chromate(VI) ions.



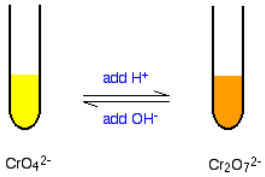
The equation for the oxidation stage is:

$$2\,[\mathrm{Cr(OH)_6}]^{3-}(\mathrm{aq}) + 3\,\mathrm{H_2O_2}(\mathrm{aq}) \longrightarrow 2\,\mathrm{CrO_4^{2-}} + 2\,\mathrm{OH^-} + 8\,\mathrm{H_2O}(\mathrm{l})$$

Some chromium(VI) chemistry

The chromate(VI)-dichromate(VI) equilibrium

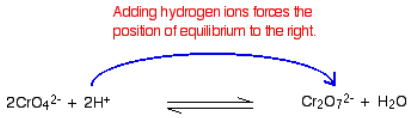
You are probably more familiar with the orange dichromate(VI) ion, $\mathrm{Cr_2O_7^{2-}}$, than the yellow chromate(VI) ion, $\mathrm{CrO_4^{2-}}$. Changing between them is easy; i f dilute sulfuric acid is added to the yellow solution it turns orange. If you add sodium hydroxide solution to the orange solution it turns yellow.



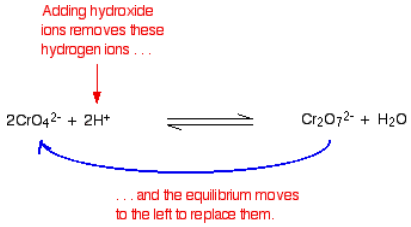
The equilibrium reaction at the heart of the interconversion is:

$$2\,\mathrm{CrO_4^{2-}} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O}$$

If you add extra hydrogen ions to this, the equilibrium shifts to the right, which is consistent with Le Chatelier's Principle.



If you add hydroxide ions, these react with the hydrogen ions. The equilibrium tips to the left to replace them.



This equilibration is also disturbed by adding base too.



Figure used with permission from Wikipedia.

Making potassium dichromate(VI) crystals

Potassium dichromate crystals can be made by a combination of the reactions we've already looked at on this page.

Starting from a source of chromium(III) ions such as chromium(III) chloride solution:

You add potassium hydroxide solution to give first a grey-green precipitate and then the dark green solution containing $[Cr(OH)_6]^{3-}$ ions. This is all described in detail further up the page. Notice that you have to use potassium hydroxide. If you used sodium hydroxide, you would end up eventually with sodium dichromate(VI).

Now you oxidize this solution by warming it with hydrogen peroxide solution. The solution turns yellow as potassium chromate(VI) is formed. This reaction is also described further up the page.

All that is left is to convert the yellow potassium chromate(VI) solution into orange potassium dichromate(VI) solution. You may remember that that is done by adding acid. This is described above if you have forgotten.

Unfortunately there is a problem here. Potassium dichromate will react with any excess hydrogen peroxide to give initially an unstable deep blue solution and it eventually gives the original chromium(III) ions again! To get around this, you first need to destroy any excess hydrogen peroxide.

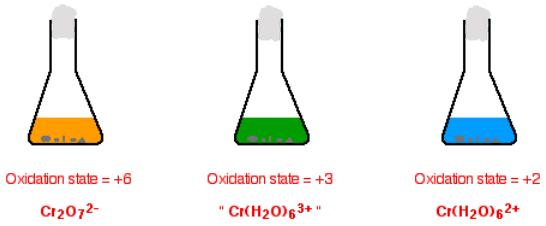
This is done by boiling the solution. Hydrogen peroxide decomposes on heating to give water and oxygen. The solution is boiled until no more bubbles of oxygen are produced. The solution is heated further to concentrate it, and then concentrated ethanoic acid is added to acidify it. Orange crystals of potassium dichromate are formed on cooling.

The reduction of dichromate(VI) ions with zinc and an acid

Dichromate(VI) ions (for example, in potassium dichromate(VI) solution) can be reduced to chromium(III) ions and then to chromium(II) ions using zinc and either dilute sulfuric acid or hydrochloric acid.

Hydrogen is produced from a side reaction between the zinc and acid. This must be allowed to escape, but you need to keep air out of the reaction. Oxygen in the air rapidly re-oxidises chromium(II) to chromium(III).

An easy way of doing this is to put a bit of cotton wool in the top of the flask (or test-tube) that you are using. This allows the hydrogen to escape, but stops most of the air getting in against the flow of the hydrogen.



The reason for the inverted commas around the chromium(III) ion is that this is a simplification. The exact nature of the complex ion will depend on which acid you use in the reduction process. This has already been discussed towards the top of the page.

Using potassium dichromate(VI) as an oxidizing agent in organic chemistry

Potassium dichromate(VI) solution acidified with dilute sulfuric acid is commonly used as an oxidising agent in organic chemistry. It is a reasonably strong oxidising agent without being so powerful that it takes the whole of the organic molecule to pieces! (Potassium manganate(VII) solution has some tendency to do that.)

It is used to:

- oxidize secondary alcohols to ketones;
- oxidize primary alcohols to aldehydes;
- oxidize primary alcohols to carboxylic acids.

For example, with ethanol (a primary alcohol), you can get either ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) depending on the conditions.

- If the alcohol is in excess, and you distil off the aldehyde as soon as it is formed, you get ethanal as the main product.

$$\mathrm{Cr_2O_7^{2-} + 8\,H^+ + 3\,CH_3CH_2OH \rightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,CH_3CHO} \qquad (4.5.1.1.1)$$

- If the oxidizing agent is in excess, and you do not allow the product to escape -e.g., by heating the mixture under reflux (heating the flask with a condenser placed vertically in the neck) - you get ethanoic acid.

$$\mathrm{2\,Cr_2O_7^{2-} + 16\,H^+ + 3\,CH_3CH_2OH \rightarrow 4\,Cr^{3+} + 11\,H_2O + 3\,CH_3COOH}$$

These equations are often simplified to concentrate on what is happening to the organic molecules. For example, the last two could be written:

$$\mathrm{CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O}$$

$$\mathrm{CH_3CH_2OH + 2\,[O] \rightarrow CH_3COOH + H_2O}$$

The oxygen written in square brackets just means "oxygen from an oxidizing agent".

Using this same reaction to make chrome alum crystals

You will find chrome alum under all sorts of different names:

- chrome alum
- potassium chromium(III) sulfate
- chromium(III) potassium sulfate
- chromium(III) potassium sulfate-12-water
- chromium(III) potassium sulfate dodecahydrate

. . . and various others!

You will also find variations on its formula. For example:

- $CrK(SO_4)_2{,}12H_2O$
- $Cr_2(SO_4)_3{,}K_2SO_4{,}24H_2O$
- $K_2SO_4{,}Cr_2(SO_4)_3{,}24H_2O$

The first of these formulae is just the other ones divided by two and rearranged a bit although the second one is easier to understand what is going on.

Chrome alum is known as a double salt. If you mix solutions of potassium sulfate and chromium(III) sulfate so that their molar concentrations are the same, the solution behaves just like you would expect of such a mixture. It gives the reactions of chromium(III) ions, of potassium ions, and of sulfate ions.

However, if you crystallise it, instead of getting mixed crystals of potassium sulfate and chromium(III) sulfate, the solution crystallizes as single deep purple crystals. These are "chrome alum". Chrome alum crystals can be made by reducing acidified potassium dichromate(VI) solution using ethanol, and then crystallizing the resulting solution. Assuming you use an excess of ethanol, the main organic product will be ethanal - and we've already seen this before (Equation 4.5.1.1.1):

$$\mathrm{Cr_2O_7^{2-} + 8\,H^+ + 3\,CH_3CH_2OH \rightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,CH_3CHO}$$

This ionic equation obviously does not contain the spectator ions, potassium and sulfate. Feeding those back in gives the full equation:

$$K_2Cr_2O_7 + 4\,HSO_4 + 3\,CH_3CH_2OH \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7\,H_2O + 3\,CH_3CHO$$

You will see that the chromium(III) sulfate and potassium sulfate are produced in exactly the right proportions to make the double salt.

In the Lab

What you do, then, is this:

You start with a solution of potassium dichromate(VI) to which has been added some concentrated sulfuric acid. The solution is then cooled by standing it in ice. An excess of ethanol is added slowly with stirring so that the temperature doesn't rise too much. When all the ethanol has been added, the solution is left over-night, preferably in a refrigerator, to crystallize. The crystals can be separated from the remaining solution, washed with a little pure water and then dried with filter paper.

Using potassium dichromate(VI) as an oxidising agent in titrations

Potassium dichromate(VI) is often used to estimate the concentration of iron(II) ions in solution. It serves as an alternative to using potassium manganate(VII) solution.

In practice

There are advantages and disadvantages in using potassium dichromate(VI).

Advantages

- Potassium dichromate(VI) can be used as a primary standard. That means that it can be made up to give a stable solution of accurately known concentration. That isn't true of potassium manganate(VII).
- Potassium dichromate(VI) can be used in the presence of chloride ions (as long as the chloride ions aren't present in very high concentration).

  Potassium manganate(VII) oxidises chloride ions to chlorine; potassium dichromate(VI) isn't quite a strong enough oxidising agent to do this. That means that you don't get unwanted side reactions with the potassium dichromate(VI) soution.

Disadvantage

- The main disadvantage lies in the color change. Potassium manganate(VII) titrations are self-indicating. As you run the potassium manganate(VII) solution into the reaction, the solution becomes colorless. As soon as you add as much as one drop too much, the solution becomes pink - and you know you have reached the end point.

  Unfortunately potassium dichromate(VI) solution turns green as you run it into the reaction, and there is no way you could possibly detect the color change when you have one drop of excess orange solution in a strongly colored green solution.

  With potassium dichromate(VI) solution you have to use a separate indicator, known as a redox indicator. These change color in the presence of an oxidising agent.

  There are several such indicators - such as diphenylamine sulfonate. This gives a violet-blue color in the presence of excess potassium dichromate(VI) solution. However, the color is made difficult by the strong green also present. The end point of a potassium dichromate(VI) titration isn't as easy to see as the end point of a potassium manganate(VII) one.

The calculation

The half-equation for the dichromate(VI) ion is:

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

. . . and for the iron(II) ions is:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Combining these gives:

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

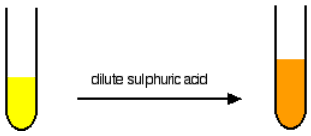
You can see that the reacting proportions are 1 mole of dichromate(VI) ions to 6 moles of iron(II) ions. Once you have established that, the titration calculation is going to be just like any other one.

Testing for chromate(VI) ions in solution

Typically, you would be looking at solutions containing sodium, potassium or ammonium chromate(VI). Most chromates are at best only slightly soluble; many we would count as insoluble. The bright yellow color of a solution suggests that it would be worth testing for chromate(VI) ions.

Testing by adding an acid

If you add some dilute sulfuric acid to a solution containing chromate(VI) ions, the color changes to the familiar orange of dichromate(VI) ions.

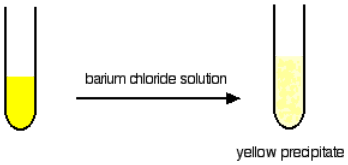


You can't rely on this as a test for chromate(VI) ions, however. It might be that you have a solution containing an acid-base indicator which happens to have the same color change!

Testing by adding barium chloride (or nitrate) solution

Chromate(VI) ions will give a yellow precipitate of barium chromate(VI).

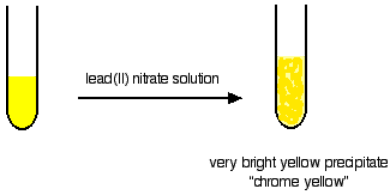
$$Ba^{2+}(aq) + CrO_4^{2+}(aq) \rightarrow BaCrO_4(s)$$



Testing by adding lead(II) nitrate solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI). This is the original "chrome yellow" paint pigment.

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$



Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 4.5.1.1: Chemistry of Chromium is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Chemistry of Chromium** by Jim Clark is licensed CC BY-NC 4.0.

4.5.1.2: Potassium Chromium Sulfate

Potassium chromium sulfate, $KCr(SO_4)_2 . 12H_2O$, or chromium alum[(1)], forms violett octaeders and is highly soluble in water.

Potassium chromium sulfate has been used in the leather industry for tanning the hides (nowadays it is replaced by basic chromium sulfate, $Cr(OH)SO_4$). The tanning process stabilizes the leather by cross linking the collagen fibers of the hide. The -COOH groups of the collagen are linked by chromium groups to form $-COO-Cr(H_2O)_4-OOC-$ bridges enhancing temperature stability (1 m^2 of cow leather contains typically about 16 g chromium).

Contributors and Attributions

- Hans Lohninger (Epina eBook Team)

4.5.1.2: Potassium Chromium Sulfate is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Potassium Chromium Sulfate** is licensed CC BY-NC-SA 4.0.

4.5.2: Chemistry of Molybdenum

The first significant practical use of this metal (discovered in 1778 by Scheele) was in the alloy used to manufacture the German artillery gun known to the Allies as Big Bertha. The metal takes its name from the Greek word molybdos, meaning "lead" because some of its compounds were once confused with similar lead compounds before Scheele's discovery. The pure metal was first isolated in 1781 by Peter Jacob Hjelm.

Chemically, molybdenum resembles a cross between Cr and W. It has a principal oxidation state of +6 although ionic compounds suggest lower states (e.g., the common ore is MoS_2).

Molybdenum contributes to the toughness and hardenability of quenched and tempered steels. It is also an essential plant nutrient. Some lands are actually barren for lack of this element in the soil.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Molybdenum** is licensed CC BY-NC-SA 4.0.

4.5.2.1: Molybdenum Disulfide

Molybdenum disulfide, MoS_2, forms a gray-black mass which is similar to graphite, both in appearance and to the touch. Like graphite MoS_2 is widely used as solid lubricant. Molybdenum disulfide occurs in nature as molybdenite (crystalline) and as jordisite (amorphous). Metallic molybdenum is produced from molybdenite.

The lubrication properties are due to a layered structure of MoS_2, where the molybdenum atoms are located between layers of sulfur atoms. The sheets of sulfur atoms exhibit only weak van der Waals interaction forces, resulting in a low coefficient of friction.

MoS_2 is diamagnetic and a semiconductor.

Contributors and Attributions

- Hans Lohninger (Epina eBook Team)

4.5.2.1: Molybdenum Disulfide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Molybdenum Disulfide** is licensed CC BY-NC-SA 4.0.

4.5.3: Chemistry of Seaborgium

The synthesis of element 106 was first reported by Soviet scientists in June of 1974. Three months later the Berkeley group claimed positive discovery of the same element. The Soviet claim was based on bombardment of three different isotopes of lead with high energy chromium-54 ions. The American group used a californium target and ions of oxygen-18. The longest lived isotope (which has no known practical uses) has a half-life of 800 milliseconds.

In early1997 the first aqueous chemistry of Sg was reported out of Germany. The most stable oxidation state in aqueous solution appears to be +6 and formation of neutral or anionic oxo or oxohalide compounds occurs just as for Mo or W. The early experiments show, as expected, that Sg is chemically like other members of group 6 and not like uranium [this goes back to an early controversy about the so-called transuranium elements: would they exhibit chemical properties similar to uranium and thus need to be removed to a separate section of the periodic table, or would they--in spite of their radioactivity--exhibit expected chemical properties of their groups? Time and research have shown the latter to be correct].

Like elements 104 and beyond, the controversy over the discovery and therefore the naming of 106 led the IUPAC to adopt the numerical symbol Unh for element 106 (unnilhexium). But in 1993 the Berkeley group gave definitive proof of their priority in synthesis and gave the name Seaborgium (Sg) after Glenn T. Seaborg. While the choice of name was lauded in general, the IUPAC was awaiting a list of names from a committee for elements 104-109. The committee rejected Seaborgium because Seaborg is still living. The Berkeley group pointed out that Einsteinium and Fermium were both named after living scientists at the time (although both died before the names were officially accepted). The committee suggested Rutherfordium (Rf) but after many complaints about the choice of names, reverted to Seaborgium.

Seaborgium is the name which the IUPAC finally approved in August 1997.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Seaborgium** is licensed CC BY-NC-SA 4.0.

4.5.4: Chemistry of Tungsten

The name for the metal tungsten is taken from the Swedish, tungsten, for "heavy stone". The symbol has its origins in the discovery of the element in the late 1700's linked to the mineral wolframite. Most German chemists still refer to the element as Wolfram (wolf's metal). Pure tungsten was eventually isolated in 1783 by brothers Juan and Fausto Elhuyar.

Tungsten is known chiefly as the metal in incandescent light bulb filaments (tungsten has the highest melting point of any metal). But a lot of tungsten is also used in the manufacture of tungsten carbide, an extremely hard material used for making cutting tools and abrasives. The metal is also alloyed with steel for very high temperature applications such as rocket engine nozzles.

Very pure tungsten is actually soft enough to be cut with an ordinary hacksaw but generally small amounts of impurities render the metal very hard and brittle. It i very similar to both Mo and Cr. It is straddled by elements having the second and third highest melting points, rhenium, Re, and tantalum, Ta.

This page deals with the extraction of tungsten from tungsten(VI) oxide, WO_3, produced from tungsten ores such as wolframite or scheelite.

Contributors and Attributions

Stephen R. Marsden

Jim Clark (Chemguide.co.uk)

Template:HideTOC

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

- **Chemistry of Tungsten** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.6: Transition Metals

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.

Topic hierarchy

4.6.1: Chemistry of Bohrium

4.6.2: Chemistry of Manganese

4.6.2.1: Chemistry of Manganese

4.6.3: Chemistry of Rhenium

4.6.4: Chemistry of Technetium

4.6: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.6.1: Chemistry of Bohrium

Element 107 (Uns) was first reported by Soviet scientists in 1976. This claim has since been substantiated by German researchers but no name was suggested and so it has been known by its numerical moniker, unnilseptium (107).

Recently, however, a committee of the IUPAC suggested the name Bohrium (after Niels Bohr). This name was finally approved in August 1997. There are no practical uses for Bohrium. All known isotopes have extremely short half-lives.

Contributors and Attributions

Stephen R. Marsden

Template:HideTOC

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

- **Chemistry of Bohrium** is licensed CC BY-NC-SA 4.0.

4.6.2: Chemistry of Manganese

The name of the 25th element comes from the Latin magnes, meaning magnet. It was discovered in 1774 by Scheele and isolated later that year by Johan Gahn. Manganese is one of the few elements that humans use on a daily basis. In 1774, a Swedish scientist named Johann Gottlieb Gahn was able to isolate manganese metal by reducing the compound of manganese dioxide. Remarkably enough, manganese has been used by humans throughout the centuries.

Introduction

In pure form Manganese is a hard, brittle, gray-white metal. It is best known as an alloying agent in steel. It enhances the ability to hot-work steel and increases resistance to impact. The Roman empire used manganese in their weapons and they were able to defeat their enemies. The hardness property of manganese helped them to create strong equipment for war. Furthermore, humans have been using manganese compounds centuries before human civilization began. The history of Manganese usage traces back to the stone age era, where nomads used it as a pigment to decorate their caves and sacred places. Manganese is an element that has helped and still helps humans to improve their personal lives in various ways.

History of Manganese

- 1771-Manganese recognized as an element by Swedish chemist Scheele
- 1774-First isolated by J.G. Gahn.
- 1799-patents granted in U.K. for using manganese in steelmaking
- 1808-Patents granted in U.k. for using manganese in steelmaking
- 1816-A German researcher observed that manganese increased the hardness of iron, without reducing its malleability or toughness.
- 1826-Prieger in Germany produced a ferromanganese containing 80% manganese in a crucible.
- 1840-J.M. Heath produced metallic manganese in England.
- 1841-Industrial-scale production of "spiegeleisen", a pig-iron containing a high percentage of manganese began.
- 1875-Commercial production of ferromanganese with a 65% manganese content. started
- 1860-Beginning of modern steel industry.
- 1868-Invention of dry cell using manganese dioxide

Where does it come from?

One may think of Manganese as initially being in metal form, however this is not the case. Manganese is not found in nature as the free metal we like to think of. Instead Manganese exists as minerals with the additions of oxides, silicates and carbonates added to the mix. Most Maganese is obtained from ores found in locations all over the world. Manganese is also known to to lie on the ocean floor in the form of nodules, which are large lumps of metallic ores.

Physical Properties

The atomic structure of Manganese includes four electron subshells.

- First subshell contains 2 electrons
- Second subshell contains 8 electrons
- Third subshell contains 13 electrons
- Four subshell contains 2 electrons

More properties of Manganese:



Symbol:	Mn
Atomic Number:	25
Mass Number:	54.93805 amu
Electron Configuration:	$[Ar]3d^5 4s^2$
Ionization Energy:	First: 717
	Second: 1509

	Third: 3248
Common Oxidation States:	+2, +3, +4, +7
Melting Point:	1245 C
Boiling Point	1862 C
Density	7470 kg/m^3

Reactions of Manganese in the world around us

Manganese is very chemically active and it has the ability to react with various elements in chemistry which we see on a day to day basis that allow for its diversity in function and uses. Because of its valence electron configuration, it allows us to use it in different and unique ways that typically other elements cannot be used in. In biological systems manganese is a crucial component of vitamin B_1.

The pure metal is produced from its most common compound (MnO_2---10th most abundant compound in the earth's crust). It can be reduced chemically or refined electrolytically. The element has at least 5 stable oxidation states with distinctive colors (as is typical of transition metals). It is commonly encountered in the laboratory as the compound $KMnO_4$ which is a strong oxidizing agent. MnO_2 catalyzes the decomposition of H_2O_2 and is sometimes used for the small scale production of oxygen gas in the lab.

Manganese and Air

By its location on the periodic table, Manganese is a little less electronegative than its neighbors which makes it a little less reactive to air. Manganese metal has the ability to burn in the presence of oxygen to form Mn_3O_4.

$$3\,\mathrm{Mn(s)} + 2\,\mathrm{O_2(g)} \rightarrow \mathrm{Mn_3O_4(s)}$$

Manganese and Nitrogen

Manganese can react in the presence of nitrogen, which is also found in the air, to form Mn_3N_2.

$$3\,\mathrm{Mn(s)} + \mathrm{N_2(g)} \rightarrow \mathrm{Mn_3N_2(s)}$$

Manganese and Water

When everything is considered under normal conditions, Manganese is not reactive with water

Manganese and Acids

Manganese dissolves readily in acidic solutions

Manganese and Halogens

Manganese reacts with the halogens of group 17 to form Manganese (II) halides. An example would be if manganese reacted with chlorine, manganese (II) chloride would form. A few example reactions are shown below, but reactions with other halogens such as with fluorine are similar.

$$Mn(s) + Cl_2(g) \rightarrow MnCl_2(s)$$

$$Mn(s) + Br_2(g) \rightarrow MnBr_2(s)$$

$$Mn(s) + I_2(g) \rightarrow MnI_2(s)$$

Nuclear chemistry of Manganese

Just like many other elements in the periodic table, specifically metals, manganese is also able to form isotopes. More isotopes than the ones listed exist. However those not shown in the table are isotopes whose half-life occur to quickly to be easily found.

Isotope	Half-life
Mn51	46.2 min
Mn52	5.591 days

Mn53	370, 000 years
Mn54	312.3 days
Mn55	stable
Mn56	2.57
Mn57	1.45 min

Uses of Manganese in our world today

Health and biology

The use of manganese in the personal health of humans and in medicine today is still as important as ever. Although many people may be wary of the importance to consume important minerals along with vitamins, many are not too familiar with the importance of the consumption of Manganese in the human diet. The existence of Manganese in the body is vital to processes on the cellular level. Without it, enzymes that are vital to life are disrupted and can cause complications in health. For example, manganese aids in the formation of connective tissue in our bodies, without it or with minimal amounts, ligaments and muscles for example are less flexible and injuries can occur more readily. However, if too much manganese is consumed then health problems such as weakness, drowsiness and even paralysis may occur. Luckily, consuming too much manganese is very rare and usually occurs to those working in mines or factories that may inhale manganese dust.

Industry and technology

The presence of Manganese in industries such as the steel industry is crucial to the success of this industry in specific. If we look back to the history of manganese presented in the beginning of this module, we can see that the use of Manganese in steel is not something recent but something from the late 1700's. Nevertheless it is still a method used today for its effects on the quality and properties of steel. Manganese is used to form an alloy in the steel which in turn results in better properties such as toughness, stiffness, wear resistance, hardness and most important strength. Manganese also helps improve the rolling and forging qualities of steel. Manganese is also responsible for coloring glass a shade of purple and can also be used in industries where glass impurities evolve due to iron impurities as Manganese can return the glass back to its normal color.

In technology, although not modern technology and as was done in 1868, Manganese is used in the invention of dry cells. It is the dioxide formed by Manganese that is used to depolarize.

Problems

1. Write out the chemical reaction between manganese and the halogen fluorine.
2. How reactive is manganese with water?
3. What is one of manganese's main uses in technology?
4. What is the electron configuration of manganese?
5. What oxidation states can manganese take?

Answers

1. $Mn_{(s)} + F_2(g) \rightarrow MnF_{2(s)}$
2. Manganese is not reactive with water under normal circumstances.
3. Manganese is known for its use in the steel industry. It is used to enhance the properties of steel to make alloys that are stronger and tougher.
4. $[Ar]3d^5 4s^2$
5. +2, +3, +4, +5, +6, +7

References

1. Pettrucci, Ralph, William Harwood, and F. Geoffrey Haring. General Chemistry: Principles and modern Applications. Upper Saddle River: Pearson Prentice Hall, 2007
2. Zumdahl, Steven S, chemistry, Fifth edition. Houghton Mifflin, New York,2000

Contributors and Attributions

- Marisol Ahumada & Abel Silva
- David Jin (UCD)

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

- **Chemistry of Manganese** is licensed CC BY-NC-SA 4.0.

4.6.2.1: Chemistry of Manganese

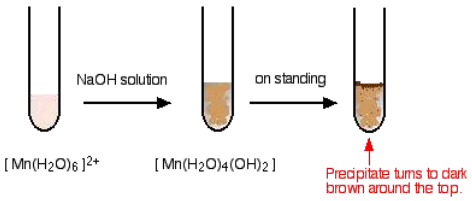
This page looks at some aspects of manganese chemistry. It includes: two simple reactions of manganese(II) ions in solution (summarized from elsewhere on the site), and the use of potassium manganate(VII) (potassium permanganate) as an oxidizing agent - including its use in titrations. The simplest ion that manganese forms in solution is the hexaaquamanganese(II) ion - $[Mn(H_2O)_6]^{2+}$.

The reaction of hexaaquamanganese(II) ions with hydroxide ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the manganese ion. Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

$$[Mn(H_2O)_6]^{2+} + 2OH^- \rightarrow [Mn(H_2O)_4(OH)_2] + 2H2O$$

In the test-tube, the color changes are:

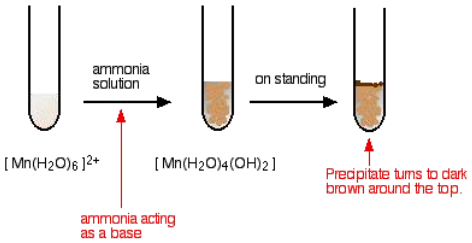


I have shown the original solution as very pale pink (the palest I can produce!), but in fact it is virtually colorless. The pale brown precipitate is oxidized to darker brown manganese(III) oxide in contact with oxygen from the air.

The reaction of hexaaquamanganese(II) ions with ammonia solution

Ammonia can act as both a base and a ligand. In this case, at usual lab concentrations, it simply acts as a base - removing hydrogen ions from the aqua complex.

$$[Mn(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Mn(H_2O)_4(OH)_2] + 2NH_4^+$$



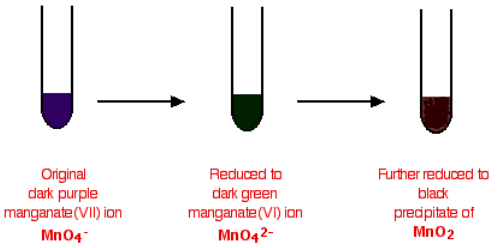
Again, I have shown the original solution as the palest pink I can produce, but in fact it is virtually colorless. The pale brown precipitate is oxidized to darker brown manganese(III) oxide in contact with oxygen from the air. There is no observable difference in appearance between this reaction and the last one.

Potassium manganate(VII) chemistry

Potassium manganate(VII) (potassium permanganate) is a powerful oxidizing agent.

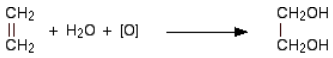
Using potassium manganate(VII) as an oxidizing agent in organic chemistry

Potassium manganate(VII) is usually used in neutral or alkaline solution in organic chemistry. Acidified potassium manganate(VII) tends to be a rather destructively strong oxidizing agent, breaking carbon-carbon bonds. The potassium manganate(VII) solution is usually made mildly alkaline with sodium carbonate solution, and the typical colour changes are:



In testing for a C=C double bond

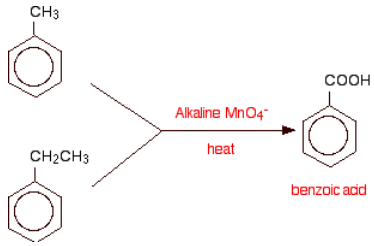
Potassium manganate(VII) oxidizes carbon-carbon double bonds, and so goes through the colour changes above. Ethene, for example, is oxidized to ethane-1,2-diol.



The oxygen in square brackets is taken to mean "oxygen from an oxidizing agent". This abbreviated form of the equation is most commonly used in organic chemistry. You are very unlikely to have to write the complete ionic equation for this reaction at this level. This isn't a good test for a carbon-carbon double bond, because anything which is even mildly reducing would have the same effect on the potassium manganate(VII) solution. You could, however, use this reaction simply as a means of making the diol.

In the oxidation of aromatic side chains

Alkaline potassium manganate(VII) solution oxidizes any hydrocarbon side chain attached to a benzene ring back to a single -COOH group. Prolonged heating is necessary. For example:



In the case of the ethyl side chain, you will also get carbon dioxide. With longer side chains, you will get all sorts of mixtures of other products - but in each case, the main product will be benzoic acid.

Using potassium manganate(VII) as an oxidizing agent in titrations

Potassium manganate(VII) solution is used to find the concentration of all sorts of reducing agents. It is always used in acidic solution. For example, it oxidizes

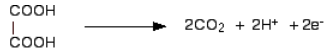
- iron(II) ions to iron(III) ions

$$Fe^{2+} \rightarrow Fe_{2+} + e-$$

- hydrogen peroxide solution to oxygen

$$H_2O_2 \rightarrow O_2 + 2H^+ 2e^-$$

- ethanedioic acid to carbon dioxide (This reaction has to be done hot.)



- sulfite ions (sulphate(IV) ions) to sulfate ions (sulfate(VI) ions)

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

In each case, the half-equation for the manganate(VII) ions in acidic solution is:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

These equations can be combined to give you an overall ionic equation for each possible reaction. That, of course, also gives you the reacting proportions. For example, when the equations are combined, you find that 1 mole of MnO_4^- ions react with 5 moles of Fe^{2+} ions. Having got that information, the titration calculations are just like any other ones.

Doing the titration

The potassium manganate(VII) solution always goes into the burette, and the other solution in the flask is acidified with dilute sulfuric acid. As the potassium manganate(VII) solution is run into the flask it becomes colourless. The end point is the first faint trace of permanent pink in the solution showing that there is a tiny excess of manganate(VII) ions present.

Problems with the use of potassium manganate(VII) solution

There are two things you need to be aware of:

- Potassium manganate(VII) cannot be used in titrations in the presence of ions like chloride or bromide which it oxidizes. An unknown amount of the potassium manganate(VII) would be used in side reactions, and so the titration result would be inaccurate. This is why you don't acidify the solution with hydrochloric acid.
- Potassium manganate(VII) isn't a primary standard. That means that it cannot be made up to give a stable solution of accurately known concentration.
- It is so strongly colored that it is impossible to see when all the crystals you have used have dissolved, and over a period of time it oxidizes the water it is dissolved in to oxygen.
- Bottles of potassium manganate(VII) solution usually have a brown precipitate around the top. This is manganese(IV) oxide - and is produced when the manganate(VII) ions react with the water.
- You have to make up a solution which is approximately what you want, and then standardize it by doing a titration. This is often done with ethanedioic acid solution, because this is a primary standard.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

This page titled 4.6.2.1: Chemistry of Manganese is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Chemistry of Manganese** by Jim Clark is licensed CC BY-NC 4.0.

4.6.3: Chemistry of Rhenium

Rhenium is a dense, silvery white metal that takes its name from the Latin, Rhenus, for the Rhine river. It was discovered in 1925 by Ida and Walter Noddack along with Otto Berg. (L. *Rhenus*: Rhine) Discovery of rhenium is generally attributed to Noddack, Tacke, and Berg, who announced in 1925 they had detected the element in platinum ore and columbite. They also found the element in gadolinite and molybdenite. By working up 660 kg of molybdenite in 1928 they were able to extract 1 g of rhenium.

Rhenium was another of the "missing" elements proposed by Mendeleev. The first sample was concentrated 100,000 fold from a gadolinium ore sample. Just enough was obtained for a spectroscopic study in which previously unseen lines were observed. The metal is acid resistant and has one of the highest melting points. But its scarcity (and therefore expense) makes practical use limited.

Contributors and Attributions

Stephen R. Marsden

- Robert Husted, Mollie Boorman

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

- **Chemistry of Rhenium** is licensed CC BY-NC-SA 4.0.

4.6.4: Chemistry of Technetium

Technetium has the distinction of being the first synthetically produced element. It was the last of the six elements predicted by Mendeleev to be discovered (in 1937 by Segrè and Perrier). Trace amounts were found in a sample of molybdenum that had been bombarded with deuterons in a cyclotron.

All known isotopes of Tc are radioactive and none appears to occur naturally on earth. However, it is produced commercially in kg quantities because very tiny amounts (55 parts per million) can transform iron into a corrosion resistant alloy. All applications of the metal involve closed systems, however, because of the radioactivity.

Pure Tc is a silvery-gray metal similar in appearance to platinum but it is normally produced in powdered form. Chemically it resembles a cross between Mn and Re. Although of little interest, compounds have been prepared in which Tc exhibits oxidation states of +4, +6 and +7.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Technetium** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.7: Transition Metals

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

Topic hierarchy

4.7.1: Chemistry of Hassium

4.7.2: Chemistry of Iron

4.7.2.1: Iron in Humans

4.7.3: Chemistry of Osmium

4.7.4: Chemistry of Ruthenium

4.7: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.7.1: Chemistry of Hassium

Like its immediate predecessors, element 108 (Hs), is of purely theoretical interest and has an extremely short half-life, decaying by spontaneous fission. It is so unstable, in fact, that it was not discovered until after element 109 had been positively confirmed.

The search for elements beyond uranium has occupied the attention of various groups of scientists around the world since the late 1940's. The principals involved hail from the laboratories at Berkeley, California, what was previously the Soviet Joint Institute for Nuclear Research at Dubna, and the Heavy-Ion Research Laboratory in Darmstadt, Germany.

Originally a committee of the IUPAC recommended that element 108 be named Hahnium, after a German scientist, Otto Hahn. That name met with some opposition and the name approved in August 1997 is Hassium, named for the German state of Hesse.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Hassium** is licensed CC BY-NC-SA 4.0.

4.7.2: Chemistry of Iron

Iron, which takes its English name from the old Anglo-Saxon and its symbol from the Latin, ferrum, was identified and used in prehistoric times. It is a very common element, fourth most abundant in the earth's crust. In addition, two of the ten most common compounds in the earth's crust are the two common oxides of iron, FeO and Fe_2O_3.

Introduction

In its pure form, iron is a silvery-white metal, distinguished by its ability to take and retain a magnetic field, and also dissolve small amounts of carbon when molten (thus yielding steel). Commercial refining of iron is based on the heating of Fe_2O_3 or Fe_3O_4 (magnetite) with a mixture of other substances in the high temperature environment of the blast furnace. The oxides are reduced to pure iron. In addition to hardening iron by adding small amounts of carbon and also some other metals to the molten iron, iron castings or forgings can be heat-treated to take advantage of the various physical properties of the different solid phases of iron.

Pure iron reacts readily with oxygen and moisture in the environment and corrodes destructively. Even alloys such as steel need protection by painting or some other coating to prevent structural failure over time.

Iron as Catalyst

The Haber Process combines nitrogen and hydrogen into ammonia. The nitrogen comes from the air and the hydrogen is obtained mainly from natural gas (methane). Iron is used as a catalyst.

$$N_{2(g)} + 3H_{2(g)} \overset{Fe}{\rightleftharpoons} 2NH_{3(g)} \tag{4.7.2.1}$$

The reaction between persulfate ions (peroxodisulfate ions), $S_2O_8^{2-}$, and iodide ions in solution can be catalyzed using either iron(II) or iron(III) ions. The overall equation for the reaction is:

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \tag{4.7.2.2}$$

For the sake of argument, we'll take the catalyst to be iron(II) ions. The reaction happens in two stages.

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+} \tag{4.7.2.3}$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \tag{4.7.2.4}$$

If you use iron(III) ions, the second of these reactions happens first. This is a good example of the use of transition metal compounds as catalysts because of their ability to change oxidation state.

Reactions of iron ions in solution

Free iron ions are compeled with water in aqueous solutions. The simplest of these complex ions are:

- the hexaaquairon(II) ion: $[Fe(H_2O)_6]^{2+}$.
- the hexaaquairon(III) ion: $[Fe(H_2O)_6]^{3+}$.

They are both acidic ions, but the iron(III) ion is more acidic.

Reactions of the iron ions with hydroxide ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the iron ions. When enough hydrogen ions have been removed, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

In the iron(II) case:

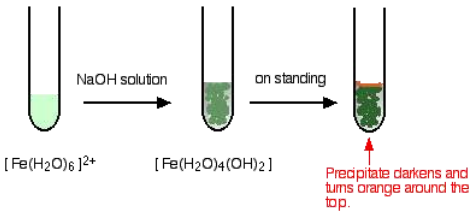
$$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O \tag{4.7.2.5}$$

In the iron(III) case:

$$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O \tag{4.7.2.6}$$

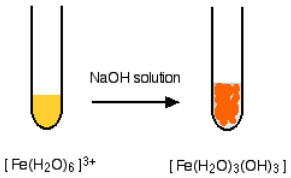
In the test-tube, the color changes are:

- In the iron(II) case:



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.

- In the iron(III) case:

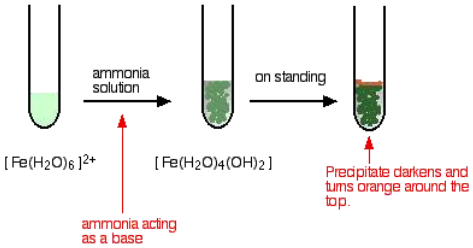


Reactions of Iron Ions with Ammonia

Ammonia can act as both a base and a ligand. In these cases, it simply acts as a base - removing hydrogen ions from the aqua complex.

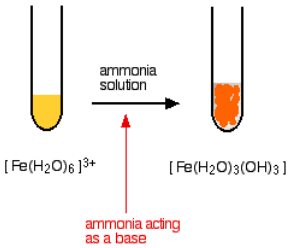
In the iron(II) case:

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$



The appearance is just the same as in when you add sodium hydroxide solution. The precipitate again changes color as the iron(II) hydroxide complex is oxidized by the air to iron(III) hydroxide. In the iron(III) case:

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$



The reaction looks just the same as when you add sodium hydroxide solution.

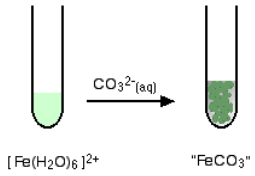
Reactions of the iron ions with carbonate ions

There is an important difference here between the behavior of iron(II) and iron(III) ions.

Iron(II) ions and carbonate ions

You simply get a precipitate of what you can think of as iron(II) carbonate.

$$Fe^{2+}(aq) + CO_3^{2-} \rightarrow FeCO_3(s)$$

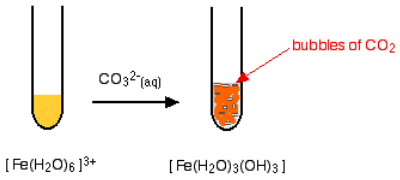


Iron(III) ions and carbonate ions

The hexaaquairon(III) ion is sufficiently acidic to react with the weakly basic carbonate ion. If sodium carbonate solution is added to a solution of hexaaquairon(III) ions, you get exactly the same precipitate as if you added sodium hydroxide solution or ammonia solution. This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex. Depending on the proportions of carbonate ions to hexaaqua ions, you will get either hydrogencarbonate ions formed or carbon dioxide gas from the reaction between the hydrogen ions and carbonate ions. The more usually quoted equation shows the formation of carbon dioxide.

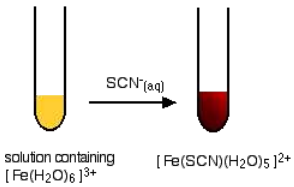
$$2[Fe(H_2O)_6^{3+} + 3CO_3^{2-} \rightarrow 2[Fe(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$$

Apart from the carbon dioxide, there is nothing new in this reaction:



Testing for iron(III) ions with thiocyanate ions

This provides an extremely sensitive test for iron(III) ions in solution. If you add thiocyanate ions, SCN^-, (e.g., from sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.



Finding the concentration of iron(II) ions in solution by Redox titration

You can find the concentration of iron(II) ions in solution by titrating with either potassium manganate(VII) solution or potassium dichromate(VI) solution. The reactions are done in the presence of dilute sulfuric acid. In either case, you would pipette a known volume of solution containing the iron(II) ions into a flask, and add a roughly equal volume of dilute sulfuric acid. What happens next depends on whether you are using potassium manganate(VII) solution or potassium dichromate(VI) solution.

Using potassium manganate(VII) solution

The potassium manganate(VII) solution is run in from a burette. At first, it turns colorless as it reacts. The end point is the first trace of permanent pink in the solution showing a tiny excess of manganate(VII) ions. The manganate(VII) ions oxidize iron(II) to iron(III) ions. The two half-equations for the reaction are:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{4.7.2.7}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \tag{4.7.2.8}$$

These combine to give the ionic equation for the reaction:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+} \tag{4.7.2.9}$$

The complete equation shows that 1 mole of manganate(VII) ions react with 5 moles of iron(II) ions. Having got that information, the titration calculations are just like any other ones.

Using potassium dichromate(VI) solution

Potassium dichromate(VI) solution turns green as it reacts with the iron(II) ions, and there is no way you could possibly detect the color change when you have one drop of excess orange solution in a strongly colored green solution. With potassium dichromate(VI) solution you have to use a separate indicator, known as a redox indicator. These change color in the presence of an oxidizing agent. There are several such indicators - such as diphenylamine sulfonate. This gives a violet-blue color in the presence of excess potassium dichromate(VI) solution.

The two half-equations are:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{4.7.2.10}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \tag{4.7.2.11}$$

Combining these gives:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + + 7H_2O + 6Fe^{3+} \tag{4.7.2.12}$$

You can see that the reacting proportions are 1 mole of dichromate(VI) ions to 6 moles of iron(II) ions. Once you have established that, the titration calculation is again going to be just like any other one.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)
- Stephen R. Marsden

This page titled 4.7.2: Chemistry of Iron is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Chemistry of Iron** by Jim Clark is licensed CC BY-NC 4.0.

4.7.2.1: Iron in Humans

Iron is an essential elements for human. **Ferritin**, an iron-storage protein found in animals and plants, contains the largest cluster currently known, an ordered aggregate $\{(FeOOH)_8(FeO\ H_2PO_4)\}_n$ containing up to 4,500 Fe(III) atoms. The cluster occurs within a protein cavity roughly 80 angstroms in diameter. Proteins in which heavy metal ions are bound directly to some of the side chains of histidine, cysteine, or some other amino acid are called metalloproteins. Two metalloproteins, transferrin and ceruloplasmin, occur in the globulin fractions of blood serum; they act as carriers of iron and copper, respectively. Transferrin has a molecular weight of 84,000 and consists of two identical subunits, each of which contains one ferric ion (Fe^{3+}) that seems to be bound to tyrosine. Several genetic variants of transferrin are known to occur in man. Another iron protein, **ferritin**, which contains 20 to 22 percent iron, is the form in which iron is stored in animals; it has been obtained in crystalline form from liver and spleen. A molecule consisting of 20 subunits, its molecular weight is approximately 480,000. The iron can be removed by reduction from the ferric (Fe3+) to the ferrous (Fe2+) state. The iron-free protein, apoferritin, is synthesized in the body before the iron is incorporated.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

4.7.2.1: Iron in Humans is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Iron in Humans** is licensed CC BY-NC-SA 4.0.

4.7.3: Chemistry of Osmium

Discovered in 1803 by Smithson Tennant (most famous for his determination that diamond is just a form of carbon), osmium is a very dense, blue-white hard metal. Its name is taken from the Greek, osme, for "odor". The oxides of osmium emit highly toxic gases and form readily when the metal is exposed to air. Thus there are few commercial applications for osmium except as a minor alloying agent where it reduces frictional wear ("osmiroid" ball point pen tips, for example).

Most osmium is recovered as a by-product of the refining of platinum and nickel ores.

Osmium tetroxide, OsO_4, is very poisonous, has a pungent smell and can cause blindness; it is a powerful oxidizing agent, and is used to stain biological materials.

Properties

Palladium is part of the the Platinum Group Metals (PGM) whic is located in the 5th and 6th rows of the transition metal section of the periodic table and includes Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum. Common characteristics include resistance to wear, oxidation, and corrosion, high melting points, and oxidation states of +2 to +4. They are generally non-toxic.

OsO_4 (Osmium Tetroxide) is a valuable catalyst in organic chemistry reactions.

- http://www.chemtube3d.com/ethene_oso4.html

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Osmium** is licensed CC BY-NC-SA 4.0.

4.7.4: Chemistry of Ruthenium

Ruthenium is a rare metal (less than 0.01 parts per million in the earth's crust). It is generally described as gray-white, hard and brittle. At room temperature it is resistant to virtually all acids. It's high melting point and brittle nature make casting difficult. Its chief commercial use is as a hardening agent in platinum jewelry.

History of Ruthenium

Element 44 (named from the Latin, ruthenia, for Russia) was originally discovered in 1807 by the Polish chemist Sniadecki, but the claim from a relative unknown was not accepted by a Paris commission and he withdrew it. It was not until 1828 that Gottfried Osann claimed to have found three new elements in his platinum samples that interest in the metal increased. Although the he could not substantiate the claim, he did not withdraw it. In 1844 Karl Klaus showed that two of Osann's metals were not new elements at all, but the third he was able to isolate and characterize.

Properties

Palladium is part of the the Platinum Group Metals (PGM) whic is located in the 5th and 6th rows of the transition metal section of the periodic table and includes Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum. Common characteristics include resistance to wear, oxidation, and corrosion, high melting points, and oxidation states of +2 to +4. They are generally non-toxic.

Applications of Ruthenium

Recently interest has grown in some compounds of ruthenium which possess the ability to convert visible light into a suitable energy source for splitting water into hydrogen and oxygen (for fuel). Work in this field is ongoing.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Ruthenium** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.8: Transition Metals

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as “cobalt blue,” and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

4.8.1: Chemistry of Cobalt
4.8.2: Chemistry of Iridium
4.8.3: Chemistry of Meitnerium
4.8.4: Chemistry of Rhodium

4.8: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.8.1: Chemistry of Cobalt

Cobalt (Co) lies with the transition metals on the periodic table. The atomic number of Cobalt is 27 with an atomic mass of 58.933195. Cobalt was first discovered in 1735 by George Brandt in Stockholm Sweden. It is used in many places today, such as, magnets materials, paint pigments, glasses, and even cancer therapy. The word cobalt is from the German word kobold, which means "goblin" or "evil spirit" this term was used by miners that was really difficult to mine and harmful to the miners health.

Physical Properties

Cobalt is a sturdy, gray metal which resembles iron and nickel. Although cobalt is ductile it is also somewhat malleable. Ductile means the metals ability to be drawn into thin wires. Malleable means is the ability of being hammered into thin sheets. Next to nickel and iron, cobalt is one of the three naturally occurring magnetic metals. When cobalt is combined with another metal to make an alloy its magnetic properties are even more apparent than the individual metal of cobalt. Cobalt's melting point is 1495 degrees C with a boiling point of 2870 degrees C. The density is 8.9 grams per cubic centimeter.

Table 1: Properties of Cobalt

Atomic Number	27
Group	9
Period	4
Mass	58.933195 g/mol
Density	8.9 $g.cm^{-3}$
Melting Point	1495 degrees C
Boiling Point	2870 degrees C
Electronegativity	1.36
Specific heat	0.568 J/mol K
Atomic Radius:	1.67Å
Covalent Radius	1.16Å
Electron Configuration	[Ar] $4s^2$ $3d^7$
Common Ions	2 (most common), 3
Crystal Structure	Hexagonal
Heat of Fusion	16.06 kJ/mol
Heat of Vaporization	377 kJ/mol

Isotopes of Cobalt

Cobalt has one naturally occurring isotope which is cobalt 59. Isotopes are two or more forms a element. Isotopes are different because of their mass number. The number written on the right of an element i.e 59 is the mass number. The mass number is the number of protons and neutrons contained in the nucleus of the atom.The number of neutrons in a atom is how elements vary, this variation is called an isotope. There are also 10 radioactive isotopes of cobalt that are currently known. A radioactive isotope which splits apart and emits radiation. Cobalt-60 is one of the most commonly used radioactive isotopes and is used in medicine to find a treat certain diseases including the *Schilling test* which determines if a patients body is making and using vitamin B_{12} effectively. Co-57,58 are also used for the same purpose. Cobalt-60 is also used to treat cancer, because the radiation it gives off kills cancer cells.

Co-56	77.3 days
Co-57	271.74 days

Co-58	70.86 days
Co-58m	9.04 hours
Co-59	Stable
Co-60	5.3 years
Co-60m	10.467 minutes
Co-61	1.7 hours

Applications of Cobalt

Cobalt's most important application is the production of super alloys. Super alloys consist of iron, cobalt, nickel, chromium, tungsten, aluminum, and titanium. Super alloys do not rust and retain their physical and chemical properties at high temperatures. Superalloys are used where metals are placed under a great deal of stress and high temperatures.Super alloys are commonly used in airplane parts such as jet engine components and gas turbines. Superalloys are used in gas turbines because is it is used to make electricity, which operates at a really high temperature. Cobalt is also used to make magnetic alloys. Cobalt magnetic alloys are used in devices that need to hold a magnetic field. An example of this is electric motors and generators. Cobalt can also be used for the production of cemented carbides. Cementation is the process where one metal is used to cover the coating of a second metal. Through the process of cementation a extremely hard, strong alloy such as those used in drilling tools is produced.

Compounds of Cobalt

Cobalt is relatively abundant in nature at around 10 to 30 parts per million. The common ores of cobalt include: cobaltite, smaltite, chloranthite, and linnaeite. The largest suppliers of cobalt are Zambia, Canada, Russia, Australia, Zaire, and Cuba. Cobalt it not currently mined in the United States.

Cobalt compounds are commonly used to make colored glass, glazes, paints, rubber, inks, cosmetics, and pottery. These compounds compounds include: cobalt oxide, cobalt potassium nitrite, cobalt aluminate, and cobalt ammonium phosphate. Cobalt compounds can also be used as catalyst. A catalyst is a substance that is used to speed up or lower a chemical reaction, by increasing or decreasing its activation energy. For all the cobalt used in the United States about 25% of them are cobalt compounds.

Health Effects of Cobalt

Cobalt is a trace mineral that the human body needs in only small amounts. When trace metals are absent in a diet this leads to health problems. Animals use trace minerals to make essential enzymes which function as catalysts. These enzymes speed up changes that occur in the human body. Enzymes are needed for living cells to function properly For example cobalt is needed for the natural production of B-12 vitamins. B-12 vitamins ensure that enough red blood cells are produced in the human body. Cobalt also affects other animals because of its lack of presence in the soil. For example sheep in Australia become infected with a disease called Coast disease, caused by cobalt deficiency. Excess cobalt can also lead to health problems. People who work around cobalt can inhale its dust which causes vomiting, diarrhea, or breathing problems. If cobalt is presence on the skin in can lead to an irritation and rash.

Chemical Properties

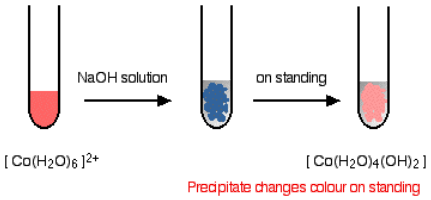
Cobalt is somewhat of a reactive element. It combines with oxygen in the air, but does not catch on fire and burn unless it is in powder form. Cobalt has the ability to react with most acids to produce hydrogen gas. However cobalt does not react with water that is at room temperature. The simplest ion that cobalt forms in solution is the pink hexaaquacobalt(II) ion - $[Co(H_2O)_6]^{2+}$. Cobalt(II) chloride is often used in humidity indicators because in dry form it is blue and when hydrated it is pink. The radioactive isotope of cobalt, Co-60, is used in portable "x-ray" devices. It actually produces gamma rays which can be used to detect internal flaws in metal in much the same way as x-rays by producing a shadowy image on film. Co-60 is also used in cancer treatment.

Ligand Exchange of hexaaquacobalt(II) ions with hydroxide ions

Hydroxide ions remove hydrogen ions from the water ligands attached to the cobalt ion. Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

$$[\mathrm{Co(H_2O)_6}]^{2+} + 2\,\mathrm{OH^-} \rightarrow [\mathrm{Co(H_2O)_4(OH)_2}] + 2\,\mathrm{H_2O}$$

In the test-tube, the color changes are:



Ligand Exchange of hexaaquacobalt(II) ions with ammonia solution

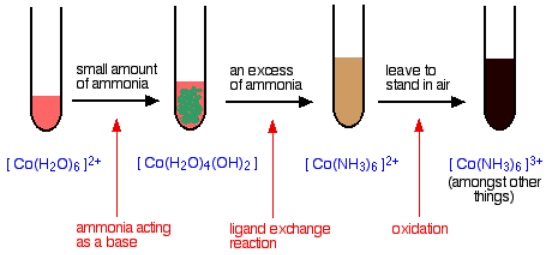
The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

$$[Co(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Co(H_2O)_4(OH)_2] + 2NH_4^+$$

That precipitate dissolves if you add an excess of ammonia. The ammonia replaces water as a ligand to give hexaamminecobalt(II) ions.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$$

The color changes are:



The hexaamminecobalt(II) complex is very easily oxidized to the corresponding cobalt(III) complex. In the test-tube this is seen as a rapid darkening to a deep red-brown solution. In fact the hexaamminecobalt(III) ion is yellow! What you see is a mixture of this ion and various other cobalt(III) ions involving ligand exchange reactions with both water molecules and negative ions present in the solution.

Another oxidation of hexaaquacobalt(II) ions

Rather than relying on oxidation by the air, you can add an oxidizing agent such as hydrogen peroxide. You can do this after the addition of ammonia as in the last case, or you can do it following addition of sodium hydroxide solution.

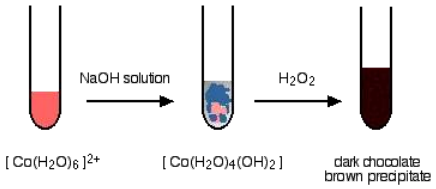
With ammonia solution and hydrogen peroxide

The reaction with ammonia solution followed by hydrogen peroxide produces the same dark reddish-brown solution as before - only faster. The equation for the oxidation of the a hexammine complex is:

$$2Co(NH_3)_6^{2+} + H_2O_2 \rightarrow 2Co(NH_3)_6^{3+} + 2OH^-$$

With sodium hydroxide solution and hydrogen peroxide

You get the variably colored precipitate of the cobalt(II) hydroxide complex when you add the sodium hydroxide solution. Addition of hydrogen peroxide produces lots of bubbles of oxygen and a dark chocolate brown precipitate.



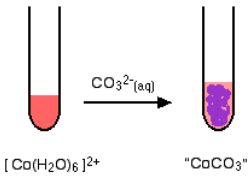
The final precipitate contains cobalt in the +3 oxidation state.

> The nature of the precipate of thie reaction is under. One resource describes it as a "hydrous Co_2O_3, i.e., cobalt(III) oxide with closely associated water. Another suggests a the priciptates is $CoO(OH)$. The oxygen seen in the reaction is produced from the decomposition of the hydrogen peroxide in a side reaction. Many things catalyze this decomposition - presumably, in this case, one or more of the various cobalt compounds present.

The reaction of hexaaquacobalt(II) ions with carbonate ions

You simply get a precipitate of what you can think of as cobalt(II) carbonate.

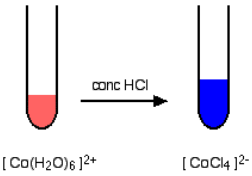
$$Co^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CoCO_3(s)$$



The the precipitate is better described as a basic carbonate with a formula of the type $xCoCO_3, yCo(OH)_2, zH_2O$. A greater discussion of general reactions between hexaaqua ions and carbonate ions is discussed elsewhere.

A ligand exchange reaction involving chloride ions

If you add concentrated hydrochloric acid to a solution containing hexaaquacobalt(II) ions, the solution turns from its original pink color to a rich blue. The six water molecules are replaced by four chloride ions.



The reaction taking place is reversible.

$$[\mathrm{Co(H_2O)_6}]^{2+} + 4\ \mathrm{Cl^-} \rightleftharpoons [\mathrm{CoCl_4}]^{2-} + 6\ \mathrm{H_2O}$$

If you add water to the blue solution, it returns to the pink color. This reaction is explored in more detail on the module addressing ligand exchange reactions.

References

1. Petrucci et al. General Chemistry: Principles & Modern Applications, 9th Edition. New Jersey: Pearson Education, Inc., 2007.
2. Newton, David. Chemical Elements. 2008-04, 2008. Print
3. "Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene - Journal of the American Chemical Society (ACS Publications)." ACS Publications - Cookie Absent. Web. 02 June 2010. <http://pubs.acs.org/doi/abs/10.1021/ja9802100>.
4. "Cobalt-catalysed Growth of Carbon Nanotubes with Single-atomic-layer Walls." Nature Publishing Group : Science Journals, Jobs, and Information. Web. 02 June 2010. <www.nature.com/nature/journal.../363605a0.html>

5. "Giant Magnetic Anisotropy of Single Cobalt Atoms and Nanoparticles -- Gambardella Et Al. 300 (5622): 1130 -- Science." Science/AAAS | Scientific Research, News and Career Information. Web. 02 June 2010. <www.sciencemag.org/cgi/conten.../300/5622/1130>.
6. "Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene - Journal of the American Chemical Society (ACS Publications)." ACS Publications - Cookie Absent. Web. 02 June 2010. <http://pubs.acs.org/doi/abs/10.1021/ja9802100>.
7. "Magnetism from the Atom to the Bulk in Iron, Cobalt, and Nickel Clusters -- Billas Et Al. 265 (5179): 1682 -- Science." Science/AAAS | Scientific Research, News and Career Information. Web. 02 June 2010. <www.sciencemag.org/cgi/conten.../265/5179/1682>.
8. In Scopus. "ScienceDirect - Journal of Catalysis : Formation of Filamentous Carbon from Iron, Cobalt and Chromium Catalyzed Decomposition of Acetylene." ScienceDirect - Home. Web. 02 June 2010. www.sciencedirect.com/science...fbd00b5adf786f

Problems

1. Is Cobalt ferromagnetic or paramagnetic?
2. What is the electron configuration of Co^{+}?
3. Who invented Cobalt? Where?
4. Why is Cobalt-60 used to treat cancer?
5. What are cobalt compounds used to make?
6. Cobalt reacts with what to produce hydrogen gas?
7. When is superalloys use preferred?
8. What are the common ores of cobalt?
9. Name one of the uses of cobalt-60, other than cancer treatment.
10. Describe the derivation of the name cobalt.

Solutions

1. Cobalt is ferromagnetic
2. $[Ar]4s^2 3d^6$
3. George Brandt in Stockholm Sweden
4. Cobalt-60 is used to treat cancer because the radiation it gives off kills cancer cells.
5. Cobalt compounds are commonly used to make colored glass, glazes, paints, rubber, inks, cosmetics, and pottery.
6. Cobalt reacts with most acids to produce hydrogen gas.
7. Superalloys are used where metals are placed under a great deal of stress and high temperatures.
8. The common ores of cobalt include: cobaltite, smaltite, chloranthite, and linnaeite
9. Cobalt-60 is used in the Schilling test which determines if a patients body is making and using vitamin B12 effectively.
10. The word cobalt is from the German word Kobold, which means "goblin" or "evil spirit" this term was used by miners that was really difficult to mine and harmful to the miners health

---

This page titled 4.8.1: Chemistry of Cobalt is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Chemistry of Cobalt** by Christine Han, Harjeet Bassi, Jim Clark is licensed CC BY-NC 4.0. Original source: https://www.chemguide.co.uk/.

4.8.2: Chemistry of Iridium

Iridium has the reputation of being the most corrosion resistant of all metals. It was discovered in 1803 by Smithson Tennant in 1803 and named for the Latin iris, or "rainbow" because it forms a large number of very colorful compounds. The pure metal is very difficult to machine into useful shapes because of its hardness and its principal use is as a hardening agent for platinum. It will withstand attack by hot aqua regia (a mixture of concentrated hydrochloric and nitric acids---which dissolves even gold) and can be used routinely at temperatures up to 2000°C.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Iridium** is licensed CC BY-NC-SA 4.0.

4.8.3: Chemistry of Meitnerium

Element 109 was first synthesized by researchers at Darmstadt, (West) Germany in August of 1983. For 10 days they hurled a beam of iron-58 ions into a bismuth-209 target. They detected the formation of one nucleus of Mt-267 which rapidly "boiled off" a neutron, reverting to Mt-266. This decayed within milliseconds to give (element 107)-262, etc. A committee of the IUPAC suggested the name Meitnerium (Mt) after the German physicist Lise Meitner. Final approval of the name and symbol was given in August 1997.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Meitnerium** is licensed CC BY-NC-SA 4.0.

4.8.4: Chemistry of Rhodium

World production of rhodium (from the Greek rhodon, "rose") is about 10 tons. While the metal itself has few applications, it is an important alloying agent used as a hardener for platinum and palladium. Rhodium was discovered in 1803 by William Hyde Wollaston who named it for the rose-red color of its salts.

Properties

Rhodium is part of the the Platinum Group Metals (PGM) whic is located in the 5th and 6th rows of the transition metal section of the periodic table and includes Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum. Common characteristics include resistance to wear, oxidation, and corrosion, high melting points, and oxidation states of +2 to +4. They are generally non-toxic. It shares the properties of these metals: high corrosion resistance, hardness and ductility. It is the rarest of the group, only occurring to the extent of about 1 part per 200 million in the earth's crust.

Contributors and Attributions

- Stephen R. Marsden
- Template:ContribChem230

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

- **Chemistry of Rhodium** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.9: Transition Metals

Group 10 metals are white to light grey in color, and possess a high luster, a resistance to tarnish (oxidation), are highly ductile, and enter into oxidation states of +2 and +4, with +1 being seen in special conditions.

Topic hierarchy

4.9.1: Chemistry of Darmstadtium
4.9.2: Chemistry of Nickel
4.9.3: Chemistry of Palladium
4.9.4: Chemistry of Platinum

4.9: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.9.1: Chemistry of Darmstadtium

As early as 1991, scientists at Berkeley reported evidence of element 110, but definitive work seems to have emerged in November of 1994 from the GSI laboratory in Darmstadt, Germany. To produce a single atom of 110, the researchers used the UNILAC accelerator to bombard a target of lead over many days with more than a billion nickel atoms. Detectors searched each collision for element 110's distinctive (predicted) decay sequence.

On August 16, 2003, at the 42nd General Assembly in Ottawa, Canada, the IUPAC Council officially approved the name for element of atomic number 110, to be known as darmstadtium, with symbol Ds. In 2001, a joint IUPAC-IUPAP Working Party (JWP) confirmed the discovery of element of atomic number 110 and this by the collaboration of Hofmann et al. from the Gesellschaft f^r Schwerionenforschung mbH (GSI) in Darmstadt, Germany (**Pure Appl. Chem.** 73, 959-967 (2001)). The most relevant experiment resulted from the fusion-evaporation using a ^{62}Ni beam on an isotopically enriched ^{208}Pb target, which produced four chains of alpha-emitting nuclides following the presumed formation of ^{269}Uun(element 110) + n. (S. Hofmann et al., **Z. Phys.** A350, 277-280 (1995)).

With the name and symbol, we now can write the reaction equation of bombardment of lead with nickel ions as:

$$^{208}\mathrm{Pb} + {}^{62}\mathrm{Ni} \rightarrow {}^{269}_{110}\mathrm{Ds} + \mathrm{n}$$

In accordance with IUPAC procedures, the discoverers at the GSI were invited to propose a name and symbol for element 110. They proposed the name **darmstadtium**, with the symbol **Ds**. Thus continues the long-established tradition of naming an element after the place of its discovery.

Contributors and Attributions

- Stephen R. Marsden
- Chung (Peter) Chieh (Chemistry, University of Waterloo)

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

- **Chemistry of Darmstadtium** is licensed CC BY-NC-SA 4.0.

4.9.2: Chemistry of Nickel

Nickel had been in use centuries before its actual discovery and isolation. As far back as 3500 BC Syrian bronzes contained a small amount of the element. In 235 BC, coins in China were minted from nickel. However there was no real documentation of the element until thousands of years later. In the 17thcentury, German miners discovered a red Colored ore they believed to contain copper. They discovered upon analysis that there was no copper but that a useless, smelly material was actually present. Thinking the ore was evil they dubbed it "Kupfernickel" or Old Nick's Copper, which meant false or bad copper. Swedish scientist Baron Axel Frederich Cronstedt in 1751 finally isolated nickel from an ore closely resembling kupfernickel. Hence, he named this new element after the traditional mineral.

At the time of its discovery nickel was thought to be useless but as its valuable properties came to light the demand for the metal increased dramatically. The usefulness of nickel as a material in alloys was eventually discovered as the strength, corrosion resistance and hardness it adds to other metals came to be appreciated. In the 1800s, the technique of silver plating was developed with a nickel-copper-zinc alloy being utilized in the process. Today, stainless steel, another nickel containing alloy, is one of the most valuable materials of the 20th century.

The U.S. five-cent piece is 25% nickel. The element is also an important alloying agent for stainless steels and in very powerful magnets. Nickel is found in the earth's crust to the extent of about 70 parts per million, about the same as copper and zinc. There is a good chance that a high proportion of the core of the earth is molten nickel.

Unlike its near neighbor copper on the periodic table, nickel is only a fair electrical conductor. But like its other neighbor, cobalt, it is very useful in making strong permanent magnets. It is also highly resistant to attack by alkalis and is used to store and transport concentrated sodium and potassium hydroxide. Nickel reacts with most acids to produce hydrogen gas and the green Ni2+ ion.

Occurrence

Nickel is the earth's 22nd most abundant element and the 7th most abundant transition metal. It is a silver white crystalline metal that occurs in meteors or combined with other elements in ores. Two important groups of ores are:

1. Laterites: oxide or silicate ores such as garnierite, $(Ni, Mg)_6\ Si_4O_{10}OH)_8$ which are predominantly found in tropical areas such as New Caledonia, Cuba and Queensland.
2. Sulfides: these are ores such as pentlandite, which contain about 1.5%, nickel associated with copper, cobalt and other metals. They are predominant in more temperate regions such as Canada, Russia and South Africa.

Canada is the world's leading nickel producer and the Sudbury Basin of Ontario contains one of the largest nickel deposits in the world.

In 1899 Ludwig Mond developed a process for extracting and purifying nickel. The so-called "Mond Process" involves the conversion of nickel oxides to pure nickel metal. The oxide is obtained from nickel ores by a series of treatments including concentration, roasting and smelting of the minerals.

In the first step of the process, nickel oxide is reacted with water gas, a mixture of H_2 and CO, at atmospheric pressure and a temperature of 50 °C. The oxide is thus reduced to impure nickel. Reaction of this impure material with residual carbon monoxide gives the toxic and volatile compound, nickel tetracarbonyl, $Ni(CO)_4$. This compound decomposes on heating to about 230 °C to give pure nickel metal and CO, which can then be recycled. The actual temperatures and pressures used in this process may very slightly from one processing plant to the next. However the basic process as outlined is common to all.

The process can be summarized as follows:

$$\mathrm{Ni} + 4\,\mathrm{CO} \xrightarrow{50^\circ C} \underbrace{\mathrm{Ni(CO)_4}}_{impure} \xrightarrow{230^\circ C} \underbrace{\mathrm{Ni}}_{pure} + 4\,\mathrm{CO}$$

Properties

Nickel is a hard silver white metal, which occurs as cubic crystals. It is malleable, ductile and has superior strength and corrosion resistance. The metal is a fair conductor of heat and electricity and exhibits magnetic properties below 345°C. Five isotopes of nickel are known.

In its metallic form nickel is chemically unreactive. It is insoluble in cold and hot water and ammonia and is unaffected by concentrated nitric acid and alkalis. It is however soluble in dilute nitric acid and sparingly soluble in dilute hydrochloric and sulfuric acids.

Nickel Compounds

Nickel is known primarily for its divalent compounds since the most important oxidation state of the element is +2. There do exist however certain compounds in which the oxidation state of the metal is between -1 to +4. Blue and green are the characteristic colors of nickel compounds and they are often hydrated.

Nickel hydroxide usually occurs as green crystals that can be precipitated when aqueous alkali is added to a solution of a nickel (II) salt. It is insoluble in water but dissolves readily in acids and ammonium hydroxide.

Nickel oxide is a powdery green solid that becomes yellow on heating. It is difficult to prepare this compound by simply heating nickel in oxygen and it is more conveniently obtained by heating nickel hydroxide, carbonate or nitrate. Nickel oxide is readily soluble in acids but insoluble in hot and cold water.

Nickel oxides

Thermal decomposition of $Ni(OH)_2$, $NiCO_3$, or $NiNO_3$ generates NiO.

Formula	Color	Oxidation State	MP	Structure / comments
NiO	green powder	Ni^{2+}	1955	NaCl

Nickel sulfides consist of NiS_2, which has a pyrite structure, and Ni_3S_4, which has a spinel structure.

All the nickel dihalides are known to exist. These compounds are usually yellow to dark brown in Color. Preparation directly from the elements is possible for all except NiF_2, which is best prepared from reaction of F_2on $NiCl_2$ at 350°C. Most are soluble in water and crystallization of the hexahydrate containing the $[Ni(H_2O)_6]^{2+}$ion can be achieved. NiF_2however is only slightly soluble in water from which the trihydrate crystallizes. The only nickel trihalide known to exist is an impure specimen of NiF_3.

Table: Nickel(II) halides Properties

Formula	Color	MP	μ (BM)	Structure
NiF_2	yellow	1450	2.85	tetragonal rutile
$NiCl_2$	yellow	1001	3.32	$CdCl_2$
$NiBr_2$	yellow	965	3.0	$CdCl_2$
NiI_2	Black	780	3.25	$CdCl_2$

Preparations

Nickel carbonate usually occurs as a light green crystalline solid or a brown powder. It dissolves in ammonia and dilute acids but is insoluble in hot water. It exhibits vigorous reaction with iodine, hydrogen sulphide or a mixture of barium oxide and air. It decomposes on heating before melting occurs.

$$Ni + F_2 \ 55°C \ /slow \rightarrow NiF_2$$
$$Ni + Cl_2 \ EtOH/ \ 20°C \rightarrow NiCl_2$$
$$Ni + Br_2 \ red \ heat \rightarrow NiBr_2$$
$$NiCl_2 + 2NaI \rightarrow NiI_2 + 2NaCl$$

Nickel carbonyl is a colorless, volatile, liquid. It is soluble in alcohol, benzene, and nitric acid but only slightly soluble in water, and insoluble in dilute acids and alkalis. Upon heating or in contact with acid or acid fumes, nickel carbonyl emits toxic carbon monoxide gas, a property exploited in preparation of nickel metal. When exposed to heat or flame the compound explodes and it can react violently with air, oxygen and bromine.

Identification of nickel compounds can be achieved by employing the use of an organic reagent dimethylglyoxine. This compound forms a red flocculent precipitate on addition to a solution of a nickel compound.

Nickel complexes

The Nickel (II) ion forms many stable complexes as predicted by the Irving Williams series. Whilst there are no other important oxidation states to consider, the Ni(II) ion can exist in a wide variety of CN's which complicates its coordination chemistry. For example, for CN=4 both tetrahedral and square planar complexes can be found. For CN=5 both square pyramid and trigonal bipyramid complexes are formed.

The phrase *"**anomalous nickel**"* has been used to describe this behavior and the fact that equilibria often exist between these forms. Some examples include:

1. addition of ligands to square planar complexes to give 5 or 6 coordinate species
2. monomer/polymer equilibria
3. square-planar/ tetrahedron equilibria
4. trigonal-bipyramid/ square pyramid equilibria.

(a) substituted acacs react with Ni^{2+} to give green dihydrates (6 coordinate). On heating, the two coordinated water groups are generally removed to give tetrahedral species. The unsubstituted acac complex, $Ni(acac)_2$ normally exists as a trimer, see below. Lifschitz salts containing substituted 1,2-diaminoethanes can be isolated as either 4 or 6 coordinate species depending on the presence of coordinated solvent.

(b) $Ni(acac)_2$ is only found to be monomeric at temperatures around 200°C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine, but in the solid state $Ni(acac)_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $Co(acac)_2$ actually exists as a tetramer.

$[Ni(acac)_2]_3$ $[Co(acac)_2]_4$

(c) Complexes of the type NiL_2X_2, where L are phosphines, can give rise to either tetrahedral or square planar complexes. It has been found that:

- L=P(aryl)3 are tetrahedral
- L=P(alkyl)3 are square planar

for L= mixed aryl and alkyl phosphines, both stereochemistries can occur in the same crystalline substance. The energy of activation for conversion of one form to the other has been found to be around 50kJ mol^{-1}. Similar changes have been observed with variation of the X group:

$Ni(P\Phi_3)_2Cl_2$	green	tetrahedral	μ =2.83 BM
$Ni(P\Phi_3)_2(SCN)_2$	red	sq. planar	μ =0 BM

where Φ is shorthand for C_6H_5. Ni^{2+}reacts with CN- to give $Ni(CN)_2.nH_2O$ (blue-green) which on heating at 180-200°C is dehydrated to yield $Ni(CN)_2$. Reaction with excess KCN gives $K_2Ni(CN)_4.H_2O$ (orange crystals) which can be dehydrated at 100°C. Addition of strong concentrations of KCN produces red solutions of $Ni(CN)_5^{3-}$.

The crystal structure of the double salt prepared by addition of $Cr(en)_3^{3+}$to $Ni(CN)_5^{3-}$ showed that two types of Ni stereochemistry were present in the crystals in approximately equal proportions. 50% as square pyramid and 50% as trigonal bipyramid.

Uses of Nickel and its Compounds

The primary use of nickel is in the preparation of alloys such as stainless steel, which accounts for approximately 67% of all nickel used in manufacture. The greatest application of stainless steel is in the manufacturing of kitchen sinks but it has numerous other uses as well. Other nickel alloys also have important applications. An alloy of nickel and copper for example is a component of the tubing used in the desalination of sea water. Nickel steel is used in the manufacture of armor plates and burglar proof vaults. Nickel alloys are especially valued for their strength, resistance to corrosion and in the case of stainless steel for example, esthetic value.

Electroplating is another major use of the metal. Nickel plating is used in protective coating of other metals. In wire form, nickel is used in pins, staples, jewelry and surgical wire. Finely divided nickel catalyzes the hydrogenation of vegetable oils. Nickel is also used in the coloring of glass to which it gives a green hue.

Other applications of nickel include:

1. Coinage

2. Transportation and construction
3. Petroleum industry
4. Machinery and household appliances
5. Chemical industry.

Nickel compounds also have useful applications. Ceramics, paints and dyes, electroplating and preparation of other nickel compounds are all applications of these compounds. Nickel oxide for example is used in porcelain painting and in electrodes for fuel cells. Nickel acetate is used as a mordant in the textiles industry. Nickel carbonate finds use in ceramic colors and glazes.

Nickel and Human Health

For an account of the limited information known about the role of nickel in human health see

- www.nutrition.org/nutinfo/
- www.vitaminsplus.com/vplus/nickel.htm
- Nickel utilisation in microorganisms - 1987 review

The first crystallization of an enzyme was reported in the 1920's. The enzyme was urease which converts urea to ammonia and bicarbonate. One source of the enzyme is the bacterium *Helicobacter Pylori*. The release of ammonia is beneficial to the bacterium since it partially neutralizes the very acidic environment of the stomach (whose function in part helps kill bacteria). In the initial study it was claimed that there were no metals in the enzyme. Fifty years later this was corrected when it was discovered that nickel ions were present and an integral part of the system. The Nobel Prize in Physiology or Medicine for 2005 was awarded to Barry J. Marshall and J. Robin Warren "for their discovery of the bacterium *Helicobacter pylori* and its role in gastritis and peptic ulcer disease".

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

This page titled 4.9.2: Chemistry of Nickel is shared under a not declared license and was authored, remixed, and/or curated by Robert J. Lancashire.

- **Chemistry of Nickel** by Robert J. Lancashire is licensed CC BY-NC-SA 4.0.

4.9.3: Chemistry of Palladium

Discovered in 1803 by William Wollaston and named after the recently discovered asteroid Pallas, palladium is a silvery-white, soft metal similar to platinum. It is a rare metal (only about 1 part per million in the earth) but occurs commonly along with copper, silver and gold.

Properties

Palladium is part of the the Platinum Group Metals (PGM) whic is located in the 5th and 6th rows of the transition metal section of the periodic table and includes Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum. Common characteristics include resistance to wear, oxidation, and corrosion, high melting points, and oxidation states of +2 to +4. They are generally non-toxic.

- Serves as the substitute catalysis for platinum in catalytic converters.
- The primary catalyst for liquid-phase hydrogenation.
- In the late 1960's, 60% of all palladium production is used in the telephone industry in the form of cross-over contacts in telephone lines. Since the shift to a fully-electronic system, palladium use has declined.
- With the possible dawn of an alternate technology in motorized vehicles, palladium has garnered a lot of attention as a possible player in fuel cell technology.
- As the price and scarcity of platinum increases, palladium has become more marketable as the primary catalyst in combustion engines.

Palladium is used as an alloying agent with gold in jewelry ("white gold") and in some dental applications in place of silver or gold. Unlike the other so-called platinum metals, palladium is more susceptible to attack by acids, even hydrochloric acid.

$$\mathrm{Pd_{(s)} + 2\,HCl \rightarrow Pd^{2+} + H_{2\,(g)} + 2\,Cl^{-}_{(aq)}}$$

"Cold Fusion"

Palladium has the curious ability to absorb large quantities of hydrogen gas (up to 900 times its own volume) and this has generated some interest in its alloys as a storage system for hydrogen as a portable fuel for automobiles. It was also prominent in the "cold fusion" controversy some years ago when it was said (apparently falsely) that when it was made to absorb heavy hydrogen (deuterium), the atoms would undergo fusion and release more energy than was put into the process.

Contributors and Attributions

- Stephen R. Marsden
- Template:ContribChem230

Template:HideToc

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

- **Chemistry of Palladium** is licensed CC BY-NC-SA 4.0.

4.9.4: Chemistry of Platinum

Independently discovered in 1735 by Antonio de Ulloa and in 1741 by Charles Wood, platinum is named from the Spanish platina or "silver". The metal is classified as precious owing to its scarcity and commercial demand. It is very heavy and silvery white and is used in laboratory instruments, jewelry, medical and dental items, and electrical contacts. Because it is immune to air oxidation the metal is often found in native form in nature. It is sometimes found in a rare, naturally occurring alloy, platiniridium.

Naturally occurring platinum is a mixture of six non-radioactive isotopes.

Properties

Platinum is part of the the Platinum Group Metals (PGM) whic is located in the 5th and 6th rows of the transition metal section of the periodic table and includes Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum. Common characteristics include resistance to wear, oxidation, and corrosion, high melting points, and oxidation states of +2 to +4. They are generally non-toxic.

- Platinum has a very high melting point, so it is often used to make containers to hold molten substances.
- Jewelers use platinum as plating and decoration because of its high ductibility.
- 80-90% of platinum uses are in the industrial or metellurgical industries.
- Platinum is a catalyst in the oxidation of ammonia (to nitric oxide) in the creation of nitric acid, which is a major ingredient in fertilizers.
- An estimated 200,000 ounces of gauze consisting of 90% platinum and 10% rhodium is used in the oxidation of ammonia for the production of nitric acid.
- Regarding pollution control, platinum works as a great oxidation catalyst for removing harmful chemicals in wire enamelling, abattoirs, meat and fish processing, and in nitric oxides released in hydrocarbon reactions.
- Platinized-anodes are used in the production of elemental chlorine.

Contributors and Attributions

- Stephen R. Marsden
- Template:ContribChem230

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

- **Chemistry of Platinum** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.10: Transition Metals

The “coinage metals”, copper, silver, and gold, have held great importance in societies throughout history, both symbolically and practically. For centuries, silver and gold have been worn by royalty to parade their wealth and power. On occasion, these metals were even used in art. Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.

Topic hierarchy

4.10.1: Chemistry of Copper
4.10.2: Chemistry of Gold
4.10.3: Chemistry of Roentgenium
4.10.4: Chemistry of Silver
4.10.4.1: Silver Chloride
4.10.4.2: Silver Nitrate

4.10: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.10.1: Chemistry of Copper

Copper occupies the same family of the periodic table as silver and gold, since they each have one s-orbital electron on top of a filled electron shell which forms metallic bonds. This similarity in electron structure makes them similar in many characteristics. All have very high thermal and electrical conductivity, and all are malleable metals. Among pure metals at room temperature, copper has the second highest electrical and thermal conductivity, after silver.

Introduction

The use of Copper dates back far into history. Copper beads have been found in what is now modern Iraq, dating back to 9000 BC. The metal is relatively easy to mine and refine, contributing to its early and widespread use. Being soft, however, it is unsuitable for making reliable tools and weapons. Early metalsmiths as far back as 3000 BC learned to combine copper with other metals to produce more durable alloys. Brass (copper and zinc) and bronze (copper and tin) are two examples. The symbol and name for copper are from the Latin *cuprum*, which literally means "from the island of Cyprus", an early source of copper ore.

Before 1982 U.S. pennies were pure copper. Now they are mostly zinc with a thin shell of copper. Most copper that is mined today is refined and drawn into wire for use in the electrical industries. A significant portion is also used in manufacturing water pipe. Copper, of course, has a characteristic color which most people recognize. It is one of the best electrical conductors and resists corrosion from most acids (except nitric and hot concentrated sulfuric). When exposed to the elements for a period of time it develops a greenish coating or patina which is copper(II) carbonate, a protective coating that prevents further wear.

Occurrence and extraction of Copper

Copper occurs both in combined state and free state and also in many ores. The important ores of copper are copper pyrites ($CuFeS_2$), cuprite and copper glance. The copper ores are mostly found in the north of India. The extraction of copper also involves many steps. The ore used for extraction is copper pyrites, which is crushed, concentrated and then heated in the presence of air. During heating the moisture gets expelled and the copper pyrites gets converted to ferrous sulfide and cuprous sulfide.

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

Blast furnace is used to heat the mixture of roasted ore, powdered coke and sand. In the blast furnace oxidation reactions takes place. Ferrous sulfide forms ferrous oxide which combines with silica and forms the slag ($FeSiO_2$).

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

Cuprous sulfide forms cuprous oxide which is partially converted to cuprous sulfide.

$$Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

This cuprous sulfide contains some amount of ferrous sulfide and this is called matte. Matte is removed from the base outlet of blast furnace. The removed matte is shifted into Bessemer converter which is lined inside with magnesium oxide. This converter has pipes through which hot air and SiO_2 are sent in. In this converter Cu_2S converts to Cu_2O and FeS converts to FeO. The ferrous oxide forms slag with SiO_2. The cuprous oxide formed reacts with Cu2S and forms copper.

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

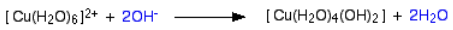
The copper thus formed is to be purified by electrolysis.

Reactions of copper(II) ions in solution

The simplest ion that copper forms in solution is the typical blue hexaaquacopper(II) ion - $[Cu(H_2O)_6]^{2+}$.

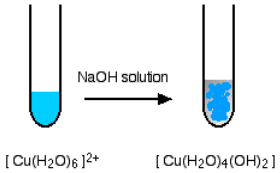
Reactions of hexaaquacopper(II) ions with Hydroxide Ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the copper ion. Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.



The color coding is to show that this is not a ligand exchange reaction. The oxygens which were originally attached to the copper are still attached in the neutral complex.

In the test-tube, the color change is:



Reactions of hexaaquacopper(II) ions with ammonia solution

The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

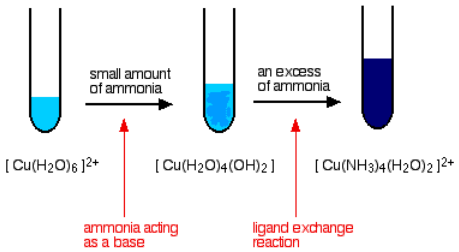
That precipitate dissolves if you add an excess of ammonia. The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions. Notice that only 4 of the 6 water molecules are replaced.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O$$

Note

You might wonder why this second equation is given starting from the original hexaaqua ion rather than the neutral complex. Explaining why the precipitate redissolves is quite complicated. You will find the explanation in full on the page about the reactions between hexaaqua ions and ammonia solution.

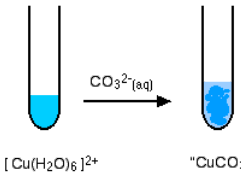
The color changes are:



The reaction of hexaaquacopper(II) ions with carbonate ions

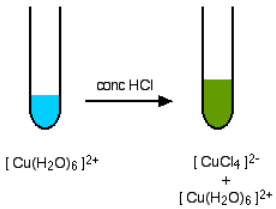
You simply get a precipitate of what you can think of as copper(II) carbonate.

$$Cu^{2+} + CO_3^{2-} \rightarrow CuCO_3(s)$$



A ligand exchange reaction involving chloride ions

If you add concentrated hydrochloric acid to a solution containing hexaaquacopper(II) ions, the six water molecules are replaced by four chloride ions.



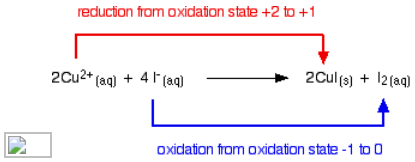
The reaction taking place is reversible.

$$Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

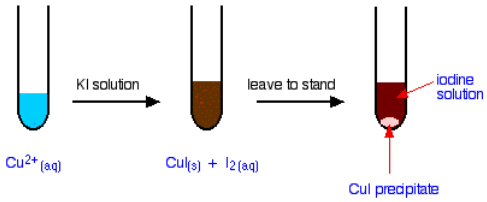
Because the reaction is reversible, you get a mixture of colors due to both of the complex ions. The color of the tetrachlorocuprate(II) ion may also be described as olive-green or yellow. If you add water to the green solution, it returns to the blue color.

The reaction of hexaaquacopper(II) ions with iodide ions

Copper(II) ions oxidize iodide ions to molecular iodine, and in the process are themselves reduced to copper(I) iodide.



The initial mucky brown mixture separates into an off-white precipitate of copper(I) iodide under an iodine solution.



Using this reaction to find the concentration of copper(II) ions in solution

If you pipette a known volume of a solution containing copper(II) ions into a flask, and then add an excess of potassium iodide solution, you get the reaction we have just described.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2(aq)$$

You can find the amount of iodine liberated by titration with sodium thiosulphate solution.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

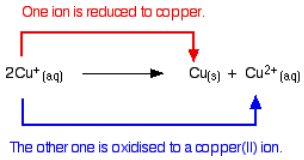
As the sodium thiosulfate solution is run in from a burette, the color of the iodine fades. When it is almost all gone, you add some starch solution. This reacts reversibly with iodine to give a deep blue starch-iodine complex which is much easier to see.

You add the last few drops of the sodium thiosulfate solution slowly until the blue color disappears. If you trace the reacting proportions through the two equations, you will find that for every 2 moles of copper(II) ions you had to start with, you need 2 moles of sodium thiosulfate solution. If you know the concentration of the sodium thiosulfate solution, it is easy to calculate the concentration of the copper(II) ions.

Some essential copper(I) chemistry

The disproportionation of copper(I) ions in solution

Copper(I) chemistry is limited by a reaction which occurs involving simple copper(I) ions in solution. This is a good example of disproportionation - a reaction in which something oxidises and reduces itself. Copper(I) ions in solution disproportionate to give copper(II) ions and a precipitate of copper. The reaction is:



Any attempt to produce a simple copper(I) compound in solution results in this happening. For example, if you react copper(I) oxide with hot dilute sulfuric acid, you might expect to get a solution of copper(I) sulfate and water produced. In fact you get a brown precipitate of copper and a blue solution of copper(II) sulfate because of the disproportionation reaction.

$$Cu_2O + H_2SO_4 \rightarrow Cu + CuSO_4 + H_2O$$

Stabilizing the copper(I) oxidation state

We've already seen that copper(I) iodide is produced as an off-white precipitate if you add potassium iodide solution to a solution containing copper(II) ions. The copper(I) iodide is virtually insoluble in water, and so the disproportionation reaction does not happen. Similarly copper(I) chloride can be produced as a white precipitate (reaction described below). Provided this is separated from the solution and dried as quickly as possible, it remains white. In contact with water, though, it slowly turns blue as copper(II) ions are formed. The disproportionation reaction only occurs with simple copper(I) ions in solution.

Forming copper(I) complexes (other than the one with water as a ligand) also stabilizes the copper(I) oxidation state. For example, both $[Cu(NH_3)_2]^+$ and $[CuCl_2]^-$ are copper(I) complexes which do not *disproportionate*. The chlorine-containing complex is formed if copper(I) oxide is dissolved in concentrated hydrochloric acid. You can think of this happening in two stages. First, you get copper(I) chloride formed:

$$Cu_2O_{(s)} + 2HCl_{(aq)} \rightarrow 2CuCl_{(s)} + H_2O_{(l)}$$

But in the presence of excess chloride ions from the HCl, this reacts to give a stable, soluble copper(I) complex.

$$CuCl_{(s)} + Cl^-_{(aq)} \rightarrow [CuCl_2]^-_{(aq)}$$

You can get the white precipitate of copper(I) chloride (mentioned above) by adding water to this solution. This reverses the last reaction by stripping off the extra chloride ion.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)
- Binod Shrestha (University of Lorraine)

This page titled 4.10.1: Chemistry of Copper is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jim Clark.

- **Chemistry of Copper** by Jim Clark is licensed CC BY-NC 4.0.

4.10.2: Chemistry of Gold

On average, a million tons of earth contain just ten pounds of gold. This scarcity, as well as its beauty and chemical properties account for its high value from ancient times. The name for the element is of Anglo-Saxon origin and the symbol comes from the Latin aurum, meaning "shining dawn".

Gold metal has a distinctive yellow color and is incredibly malleable and ductile. A single ounce of pure gold can be beaten out to a sheet that is about 300 feet square!! Pure gold is easily cut with a knife. Few elements react with gold under normal conditions and so most gold is recovered as small flakes of the pure element.

Gold is a very good conductor and is often used to plate electrical contacts since it resists corrosion so well. It also is a good reflector of heat-carrying infra-red radiation.

The world's oceans contain billions of tons of gold but it is too widely dispersed to be recovered (two-tenths of an ounce per million tons of water).

Gold will not react with either $H_2SO_{4(aq)}$ or $HNO_{3(aq)}$, rather it will react with what is called *aqua regia*, which is one part HNO_3 and three parts HCl. For example,

$$Au_{(s)} + 4H^+_{(aq)} + NO^-_{3(aq)} + 4Cl^-_{(aq)} \rightarrow [AuCl_4]^-_{(aq)} + 2H_2O_{(l)} + NO_{(g)}$$

Note: The group 11 metals do not react with hydrochloric acid.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Gold** is licensed CC BY-NC-SA 4.0.

4.10.3: Chemistry of Roentgenium

Announcement of the discovery of element 111 was made in the popular press in January of 1995. Reports from the GSI labs in Germany indicate that nickel ions were used to bombard a bismuth target. The IUPAC in 2004 confirmed the discovery by S. Hoffmann and his coworkers in Darmstadt, Germany. The researchers proposed the name Roentgenium, with symbol Rg. Final approval was given in November 2004.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Roentgenium** is licensed CC BY-NC-SA 4.0.

4.10.4: Chemistry of Silver

Silver (name from the Anglo-Saxon sioful, symbol from the Latin argentium) is considered a precious metal. It is found only to the extent of 0.05 parts per million in the earth (i.e., you have to dig up 20 million shovels full of dirt to get one shovel full of silver!). Knowledge of the metal is of ancient origins. Refining methods are mentioned in the Hebrew scriptures and ancient Egyptian writing. Silver was once considered more valuable than gold, probably because gold was easier to locate and refine at the time. Silver is ten times more abundant than gold.

Contributors and Attributions

Stephen R. Marsden

Binod Shrestha (University of Lorraine)

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

- **Chemistry of Silver** is licensed CC BY-NC-SA 4.0.

4.10.4.1: Silver Chloride

Silver chloride, AgCl, is a white crystalline solid which is well known for its low solubility in water. AgCl occurs naturally as the mineral chlorargyrite. Silver chloride converts to silver and chlorine, when subjected to sunlight or heating.

AgCl adopts the fcc NaCl structure, in which Ag^+ ions are surrounded by octahedrons of six chloride ligands.

Contributors and Attributions

- Hans Lohninger (Epina eBook Team)

4.10.4.1: Silver Chloride is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Silver Chloride** is licensed CC BY-NC-SA 4.0.

4.10.4.2: Silver Nitrate

Silver nitrate, $AgNO_3$, is the least expensive silver salt and is relatively stable to light. It easily dissolves in water (2150 g/L at 20 °C). As the nitrate can be easily replaced by other ligands $AgNO_3$ is a versatile starting point for the synthesis of other silver compounds.

Silver nitrate can be prepared by dissolving silver in with nitric acid:

$3\ Ag + 4\ HNO_3 \longrightarrow 3\ AgNO_3 + NO + 2\ H_2O$

When a sheet of copper is put into a silver nitrate solution, the silver nitrate reacts with copper to form hairlike crystals of metallic silver and a blue solution of copper nitrate:

$2\ AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\ Ag$

$AgNO_3$ reacts with solutions of halide ions to give a precipitate of AgX (X = Cl, Br, I), which are used in photographic films.

When heated, silver nitrate decomposes into metallic silver, oxygen and nitrogen oxide:

$2\ AgNO_3 \longrightarrow 2\ Ag + O_2 + 2\ NO_2$

Silver salts have antimicrobial properties and are commonly used to disinfect drinking water. When diluted silver nitrate is braught into contact with skin, the skin becomes brown/black after a short time due to elementary silver which is introduced into the skin according to the following reaction:

$AgNO_3 + H\ (\text{from the skin}) \longrightarrow Ag + HNO_3$

Concentrated solutions of $AgNO_3$ will cause burns due to the same reaction.

Contributors and Attributions

- Hans Lohninger (Epina eBook Team)

4.10.4.2: Silver Nitrate is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Silver Nitrate** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

4.11: Transition Metals

Group 12 elements have partially filled (n − 1)d subshells, and hence are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Group 12 metals tend have low melting and boiling points (due to the weak metallic bonding of the ns^2 electrons) and charges of +2 or +1.

Topic hierarchy

- 4.11.1: Chemistry of Cadmium
  - 4.11.1.1: Cadmium Sulfide
- 4.11.2: Chemistry of Copernicium
- 4.11.3: Chemistry of Mercury
- 4.11.4: Chemistry of Zinc

4.11: Transition Metals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.11.1: Chemistry of Cadmium

This module is created to provide information about Cadmium, which can be very helpful to know as this transition metal is poisonous and can harm those who do not handle it with caution.

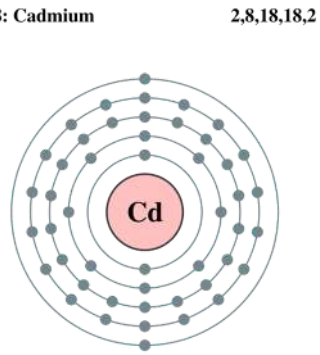
Introduction

Cadmium, a transition metal, has the chemical symbol of Cd. Cadmium is located in the d-block and 12 group of the periodic table possessing an atomic number of 48 and an atomic mass of 112.411g. Cadmium was discovered in Germany in 1817, by a German scientist, Friedrich Strohmeyer. This element was very commonly used as a sacrificial anode to protect iron and steel from corroding and is also used in nickel-cadmium batteries. Cadmium is highly toxic so it should be used and handled with great caution.

General Properties of Cadmium

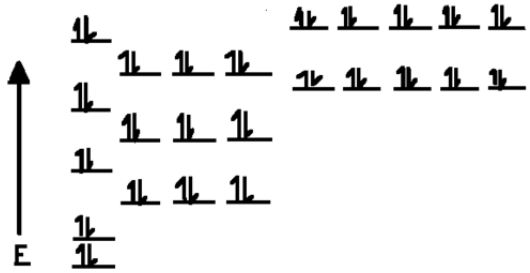
- Chemical Symbol: Cd
- Atomic Number: 48
- Atomic Mass: 112.411
- Group Number: 12
- Period Number: 5
- Electronegetivity: 1.69
- Standard State: Solid
- Standard Color: Silvery Grey Metallic
- Density: 8.65 g/cm^3
- Melting Point: 320.9 ^oC
- Boiling Point: 767^oC
- Most common Oxidation State: +2
- Heat of Fusion: 6.192 kJ mol^{-1}
- Heat of Vaporization: 99.87 kJ mol^{-1}

Atomic Structure



Electron Configuration of Cadmium

Cd: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s2\ 4d^{10}$ or [Kr] $4d^{10} 5s^2$



Common Isotopes

Cadmium has a total of eight naturally occuring isotopes. These are ^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd,^{114}Cd, ^{116}Cd. Of these eight istopes, ^{114}Cd and ^{112}Cd are the most common with an abundance of 29% and 24% respectively.

Metallic Characteristics

Cadmium metal is soft and malleable when pure and is used mostly for electroplating steel (corrosion resistance) and in the manufacture of bearings. Cadmium compounds are also found in oil paints where they provide some brilliant colors (e.g., "cadmium yellow"). In its solid state, this metal is a silvery grey color. Cadmium is a very good electricity conductor, as well as very resistance to corrosion, making it an excellent sacrificial anode for metals such as iron and steel.

Like zinc and tin, cadmium metal "cries" or emits a high pitched sound when bent rapidly. Most cadmium today is recovered as a by-product of the zinc refining process.

Natural Occurrences

Cadmium never occurs in nature in its elemental form. It is always found in a compound with another element. The most common natural compounds of Cadmium are Cadmium Sulfide, Cadmium Carbonate, and Carbon Oxide. Carbon Sulfide, also known as the mineral Greenockite, is the most well known source of Cadmium. Cadmium is also found in the Earth's Crust in amounts of about 0.1 to .2 ppm, a very smallamount. Most of the Cadmium that is obtained is through a process known as Zinc refinement, which uses their differing melting points.

Common Reactions with Cadmium

Cadmium forms several important compounds in nature:

- Cadmium Hydroxide ($Cd(OH)_2$): This compound is seen in the Nickel-Cadmium battery and forms precipitate in the presense of a Nitric Acid solution.



- Cadmium Oxide (CdO): This compound in used in a variety of reactions including acting as a catalyst in redox reactions, hydrogenation reactions, polymerization and cleavage. Cadmium Oxide is heat resistant so it can be very useful in heat-resistant plastics, as well as other coatings for plastic. This compound is all seen in certain enamels and batteries.
- Cadmium Sulfate ($CdSO_4$): This compound, like many other compounds of Cadmium is used in electroplating, pigments, fluorescents, and batteries, specifically the Weston Cell.

These three compounds have the most significant use in society; however, a few other compounds that exist in nature are Cadmium Cyanide, Cadmium Chloride, Cadmium Carbonate, and Cadmium Nitrate.

Common Uses

Cadmium's s most known to be used in Nicad, or Nickel-Cadium rechargeble batteries, which is the second most widely used battery, seen in airplanes, telephones, power tools, cd players, computers, and even radar stations. In this battery, Cadmium takes the form of Cadmium hydroxide. Cadmium is also used in coatings, pigments, plastics, and in alloys. The most commonly formed alloys are with silver, copper, and zinc mainly because Cadmium lowers the melting point allowing them to be suitable for the hard soldering of metals. In past years, Cadmium was used in electroplating of steel to protect from corrosion; however, that is not as common.

Hazards and Toxicity

Cadmium is a very toxic metal, therefore needs to be handled with great caution. Cadmium can enter the human body through smoking cigarettes, contaminated water due to landfills, certain foods such as shellfish, and mostly through handling the metal itself. This metal when inhaled or digested can cause many health affects, including vomiting, nausea, diarrhea, dry throat, and headaches. More serious affects are still being investigated, but is thought to cause high blood pressure, cancer, heart and liver disease.

References

1. Schulte-Schrepping, K.-H. and Piscator, M. 2000. Cadmium and Cadmium Compounds. Ullmann's Encyclopedia of Industrial Chemistry.Print.
2. Newton, David E. "Cadmium." *Chemical Elements: From Carbon to Krypton*. Vol. 1. Detroit: U.X.L., 1999. 81-86. Print.
3. Young, Jay A. "Cadmium." Journal of Chemical Education 2005 82 (4), 521. Print.

Problems

1. What is the electron configuration of Cd^{2+}? Draw the orbital filled diagram for this ion.
2. What is an example of a balanced chemical reaction for the formation of Cadmium hydroxide? Don't forget to include phases.
3. Electroplating was a common use of Cadmium, explain what electroplating means and how is it beneficial?
4. Explain the term of an isotope in regards to Cadmium.
5. What are the characteristics of a metal? Does Cadmium show these characteristics?

Solutions to Problems

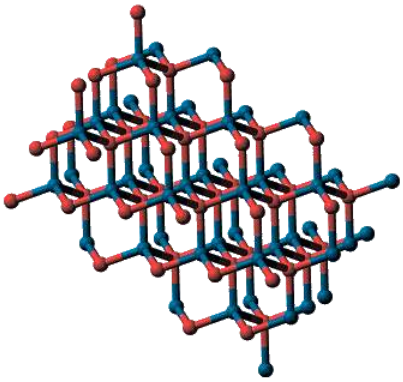
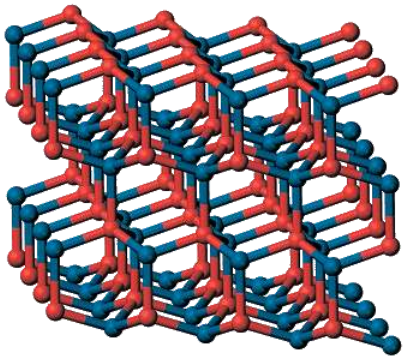
1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$
2. $Cd(NO_3)_2 + 2\ NaOH \rightarrow Cd(OH)_2 + 2\ NaNO_3$
3. Electroplating is the using of one metal to fully cover or plate another metal to protect it from corrosion. For example, the use of Cadmium to electroplate steel to protect it from corroding.
4. An isotope is a naturally occuring form of Cadmium where there is a differing numbers of neutrons, however, the same number of protons.
5. The characteristics of a metal include good conductors of heat and electricity, tendency to lose electrons, high melting points, are ductile and malleable. Cadmium does posses these characteristics and is a good example of a metal.

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

- **Chemistry of Cadmium** is licensed CC BY-NC-SA 4.0.

4.11.1.1: Cadmium Sulfide

Cadmium sulfide (CdS) exists in two natural forms: greenockite and hawleyite, which differ in their crystal structure. Greenockite forms hexagonal crystals with the wurtzite structure, hawleyite has the sphalerite (zinc blende) structure.

	
Hawleyite (cubic)	Greenockite (hexagonal)

Cadmium sulfide is a direct band gap semiconductor with E_g = 2.42 eV at room temperature. CdS is used in optoelectronics (photosensitive and photovoltaic devices). One simple use is as a photoresistor whose electrical resistance changes with incident light levels. Mixed with zinc sulfide, cadmium sulfide acts as a phosphor with long afterglow.

Cadmium sulfide was used as a pigment in paints as far back as 1819. Synthetic cadmium sulfide pigments are valued for their good thermal stability in many polymers, for example in engineering plastics. By adding selenium it is possible to obtain colors ranging from a greenish yellow to red violet.

Contributors and Attributions

- Hans Lohninger (Epina eBook Team)

4.11.1.1: Cadmium Sulfide is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Cadmium Sulfide** is licensed CC BY-NC-SA 4.0.

4.11.2: Chemistry of Copernicium

Element 112 was synthesized in 1996 at the GSI in Darmstadt, Germany by Hofmann, et. al. Lead was bombarded with zinc atoms to achieve a mass total of 277. In July of 2009 the name "copernicium" and symbol "Cn" (in honor of Copernicus) were submitted to the IUPAC.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Copernicium** is licensed CC BY-NC-SA 4.0.

4.11.3: Chemistry of Mercury

Mercury (Hg) is a transition metal element that is unique because it is the only metal element that exist in a liquid form at room temperature. Due to this property, it is used in thermometers, barometers, gas-pressure regulators, electrodes, and electrical relays and switches.

Contributors and Attributions

- Tam Nguyen (UC Davis)

Binod Shrestha (University of Lorraine)

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

- **Chemistry of Mercury** is licensed CC BY-NC-SA 4.0.

4.11.4: Chemistry of Zinc

The name for zinc is of German origins, zink. It has been known since pre-historic times and compounds as well as the metal had been used for many years before anyone ever thought about elements at all! **Zinc (Zn)** is a blue-white metal of moderate strength, hardness and ductility. Zinc is one of the least common elements and is mostly produced through electrolysis of aqueous zinc sulfate. About one third of all metallic zinc is used to manufacture galvanized nails. Because of its low melting point and its ability to form bonds with iron or steel, it serves to coat the metal and protect it from corrosion. Metallic zinc is also used to make dry cell batteries.

Physical Properties

Pure zinc is a bluish-silver and ductile metal with a low melting and boiling point. Most zinc today is obtained from ZnS, extracted from zinc blende ore and roasted to remove the sulfur. Zinc can also be obtained by electrolysis of aqueous zinc sulfate, a common laboratory exercise.



Figure 1: *Brass die, along with zinc and copper samples. from Wikipedia*

Zinc plays a huge part in the production of alloys. One of the best known zinc alloy is brass, which contains between 55-95% copper. Zinc also takes part in manufacturing solder, which has a relatively low melting point. Solder is used to join electrical components, as well as pipes and other metals.

Chemistry Properties

Zinc is reasonably resistant to corrosion and is used as a covering for baser metals like iron ("galvanizing"). Zinc can be readily cast or molded. Zinc has many unique characteristics. For example, its vapor burns in air with a green flame, forming zinc oxide. Zinc oxide is a common zinc compound that is used in paints, cosmetics, plastics and more. Metallic zinc reacts with weak acids very slowly. Sulfur has a strong affinity for zinc. When heated, the two powders react explosively to form zinc sulfide. Zinc sulfide is used to make television screens and fluorescent light bulbs.

Zinc also reacts with halogens. However, as the electronegativity decreases among the halogen group, the reactivity with zinc decreases. Thus, the most electronegative of the halogens (Fluorine) reacts with zinc violently, while the less electronegative halogen (Iodine) only generates a small amount of heat. Interestingly, properties of zinc are strongly affected by impurities such as lead, cadmium and iron. Also, zinc is most often used as a reducing agent in chemical reactions and it forms complex ions with ammonia and cyanide ions.

References

1. Gorodetsky, Malka; Singerman, Ammon. "Electroforming: An improvised experiment on electroplating." *J. Chem. Educ.***1980**, *57*, 514.

Contributors and Attributions

- Tabatha Schnelker
- Stephen R. Marsden

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

- **Chemistry of Zinc** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

5: Reactions of Complexes

5.1: Introduction to Reactions of Metal Complexes
5.2: Substitutions Reactions
5.2.1: Introduction to Substitution Reactions
5.2.2: Inert and Labile Complexes
5.2.3: Mechanistic Possibilities
5.3: Kinetics Hint at the Reaction Mechanism
5.3.1: Rate Law for Dissociative Mechanisms
5.3.2: Rate Laws for Interchange Mechanisms
5.3.3: Rate Law for Associative Mechanisms
5.3.4: Preassociation Complexes
5.3.5: Activation Parameters
5.3.6: Some Reasons for Differing Mechanisms
5.4: Experimental Evidence in Octahedral Substitutions
5.4.1: Dissociation
5.4.2: Linear Free Energy Relationships
5.4.3: Associative Mechanisms
5.4.4: The conjugate base mechanism
5.4.5: The Kinetic Chelate Effect
5.5: Stereochemistry of Octahedral Reactions
5.5.1: Substitution in trans-en octahedral complexes
5.5.2: Substitution in cis-en octahedral complexes
5.5.3: Isomerization of Chelate Rings
5.6: Substitutions in Square Planar Complexes
5.6.1: Kinetics and Stereochemistry of Square Planar Reactions
5.6.2: Evidence for Associative Reactions
5.7: The Trans Effect
5.8: Redox Mechanisms
5.8.1: Outer Sphere Electron Transfer
5.8.2: Inner Sphere Electron Transfer
5.9: Reactions of Coordinated Ligands
5.9.1: Metal-catalyzed Hydrolysis
5.9.2: Template Reactions
5.9.3: Electrophilic Substitutions

This page titled 5: Reactions of Complexes is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.1: Introduction to Reactions of Metal Complexes

Although there are a vast array of reactions that occur at transition metal centers, we will touch on only a subset of the possibilities. This chapter will focus on the reactions of octahedral and square planar metal complexes, and the reactions will be divided into three types:

1. **Substitution reactions at the metal center**: these are reactions in which one ligand is replaced with another ligand within the metal's inner coordination sphere.
2. **Redox**: these are reactions in which the metal oxidation state formally changes by gaining or loosing electrons.
3. **Ligand reactions**: these are reactions that occur primarily on the ligands that are bound to metal ions.

Review of reaction coordinate diagrams and terms

Before we begin our discussion of reactions, let's review some of the vocabulary and models that chemists use to understand reactions.

A chemical reaction can be represented with a reaction coordinate diagram in which the total potential energy of a state is plotted in the vertical y axis, and the "**reaction coordinate**" (sometimes also referred to as "reaction progress", or "extent of reaction") is plotted on the horizontal x axis. The reaction coordinate is often drawn as the progress of a reaction from reactants (R) on the left to products (P) on the right.* Examples of reaction coordinate diagrams for a one-step and a two-step reaction are shown in Figure 5.1.1. Notice the difference in the reaction profile that depends on the number of reaction steps. A one-step reaction has one "hill" shape, while a two step reaction takes on a "saddle" shape.

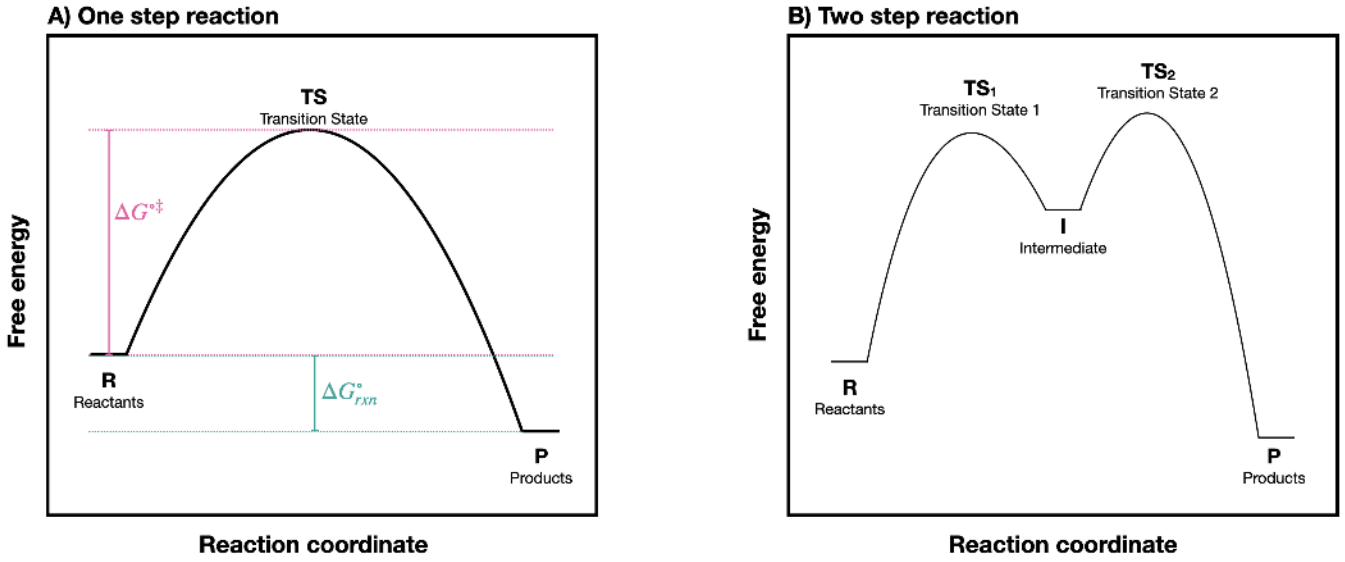


Figure 5.1.1: Examples of a reaction coordinate diagram for a one-step reaction (left), and a two-step reaction (right). (CC-BY-SA; Kathryn Haas)
*Many students find it helpful to envision the horizontal axis in an reaction coordinate diagram as being analogous to the progress bar at the bottom of a youtube video.

Thermodynamics

The difference in energy between reactants (R) and products (P) indicates whether reactants or products will dominate at thermodynamic equilibrium. At standard conditions, this difference is the standard Gibbs Free Energy of the reaction (ΔG°_{rxn} or ΔG°). The Gibbs free-energy change is a combination of enthalpy change (ΔH°) and entropy change (ΔS°):

$$\Delta G^{\circ} = \Delta H^{o} - T\Delta S^{o}$$

where

- T is the temperature in Kelvin (recall that the Kelvin temperature is simply the Celsius temperature plus 273.15).
- Enthalpy change (ΔH°) is the heat released or absorbed by the reaction.

- Entropy change (ΔS°) is the change in disorder from reactants to products. In a reaction in which one molecule cleaves into two smaller molecules, for example, disorder increases, so ΔS° is positive.

The standard Gibbs free energy change for a reaction can be related to the reaction's equilibrium constant K_{eq} by the equation:

$$\Delta G^\circ = -RT \ln K_{eq}$$

where R is the gas constant (8.314 J/mol×K) and T is the temperature in Kelvin (K).

A negative value for ΔG°_{rnx} (an exergonic reaction) corresponds to K_{eq} being greater than 1, an equilibrium constant which favors product formation. Conversely, an endergonic reaction has a positive value of ΔG°, and a K_{eq} between 0 and 1.

Kinetics

The highest point between two energy minima is a transition state (TS). The difference in energies of the reactant and the highest-energy TS is the standard free energy of activation ($\Delta G^{\circ\ddagger}$). The activation energy, in combination with the temperature at which the reaction is being run, determines the rate of a reaction: the higher the activation energy, the slower the reaction. The rate constant (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. The relationship between activation energy and the rate constant, k, is given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{or} \qquad \ln k = \ln A - \frac{E_A}{RT}$$

A rate law is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The rate is defined as the change in reactants or products over time. For example, in a reaction of two reactants (R_1 and R_2) to form product (P), a rate law could be written as follows:

$$\frac{d[\mathrm{P}]}{dT} = \mathrm{k}[\mathrm{R}_1][\mathrm{R}_2]$$

The rate law above is second order overall, and first order with respect to both R_1 and R_2. The order indcates the power of reactant concentrations for individual reactants or overall for the reaction.

In a one-step reaction, the product is formed in one step. There is an energy barrier to overcome so that this process can happen. At the height of that energy barrier is the TS. In a one-step reaction, there is one transition state. In contrast, in a two-step reaction, there are two transition states and an intermediate (denoted by the letter I). The first step from R to I, passes over transition state TS_1, is endergonic. The second step passing through transition state TS_2 is exergonic. The intermediate (I) is thus depicted as an energy 'valley' (a local energy minimum) situated between the two energy maxima; TS_1 and TS_2.

In Figure 5.1.1B, notice that the energy barrier for the first step is larger than the energy barrier for the second step. This means that the first step is slower than the second. In a multi-step reaction, the slowest step - the step with the largest energy barrier - is referred to as the rate-limiting or rate-determining step. The rate-determining step can be thought of as the 'bottleneck' of the reaction: a factor which affects the rate-determining step will affect the overall rate of the reaction. Conversely, a factor which affects only a much faster step will not significantly affect the rate of the overall reaction.

Summary and Key Terms

Reaction coordinate diagrams convey some very important ideas about how the reaction can proceed, and about the thermodynamics and kinetics of the reaction. In the sections that follow, the following key terms will be used:

Description of Key Terms

Reactants (R): The molecular species that are the starting materials for a chemical reaction. These are often written at the left side of a reaction coordinate diagram.

Products (P): The molecular species that result from a chemical reaction. These are often written at the right side of a reaction coordinate diagram.

Transition State (TS): a transition state is the transient species that exists at an energy maximum. In other words, TS's are highest-energy structures along a reaction pathway. Hammond's postulate suggests that the structure of a transition state should

resemble the lower-energy species (R, P, or I) adjacent to it along the reaction coordinate, and most closely resembles the structure of the species closest in energy.

Intermediate (I): an intermediate is a high-energy structure at a local minimum. Intermediates are sometimes thought of as long-lived transition states. Unlike transition states, intermediates sometimes exist long enough and in high enough concentration to be detectable experimentally.

Microscopic reversibility: if a reaction can proceed in the forward direction from R to P, then in principle, it can also proceed in the reverse direction from P to R. There may be many possibilities for how a reaction *could* happen, but the lowest-energy pathway in the forward direction is also the lowest energy pathway in the reverse direction. In other words, the reactions passes through the same lowest-energy I and TS in the forward and reverse directions.

Steady-State Approximation: the concentration of an intermediate is assumed to react as quickly as it forms. This approximation allows us to assume that concentration of an intermediate remains "steady" throughout the reaction progress. This approximation is useful for analysis of reaction kinetics.

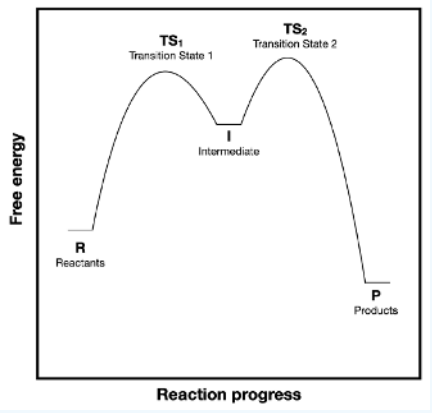
Order: The order of a reaction indicates the power of total reactant concentration in a kinetic rate law. The order of a reactant indicates that reactant's power in the rate law. For example, is a rate law that is $\mathrm{Rate}=\mathrm{k}[\mathrm{A}]^2[\mathrm{B}]$, the reaction is second order in A, first order in B and third order overall. If there were also a reactant, C, that was not part of the rate law, the reaction would be zero order with respect to C.

? Exercise 5.1.1

Figure 5.1.1 is replicated below for convenience. This figure shows a reaction coordinate diagram for a two-step reaction.

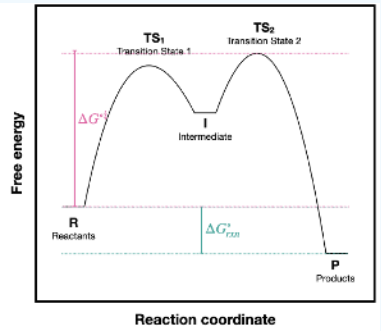
a. (ΔG°) and $\Delta G^{\circ\ddagger}$) are labeled on Figure 5.1.1*A*, but not on Figure 5.1.1*B*. Add the appropriate labels to diagram B. (copied below for convenience).

b. Consider the energy barriers for the first and second steps and explain why the steady-state approximation is a valid assumption.

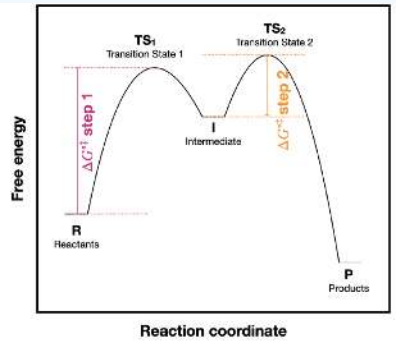


Answer

a) The activation energy for this reaction is the difference between R and TS_2 because TS_2 is the highest energy along the reaction pathway.



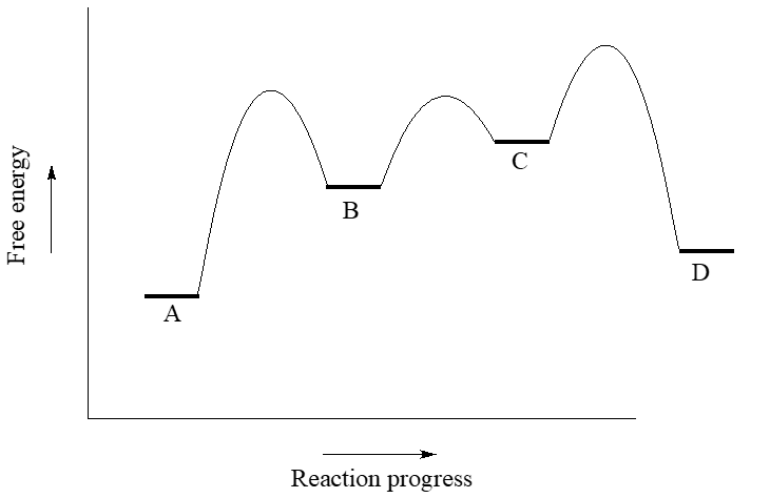
b) The activation energy for step 2 is much smaller than for step 1. This tells us that step 2 occurs faster than step 1. So, the concentration of intermediate should not increase over the course of the reaction, and it should react at least as fast as it is formed. The fact that the activation barrier for step 2 is less than for step one allows us to assume that [I] does not change over the course of the reaction. This should generally be true for all intermediates.



Exercise 5.1.1

Use the reaction coordinate diagram below to answer the questions.

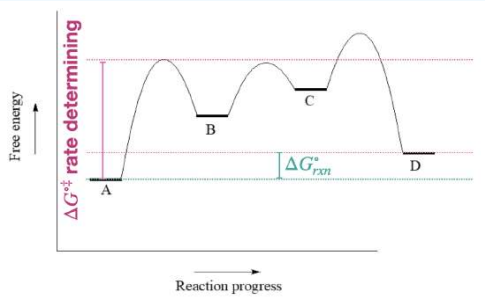
a. Is the overall reaction endergonic or exergonic in the forward (A to D) direction?
b. How many steps does the reaction mechanism have?
c. How many intermediates does the reaction mechanism have?
d. Redraw the diagram if necessary. Add a label showing the energy barrier for the rate-determining step of the forward reaction.
e. Add a label showing ΔG°_{rxn} for the reverse reaction (D to A).
f. What is the fastest reaction step, considering both the forward and reverse directions?



Answer

a. Is the overall reaction endergonic or exergonic in the forward (A to D) direction?
b. How many steps does the reaction mechanism have?
c. How many intermediates does the reaction mechanism have?
d. The first step is rate determining since it has the largest activation barrier.

e. ΔG°_{rxn} for the reverse reaction (D to A) is the same as for the froward direction, with a revers of its sign.



f. The fastest step has the lowest barriers: this would be the step to/from B and C.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

Curated or created by Kathryn Haas

This page titled 5.1: Introduction to Reactions of Metal Complexes is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **6.3: A Quick Review of Thermodynamics and Kinetics** by Tim Soderberg is licensed CC BY-NC-SA 4.0. Original source: https://digitalcommons.morris.umn.edu/chem_facpubs/1/.

SECTION OVERVIEW

5.2: Substitutions Reactions

5.2.1: Introduction to Substitution Reactions

5.2.2: Inert and Labile Complexes

5.2.3: Mechanistic Possibilities

This page titled 5.2: Substitutions Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.2.1: Introduction to Substitution Reactions

Ligand substitution refers to the replacement of one ligand in a coordination complex with another ligand.



Figure 5.2.1.1: Substitution of one ligand for another in a coordination complex.

Remember, a ligand in coordination chemistry is just a Lewis base that binds to a metal atom or ion. It does so by donating a lone pair (or other pair of electrons). Generallly, this donation is reversible. The donor can always take its electrons back. Typically, there may be some balance between the metal's need for more electrons and the donor's attraction for its own electrons; donor atoms are frequently more electronegative than the metal.

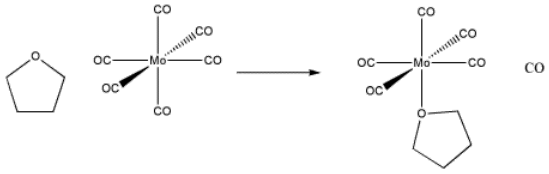


Figure 5.2.1.2: An example of ligand substitution. THF replaces a carbon monoxide in this molybdenum complex.

Even though the reaction is pretty simple, it can occur in different ways.

That is, the elementary steps involved in the reaction can occur in different orders. The elementary reactions are the individual bond-making or bond-breaking events that lead to an overall change. Sometimes the order of steps is referred to as the mechanism or the mechanistic pathway.

- The mechanism is the order of elementary reaction steps.
- Elementary reaction steps are individual bond-making and breaking steps.

You may have seen reaction mechanisms before. For example, carbonyl addition chemistry can involve lengthy mechanisms, in which a number of proton transfers and other bond-making and bond-breaking steps must occur to get from one state to another. Because ligand substitution is simpler than that, it is a good place to study mechanism in a little more depth, without getting overwhelmed by the details.

The sequence of steps in the mechanism influences how different factors will impact the reaction. For example, changing concentrations of different components in a reaction mixture can affect the time it takes for a reaction to finish.

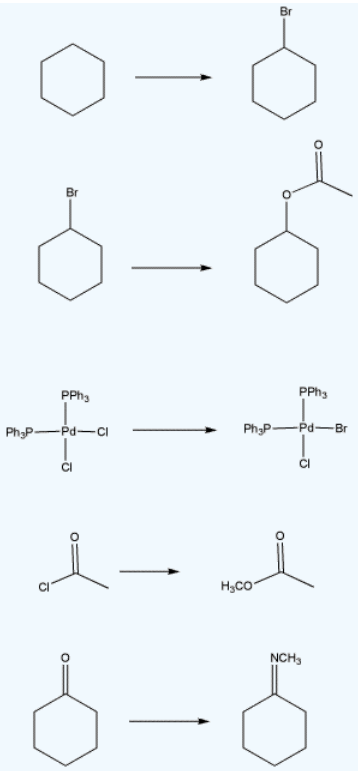
- The mechanism can have a dramatic impact on the outcome of the reaction under different circumstances.

These kinds of considerations have a dramatic impact on industrial processes such as pharmaceutical production. In that setting, chemical engineers need to make decisions about how much of each reactant must be admitted to a reaction mixture and how long they should be allowed to react together. If they allow the reaction to proceed for too, long, there may be “side-reactions” that start to occur, interfering with the quality of the product, and they will waste valuable time in the production pipeline. If they don’t allow it to react long enough, the reaction may not finish, and the product will be contaminated with leftover starting materials.

In this chapter, we will look at how this simple reaction can occur in different ways. We will see some different methods that are used to tell which way the reaction occurs (i.e. evidence of what is really happening). We will also look at some different factors that may influence whether the reaction is likely to occur one way or the other (i.e. reasons it is happening that way, or reasons we expect it will happen that way).

? Exercise 5.2.1.1

Some kind of substitution occurs in each of the following reactions: an atom or group replaces another. In each case, identify what is being replaced, and what replaces it.



Answer a

a bromine atom replaces a hydrogen atom

Answer b

an acetate group (ethanoyl ester) replaces a bromine atom

Answer c

a bromine atom replaces a chlorine atom (or ions)

Answer d

a methoxy group replaces a chlorine atom

Answer e

a methylamino group replaces an oxygen atom

This page titled 5.2.1: Introduction to Substitution Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.1: Introduction to Substitution** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

5.2.2: Inert and Labile Complexes

Kinetics of Substitution Reactions

Kinetics is a branch of chemistry that is concerned with the rates of chemical reactions. In this section, we will discuss the rates of metal-ligand (M-L) substitution reactions.

Let's start with some examples. In the table below are three examples of ligand substitution reactions of hexaaquo metal complexes to form hexaammine complexes. These reactions are nearly identical with the exception of the metal ion. The products are thermodynamically favored in all cases.

Reaction	Rate constant (k)	Labile or Inert
$[\mathrm{Ni(OH_2)}]^{2+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Ni(NH_3)_6}]^{2+}$	$k = 10^{4} s^{-1}$ (1 ns)	Labile (happens in < 1 min)
$[\mathrm{Cr(OH_2)}]^{3+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Cr(NH_3)_6}]^{3+}$	$k = 10^{-3} s^{-1}$ (6 days)	Inert (slow, takes hours)
$[\mathrm{Cu(OH_2)}]^{2+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Cu(NH_3)_6}]^{2+}$	$k = 10^{8} s^{-1}$	Very Labile (happens in seconds)

Definitions

- **Kinetically Labile** - Metal complexes that undergo "kinetically fast" substitution reactions are **kinetically labile**. Taube suggested that these are reactions in which half of the reactant is consumed in one minute or less ($t_{1/2}$ <1 min).
- **Kinetically Inert** - Metal complexes that undergo "kinetically slow" substitution reactions are **kinetically inert** or **non-labile**. Taube suggested that these are reactions in which $t_{1/2}$ >1 min.

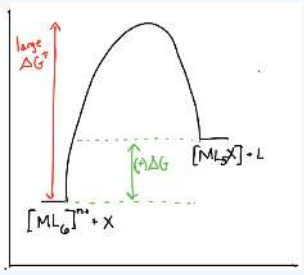
A common pitfall is to confuse the meaning of kinetic terms, like *labile* and *inert*, with thermodynamic terms, like *stable* and *unstable*. It is important to distinguish between kinetics and thermodynamics. For example, the complex $[Fe(H_2O)Cl]^{2+}$ has a large formation constant and is thermodynamically stable; yet it is also labile. On the other hand, the complex $[Co(NH_3)_6]^{3+}$ is unstable in acidic aqueous solution and decomposes spontaneously to $[Co(H_2O)_6]^{3+}$; yet it decomposes slowly because it is inert. It is good practice to use clear terms such as "*kinetically* labile" or "*kinetically* inert" and "*thermodynamically* stable" and "*thermodynamically* unstable".

Exercise 5.2.2.1

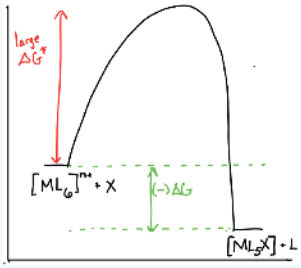
Draw the reaction coordinate diagrams for a reaction of the form $[ML_6]^{n+} + X \rightleftharpoons [ML_5X]^{n+} + L$ in the following scenarios:

a. $[ML_6]^{n+}$ is theromdynamically stable and kinetically inert.
b. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically inert.
c. $[ML_6]^{n+}$ is theromdynamically stable and kinetically labile.
d. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically labile.

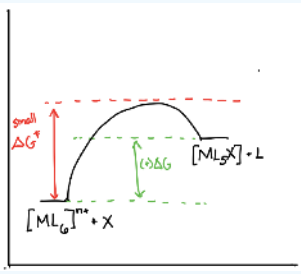
Answer a)



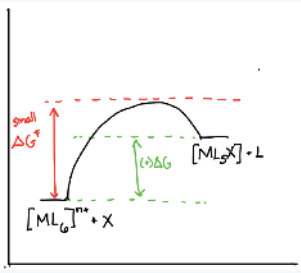
Answer b)



Answer c)



Answer d)



Factors that affect rates of substitution reactions:

Some of the factors that affect the kinetic rates of ligand substitution are the same factors that affect thermodynamic stability (see Chapter 10). The same factors that make a complex stable can also make it more inert. Why are kinetic factors related to thermodynamic stability? It is because the structure and stability of the reactant complex is related to the structure and stability of the transition state. The reactant complex must change its geometry to form an intermediate or transition state. When the reactant is particularly stable, it can result in a higher activation energy associated with moving away from the stable configuration. However, it is incorrect to assume that stability is *always* correlated with reaction rates. Kinetic and thermodynamic factors are related, yet separate.

There are three important factors that influence kinetic rate of substitution:

1. Ligand Field Stabilization Energy (LFSE): Electron configurations that place electrons in higher-energy orbitals (particularly antibonding orbitals) result in more labile complexes. As long as there are not electrons in higher-energy orbitals, the lability correlates roughly with LFSE. The more negative the LFSE, the more inert.
2. Coulombic attraction between the metal and ligand: In general, higher charge density on the metal ion or on the ligand(s) leads to stronger electrostatic attraction between metal and ligand. Stronger Coulombic attraction generally leads to slower dissociation steps and faster association steps. The effect that these have on the reaction rate depends on elementary steps that take part in the rate-determine step(s).
3. Denticity: Multi-dentate ligands create particularly inert complexes as a result of the kinetic chelate effect.

All three considerations are described in more detail below.

Exercise 5.2.2.2

In which compound from each pair would you expect the strongest ionic bonds? Why?

a) LiF vs KBr
b) $CaCl_2$ vs. KCl

Answer a

The ions in LiF are both smaller than in KBr, so the force of attraction between the ions in LiF is greater because of the smaller separation between the charges.

Answer b

Calcium has a 2+ charge in $CaCl_2$, whereas potassium has only a + charge, so the chloride ions are more strongly attracted to the calcium than to the potassium.

Taube's observations of metal complex substitution rates

Henry Taube (Nobel Prize, 1983) tried to understand kinetic lability by comparing the factors that govern bond strengths to observations about the rates of reaction of coordination complexes. He saw some things that were unsurprising. He also drew some new conclusions based on ligand field theory.

Taube observed that **many M^{+1} ions (M = metal) are more labile than many M^{+3} ions**, in general. That isn't too surprising, since metal ions function as electrophiles (Lewis acids) and ligands function as nucleophiles (Lewis bases) in forming coordination complexes. In other words, *metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly*. However, there were exceptions to that general rule. For example, Taube also observed that Mo_5^+ compounds are more labile than Mo_3^+ compounds. So, there must be more going on here than *just* the effects of electrostatic attraction.

Another factor that governs ionic bond strengths is the *size of the ion*. Typically, **ions with smaller atomic radii form stronger bonds** than ions with larger radii. Taube observed that Al^{3+}, V^{3+}, Fe^{3+} and Ga^{3+} ions are all about the same size. All these ions exchange ligands at about the same rate. That isn't surprising, because they have the same charge and the same radius. However, Cr^{3+} is also about the same size as those ions and it also has the same charge, but it is much less labile. Once again, there are exceptions to our regular expectations based on simple electrostatic considerations. Furthermore, 4d and 5d transition metals (Y→Cd, and Ac→Hg) are much more inert than 3d transition metals (Sc→Zn). This is unexpected when we consider size; the 4d and 5d metals are much larger than the 3d metals. This unexpected behavior tells us that electrostatics alone cannot predict lability.

Taube came up with a hypothesis that could explain the seeming contradictory oservations described above: *kinetic lability must be affected by d-electron configuration*. This idea forms the basis of Taube's rules about lability.

For example, metals like Ni^{2+} and Cu^{2+} are very labile. The d orbital splitting diagrams for those compounds would have d electrons in the e_g set. Remember, the e_g set arises from interaction with the ligand donor orbitals; this set corresponds to a σ antibonding level.

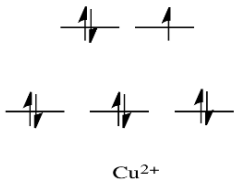


Figure 5.2.2.1: d^9-electron configuration assuming octahedral geometry.

By comparison, V^{2+} is rather inert. The d orbital splitting diagram in this case has electrons in the t_{2g} set, but none in the e_g set.

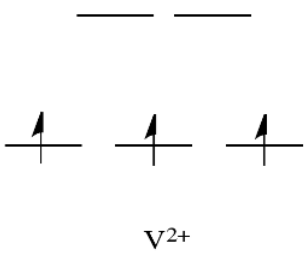


Figure 5.2.2.2: d^3-electron configuration assuming octahedral geometry.

So, having electrons in the higher energy, antibonding e_g level weakens the bond to the ligand, so the ligand can be replaced more easily. In the absence of those higher energy electrons, the bond to the ligand is stronger, and the ligand isn't replaced as easily.

On the other hand, metals like Ca^{2+}, Sc^{3+} and Ti^{4+} are pretty labile. The d orbital splitting diagrams in those cases are pretty simple: there are no d-electrons at all in these ions.

That means having no electrons in these mostly non-bonding levels leaves the complex susceptible to ligand replacement. But it's hard to see why population of an orbital that is mostly non-bonding would have an effect on ligand bond strength.

Instead, this factor probably has something to do with the part of ligand substitution that we have ignored so far. Not only does one ligand need to leave, but a second one needs to bond in its place. So, having an empty orbital for the ligand to donate electrons into (or, put another way, not having electrons in the way that may complicate donation from the ligand) makes that part of the reaction easier.

Exercise 5.2.2.3

Consider all possible electron configurations for octahedral complexes (d^0 to d^{10}, high spin and low spin cases): predict whether each case would be inert, intermediate, or labile.

Answer

	Kinetically Inert (Slow)	Kinetically Labile (Fast)
d^n electron count and ligand field strength	Octahedral configurations with empty e_g orbitals: • d^3 • low-spin d^4, d^5, d^6 Strong-field d^8 (square planar)	Octahedral configurations with occupied e_g orbitals: • d^1, d^2, d^7, d^9, d^10 • high-spin d^4, d^5, d^6 Weak-field d^8 (usually tetrahedral)

Exercise 5.2.2.4

Put the metal ions in order of decreasing reaction rate (from labile to inert):

a) Al^{3+}, Na^{+}, Mg^{2+}

b) $Ca^{2+}, Mg^{2+}, Sr^{2+}$

Answer (a)

Most Labile to most inert: $Na^{+} > Mg^{2+} > Al^{3+}$

These are metal ions with similar size and varying charge. They are in order of increasing charge and increasing density from left to right.

Answer (b)

Most labile to most inert: $Sr^{2+} > Ca^{2+} > Mg^{2+}$

These metal ions have the same charge, and vary in size. They are in order of decreasing charge and increasing charge density from left to right.

Exercise 5.2.2.5

Some metals, like Mn^{2+}, can be either labile or inert, depending on whether they are high spin or low spin. Explain why using d orbital splitting diagrams.

Answer

Add texts here. Do not delete this text first.

Exercise 5.2.2.6

Predict whether the following metals, in octahedral complexes, are labile or not.

a) Co^{3+} (high spin)

b) Co^{3+} (low spin)

c) Fe^{2+} (low spin)

d) Fe^{2+} (high spin)

e) Zn^{2+}

Answer

Answer a

labile (electrons in higher energy d orbital set)

Answer b

not labile (all electrons in lower energy d orbitals)

Answer c

not labile (all electrons in lower energy d orbitals)

Answer d

labile (electrons in higher energy d orbital set)

Answer e

labile (electrons in higher energy d orbital set)

Generalizations for how metal ion affects kinetics:

These are some generalizations about how the kinetics of substitution is affected by the metal ion identity and the d^n electron configuration.

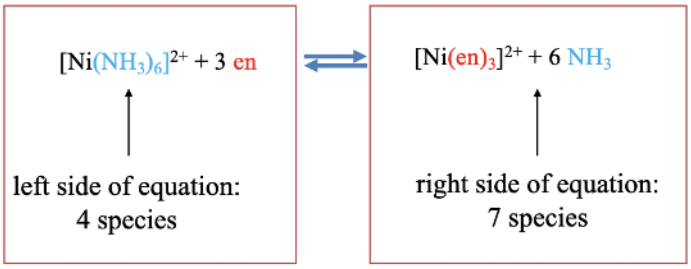
1. s-block metals are very labile, except for those with very high charge density (eg. $Mg^{2+}\ is\ inert$)
2. d^{10} metals are labile (eg: Zn^{2+}, Cu^{+}, Hg^{2+})
3. Other ions with a full shell are labile (eg: Ln^{3+} of f-block)
4. 3d M^{2+}, *when high spin*, are generally labile (eg. $Cu^{2+}is\ very\ labile$)
5. 4d and 5d are usually inert due to higher LFSE (low spin, high LFSE)
6. M^{2+} is more labile than the same metal as M^{3+}
7. d^3 and low spin d^6 are inert (eg. Cr^{3+}, Co^{3+}, low spin Fe^{2+})

Chelate Complexes

In addition to considering factors related to the metal ion and charge or covalent character of metal-ligand bonds, an important consideration is the effect a chelate ligand on reaction kinetics. This effect is also discussed in more detail later in this chapter (Section 12.4.5).

Recall the Thermodynamic Chelate Effect

Chelating complexes tend to be more stable than complexes with monodentate ligands. This is called the “thermodynamic chelate effect”. The effect deserves an explanation. The explanation is the increase of entropy that occurs when two or more monodentate ligands are replaced by a chelating ligand. The entropy increases because the overall number of particles increases as the substitution takes place.



$\Delta S° = +88\ J\ K^{-1}\ mol^{-1}$

Figure 5.2.2.3: Example of the thermodynamic chelate effect

For example, the substitution of six ammine ligands in the hexaammine nickel (2+) complex by three ethylenediamine chelating ligands increases the number of molecules from four to seven, and hence the entropy increases, in this case by 88 J K^{-1} and mol^{-1} (Figure 5.2.2.3)

The Kinetic Chelate Effect

In addition to the thermodynamic chelate effect, there is the kinetic chelate effect. Chelate complexes are frequently more inert than complexes with monodentate ligands. Chelate complexes are more inert for two reasons (Figure 5.2.2.4).

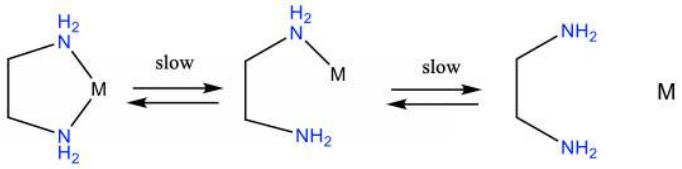


Figure 5.2.2.4: Illustration of the kinetic chelate effect

Firstly, the whole ligands needs to rotate and bend in order to cleave the first metal-ligand bond. This requires time and slows the kinetics of the bond cleavage. The second reason is that the detached donor atom cannot leave the proximity of the complex because the ligand is still attached via the other donor atom. This increases the probability of the re-formation of the metal-ligand bond which decreases the probability of both bonds being cleaved.

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

Curated or created by Kathryn Haas

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 5.2.2: Inert and Labile Complexes is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **9.1: Substitution Reactions and their Mechanisms** by Kai Landskron is licensed CC BY 4.0.

5.2.3: Mechanistic Possibilities

A mechanism is the sequence of elementary steps by which a reaction proceeds. There are two aspects that describe the mechanism of a substitution reaction. One is called the **stoichiometric mechanism**, and the other one is called the **intimate mechanism**. The *stoichiometric* part of the mechanism is defined by the identity of the intermediate, or lack thereof. The *intimate* part of the mechanism is defined by the rate limiting step, and how the rate is dependent on the identity of the incoming ligand.

Stoichiometric Mechanisms

The *stoichiometric* part of the mechanism is **defined by the identity of the intermediate, or lack thereof**. There are three classes of stoichiometric mechanisms based on the type of intermediates that can be characterized. If the intermediate can be isolated it is either an Associative (higher-coordination number intermediate) or Dissociative (lower-coordination number intermediate) reaction. On the other hand, if the intermediate cannot be isolated because it is short-lived (or does not exist) the reaction is classified as Interchange.

Associative (A) Mechanism

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating **an intermediate with a higher coordination number**. The leaving group leaves in a second step to form the product. The generic reaction below illustrates the steps of an associative mechanism. Note that the intermediate, $\mathrm{ML_nXY}$, has a higher coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} \text{Overall Reaction:} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \hline \text{Step 1 (Association):} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nXY} \\ \text{Step 2 (Dissociation):} \quad & \mathrm{ML_nXY \rightleftharpoons ML_nY + X} \end{aligned}$$

Associative mechanisms are typical of square planar, d^8 complexes. The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **higher coordination number** than the reactant complex.

Dissociative (D) Mechanism

Dissociative (D) mechanisms involve a first step where a bond between the metal ion and the leaving group breaks, creating **an intermediate with a lower coordination number.** The entering group enters in a second step to form the product. The generic reaction below illustrates the steps of a dissociative mechanism. Note that the intermediate, $\mathrm{ML_n}$, has a lower coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} \text{Overall Reaction:} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \hline \text{Step 1 (Dissociation):} \quad & \mathrm{ML_nX \rightleftharpoons ML_n + X} \\ \text{Step 2 (Association):} \quad & \mathrm{ML_n + Y \rightleftharpoons ML_nY} \end{aligned}$$

The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **lower coordination number** than the reactant complex.

Interchange (I) Mechanism

Interchange (I) Mechanisms take place in one concerted step where the entering group enters as the leaving group leaves. Bond formation and bond breaking occur simultaneously. In the case of an interchange mechanism, no intermediate is detectable. This means that either there is no intermediate, or that the intermediate is too high-energy and short-lived to be detected. The generic reaction below illustrates the single step of an interchange mechanism. Note that the species, $\mathrm{[Y\cdots ML_n\cdots X]^{\ddagger}}$, can be defined as either a transition state or a very short-lived intermediate. The distinction between these two possibilities is difficult; *when the intermediate is undetectable it is not considered a true intermediate*.

$$\begin{aligned} \text{Overall Reaction:} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \hline \text{Step 1 (Concerted):} \quad & \mathrm{ML_nX + Y \rightleftharpoons [Y\cdots ML_n\cdots X]^{\ddagger} + \rightleftharpoons ML_nY + X} \end{aligned}$$

The interchange mechanism is common for many six-coordinate (octahedral) metal complexes. The hallmark feature that distinguishes the interchange mechanism from other possible mechanisms is the **absence of a detectable intermediate**. If an intermediate is detected, the mechanism is considered associative (A). Another piece of evidence that can indicate an interchange mechanism is stereochemical changes from reactant to product. If specific sterochemistry (ie cis or trans relationships) is changed, it may be taken as evidence that an intermediate exists long enough to allow rearrangement to occur.

Distinguishing A, D, and I Mechanisms

Figure 5.2.3.1 shows examples of possible reaction profiles for each of the stoichiometric mechanisms described above. The profile of A and D mechanisms can be similar; they each require an intermediate, and the primary difference between A and D is the sequence of steps. An I mechanism lacks a true intermediate. These three cases can be difficult to distinguish experimentally, and especially if characterization of an intermediate is difficult. Notice that the reaction coordinate diagram for A and D pathways, shown in Figure 5.2.3.1, are similar. The only necessary difference between them is in the identity of the intermediate species.

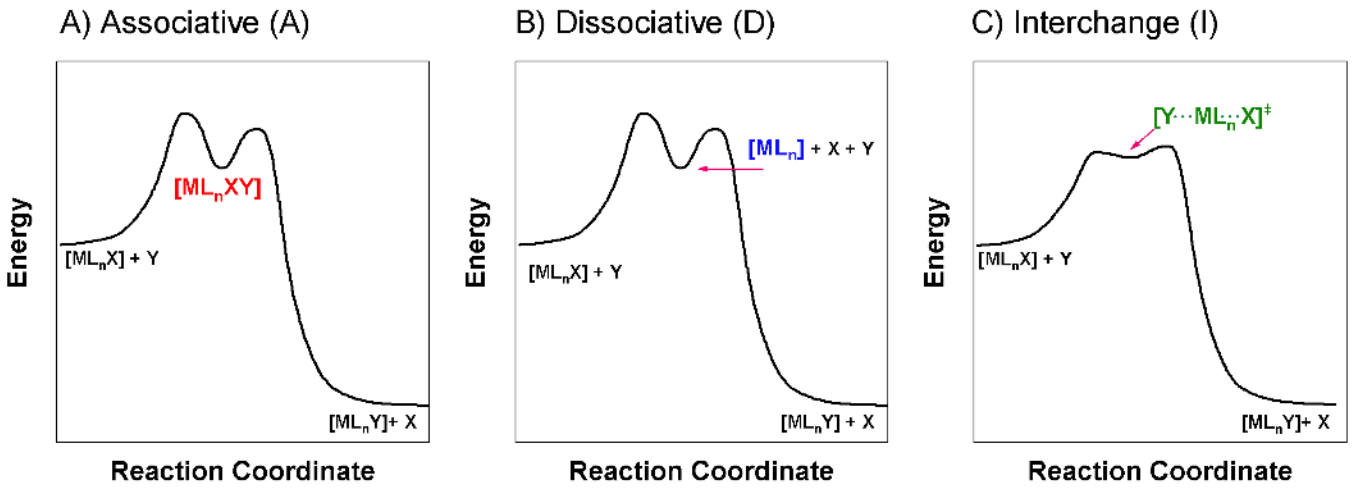


Figure 5.2.3.1: Example reaction coordinate diagrams for generic reactions that proceed through associative, dissociative, or interchange mechanisms. (Panel A) A reaction proceeds through an Associative pathway if it forms an intermediate with higher coordination number than its reactant complex. Here, an exergonic reaction is shown, where intermediate $[ML_nXY]$ has a higher coordination number than reactant $[ML_nX]$. (Panel B) A reaction proceeds through a Dissociative pathway if it forms an intermediate of lower coordination number than its reactant. Here, an exergonic reaction is shown where intermediate, $[ML_n]$, has lower coordination number than the reactant complex, $[ML_nX]$. (Panel C) A reaction proceeds through an Interchange pathway if there is no true intermediate and the reaction proceeds in one step where bonds are broken and formed simultaneously. Shown here is an exergonic reaction where there is a high-energy species that is too unstable to be isolated; thus it is not a true intermediate and is considered equivalent to a transition state. (CC-BY-SA; Kathryn Haas).

Intimate Mechanisms

The intimate mechanism is defined by characteristics of the rate-limiting step. The reaction is classified as associatively-activated (using a subscript, a) if the rate changes by more than 10-fold as the entering group is varied. The reaction is classified as dissociatively-activated (using a subscript, d) if the rate changes by less than 10-fold as the entering group is varied.

Associatively-Activated Mechanisms

The rate-limiting step of an associatively activated pathway is formation of a bond between the entering group and the central metal ion. These reactions also require formation of an encounter complex in a pre-equilibrium step prior to bond forming or bond breaking steps discussed here (see Eigen-Wilkins Mechanism).

Associatively-activated A and I (A_a and I_a)

In the case of an associatively-activated associative pathway (**A_a**) or an associatively-activated interchange pathway (**I_a**), the rate-limiting step is the association of the entering group (Y) with the reactant, ML_nX. In the case of the A_a pathway, it is the first step (bolded) below.

A_a Mechanism

Step 1 (Association): $\mathbf{ML_nX + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_nXY}$ **$\Longleftarrow$ RATE LIMITING ASSOCIATION**

Step 2 (Dissociation): $ML_nXY \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY + X$

In the case of A_a, the first step shown above is slower than the second step ($k_1 < k_2$). In this case, an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between A_a and I_a mechanisms is often impossible.

Associatively-activated D (D_a)

In the case of an associatively-activated dissociative reaction (**D_a**), the rate limiting step is the association of the entering group (Y) with the intermediate ML_n; the second step (bolded) in the mechanism shown below:

D_a Mechanism

Step 1 (Dissociation): $ML_nX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_n + X$

Step 2 (Association): $\mathbf{ML_nX + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML_nY}$ **$\Longleftarrow$ RATE LIMITING ASSOCIATION**

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$).

? Exercise 5.2.3.1

Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_a, I_a, and D_a pathways. Use these diagrams to explain why it is impossible to distinguish between A_a and I_a.

Hint

Notice that the reaction coordinate diagrams for A and D pathways, shown in Figure 5.2.3.1, are similar. The only necessary difference between them is the identity of the intermediate. These diagrams can be modified to represent associatively-activated pathways by altering the relative energy of the transition state for the associative step; the energy barrier for the associative step must be greater than that of the dissociative step. In other words, the difference between Aa, Da is in the relative energies of the first and second transition states. In the case of Ia, the diagram could be similar to the I profile shown in Figure 5.2.3.1, with the exception that the energy barrier for making the M-Y bond is greater than the energy barrier for breaking the M-X bond.

Answer

The three reaction coordinate diagrams shown in the figure below represent A_a, I_a, and D_a mechanisms respectively. If your diagram does not match this perfectly, that may be OK. The important features are:

- A_a: This reaction profile should show an intermediate with higher coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for formation of this intermediate is the associative step, and therefore it should also be the rate-limiting step for an A_a mechanism; in other words, the first step should have the highest energy barrier.
- I_a: This reaction profile should lack a stable intermediate. The energy barrier for creating of the M-Y bond must be rater-limiting. The diagram shown below is an acceptable solution, but a diagram like shown in Panel C of Figure 5.2.3.1is also correct. It is not clear from the diagram alone whether bond breaking or bond making are rate-limiting; this nuance would lie primarily in the identity of the transition state, and whether the M-Y bond is stronger or weaker than the M-X bond in the transition state.

- D_a: This reaction profile should show an intermediate with lower coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for association of the entering group with the intermediate (the second step) must be rate-limiting in a D_a mechanism. In other words, the second step should have the highest energy barrier.

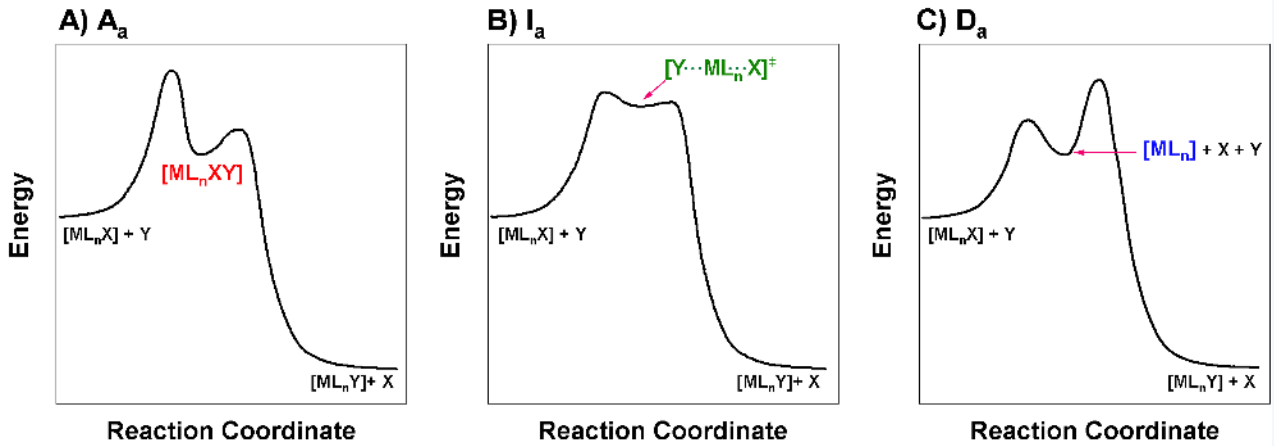


Figure for Excercise 5.2.3.1: Reaction coordinate diagrams for associatively-activated mechanisms. (A) Associatively-activated associative, Aa. (B) Associatively-activated interchange, Ia. (C) Associatively-activated dissociative, Da. (CC-BY-SA; Kathryn Haas)

The A_a and I_a mechanisms have different reaction profiles while still the rate-limiting step is the initial association of the incoming ligand to the metal center. These two types of mechanisms are difficult to distinguish because in the case of A_a, there is a relatively small energy barrier for reaction of the intermediate to form product; thus this intermediate is not long-lived and would be difficult to detect. Experimental distinction between A_a and I_a lies in the detection and characterization of this intermediate, and since it may be elusive in A_a, it is difficult to unambiguously determine whether an associatively-activated mechanism is A_a or I_a.

Dissociatively-Activated Mechanisms

When the rate-determining step is the breaking of a bond between the central metal ion and the leaving group, it is considered a dissociatively-activated (subscript d) mechanism. The rates of these reactions are largely independent of the identity of the incoming ligand.

Dissociatively-activated A (A_d)

In the case of a dissociatively-activated associative pathway ($\mathbf{A_d}$), the rate-limiting step is the dissociation of the leaving group (X) from the intermediate, ML_nXY; the second step (bolded) below.

$$\begin{array}{c} \mathrm{A_d\ Mechanism} \\ \hline \text{Step 1 (Association):} \quad \mathrm{ML_nX + Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_nXY} \\ \mathbf{Step\ 2\ (Dissociation):} \quad \mathbf{ML_nXY} \underset{\mathbf{k_{-2}}}{\overset{\mathbf{k_2}}{\rightleftharpoons}} \mathbf{ML_nY + X} \quad \Longleftarrow \mathbf{RATE\ LIMITING\ DISSOCIATION} \end{array}$$

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$.

Dissociatively-activated D and I (D_a and I_a)

In the case of a dissociatively-activated dissociative reaction ($\mathbf{D_d}$), or a dissociatively-activated interchange pathway ($\mathbf{I_d}$), the rate limiting step is the dissociation of the leaving group (X) from the reactant, ML_nX. For D_d the rate limiting step is the first step (bolded) in the mechanism shown below:

D_d Mechanism

Step 1 (Dissociation): $\mathbf{ML_nX \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} ML_n + X}$ **⟸ RATE LIMITING DISSOCIATION**

Step 2 (Association): $ML_nX + Y \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} ML_nY$

In the case of D_d, the first step shown above is slower than the second step ($k_1 < k_2$ and an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between D_d and I_d mechanisms is often impossible.

Exercise 5.2.3.2

You should complete Excercise 5.2.3.1before attempting this excercise.
Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_d, I_d, and D_d pathways.

Answer

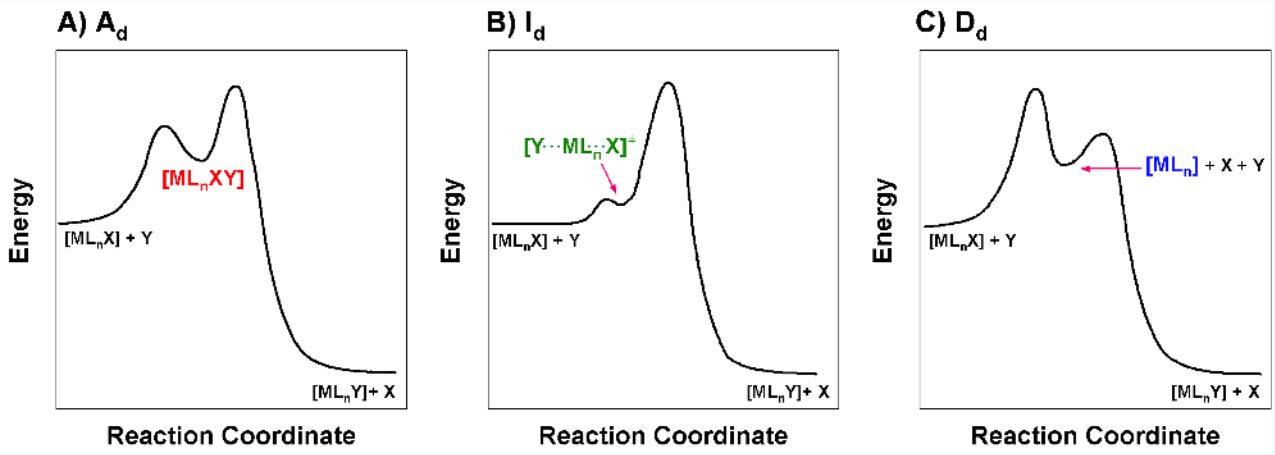


Figure for Excercise 5.2.3.2: Reaction coordinate diagrams for dissociatively-activated mechanisms. (A) Dissociatively-activated associative, Ad. (B) Dissociatively-activated interchange, Id. (C) Dissociatively-activated dissociative, Dd. (CC-BY-SA; Kathryn Haas)

Curated or created by Kathryn Haas

This page titled 5.2.3: Mechanistic Possibilities is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

SECTION OVERVIEW

5.3: Kinetics Hint at the Reaction Mechanism

Since the different mechanisms have different rate-limiting steps, there are kinetic consequences for each type of mechanism. We can used kinetic data, therefore, to help distinguish the mechanism of a reaction. However, the information gleaned from rate laws alone can be ambiguous. For example, what does it mean if a reaction depends on on the concentration of incoming ligand? How can we distinguish between an associative mechanism (A), and an associatively-activated dissociative mechanism (D_a?

5.3.1: Rate Law for Dissociative Mechanisms

5.3.2: Rate Laws for Interchange Mechanisms

5.3.3: Rate Law for Associative Mechanisms

5.3.4: Preassociation Complexes

5.3.5: Activation Parameters

5.3.6: Some Reasons for Differing Mechanisms

This page titled 5.3: Kinetics Hint at the Reaction Mechanism is shared under a CC BY-SA license and was authored, remixed, and/or curated by Kathryn Haas.

5.3.1: Rate Law for Dissociative Mechanisms

Derrivation of the Rate Law

A Dissociative (D) mechanism is two steps in which the first step is the dissociation of a ligand. The intermediate, $\mathrm{ML_n}$, has a lower coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{array}{rl} \text{Step 1 (Dissociation):} & \mathrm{ML_nX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_n} + \mathrm{X} \\ \text{Step 2 (Association):} & \mathrm{ML_n} + \mathrm{Y} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML_nY} \\ \hline \text{Overall Reaction:} & \mathrm{ML_nX} + \mathrm{Y} \rightleftharpoons \mathrm{ML_nY} + \mathrm{X} \end{array}$$

If we assume that $k_{-2} << k_2$, the rate law for the formation of products is the rate law of the second step.

$$\frac{d\left[\mathrm{ML}_n\right]}{dt} = k_2[\mathrm{ML_n}][\mathrm{Y}]$$

We can assume that the concentration of the intermediate is small enough that it would be difficult or impossible to measure its concentration. Here, we can evoke the steady-state approximation and assume that the concentration, $[\mathrm{ML_n}]$, is approximately unchanging over the course of reaction. The $[\mathrm{ML_n}]$ depends on k_1, k_{-1} and k_2. These assumption are expressed mathematically as follows.

$$\frac{d\left[\mathrm{ML}_n\right]}{dt} = k_1\left[\mathrm{ML}_n\mathrm{X}\right] - k_{-1}\left[\mathrm{ML}_n\right]\left[\mathrm{X}\right] - k_2\left[\mathrm{ML}_n\right]\left[\mathrm{Y}\right] = 0$$

We can then use the equation above to solve for $[\mathrm{ML_n}]$.

$$\mathrm{ML_n} = \frac{k_1\left[\mathrm{ML}_n\mathrm{X}\right]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

Then substitution this into the rate law given above for the second step of the mechanism. This would yield a rate law that depends only on species with measurable concentrations.

$$\frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = \frac{k_2k_1\left[\mathrm{ML}_n\mathrm{X}\right]\left[\mathrm{Y}\right]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

The rate law above suggests that the rate of product formation has an inverse relationship to the concentration of the outgoing ligand, X. This is one piece of evidence that can be used to distinguish a Dissociative mechanism; that is if the rate of reaction decreases as [X] in solution is increased it is evidence of a D mechanism. This rate law also suggests that ther is a complicated dependence of the reaction rate on the concentration of incoming ligand, Y. The importance of [Y] compared to [X] depends mathmatically on the weight of the two values in the demoninator of the rate law. If [X] >> [Y], then a valid approximation is to assume that the $k_2[\mathrm{Y}]$ term is relatively small and simplify the rate law by dropping it out completely.

$$\text{If } \mathrm{X} >> \mathrm{Y}\text{, then simplify: } \frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = \frac{k_2k_1\left[\mathrm{ML}_n\mathrm{X}\right]\left[\mathrm{Y}\right]}{k_{-1}[\mathrm{X}]}$$

The resulting rate law (above) has a simpler dependence on [Y]; that is when [X] is large, the reaction rate is directly related to [Y].

The opposite extreme is under conditions of high [Y]. This yields a rate law that is first order in its dependence on the reactant metal complex. When [Y] is large, and the $k_{-1}[\mathrm{X}]$ term is relatively insignificant, the rate law can be simplified to the pseudo-first order rate law as follows.

$$\text{If } \mathrm{Y} >> \mathrm{X}\text{, then simplify: } \frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = k_1[\mathrm{ML_nX}]$$

The best type of experimental evidence to determine a dissociative mechanism would be a systematic study of the dependence of rate on both [X] and [Y]. However, the dissociative reaction is unique in that it displays this type of saturation kinetics at high concnetration of the incoming ligand, and so the study of how a reaction rate behaves under high [Y] is common.

First-order reactions

Under conditions of high [Y], the a reaction following a D mechanism is said to follow "first order" kinetics. This type of reaction is sometimes called a first order reaction. That means the rate law depends on only one concentration term.

Why does the dissociative mechanism depend on concentrations in this specific way?

The rate depends on one molecule losing a ligand. Once it does so, a second ligand can replace the one that left. However, losing a ligand may be harder to do than gaining a new one. To lose a ligand, a bond must be broken, which costs energy. To gain a new ligand, a bond is made, releasing energy. That first step is harder to do, so it takes longer. It is a bottleneck that slows the reaction down. It is called the rate-determining step.

- The rate-determining step is the slow step of the reaction.
- The rate-determining step controls the rate of the overall reaction; everything else has to wait for that step to happen.
- Once the rate-determining step has occurred, everything else follows very quickly.

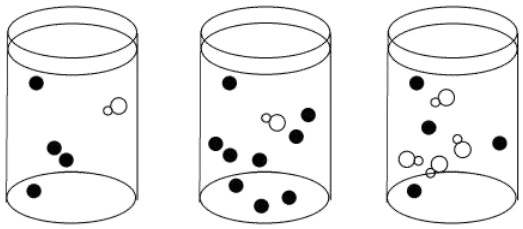


Figure 5.3.1.1: A bottleneck in a reaction. If the reaction must wait for the white molecule to dissociate, it doesn't matter how many black molecules there are; the reaction still goes just as slow. However, the more white molecules there are, the more frequently they will be able to react with the black molecules as dissociation occurs.

No collision is necessary for the metal complex to lose a ligand. Instead, a bond in the metal complex has to break. That just takes time and energy. As a result, concentration of the incoming ligand matters very little.

We should think a little more about energy requirements, available energy and reaction rate. It takes a certain amount of energy to break a bond. Over any given period of time, a specific amount of energy is available in the surroundings to use. That energy is not available uniformly. Some molecules will get more energy from their surroundings and others will get less. There will be a statistical distribution, like a bell curve, of energy available in different molecules. That means bond-breaking events are governed by statistics.

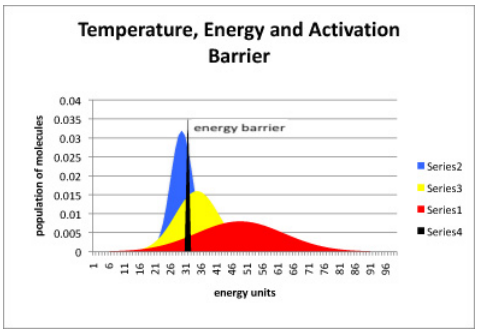


Figure 5.3.1.2 The relationship between temperature, energy available, and energy barrier. The black line represents energy needed to start the reaction, also called the energy barrier or the activation barrier. The blue curve is the distribution of available energy in a group of molecules at a cooler temperature. The yellow curve is for a group of molecules that is a little warmer, and the red curve even warmer.

In figure 5.3.1.2 most of the molecules at the low temperature (blue) do not have enough energy to begin the reaction. A small portion do, and so the reaction will proceed, but very slowly. In the yellow curve, there is more energy available, and so a large fraction of molecules have the energy necessary to begin the reaction. In the red curve, the vast majority have sufficient energy to react. Thus, one of the factors governing how quickly a reaction will happen is the energy needed, or activation barrier. A second factor is the energy available, as indicated by the temperature.

Of course, even if there is enough energy for the reaction, the reaction might not occur yet. Energy is necessary but not sufficient to start a reaction. There are also statistical factors in terms of whether a molecule has its energy allotted into the right places, or in

some cases, whether two molecules that need to react together are oriented properly.

Suppose at a given temperature it takes a specific amount of time for half the molecules to gain enough energy so that they can undergo the reaction. That amount of time is called the half life of the reaction. After one half life, half the molecules have reacted and half remain. After a second half life, half the remaining molecules (another quarter, for three quarters of the original material in all) have also reacted, and a quarter still remain. After a third half life, half the remaining ones (another eighth, making it seven eighths reacted in total) will have reacted, leaving an eighth of the original material behind.

- Exponential decay is based on a statistical distribution of energy availability.
- The concept of half life is related to exponential decay.
- It takes a fixed period of time for a half of the metal complex obtain enough energy to dissociate.

Thus, the time it takes for the reaction to happen does not really depend on the concentration of anything.

However, the change in *concentration* over time -- the quantity that we can usually measure most easily -- depends on the original concentration, and for that reason the concentration of the metal complex appears in the rate law.

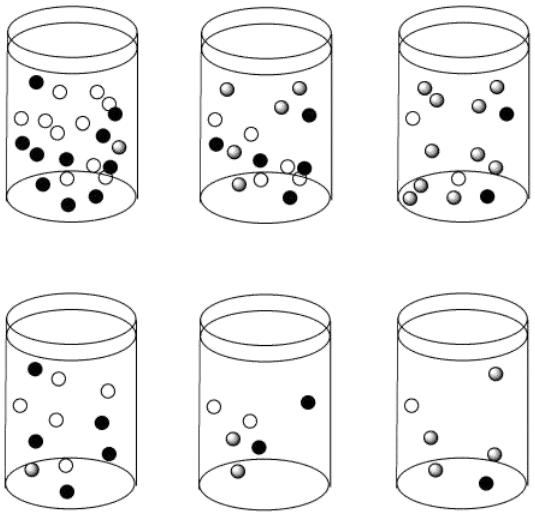


Figure 5.3.1.3 The reactions in the top row and bottom row are proceeding with the same half-life as we move from left to right. However, the top row starts out more concentrated than the bottom row. As a result, the *concentrations* in the top row are changing more quickly than in the bottom row.

Suppose the half life for a particular case of ligand substitution is one second. After a half life, a 1 M solution becomes 0.5 M, so the rate of change in concentration per time is 0.5M/s. But after the same half life, a 0.5 M solution becomes 0.25 M, so the change in concentration is 0.25 M/s.

? Exercise 5.3.1.1

If a first order reaction has a half-life of 120 seconds, how much of the original material is left after

a) four minutes? b) six minutes? c) eight minutes? d) ten minutes?

Answer a

4 minutes = 240 seconds = 2 x 120 second = 2 half lives.

Material left = 50% x 50% = 0.5 x 0.5 = 0.25 = 25% left

Answer b

6 minutes = 360 seconds = 3 x 120 second = 3 half lives.

Material left = 0.5 x 0.5 x 0.5 = 0.125 = 12.5% left

Answer c

8 minutes = 480 seconds = 4 x 120 second = 4 half lives.

Material left = 0.5 x 0.5 x 0.5 x 0.5 = 0.0625 = 6.25% left

Answer d

10 minutes = 600 seconds = 5 x 120 second = 5 half lives.

Material left = 0.5 x 0.5 x 0.5 x 0.5 x 0.5 = 0.03125 = 3.125% left

Exercise 5.3.1.2

Given the first-order dissociative rate law above, what would happen to the reaction rate for substitution in each of the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is halved
c. the concentration of ligand is doubled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is halved

Answer a

Dissociative Rate Law: Rate = $[ML_n]$, if ML_n is the complex. There is no dependence on [X], if X is the new ligand.

Rate will double: Rate = 2 x $[ML_n]_0$, if $[ML_n]_0$ is the original concentration.

Answer b

Rate will be halved: Rate = 0.5 x $[ML_n]_0$.

Answer c

Rate will triple: Rate = 3 x $[ML_n]_0$.

Answer d

Rate will be halved: Rate = 0.5 x $[ML_n]_0$.

Exercise 5.3.1.3

Plot graphs of initial rate vs concentration to show what you would see in dissociative substitution.

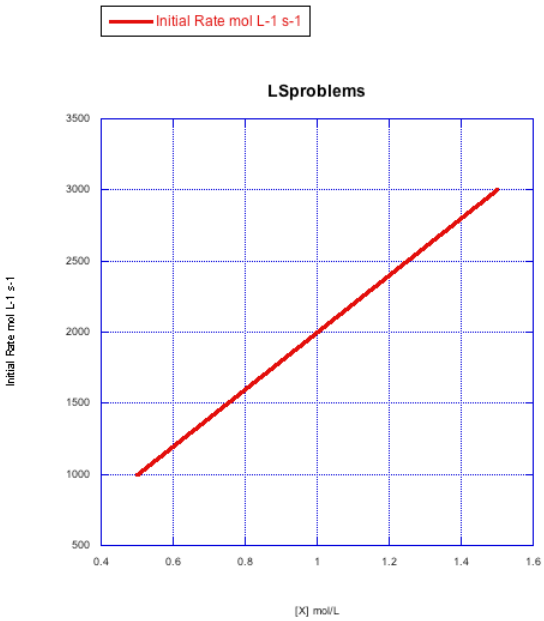
a) The concentration of metal complex, $[ML_n]$, is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

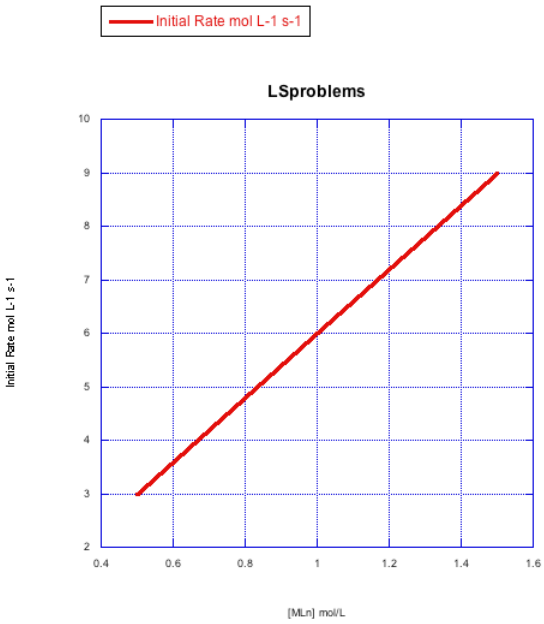
b) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L

Exercise 5.3.1.4

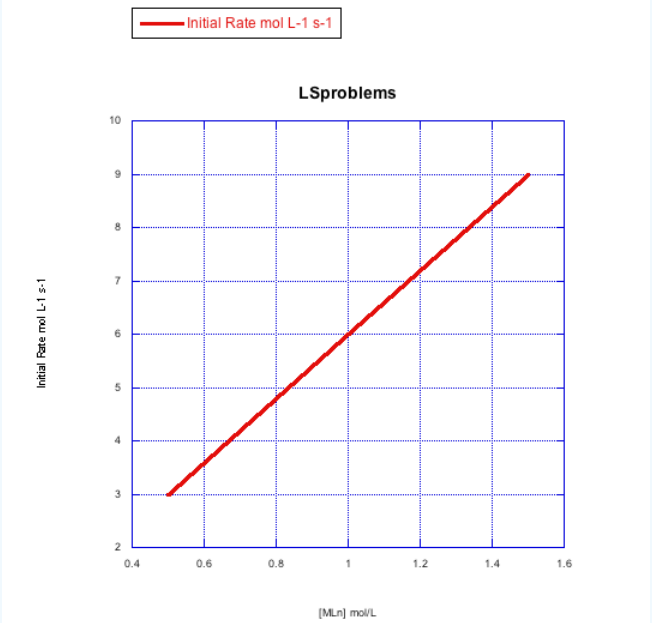
Given the following sets of initial rate data, determine whether each case represents a dissociative substitution. [MLn] = concentration of the coordination complex; [X] = concentration of incoming ligand.

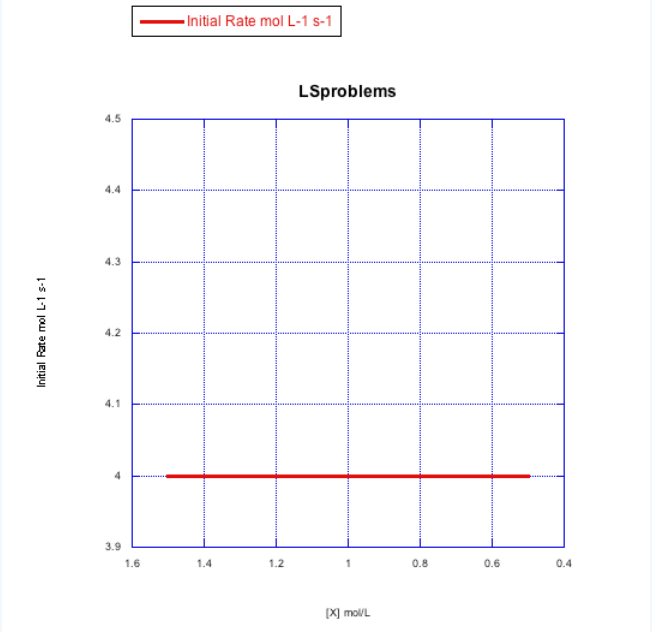
a)


Initial Rate mol L-1 s-1
LSproblems
Initial Rate mol L-1 s-1
3500
3000
2500
2000
1500
1000
500
0.4
0.6
0.8
1
1.2
1.4
1.6
[X] mol/L


Initial Rate mol L-1 s-1
LSproblems
Initial Rate mol L-1 s-1
10
9
8
7
6
5
4
3
2
0.4
0.6
0.8
1
1.2
1.4
1.6
[MLn] mol/L

b)





Answer a

The rate increases with both concentration of metal complex and incoming ligand. This looks like an associative mechanism.

Answer b

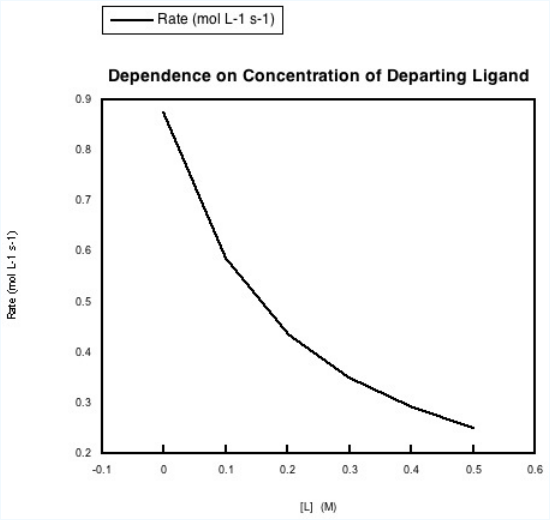
The rate depends on concentration of the metal complex, but not the incoming ligand. This looks like a dissociative mechanism.

Answer c

The rate depends on the concentration of incoming ligand, but not the metal complex. Whatever is going on here, it isn't a simple dissociative mechanism.

Exercise 5.3.1.5

In the following data, the concentration of the metal complex and the incoming ligand were held constant, but more of the departing ligand was added to the solution.



a) Explain what the data says about rate dependence on this concentration.

b) Explain this rate dependence in terms of the reaction.

Answer a

The rate of the reaction is depressed when the concentration of the departing ligand is increased.

Answer b

This dependence could indicate an equilibrium in the dissociative step. The more departing ligand is added, the more the equilibrium is pushed back towards the original metal complex. With less dissociated metal complex around, the entering ligand cannot form the new complex as quickly.

Exercise 5.3.1.6

In certain solvents, such as THF, acetonitrile and pyridine, the rate law for substitution often appears to be Rate = $k_1[ML_n] + k_2[ML_n][X]$, in which X is the incoming ligand and ML_n is the metal complex.

a) What do these solvents have in common?

b) What is a possible explanation for this rate law?

c) This rate law has been shown to be consistent with an entirely associative mechanism. How is that possible?

Answer a

These solvents all have lone pairs. They could be Lewis bases or nucleophiles.

Answer b

It looks like two competing mechanisms. On term suggests a dissociative mechanism, whereas the other term suggests a dissociative mechanism. They could be happening in competition with each other.

Answer c

On the other hand, it could be that there is one mechanism with two different nucleophiles. If the incoming ligand is the nucleophile, the term on the right shows up in the rate law. If the solvent is the nucleophile, forming a third complex, the term on the left shows up in the rate law. That's because we would typically change the amount of metal complex and the amount of ligand that we add to the solution in order to determine the rate law, but we wouldn't normally be able to change the concentration of the solvent, so it would be a constant. (How could you confirm this explanation in an experiment?)

This page titled 5.3.1: Rate Law for Dissociative Mechanisms is shared under a CC BY-SA license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.4: Dissociative Mechanism and Kinetics** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

5.3.2: Rate Laws for Interchange Mechanisms

Interchange (I) Mechanisms take place in one concerted step where there is no intermediate, or the intermediate is elusive. The reactio nessentially occurs in once step in which bond forming and bond breaking is concerted, as shown below. The species, $[\mathrm{Y}\cdots\mathrm{ML_n}\cdots\mathrm{X}]^{\ddagger}$, can be defined as either a transition state or a very short-lived intermediate.

$$\text{Step 1 (Concerted):} \quad \mathrm{ML_nX + Y} \rightleftharpoons [\mathrm{Y}\cdots\mathrm{ML_n}\cdots\mathrm{X}]^{\ddagger} + \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_nY + X}$$

The rate law of this one-step reaction depends on whether the relative rates of the forward and reverse reactions. When the reaction is practically irreversible, then the rate depends only on the formation of product, and not its reaction to re-form product. In this case, the rate law is a simple second-order rate law.

$$\frac{d[\mathrm{ML_nY}]}{dt} = k_1[\mathrm{ML_nX}][\mathrm{Y}]$$

On the other hand, if the rate of re-formation of reactant is significant, then the rates of forward and reverse reactions must be considered in the rate law.

$$\frac{d[\mathrm{ML_nY}]}{dt} = k_1[\mathrm{ML_nX}][\mathrm{Y}] - k_{-1}[\mathrm{ML_nX}][\mathrm{X}]$$

In the latter case where there is a dependence of rate on both [X] and [Y], an effective strategy is to employ the condition where solution concentration of both [X] and [Y] are simultaneously high so that the reaction is effectively a competition of two pseudo-first order reactions that depend primarily on the metal complex concentrations. In such a case as this, another helpful piece of information is the equilibrium constant for the reaction ($K = \frac{k_1}{k_{-1}}$). The rate law is written below.

$$\text{When [X] and [Y] are very high:} \quad \frac{d[\mathrm{ML_nY}]}{dt} = k_1[\mathrm{ML_nY}] - k_{-1}[\mathrm{ML_nX}] = -\frac{d[\mathrm{ML_nX}]}{dt}$$

One distinguishing feature of an I mechanism compared to a D mechanism can be determined from such an experiment under high concentration of X and Y. In the case of a D mechanism and sufficiently high concentration of incoming ligand, [Y], the reaction demonstrations saturation kinetics to give a pseudo-first order rate law depending only on the concentration of reactant metal complex. In the case of I, the reaction rate is not a simple first order rate law because even under high [Y] and [X], there is a dependence of rate on concentration of the product complex.

Reactions that are I_a or I_d are distinguished by the relative strength of the M-X and M-Y bond in the transition state. These reactions can be distinguished by varying the Identities of X and Y to determine how the reaction rate depends on identity of X and Y. If there is a large dependence on the incoming ligand, and less so on the outgoing ligand, it could be classified as an I_a mechanisms. The opposite is also true.

This page titled 5.3.2: Rate Laws for Interchange Mechanisms is shared under a CC BY-SA license and was authored, remixed, and/or curated by Kathryn Haas.

5.3.3: Rate Law for Associative Mechanisms

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating an intermediate, $\mathrm{ML_nXY}$, with a higher coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} &\text{Step 1 (Association):} && \mathrm{ML_nX + Y} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_nXY} \\ &\text{Step 2 (Dissociation):} && \mathrm{ML_nXY} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML_nY + X} \\ \hline &\text{Overall Reaction:} && \mathrm{ML_nX + Y} \rightleftharpoons \mathrm{ML_nY + X} \end{aligned}$$

To determine the rate law, we can use a similar process as we followed for D mechanisms, which are also two steps. Assuming that $k_2 >> k_{-2}$, the rate of formation of product from the second step is:

$$\frac{d[\mathrm{ML_nY}]}{dt} = k_2[\mathrm{ML_nXY}]$$

The steady state approximation allows us to assume that the intermediate is in low concentration (too low to be reliably measured) and that it is unchanging. We can use the rate law for the first step to find $[\mathrm{ML_nXY}]$ in terms of species that can be reliably measured.

$$\frac{d[\mathrm{ML_nXY}]}{dt} = k_1[\mathrm{ML_nX}][\mathrm{Y}] - k_{-1}[\mathrm{ML_nXY}] - k_2[\mathrm{ML_nXY}] = 0$$

...solving this first-step rate law for $[\mathrm{ML_nXY}]$ gives $[\mathrm{ML_nXY}] = \dfrac{k_1[\mathrm{ML_nX}][\mathrm{Y}]}{k_{-1} + k_2}$

And then substitution $[\mathrm{ML_nXY}]$ into the rate law for the second step, and let $k = \frac{k_1 k_2}{k_{-1}+k_2}$ to gives the overall rate law below.

$$\frac{d[\mathrm{ML_nY}]}{dt} = \frac{k_1 k_2[\mathrm{ML_nX}][\mathrm{Y}]}{k_{-1} + k_2} = k[\mathrm{ML_nX}][\mathrm{Y}]$$

This overall rate law is second order, and first order with respect to each of the reactants. This means that there is a direct (linear) relationship between concentration of either reactant and the rate of reaction.

Why does the associative mechanism depend on concentrations in this specific way?

This is a case of two molecules coming together. If both compounds are dissolved in solution, they must “swim around” or travel through the solution until they bump into each other and react. The more concentrated the solution is, or the more crowded it is with molecules, the more likely are the reactants to bump into each other. If we double the amount of new ligand in solution, an encounter between ligand and complex becomes twice as likely. If we double the amount of metal complex in solution, an encounter also becomes twice as likely.

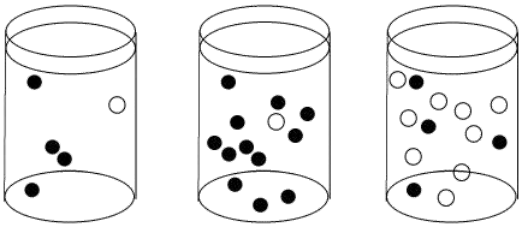


Figure 5.3.3.1 The effect of concentration on collision probability. In the first beaker, there is a chance that a black molecule and white molecule will meet and react together. The chance of a meeting is much higher in both the second beaker, where there are lots more black molecules, and in the third beaker, where there are many more white molecules.

Exercise 5.3.3.1

Given the associative rate law above, what would happen to the reaction rate for an associative substitution in the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is doubled
c. the concentration of ligand is tripled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is doubled

Answer a

Associative Rate Law: $Rate = [ML_n][X]$, if ML_n is the complex and X is the new ligand.

Rate will quadruple: $Rate = (2 \times [ML_n]_0) \times (2 \times [X]_0) = 4 \times [ML_n]_0[X]_0$, if $[X]_0$ and $[ML_n]_0$ are the original concentrations.

Answer b

Rate will sextuple: $Rate = (3 \times [ML_n]_0) \times (2 \times [X]_0) = 6 \times [ML_n]_0[X]_0$.

Answer c

Rate will nonuple: $Rate = (3 \times [ML_n]_0) \times (3 \times [X]_0) = 9 \times [ML_n]_0[X]_0$.

Answer d

Rate will stay the same: $Rate = (0.5 \times [ML_n]_0) \times (2 \times [X]_0) = 1 \times [ML_n]_0[X]_0$.

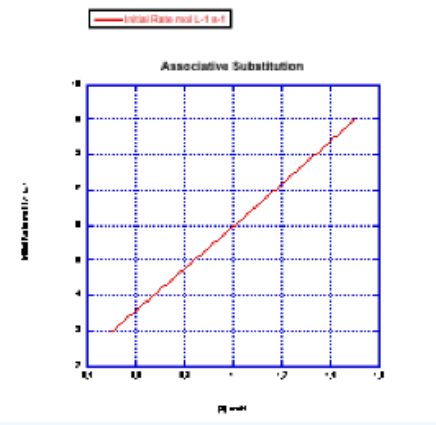
Exercise 5.3.3.2

Plot graphs of initial rate vs. concentration to show what you would see in associative substitution.

a) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

b) The concentration of metal complex, $[ML_n]$, is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

Answer



Exercise 5.3.3.3

In the previous problem, the experiment was run in a particular way for particular reasons.

a) Why was one concentration held constant while the other one was changed? Why not change both?

b) Why does the graph report "initial rate" -- just the rate at the very beginning of the reaction?

Answer a

Changing both concentrations at once would leave some doubt about whether one concentration had affected the rate, or the other concentration, or both. In practice, one concentration is usually held constant while the other is kept in excess and varied.

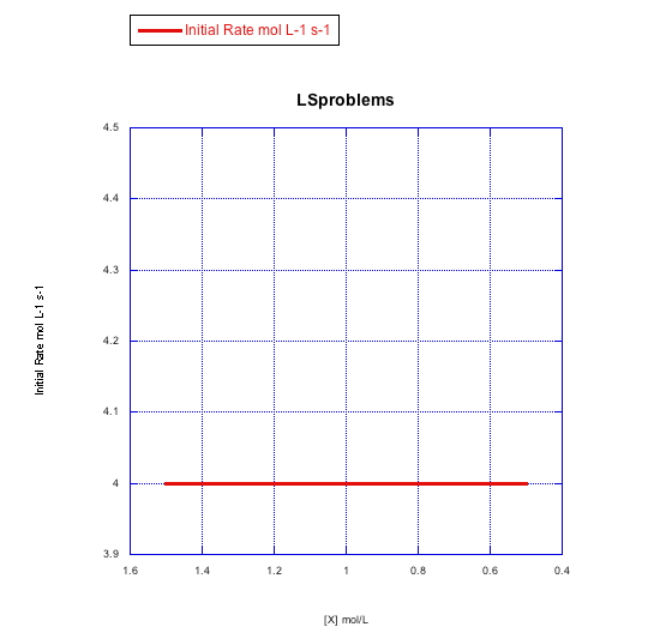
Answer b

Rate changes over time because the concentrations of reactants change as they are consumed. By reporting only the initial rate (usually meaning less than 5% or 10% complete, but possibly even less than that if a lot of data can be gathered very quickly), the concentrations are still about what you started with. That means you can report a rate that corresponds to a given concentration with confidence.

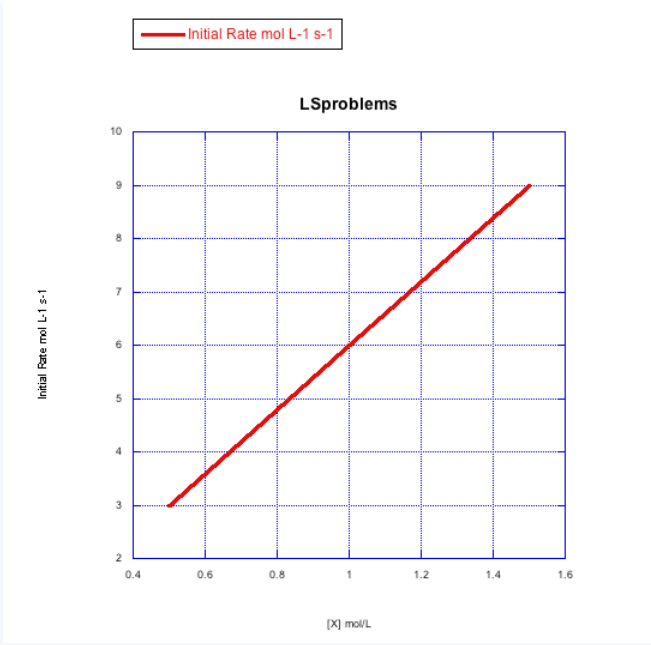
Exercise 5.3.3.4

Given the following sets of initial rate data (rates measured at the beginning of a reaction), determine whether each case represents an associative substitution.

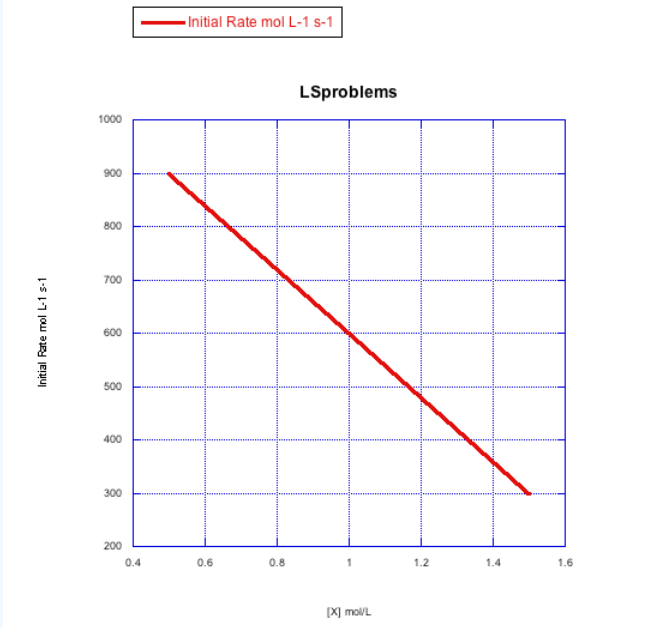
a)



b)

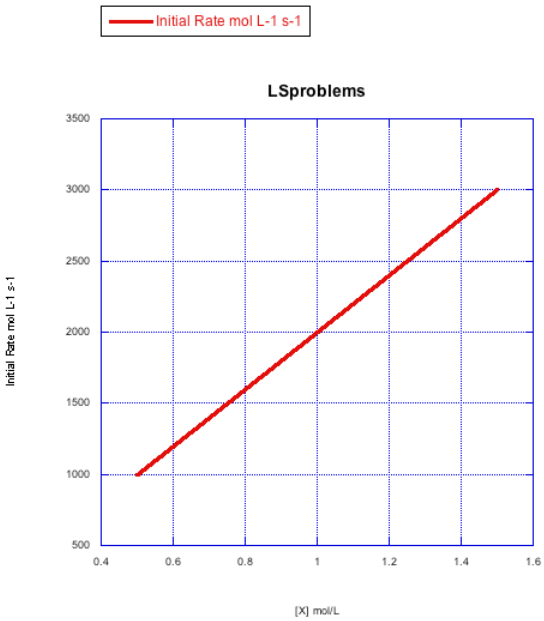


c)



d)

https://chem.libretexts.org/@go/page/429271



Answer a

The rate would change with the ligand concentration if associative. This rate is constant over a range of ligand concentrations, so the reaction is not associative.

Answer b

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

Answer c

The rate changes over the concentration range, but it decreases. This is the opposite of what should happen. This reaction does not follow a simple associative pathway.

Answer d

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

? Exercise 5.3.3.5

What information can be gained from the slopes of lines in Exercise 5.3.3.4?

Answer

Because $Rate = k[ML_n][L]$ is held constant while [L] is varied, then the slope of the line is k [ML_n]. Since you would know the value of [ML_n], you could obtain the rate constant from the quantity (slope/ [ML_n]).

Note that the rate law for an A mechanism, and a reversible I mechanism are of the same form: they are each first order with respect to each reactant. Thus, an unambiguous determination between the two is difficult because it would require detection of the

intermediate, which exists only at a very low concentration.

This page titled 5.3.3: Rate Law for Associative Mechanisms is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.3: Associative Mechanism and Kinetics** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

5.3.4: Preassociation Complexes

Most octahedral complexes react through either an associative or dissociative interchange mechanism (I_a or I_d). Although the rate laws should be different for these two cases, it is difficult to distinguish between them. The difficulty lies in the seemingly conflicting observations from experiments performed under limiting conditions of the incoming ligand. For example, in the case of the reaction of hexaaquochromium(III) ($[Cr(H_2O)_6]$) with ammonia (NH_3), the rate laws determined at high and low concentrations of the incoming ligand give different apparent rate laws. Under most conditions, the rate law appears to indicate a dissociative mechanism (ie rate is independent of the $[NH_3]$). But, at very high $[NH_3]$, the rate law appears to indicate an associative mechanism (ie the rate depends on $[NH_3]$).

This information might seem contradictory. However, it can be explained by the formation of a transient ion pair, usually called an encounter complex, in a step prerequisite to the rate-determining step(s). The Eigen-Wilkins Mechanism is based on this idea.

The Eigen-Wilkins mechanism

The Eigen-Wilkins *mechanism* is also a rate law, and it governs the reactions of octahedral metal complexes. This mechanism does not define the rate-limiting step; rather, it defines the existence of a pre-equilibrium step (ie an initial step that is *not rate-determining*) that results in formation of an encounter complex. The encounter complex is a short-lived ion pair of the metal complex and the incoming ligand; it is an intermediate formed through Coulomb interactions. For the conversion of a generic metal complex, where X is the leaving group and Y is the entering group, the overall reaction, pre-equilibrium step, and formation of products from the encounter complex are shown below:

	CHEMICAL EQUATION	EQUILIBRIUM EXPRESSION
Formation of Encounter Complex	$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (ML_5X \cdot Y)$	$K_E = \frac{[(ML_5X \cdot Y)]}{[ML_5X][Y]}$
Formation of Products:	$(ML_5X \cdot Y) \xrightarrow{k_2} ML_5Y + X$	$K_2 = \frac{[ML_5Y][X]}{[(ML_5X \cdot Y)]}$
Overall Reaction:	$ML_5X + Y \rightleftharpoons ML_5Y + X$	$K = \frac{[ML_5Y][X]}{[ML_5X][Y]}$

Fast pre-association

One possibility (that is most common) is that k_1 and $k{-}1$ are much larger than k_2. In this case, the encounter complex forms quickly, and once it forms, it also can quickly fall apart to re-form the reactant complex. When k_2 is relatively small then reaction of the encounter complex to form the product is the rate-determining step, and sometimes the concentration of encounter complex can be experimentally determined. However, it is rare that this is the case. A second, more common scenario iis that k_2 is also relatively large. Assuming that the formation of the encounter complex is still a fast step, then the rate still depends on the reaction of that encounter complex to form product. In either case, one path for deriving the rate laws is given below. The rate of formation of the product is defined by the second step:

$$\text{Rate} = \frac{d[ML_5Y]}{dt} = k_2[(ML_5X \cdot Y)]$$

Although the encounter complex may exist in high enough concentration to be detected, that is rare and technically difficult. Rather, the concentration of the encounter complex can be determined by manipulation of the equilibrium constant expression and some helpful assumptions. The equilibrium constant for formation of the encounter complex is:

$$K_E = \frac{[(ML_5X \cdot Y)]}{[ML_5X][Y]}$$

This can be rearranged to solve for concentration of the encounter complex.

$$[(ML_5X \cdot Y)] = K_E[ML_5X][Y] \tag{5.3.4.1}$$

...and we can re-write the rate experssion to remove the encounter complex from the expression. But by doing so, we remove the problem of the unmeasurable encounter complex being in the expression, but add the problem of the reactant metal complex being part of the expression:

$$\text{Rate} = k_2 K_E [\text{ML}_5\text{X}][\text{Y}]$$

The problem is that we don't precisely know what the value of $[\text{ML}_5\text{X}]$. We only know the total amount we initially added. But, we assume that k_1 is large, and so the initial concentration of the metal complex may change immediately to produce some of the encounter complex. As long as k_2 is relatively small, we can assume that the initial total concentration of metal complex at the start of reaction consists primarily of the reactant complex plus the encounter complex:

$$[\text{M}]_{\text{total}} = [\text{ML}_5\text{X}] + [(\text{ML}_5\text{X} \cdot \text{Y})]$$

We can substitute XXX into XXX to remove the encounter complex from the expression, then rearrange to solve for the reactant metal ion concentration, $[\text{ML}_5\text{X}]$:

$$\begin{aligned} [\text{M}]_{\text{total}} &= [\text{ML}_5\text{X}] + K_E[\text{ML}_5\text{X}][\text{Y}] \\ &= [\text{ML}_5\text{X}](1 + K_E[\text{Y}]) \\ [\text{ML}_5\text{X}] &= \frac{[\text{M}]_{\text{total}}}{1+K_E[\text{Y}]} \end{aligned}$$

Now this allows us to do one more substitution into the rate expression to get the rate into terms of constants and solution concentrations that are known:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{1 + K_E[\text{Y}]}$$

This rate expression is complex, but can be simplified under extremely high or low concentrations of the incoming ligand, [Y].

High [Y]: If the recation proceeds at high concentration of Y, then the denominator, $1 + K_E[\text{Y}]$ becomes approximately $K_E[\text{Y}]$. The expression is simplified to a first-order rate law under high [Y]:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{K_E[\text{Y}]} = k_2[\text{M}]_{\text{total}}$$

This would allow determination of k_2 because the rate could be directly observed by varying the concentration of $[\text{M}]_{\text{total}}$ at high [Y].

Low [Y]: If the reaction is run at very low [Y], then the denominator, $1 + K_E[\text{Y}]$ becomes approximately 1. We can let the observed rate constant, $k_{obs} = k_2 K_E$ to get a simplified second-order rate law under very low [Y]:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{K_E[\text{Y}]} = \frac{d[\text{ML}_5\text{Y}]}{dt} = k_{obs}[\text{M}]_{\text{total}}[Y]$$

The observed rate constant can be measured experimentally, and K_E can be determined theoretically ($k_{obs} = k_2 K_E$)

This page titled 5.3.4: Preassociation Complexes is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

5.3.5: Activation Parameters

The rate law shows how the rate of a reaction depends on concentrations of different species in solution. The proportionality constant, k, is called the rate constant. It contains other information about the energetic requirements of the reaction.

All reactions must overcome activation barriers in order to occur. The activation barrier is the sum of the energy that must be expended to get the reaction going. An activation barrier is often thought of, cartoonishly, as a hill the molecule has to climb over during the reaction. Once, there, it can just slide down the other side of the hill to become products. At the top of the hill, the molecule exists in what is called the "transition state". At the transition state, the structure is somewhere between its original form and the structure of the products.

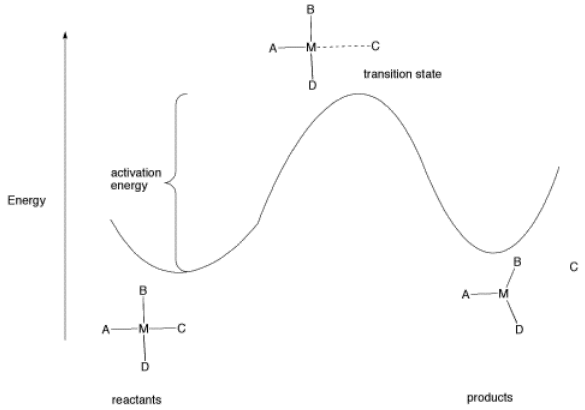


Figure 5.3.5.1: The activation barrier for a ligand dissociation step.

The type of diagram shown in figure LS6.1 is sometimes called a "reaction progress diagram". It shows energy changes in the system as a reaction proceeds. One or more activation barriers may occur along the reaction pathways, as various elementary steps occur in the reaction. In the above case, it is easy to imagine the source of the energy barrier, because some energy must be expended to break the bond to ligand C.

However, after that barrier is passed, energy is lowered again. This can happen for several reasons. Once C has separated from the metal complex, it is free to vibrate, tumble, roll and zip around all on its own. That means it can put its energy into any of those modes, independently of the metal complex. As a result, the entropy of the system increases. That lowers the overall "free energy" of the system. In addition, there may be some relief of crowding as the molecule changes from a four-coordinate complex to a three-coordinate complex, so strain energy is also lowered.

? Exercise 5.3.5.1

Make drawings depicting the relationship between reaction progress and energy for the following cases:

a) a new ligand binds to a four-coordinate complex, forming a five coordinate complex.

b) a two-step process in which a new ligand binds to a four-coordinate complex, forming a five coordinate complex, and then an old ligand dissociates to form a new, four-coordinate complex.

The rate constant gives direct insight into what is happening at the transition state, because it gives us the energy difference between the reactants and the transition state. Based on that information, we get some ideas of what is happening on the way to the transition state.

The rate constant can be broken down into pieces. Mathematically, it is often expressed as

$$k = (\frac{RT}{Nh})e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

In which R = the ideal gas constant, T = temperature, N = Avogadro's number, h = Planck's constant and $\Delta G^{\ddagger}$ = the free energy of activation.

The ideal gas constant, Planck's constant and Avogadro's number are all typical constants used in modeling the behaviour of molecules or large groups of molecules. The free energy of activation is essentially the energy requirement to get a molecule (or a

mole of them) to undergo the reaction.

Note that k depends on just two variables:

- $\Delta G^{\ddagger}$ or the energy required for the reaction
- T or the temperature of the surroundings, which is an index of the available energy

The ratio of activation free energy to temperature compares the energy needs to the energy available. The more energy available compared to the energy needed, the lower this ratio becomes. As a result, the exponential part of the function becomes larger (since the power has a minus sign). That makes the rate constant bigger, and the reaction becomes faster.

The activation free energy is constant for a given reaction. It can be broken down in turn to:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

in which $\Delta H^{\ddagger}$ = activation enthalpy and $\Delta S^{\ddagger}$ = activation entropy.

The activation enthalpy is the energy required for the reaction. The activation entropy deals with how the energy within the molecule must be redistributed for the reaction to occur. These two parameters can be useful in understanding events leading to the transition state.

For example, in ligand substitution, an associative pathway is marked by low enthalpy of activation but a negative entropy of activation. The low enthalpy of activation results because bonds don't need to be broken before the transition state, so it doesn't cost much to get there. That's favorable and makes the reaction easier. However, a decrease in entropy means that energy must be partitioned into fewer states. That's not favorable and makes the reaction harder. The reason the energy must be redistributed this way is that two molecules (the metal complex and the new ligand) are coming together to make one bigger molecule. They can no longer move independently of each other, and all of their combined energy must be reapportioned together, with a more limited range of vibrational, rotational and translational states to use for that purpose.

- Associative pathway: more bond making than bond breaking; lower enthalpy needs
- Associative pathway: two molecules must be aligned and come together; fewer degrees of freedom for energy distribution; decrease in entropy

On the other hand, the dissociative pathway is marked by a higher enthalpy of activation but a positive entropy of activation. The higher enthalpy of activation results because a bond must be broken in the rate determining step. That's not favorable. However, the molecule breaks into two molecules in the rate determining step. these two molecules have more degrees of freedom in which to partition their energy than they did as one molecule. That's favorable.

- Dissociative pathway: more bond breaking in rate determining step, higher enthalpy needs
- Dissociative pathway: one molecule converts to two molecules in rate determining step, greater degrees of freedom in two independently moving molecules, entropy increases

Thus, looking at the activation parameters can reveal a lot about what is going on in the transition state.

? Exercise 5.3.5.2

What factor(s) other than entropy might raise the free energy of the transition state going into an associative step between a metal complex and an incoming ligand? (What factor might make the first, associative step slower than the second, dissociative step?)

Answer

The metal centre is becoming more crowded as the new ligand arrives, so an increase in energy owing to steric hindrance may also play a role in the transition state energetics.

? Exercise 5.3.5.3

Other mechanisms for ligand substitution are also possible. The following case is referred to as an associative interchange (I_A).



a) Describe in words what happens in an associative interchange.

b) Predict the rate law for the reaction.

c) Qualitatively predict the activation entropy and enthalpy, compared with

i) an associative mechanism and

ii) a dissociative mechanism.

Answer a

The new ligand, B, is arriving at the same time as the old ligand, A, is departing. We might also describe it as new ligand B pushing old ligand A out of the complex.

Answer b

$Rate = k[ML_5A][B]$, which looks like an associative rate law.

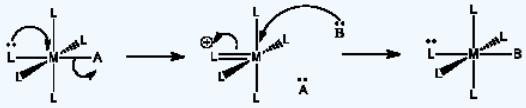
Answer c

This is a thought-provoking question without a definite answer. Associative mechanisms typically have lower activation enthalpy than dissociative mechanisms, because there has also been some bond-making prior to the bond-breaking in the rate determining step. The associative interchange would be a little more like the associative mechanism than dissociative. The mix of bond-making and bond-breaking at the transition state would make the enthalpy of activation relatively low.

Associative mechanisms have negative activation entropies, whereas dissociative mechanisms have positive activation entropies. The associative interchange could be in between the two, given that the elementary step would be close to entropically neutral overall. What happens at the transition state is a little harder to imagine, but it might reflect the small changes in entropy through the course of the reaction, producing a small entropy of activation. On the other hand, if the incoming ligand is forced to adopt some specific approach as it comes into the molecule (to stay out of the way of the departing ligand, for example) then that restriction could show up as a small negative activation entropy.

? Exercise 5.3.5.4

For the following mechanism:



a) Describe in words what is happening.

b) Predict the rate determining step.

c) Predict the rate law for the reaction.

d) Qualitatively predict the activation entropy and enthalpy, compared with

i) both an associative mechanism and

ii) a dissociative mechanism.

e) Suggest some ligands that may be able to make this mechanism occur.

Answer a

The lone pair donation from one ligand appears to push another ligand out.

Answer b

The first step is probably rate determining, because of the bond breaking involved.

Answer c

If the first step is rate determining, $Rate = k[ML_5A]$.

Answer d

Another question without a very clear answer. Compared with an associative mechanism, the activation entropy is probably much more positive, because additional degrees of freedom are being gained as the molecule heads over the activation barrier and one of the ligands separates to be on its own. However, the activation entropy may be less positive than in a regular dissociation, because in this case the breaking of one bond has to be coordinated with the formation of another.

The enthalpy of activation has both a bond-making and bond-breaking component, a little like in an associative mechanism. However, the amount of bond making here is probably less important, because pi bonds are typically not as strong as sigma bonds. The activation enthalpy is probably higher than an associative pathway but not as high as a dissociative one.

Answer e

The donor ligand must have a lone pair. Oxygen donors would be good candidates, because even if one lone pair is already donating in a sigma bond, an additional lone pair may be available for pi donation. The same thing is true for halogen donors. It would also be true for anionic nitrogen donors but not for neutral nitrogen donors, because a neutral nitrogen has only one lone pair.

This page titled 5.3.5: Activation Parameters is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.5: Activation Parameters** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

5.3.6: Some Reasons for Differing Mechanisms

We usually look for physical reasons why a given compound might undergo a reaction via one mechanism and not another. That ability adds to our understanding of chemistry. If we can take information and give it predictive value, then we may be able to make educated decisions about what is probably happening with new reactions.

Why might a reaction undergo a dissociative reaction rather than an associative one? What factors might prevent an associative pathway?

One reason may be that there is not enough room. In an associative step, an additional ligand comes in and binds to the metal. If it is already crowded, that may be difficult.

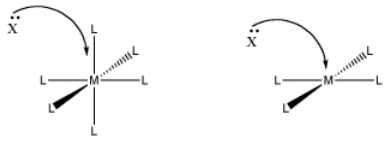


Figure 5.3.6.1: The role of steric crowding in ligand substitution. In one of these cases, the associative mechanism is less favored because of crowding that will occur in the transition state.

- Steric crowding may lead to a dissociative, rather than associative, mechanism.

Another reason has to do with electronics. Maybe the compound cannot easily accept an additional bonding pair. That may be the case if the compound already has eighteen electrons.

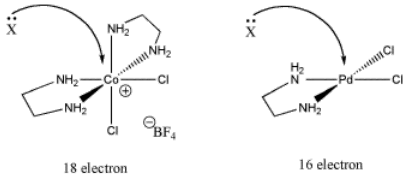


Figure 5.3.6.2 The role of electron count in ligand substitution. In one of these cases, the associative mechanism is less favored because the metal is already electronically saturated.

- Electronic saturation may lead to a dissociative, rather than associative, mechanism.

However, if there is less crowding, and more electrons can be accommodated, an associative pathway may result.

? Exercise 5.3.6.1

i) Draw structures for the following reactions. Pay attention to geometry.

ii) Predict whether each of the substitutions would occur through associative or dissociative mechanisms.

a) $AuCl_3py + Na\ N_3 \rightarrow Na^+\ [AuCl_3N_3]^- + py$

b) $Rh(C_2H_4)_2(acac) + C_2D_4 \rightarrow Rh(C_2D_4)_2(acac) + C_2H_4$

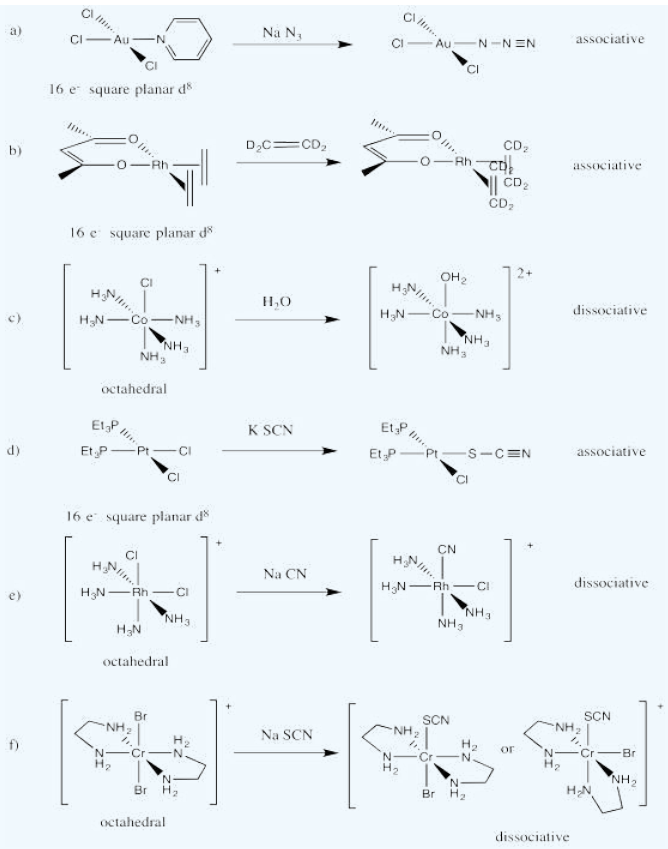
c) $[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_{2)}]^{2+} + Cl^-$

d) *trans*-$(Et_3P)_2PtCl_2 + {}^-SCN \rightarrow$ *trans*-$(Et_3P)_2PtCl(SCN) + Cl^-$

e) $Rh(NH_3)_4Cl_2^+ + {}^-CN \rightarrow Rh(NH_3)_4Cl(CN)^+ + Cl^-$

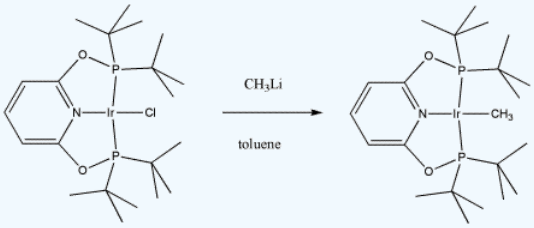
f) *trans*-$[Cr(en)_2Br_2\ ]^+ + {}^-SCN \rightarrow$ *cis*- and *trans*-$[Cr(en)_2Br(SCN)]^+ + Br^-$

Answer



Exercise 5.3.6.2

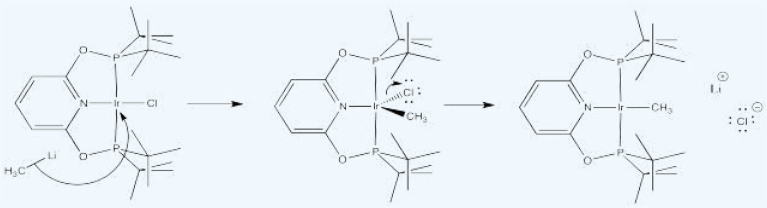
Maurice Brookhart of UNC, Chapel Hill, makes organometallic compounds in order to study fundamental questions about reactivity. In this case, he has reported making a new compound capable of "C-H activation", a reaction in which unreactive C-H bonds can be forced to break. This process holds the future promise of converting coal and natural gas into important commodities currently obtained from petroleum.



a) Draw, with curved arrows, a mechanism for the ligand substitution in the synthesis of this C-H activating complex.

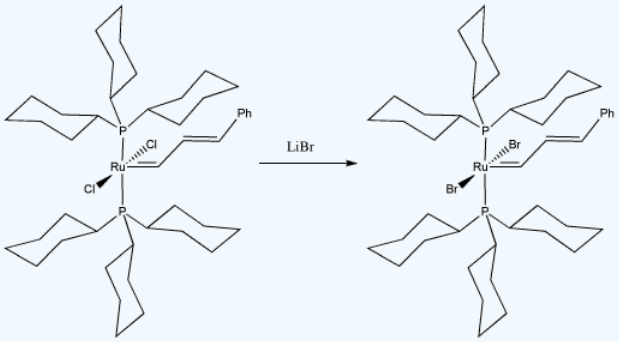
b) Explain your reasons for your choice of reaction mechanism.

Answer



Exercise 5.3.6.3

Bob Grubbs of Cal Tech was awarded the Nobel Prize in chemistry for his development of catalysts for olefin metathesis. Olefin metathesis is important both in the reforming of petroleum and in the synthesis of important commodities such as pharmaceuticals. In the following study, he replaced chlorides on a "Grubbs Generation I catalyst" to study the effect on the olefin metathesis reaction.

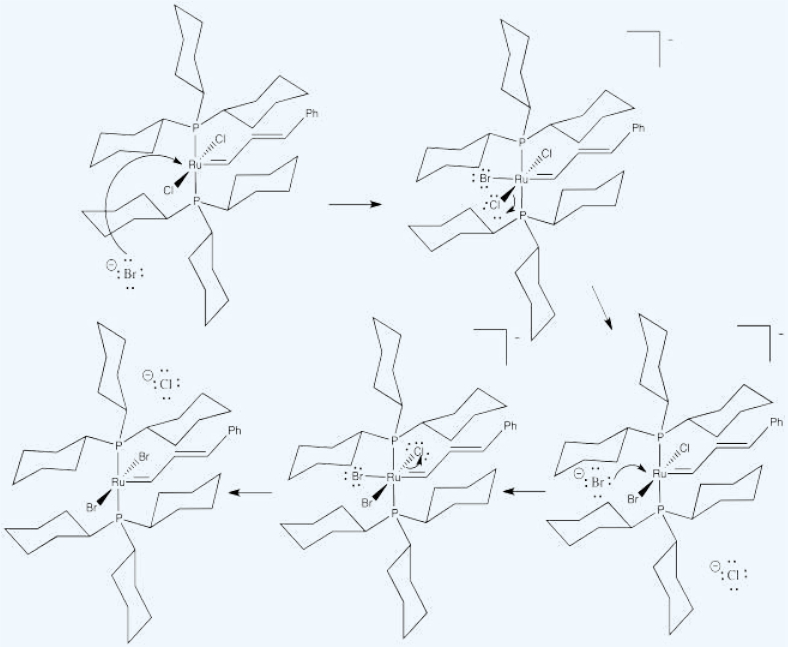


a) Draw, with curved arrows, a mechanism for the ligand substitution in this complex.

b) Explain your reasons for your choice of reaction mechanism.

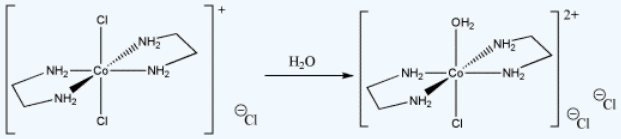
c) What factor(s) do you think Grubbs hoped to study by making this substitution in the catalyst?

Answer



Exercise 5.3.6.4

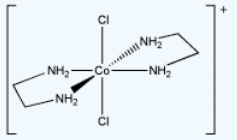
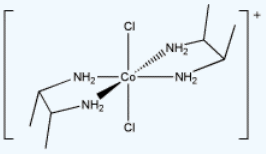
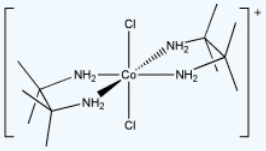
Sometimes, kinetic studies can give insight into a reaction if controlled changes in the reaction produce measurable results.



a) Draw, with curved arrows, a mechanism for the ligand substitution in this reaction.

b) Explain your reasons for your choice of reaction mechanism.

c) Explain the following kinetic data.

complex	substitution rate constant
	$3.2 \times 10^{-5}\ s^{-1}$
	$4.1 \times 10^{-3}\ s^{-1}$
	too fast to measure easily

Exercise 5.3.6.5

Several different structures were proposed for $Ni(cysteine)_2^{2-}$. Kinetic studies of substitution in this complex showed the rate was dependent in the concentration of both the metal complex and the incoming ligand. Which structure do you think is correct? Why?

This page titled 5.3.6: Some Reasons for Differing Mechanisms is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.6: Some Reasons for Differing Mechanisms** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

5.4: Experimental Evidence in Octahedral Substitutions

This section will review some of the common experiments that can provide evidence supporting different mechanisms, with a focus on the reactions of octahedral complexes.

This page titled 5.4: Experimental Evidence in Octahedral Substitutions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.4.1: Dissociation

Consider what must happen for the simplest case of a purely dissociative (D) reaction mechanism for an octahedral metal complex. The first step, and the rate-limiting step must be dissociation of one ligand to form an intermediate with a lower coordination number. Such a situation, where an octahedral complex looses a ligand, X, to become a square pyramidal intermediate is shown below in Figure 5.4.1.1.

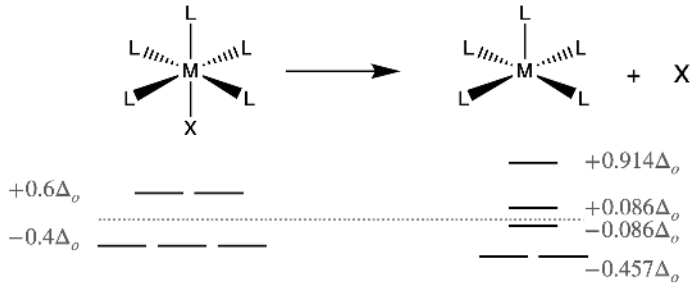


Figure 5.4.1.1: Dissociation of a ligand to form a square pyramidal intermediate. This would be the first step of a dissociative (D) reaction mechanism. The Ligand Field Activation Energy (LFAE) can be calculated from the splitting energies of the octahedron compared to the square planar intermediate. (CC-BY-SA; Kathryn Haas)

If the dissociation of a ligand is rate-determining, factors that lower the energy of the transition state or intermediate structures will speed the reaction rate. Here we could consider the differences in ligand-field stabilization energy (LFSE). The difference between the LFSE of the octahedral reactant and that of the intermediate is defined as the ligand field activation energy (LFAE). The LFAE can be calculated for a given d-electron count for an octahedral reactant and a square pyramidal intermediate using the information provided in Figure 5.4.1.1. Metal ions with particularly low (more negative) LFAE values tend to be more labile, while those with particularly high (less negative) values tend to be more inert. However, most octahedral complexes are expected to react through dissociative mechanisms due to the unfavorable steric crowding that must occur during an associative pathway.

The ease by which the M-X bond is broken will also influence rate of a dissociative reaction, and this can be probed experimentally. The following experiments can give evidence that support the argument that a reaction occurs by a dissociative pathway, or that it is dissociatively activated.

Experimental evidence that supports dissociative mechanism

1. Identity of the entering ligand has little effect on reaction rate.

If dissociation is the rate-determining step, the identity of the entering ligand, Y, should have little effect on the reaction rate. Therefore, an experiment that varies Y while holding X constant can indicate whether or not Y is involved in the rate-determining step. If the identity of Y has little effect on rate, then it must not be involved in the rate-determining step. Such experimental evidence can be taken as evidence of a dissociative mechanism. For example, the rate constants for reaction of $[Cr(NH_3)_5H_2O]^{3+}$ with different incoming ligands, shown below, has rate constants of similar magnitude (they are approximately within one order of magnitude), indicating a dissociatively activated mechanism. In this case, other lines of evidence suggest this is a reaction with a I_d mechanism.

$$[Cr(NH_3)_5H_2O]^{3+} + Y^- \rightleftharpoons [Cr(NH_3)_5Y]^{2+} + H_2O$$

Table 5.4.1.1: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry, 5th edition*, pg 449.

Entering Ligand, Y^-	Rate Constant, k_1 $(10^{-4} M^{-1} s^{-1})$
NCS^-	4.2
Cl^-	0.7
Br^-	3.7
$CF_3CO_2^-$	1.4

2. Steric Crowding of the Metal Complex

Steric crowding of the metal complex would inhibit a dissociative pathway through steric crowding of the entering ligand. However, steric crowding can increase the stability of the intermediate after dissociation of the ligand from the crowded octahedral complex. If the reaction rate increases with steric crowding of the reactant complex, this is taken as evidence to support a dissociative mechanism.

3. Volume of Activation

One molecule generally takes up less space than two sperate molecules. This usually holds true in solution. Measurement of a rate constant's dependence on pressure can be used to determine the volume of activation (ΔV_{act}) and give insight into the mechanism of that reaction. In a dissociation mechanism, the dissociation causes one metal complex to become two separate molecules. Thus, the intermediate should, in principle, take up more space than the reactant complex. In a situation like this, we expect that the rate of reaction should decrease with increasing pressure, giving a positive value for ΔV_{act}. However, solvation of ions can influence volume, and this should be considered in interpretation of pressure-dependence data.

4. Increased coulombic attraction with the leaving group decreases reaction rate.

Couloubic (electrostatic) attraction between the dissociating ligand, X, and the metal complex should slow ligand dissociation. Coulombic attraction increases with increased magnitude of charges and with decreased distance. If the reaction rate slows with increased charge of the metal ion or the ligand itself, this is taken as evidence of a dissociative mechanism. Likewise, if rate decreases as the radius of the central metal ion is decreased, this is evidence to support a dissociative mechanism.

5. Increased strength of the M-X bond decreases reaction rate.

Free energy relationships between the formation constant of M-X and the kinetic rate constant of the reaction can provide evidence to support a dissociative mechanism (Discussed in the next section).

This page titled 5.4.1: Dissociation is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.4.2: Linear Free Energy Relationships

The Linear Free Energy Relation (LFER) is a tool that can indicate the importance of bond breakage or bond formation in the rate-determining step. In the case of a dissociative mechanism, for example, bond breaking is critical for reaction progress. Therefore, the strength of the M-X bond influences not only the extent to which the reaction will happen, but also the rate. Although thermodynamic stability of a complex does not necessarily indicate the kinetic rate at which it will react, there is a relationship between bond stability and the rate of reaction *if the breaking or formation of that bond is involved in the rate-determining step*. The relationship can be stated as follows:

$$ln\ k = ln\ K + c$$

And this relationship can be justified using the Arrhenius equation and equation for the temperature-dependence of the equilibrium constant.

$$\ln k = \ln A - \frac{E_A}{RT} \quad \text{and} \quad \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

In an experiment designed to test the Linear Free Energy Relationship, several reactions would be conducted under nearly identical conditions, where only the identity of the leaving group, X, is varied. In these experiment, the temperature would be constant and the same in each case. If we assume that the pre-exponential factor, A is the same for each reaction condition (and it should be at identical temperatures for analogous reactions), then the $\ln K$ term of the Arrhenius equation becomes proportional to the activation energy, E_a (and proportional to Gibb's energy of activation, $\Delta G^\ddagger$, and Gibb's energy ΔG). And since the Gibb's energy is related to the equilibrium constant, K, by $\Delta G = RT \ln K$, the value of K and k should be correlated. Likewise, if T is constant over the reaction conditions and ΔS° is similar across the analogous reactions (which it should be), then $\ln K$ becomes proportional to enthalpy, ΔH°, which is proportional to Gibb's free energy of reaction ΔG°.

If a Linear Free Energy Relation plot of $\ln K$ vs $\ln k$ is linear, but with a slope less than one, it indicates a dissociative mechanism with some degree of associative character (for example, an I_d mechanism or a mechanism involving the formation of preassociation complex). If the plot of $\log K$ vs $\log k$ for the reactions is linear, this is evidence that the reaction is dissociative. An example for a linear free energy plot is shown in Figure 5.4.2.1for the hydrolysis of $[\mathrm{Co(NH_3)_5X]_2^+}$ (this is the substitution of $\mathrm{X^-}$ with $\mathrm{H_2O}$).

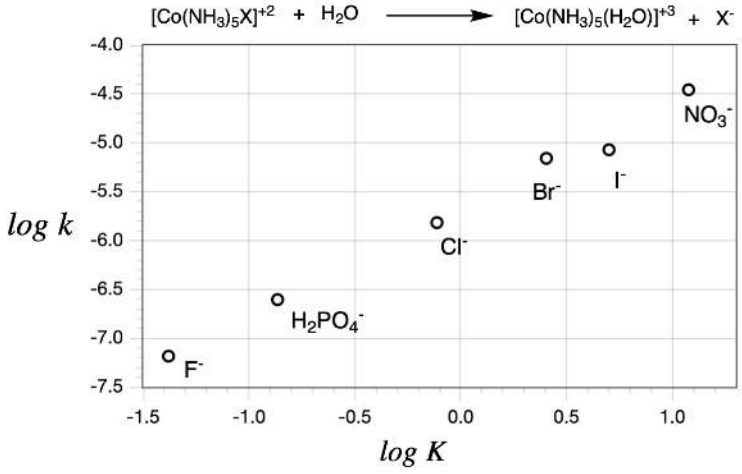


Figure 5.4.2.1: Linear Free Energy relationship lot for $[\mathrm{Co(NH_3)_5X]_2^+}$ where $\mathrm{X^-}$=$\mathrm{F-, H_2PO_4-, Cl-, Br-, I-, NO_3^-}$. This is summarized in Cooper H. Langford, *Inorganic Chemistry* **1965** *4* (2), 265-266, DOI: 10.1021/ic50024a041. (CC-BY-SA; Kathryn Haas)

When the slope is approximately 1, as it is in the case of $[\mathrm{Co(NH_3)_5X]_2^+}$ in Figure 5.4.2.1, it indicates that the variation of the $\mathrm{X^-}$ leaving group has a similar effect on the magnitude of both ΔG (thermodynamic, related to K) and $\Delta G^\ddagger$ (kintetic, related to k). In other words, a slope close to 1 indicates a purely dissociative pathway (D). This data shown in Figure 5.4.2.1, for example, is evidence of a dissociative mechanism for $[\mathrm{Co(NH_3)_5X]_2^+}$.

The argument that a reaction is dissociative can also be supported by evidence showing little effect of the incoming ligand on reaction rate. For example, data supporting the argument that $[Co(NH_3)_5H_2O]^{+}_{3}$ reacts by a dissociative pathway is shown below. The data show that variation of the identity of the incoming ligand, Y^{-}, has little effect on the rate constant (they are approximately within one order of magnitude).

$$\text{For the reaction: } [Co(NH_3)_5H_2O]^{3+} + Y^{m^-} \rightleftharpoons [Co(NH_3)_5Y]^{(3\ -m)^+} + H_2O$$

Table 5.4.2.1: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo cobalt(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry, 5th edition*, pg 448.

Entering Ligand, Y^{-}	Rate Constant, k_1 $(10^{-6}s^{-1})$ (pseudo-first order with excess $[Y^{-}]$)
H_2O	100
N_3^-	100
SO_4^{2-}	24
Cl^-	21
NCS^-	16

This page titled 5.4.2: Linear Free Energy Relationships is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.4.3: Associative Mechanisms

Associative mechanisms tend to be less common for octahedral complexes as a result of steric hindrance of the metal ion by six ligands. However, reactions of octahedral complexes with associative character are more likely if the ligands have low steric bulk and/or the central metal ion is larger with longer bonds (as in the case of $4d$ and $5d$ metal ions). Reactions of octahedrons have also been observed in cases of low d-electron count or low electron density around the central ion, presumably making nucleophilic reaction more favorable. If an octahdral complex is determined to have associative character, in most cases it is associatively-active interchange (I_a).

The evidence that supports arguments for associative mechanisms is somewhat the opposite as that which would support dissociative character. One typical piece of evidence that supports an associative pathway is **a large effect of the incoming ligand on the reaction rate constant**. For example, in the reaction of hexaaquo chromium (III) ion ($[\mathrm{Cr(H_2O)_6}]^3+$) with various incoming ligands (shown below), rate constants vary by several orders of magnitude. This data is evidence of an associative mechanism (I_a). In contrast, the reaction of pentaamineaquo chromium (III) ion ($[\mathrm{Cr(NH_3)_5H_2O}]^3+$) occurs by an associative mechanism (data shown in Section 12.4.1). The difference in reaction mechanisms for different chromium (III) complexes can be justified by the different electron densities around their metal ion center. The ammine ligand is a stronger sigma donor and thus the metal center is more electron rich in the case of $[\mathrm{Cr(NH_3)_5H_2O}]^3+$. Nucleophilic reaction by an incoming ligand is thus more likely in the case of $[\mathrm{Cr(H_2O)_6}]^3+$, which has a more electrophilic center.

$$[\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{Y^-} \rightleftharpoons [\mathrm{Cr(H_2O)_5Y}]^{2+} + \mathrm{H_2O}$$

Table 5.4.3.1: Rate Constants for Exchange of Aquo Ligand of hexaaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry, 5th edition*, pg 449.

Entering Ligand, $\mathrm{Y^-}$	Rate Constant, k_1 $(10^{-4} M^{-1} s^{-1})$
$\mathrm{NCS^-}$	180
$\mathrm{NO_3^-}$	73
$\mathrm{Cl^-}$	2.9
$\mathrm{Br^-}$	0.9
$\mathrm{I^-}$	0.08

Another piece of evidence that can support associative mechanisms is the temperature-dependence of the rate law, which in turn can yield the entropy of activation (represented as $\Delta S^{\ddagger}$ or ΔS_{act}). When an incoming ligand associates with a metal complex and two molecules beome one, there would be a negative change in the entropi (entropy decreases). A negative value for the entropy of activation indicates an associative pathway. An example of this is in the substitution of the aquo ligand in $[\mathrm{Ru(EDTA)(H_2O)}]^-$, which has a negative value of $\Delta S^{\ddagger}$, indicating an I_a mechanism.

This page titled 5.4.3: Associative Mechanisms is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.4.4: The conjugate base mechanism

The substitution reaction of acidic octahedral complexes (with ligands that can donate a proton) can be catalyzed in the presence of hydroxide ion (OH^-. Through an initial acid-base reaction, the metal complex can be deprotonated to its conjugate base. The deprotonation increases electron density on the metal center, facilitating the loss of the leaving group ligand, especially when the leaving ligand is trans to the deprotonation site. This mechanism is referred to as the **conjugate-base mechanism** or the $\mathbf{S_N1CB}$ (**S**ubstitution, **N**ucleophilic, first-order in the **C**onjugate **B**ase mechanism) mechanism. Although it involves a dissociative rate-limiting step, the rate law is consistent with the second-order kinetics because the rate also depends on the initial reaction of the base with the metal complex. In this mechanism, the first step is formation of the conjugate base of the metal complex by deprotonation of one of its ligands. This is a case where numerous lines of evidence are necessary to establish the mechanism.

Cobalt pentammine complexes, $Co(NH_3)_5X^{n+}$, have been studied extensively and are found to react through the conjugate-base mechanism. The way in which the actual mechanism was determined, and how other possible mechanism were ruled out are described below.

Evidence under acidic aqueous conditions

In acidic aqueous solutions, the reaction

$$[Co(NH_3)_5X]^{2+} + Y^- \longrightarrow [Co(NH_3)_5Y]^{2+} + X^-$$

was found to proceed through an aquo complex intermediate, $[Co(NH_3)_5OH_2]^{3+}$, which is also the dominant product despite the identity of the incoming ligand. In other words, to form the product of the reaction above, there are two substitution steps necessary (shown below).

$$[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(OH_2)]^{3+} + X^- \quad \text{(step 1, form aquo intermediate)}$$

$$[Co(NH_3)_5(OH_2)]^{3+} + Y^- \rightleftharpoons [Co(NH_3)_5Y]^{2+} + H_2O \quad \text{(step 2, form final product)}$$

The first step in the reaction is the breaking of a $Co-X$ bond and the formation of a $Co-OH_2$ bond (step 1). Subsequently, Y^- can replace the aquo group (step 2).

In aqueous solution, water is always present at a much higher concentration than the various possible entering groups Y^-, so it is reasonable that the aquo complex should be favored in the competition to form the new bond to $Co(III)$. Nevertheless, the strength of the $Co-Y$ bond should depend on the nucleophilicity of Y^- in these substitution reactions. Thus, the amount of $[Co(NH_3)_5Y]^{2+}$ product should increase with increasing nucleophilicity of Y^-. The fact that the aquo complex is the predominant reaction product despite the identity of Y^- strongly suggests that the the $Co-X$ bond breaking is more important in the reaction outcome than formation of the new bond to the incoming Y^-.

This evidence indicates dissociative character in the reaction. But the nature of the substitution mechanism is still unclear. For example, is the original $Co-X$ bond completely broken before the new $Co-OH_2$ bond has begun to form so that $Co(NH_3)_5^{3+}$ is a true intermediate? Does the mechanism involve a transitory intermediate where bonds are breaking and forming in a concerted fashion?

Evidence under basic aqueous conditions

The evidence of reaction mechanism under basic conditions is seemingly contradictory to what is described above. When the entering group, Y^-, is the hydroxide ion, the reaction is

$$Co(NH_3)_5X^{n+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{q-}$$

Substitution by hydroxide ion is kinetically faster than by the aquo ligand in acidic solutions, and the rate is law found to be second-order:

$$\frac{d\left[Co(NH_3)_5OH^{2+}\right]}{dt} = k\left[Co(NH_3)_5X^{n+}\right]\left[OH^-\right]$$

This rate law is consistent with an associative reaction involving nucleophilic attack by the hydroxide ion at the cobalt center. In an associative interchange mechanism, the $Co-OH$ bond formation occurs simultaneously with breaking of the $Co-X$ bond. However, just as in the case above, the hydroxo complex dominates even in the presence of Y^-. Thus, the hydroxide ion seems to be a uniquely effective nucleophile toward cobalt(III). However, nucleophilic displacements have been investigated on many other electrophile, and in general, hydroxide is not a particularly effective nucleophile toward other electrophilic centers. So, assignment of an associative mechanism to this reaction is reasonable only if we can explain why hydroxide is uniquely reactive in this case and not in others.

The conjugate-base mechanism

An alternative mechanism, referred to as the **conjugate-base mechanism** or the $\mathbf{S_N1CB}$ (**S**ubstitution, **N**ucleophilic, first-order in the **C**onjugate **B**ase mechanism) mechanism, is also consistent with the second-order rate law. In this mechanism, the first step is formation of the conjugate base of the metal complex by deprotonation of one of its ligands. An important requirement of this mechanism is the presence of a metal-bound ligand with acidic protons (including amine, ammine, or aquo ligands). Under basic conditions the mecahnism is catalyzed by hydroxide ion.

In the case of $[Co(NH_3)_5OH_2]^{3+}$ reacting under basic conditions, the hydroxide removes a proton from one of the ammine ligands to give a six-coordinate conjugate base intermediate (step 1 below). This conjugate base intermediate contains an amido (NH_2^-) ligand which is a π-donor ligand, allowing facilitated dissociation of one of the other ligands (particulary the ligand in the trans position). This intermediate loses the leaving group X^- in the rate determining step to form a five-coordinate intermediate, $Co(NH_3)_4NH^{2+}$ (step 2 below). This five-coordinate intermediate quickly picks up a water molecule from the bulk solution to give the aquo complex (step 3 below). In a series of proton transfers to (step 4) and from (step 5) the aqueous solvent, the aquo complex rearranges to the final product. The mechanism is shown below for $[Co(NH_3)_5OH_2]^{3+}$ reacting with Cl^-:

$$[Co(NH_3)_5Cl^{2+} + OH]^- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^+ + H_2O \qquad \text{(step 1, conjugate base)}$$

$$[Co(NH_3)_4(NH_2)Cl]^+ \rightleftharpoons [Co(NH_3)_4(NH_2)]^{2+} + Cl^- \qquad \text{(step 2, dissociation)}$$

$$Co(NH_3)_4(NH_2)^{2+} + H_2O \rightleftharpoons Co(NH_3)_4(NH_2)(OH_2)^{2+} \qquad \text{(step 3, association)}$$

$$Co(NH_3)_4(NH_2)(OH_2)^{2+} + OH^- \rightleftharpoons Co(NH_3)_4(NH_2)OH^+ + H_2O \qquad \text{(step 4, proton transfer)}$$

$$Co(NH_3)_4(NH_2)OH^+ + H_2O \rightleftharpoons Co(NH_3)_5OH^{2+} + OH^- \qquad \text{(step 5, proton transfer)}$$

The evidence in favor of the S_N1CB mechanism is persuasive. It requires that the ammine protons be acidic, so that they can undergo the acid–base reaction in the first step. That this reaction occurs is demonstrated by proton-exchange experiments. In basic D_2O, the ammine protons undergo $H-D$ exchange according to

$$[Co(NH_3)_5Cl]^{2+} + D_2O \rightleftharpoons [Co(ND_3)_5Cl]^{2+} + HDO$$

The ammine protons are also necessary; the reaction does not occur for similar compounds, like $Co(2\,,2\,'-\text{bipyridine})_2(O_2CCH_3)_2^+$, which lack acidic protons on the nitrogen atoms that are bound to cobalt (*i.e.*, there are no $H-N-Co$ moieties).

The evidence that $Co(NH_3)_4(NH_2)^{2+}$ is an intermediate is also persuasive. When the base hydrolysis reaction is carried out in the presence of other possible entering groups, Y^{p-}, the *rate* at which $[Co(NH_3)_5X]^{n+}$ is consumed is unchanged, but the product is a mixture of $[Co(NH_3)_5OH]^{2+}$ and $[Co(NH_3)_5Y]^{n+}$. If this experiment is done with a variety of leaving groups, X^{q-}, the proportions of $[Co(NH_3)_5OH^{2+}]$ and $[Co(NH_3)_5Y]^{n+}$ are constant despite which leaving group exists in the reactant complex. These observations are consistent with the hypothesis that all reactants, $[Co(NH_3)_5X]^{n+}$, give the same intermediate, $[Co(NH_3)_4(NH_2)]^{2+}$. The product distribution is always the same, because it is always the same species undergoing the product-forming reaction.

This page titled 5.4.4: The conjugate base mechanism is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **5.16: The Mechanism of the Base Hydrolysis of $Co(NH_3)_5X^{n+}$** by Paul Ellgen is licensed CC BY-SA 4.0. Original source: https://www.amazon.com/Thermodynamics-Chemical-Equilibrium-Paul-Ellgen/dp/1492114278.

5.4.5: The Kinetic Chelate Effect

We discussed the increased thermodynamic stability of chelating ligands in a previous section on the chelate effect (Section 10.1.1). This thermodynamic benefit is related to a change in the rate of binding and dissociation events called the kinetic chelate effect. This effect was also mentioned earlier in this chapter (Section 12.2.2).

Recall that there is a relationship between the equilibrium constant and rate constants of any chemical reaction. The relationship is demonstrated below for a general reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$\text{forward rate} = k_f[A]^a[B]^b$$

$$\text{reverse rate} = k_r[C]^c[D]^d$$

At equilibrium, the rate of the forward reactions is equal to the rate of the reverse reaction. Therefore:

$$\text{forward rate} = \text{reverse rate}$$

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

Rearrangement of the equation above gives:

$$\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_{eq}$$

Because chelating ligands have larger values of K_{eq} than analogous monodentate ligands, there must also be a change in the relative rates of the forward (binding) and reverse (dissociation) reactions. In fact, there is a kinetic benefit that makes a metal bound to a polydentate ligand more inert than the analogous complex with monodentate ligands: this is called the ***kinetic chelate effect***.

The kinetic chelate effect is a result of a slower first dissociation step and faster re-association step relative to that of a monodentate ligand. The complete dissociation of a bidentate ligand, for example, would require two dissociation steps (see first reaction in figure below). It is the first dissociation step that is slower in a bidentate ligand ($k_1 < k_1'$ in the figure below). This first dissociation step is slower in part because the chelate would have to rotate to move the free ligand away from the open coordinate site on the metal ion. For the same reason, the reverse of this step (association) is faster than the association of a monodentate ligand ($k_{-1} > k_{-1}'$).

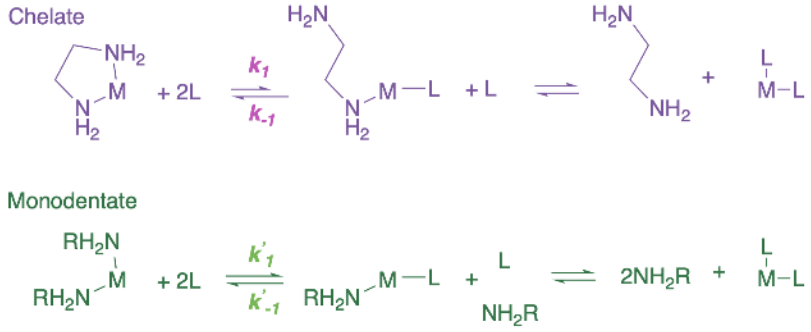


Figure 5.4.5.1: Step-wise dissociation of a bidentate ligand and analogous monodentate ligands. (CC-BY-SA; Kathryn Haas)

(1) Carter, M. J.; Beattie, J. K. Kinetic Chelate Effect. Chelation of Ethylenediamine on Platinum(II). Inorg. Chem.1970, 9 (5), 1233–1238. https://doi.org/10.1021/ic50087a044.

Curated or created by Kathryn Haas

This page titled 5.4.5: The Kinetic Chelate Effect is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.5: Stereochemistry of Octahedral Reactions

The stereochemical outcomes of a reaction can depend on numerous factors. For simplicity, the discussion in this section will be limited to octahedral complexes that react through dissociative mechanisms, with emphasis on those that occur through the limiting case of a dissociative (*D*) mechanism. In light of this focus, the reactions of Co(III) complexes, particularly those with ethylenediamine ligands, provide appropriate examples of well-characterized systems.

In the purely dissociative case, the octahedral metal complex completely loses one ligand to become a five-coordinate intermediate. Therefore, the structure of the product depends primarily on the structure of the intermediate and its interaction with the entering ligand. The outcome of a *D* reaction should not be influenced by the identity of the leaving group. However, the identity of the entering group and the reaction conditions are appropriate considerations. For example, under basic aqueous conditions, the conjugate base mechanism can alter the stereochemical outcome compared to the same reaction under more acidic conditions.

Structure of the intermediate

When an octahedral metal complex reacts through a *D* mechanism, a six-coordinate metal complex forms a five-coordinate intermediate, which goes on to react with the entering group. The structure of that 5-coordinate intermediate has a major influence on the stereochemistry of the product. Recall from a previous section (Section 9.4) that 5-coordinate metal complexes can adopt either a **square pyramidal** or **trigonal bipyramidal geometry**. * In general, if the intermediate adopts a square pyramidal structure, the incoming ligand will enter at the same site where the leaving group was lost, and stereochemistry is retained from reactant to product. On the other hand, if the intermediate structure is a trigonal pyramid, at least some of the product will not retain the original configuration.

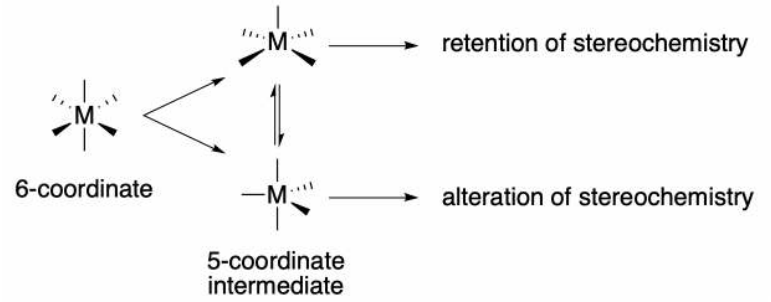


Figure 5.5.1: In the context of a substitution reaction, the loss of a ligand from an octahedral complex results in a five-coordinate intermediate. When the intermediate structure is a square pyramid, the new ligand enters so that the original sterochemistry is retained. The adoption of a trigonal bipyramid leads to changes in the stereochemistry of at least some of the product compared to the reactant. (CC-BY-SA; Kathryn Haas)

* Note: Recall from a previous section (Section 9.4) that square pyramid and trigonal bipyramid geometries typically have similar energies and readily interconvert through pseudorotation. However, during a D reaction, the intermediate exists for such a short moment in time, that interconversion is assumed not to occur unless there is an unusually long-lived intermediate.

Cis vs trans reactants

This section will present generalizations for the stereochemical consequences of substitution in *trans*-bisethylenediamine (*trans*-en) and *cis*-bisethylenediamine (*cis*-en) octahedral Co(III) complexes. Cis-en complexes tend to retain a square pyramidal intermediate structure and retain the cis stereochemistry of the product, except when the conjugate base mechanism promotes isomerization. On the other hand, trans-en complexes are more likely to undergo stereochemical rearrangments through a trigonal pyramidal intermediate. However, especially in the case of trans-en complexes, the product ratios are a result of mixtures of intermediates.

This page titled 5.5: Stereochemistry of Octahedral Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.5.1: Substitution in trans-en octahedral complexes

The reaction of metal complexes of the form $[\mathrm{M(en)_2LX}]^{n+}$ have multiple possible pathways in terms of the structure of the intermediate.

When the X ligand departs from a trans complex, the most likely case is that the L ligand will remain in the axial position. In that case, there is one primary structure for the square pyramidal intermediate. Reaction of that intermediate with the incoming ligand, Y, will result in retention of trans stereochemistry.

An alternative possibility is that the intermediate adopts a trigonal bipyramidal structure. In that case, the outcome of the reaction depends on which of the possible trigonal bipyramidal structures exist and their relative amounts. There are two chemically distinguishable positions on the trigonal bipyramid; the axial and equatorial positions. The remaining L ligand can occupy either the axial position, which has a slightly longer bond, or the equatorial positions, which are slightly closer to the metal and more sterically hindered in space. To adopt either of the trigonal bipyramidal structures, rearrangement of the complex is necessary. It is more likely that the rearrangement will result in the trans ligand being in the equatorial position, since that requires less distortion of the original positions of each ligand (this is not obvious from the structures in Figure 5.5.1.1). A trigonal structure with axial L requores one of the en ligand nitrogens to move by 90 degrees, while a structure with equitoral L requires only 30 degree movement from any ligand. As a result, the trigonal bipyramid with equitorial L (bottom of Figure 5.5.1.1) is the dominant trigonal bipyramidal structure. That structure can produce three optical isomers from the three different angles of ligand Y entering along the equitorial plane. When Y enters trans to L, it produces the trans product. When Y enters cis to L, it produces either of the two cis optical isomers. The cis-$\Lamda$ and $cis-\Delta$ isomers are equally likely, and are produced as a racemic miture from an optically inactive starting trans reactant. The expected ratios of cis to trans are 2:1.

Regarding the trigonal bipyramidal intermediates, the identity of L influences its preference for the axial or equatorial positions. For example, π-donor ligands prefer equatorial positions due to the shorter bond lengths involved in π-donor interactions. Thus, when L is a strong π-donor, reaction products are more likely to come from the trigonal intermediate with an equatorial L. This last point is relevant to reactions where the conjugate base mechanisms is at play. The deprotonated ligand that results from the conjugate base mechanism is a stronger π-donor, and has preference for occupation of the equatorial positions of a trigonal bipyramidal intermediate. Even in cases where the square pyramid is typically preferred, the conjugate base mechanism can result in preference for a trigonal intermediate.

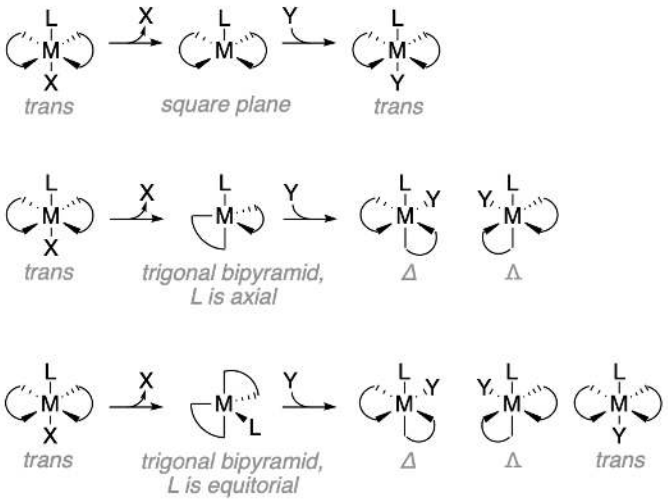


Figure 5.5.1.1: Three different possibilities for the five-coordinate intermediate yield different possibilities for the stereochemistry of the product complex. The possibility of a square pyramid with basal ligand is not shown and is considered less likely than the three pathways shown because it would require a long-lived intermediate to allow time for the rearrangement of the square planar intermediate shown. (CC-BY-SA; Kathryn Haas)

The actual proportion of reaction products of a given stereochemistry depends on the extent to which each of the possible intermediates leads to the products. However, the expected percentages of cis-trans from any single intermediate is rarely found in experimental data (See Table 5.5.1.1).

Table 5.5.1.1 gives the % of trans stereochemistry retained in the displacement of Cl^- by either H_2O or OH^- in a series of $trans-[Co(en)_2LCl]^+$ complexes where the identity of the *trans* ligand, L^-, is varied.

The reactions run under acidic conditions is shown below, and its data is shown in the middle column in Table 5.5.1.1:

$$trans-[Co(en)_2LCl]^+ + H_2O <==> [Co(en)_2L(H_2O)]^{2+} + Cl^-$$

The reactions run under basic conditions is shown below, and its data is shown in the right column in Table 5.5.1.1:

$$trans-[Co(en)_2LCl]^+ + OH^- <==> [Co(en)_2L(OH)]^+ + Cl^-$$

Table 5.5.1.1: % trans product under different conditions

L^-	% trans product under acidic conditions (stereochemistry of reactant is retained)	% trans product under basic conditions (stereochemistry of reactant is retained)
OH^-	25	6
NCS^-	30-50	24
Br^-	50	100
Cl^-	65	95
NH_3^-	100	24
NO_2^-	100	94
Data from Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed.* Pearson: Boston, 2014, p. 459.		

5.5.1: Substitution in trans-en octahedral complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.5.2: Substitution in cis-en octahedral complexes

The D substitution reactions of cis complexes occur through the same intermediate structures described above for trans complexes. For example, the reaction,

$$\text{cis}-[\text{M(en)}_2\text{LX}]^+ + \text{Y}^- \longrightarrow [\text{Co(en)}_2\text{LY}]^{2+} + \text{X}^-$$

can proceed through square planar or trigonal bipyramidal intermediates. Complete the exercise below.

? Exercise 5.5.2.1

Follow the example of Figure 12.5.1.1 to sketch the possible reaction intermediates and products for $\text{cis}-[\text{M(en)}_2\text{LX}]^+ + \text{Y}^-$. Which intermediates are most likely? In the case of each trigonal bipyramid, what would be the ratios of products if ligand attack from the three angles along the trigonal plane are equally likely?

Answer

Add texts here. Do not delete this text first.

Table 5.5.2.1 gives the % of cis stereochemistry in the displacement of Cl^- by either H_2O or OH^- in a series of $\text{cis}-[\text{Co(en)}_2\text{LCl}]^+$ complexes where the identity of the *trans* ligand, L^-, is varied.

The reactions run under acidic conditions is shown below, and its data is shown in the middle column in Table 5.5.2.1:

$$\pm\text{cis}-[\text{Co(en)}_2\text{LCl}]^+ + \text{H}_2\text{O} <==> [\text{Co(en)}_2\text{L(H}_2\text{O)}]^{2+} + \text{Cl}^-$$

The reactions run under basic conditions is shown below, and its data is shown in the right column in Table 5.5.2.1. Note that in all but one case, the reactions run under basic conditions were done so using optically pure starting material, and gave an optically active product.

$$\Delta-\text{cis}-[\text{Co(en)}_2\text{LCl}]^+ + \text{OH}^- <==> [\text{Co(en)}_2\text{L(OH)}]^+ + \text{Cl}^-$$

Table 5.5.2.1: % cis product under different conditions

L^-	% cis product under acidic conditions from racemic cis reactant (stereochemistry of reactant is retained)	% cis and trans product under basic conditions from $\Delta - cis$ starting material (stereochemistry of reactant is retained)
OH^-	100	61% $\Delta - cis$ | 36% $\Lambda - cis$ | 3% trans
NCS^-	100	56% $\Delta - cis$ | 24% $\Lambda - cis$ | 20% trans
Br^-	100	-
Cl^-	100	21% $\Delta - cis$ | 16% $\Lambda - cis$ | 63% trans
NH_3^-	-	60% $\Delta - cis$ | 24% $\Lambda - cis$ | 16% trans
NO_2^-	100	46% $\Delta - cis$ | 20% $\Lambda - cis$ | 34% trans
Data from Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed.* Pearson: Boston, 2014, p. 459.		

Under acidic conditions, and when the conjugate base mechanism is unlikely, the product specifically retains the stereochemistry of the starting material. This data (middle column above) indicates that the D reaction of the cis isomer, in contrast to trans, reacts exclusively through the square pyramidal intermediate under acidic conditions. This is because in every case, the ligand trans to the X leaving group is an amine from the en ligand, which is not a π donor. The ligand cis to the leaving group (L) has no influence on the reaction outcome under acidic conditions.

Under basic conditions, where the conjugate base mechanism is possible, cis stereochemistry is not entirely retained, and the cis products are produced in approximately a 2:1 ration of $Delta : \Lambda$ from a $Delta$ reactant.

Exercise 5.5.2.1

Consider the data in the right colum of Table 5.5.2.1. What does the presence of trans product and a 2:1 ratio of the two cis isomers indicate about the intermediates of reaction under basic conditions?

Answer

Add texts here. Do not delete this text first.

5.5.2: Substitution in cis-en octahedral complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.5.3: Isomerization of Chelate Rings

Recall that the stereoisomers of octahedral complexes with two and three bidentate ligands were discussed previously (Section 9.3). This page will discuss the interconversion of stereoisomers, which can occur through two primary mechanisms involving either (1) bond breaking and bond making steps, and (2) twisting.

Isomerization through dissociative substitution

One way to convert one steroisomer to another is through bond breaking and bond re-making steps. This type of structural rearrangement is essentially a substitution reaction, as described previously in this chapter, except that the leaving group and entering group are the same ligand. Evidence for this type of mechanism comes from the study of isotopically labeled amibidentate ligands (those that have different modes of coordination). For example, an acetyl group with a labeled CD_3 can be added as an "outside" group (adjacent to the coordinating groups) in a tris(acac)cobalt(III) complex. The labeled group moves to the "inside" (directly coordinated to the metal ion) during isomerization from an optically pure solution to a racemic mixture. This change can only occur through bond breaking and re-forming steps.

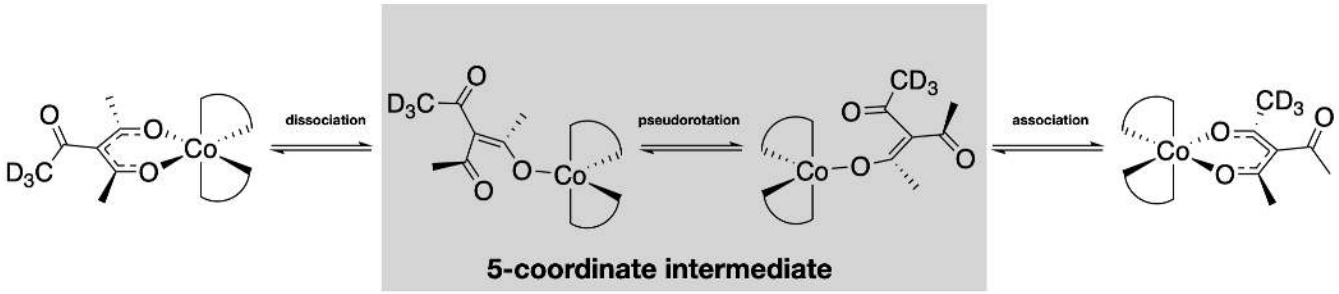


Figure 5.5.3.1: The rearangement of a CD_3 group from an "outer acetyl" to one directly coordinating to the metal complex of an CD_3-labeled acetyl group on acetylacetone (acac) provides evidence of isomerization through a mechanism related to dissociative substitution. (CC-BY-SA; Kathryn Haas)

Isomerism through twisting

The second pathway of isomerism is through twisting; it does not involve bond breaking or bond forming. Twisting that causes interconversion of octahedral isomers was also discussed in Chapter 9. A figure from that chapter is re-posted here for convenience.

An octahedroal coordination sphere is just a trigonal antiprism in which all edge lengths are identical. Rotation of one triangular face relative to its opposite until the two are eclipsed gives a triganal prismatic geometry. In fact, since continuation of this rotation gives another octahedral complex the trigonal prismatic geometry is an intermediate in isomerization reactions involving octahedral complexes. In tris- and bis-chelates such isomerizations are said to occur by a **Bailar twist** or a **Ray-Dutt twist**, which differ only in the relationship between the chelate rings and the faces twisted.

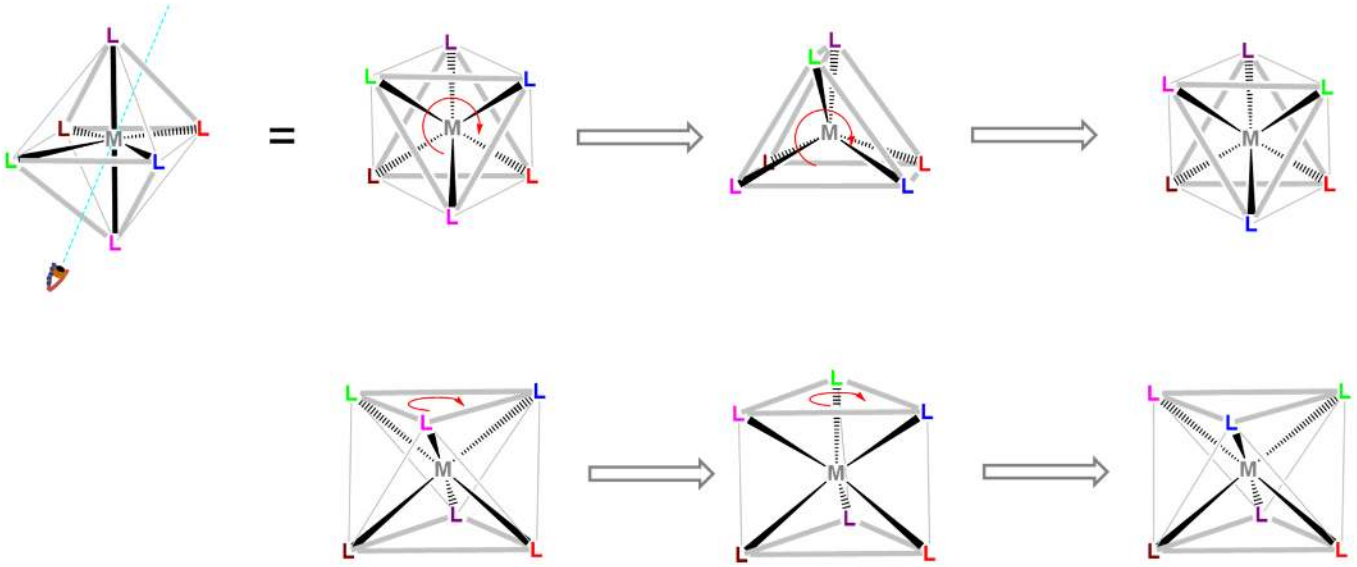


Figure 5.5.3.2. Since an octahedron is a trigonal antiprism a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is thermally or photochemically accessible twists like these provide one pathway for isomerisation reactions involving octahedral complexes. In tris- and bis-chelates such isomerizations are said to occur by Bailar and Ray-Dutt twists, which differ only in the relationship between the chelate rings and the faces twisted. Top: View down looking down an axis bisecting a pair of opposing faces. Bottom: View perpendicular to that shown at top. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

5.5.3: Isomerization of Chelate Rings is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.5: Coordination Numbers and Structures** by Stephen M. Contakes is licensed CC BY 4.0.

5.6: Substitutions in Square Planar Complexes

Substitutions in square planar complexes tend to occur through mechanisms with associative character, although the degree of associative character may vary (eg A, I_a, I_d. The outcome of square planar substitutions depend on the identities of the leaving group, the ligand trans to the leaving group, and the entering group. The reactions of Pt(II) are well studied and will serve as the primary examples in this section. Pt(II) complexes are of particular interest because of their role as effective chemotherapeutics in the treatment of several types of solid tumor cancers.

The generic chemical equation for substitution in a square planar complex is shown below, where X is the leaving group, Y is the entering group, and $[\mathrm{ML_3X}]$ is the reactant complex:

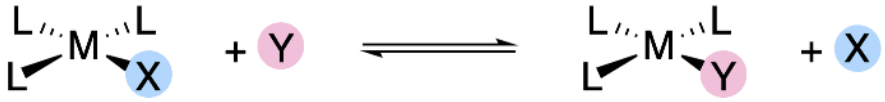


Figure 5.6.1: Generic form of square planar metal complex undergoing a substitution reaction. (CC-BY-SA; Kathryn Haas)

This page titled 5.6: Substitutions in Square Planar Complexes is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.6.1: Kinetics and Stereochemistry of Square Planar Reactions

Kinetics

In general, the reaction kinetics of square-planar associative substitution takes the form of the following rate law, which has two terms:

$$\frac{d[\mathrm{ML_3Y}]}{dT} = k_1[\mathrm{ML_3X}] + k_2[\mathrm{ML_3X}][\mathrm{Y}]$$

Each of the terms corresponds to one of the two possible reaction pathways. The term, $k_2[\mathrm{ML_3X}][\mathrm{Y}]$, is second-order, and corresponds to a simple associative pathway. The $k_1[\mathrm{ML_3X}]$ term is first-order, although it also corresponds to an associative pathway. The reason it appears to be first order is because square planar complexes can react through a solvent-assisted pathway where bulk solvent replaces the leaving group, and then is replaced by the entering group (Figure 5.6.1.2). Because solvent concentration does not appreciably change as the reaction proceeds, it is not part of the rate law term even though it is involved in the rate-determining association. The step in which solvent is substituted by the entering group must happen faster than the solvent-assisted replacement of X.

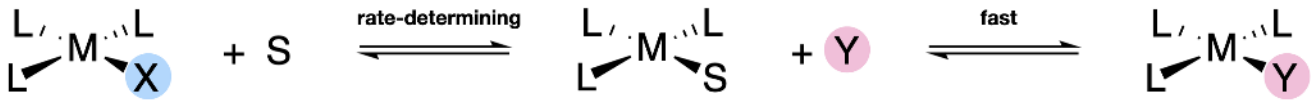


Figure 5.6.1.2: Solvent-assisted substitution pathway where X is the leaving group, Y is the entering group, and S is solvent. (CC-BY-SA; Kathryn Haas)

The kinetic rate constats in square planar substitution can depend on the identities of the leaving group, the ligand trans to the leaving group, and the entering group. The ligands that are in the cis positions with respect to the leaving group do not have a significant affect on the rate, and these are referred to as spectator ligands.

Stereochemistry

Square planar complexes react to give products in which the stereochemistry of the reactant is retained. In other words, a *trans*-reactant will give a *trans*-product, and a *cis*-reactant will give a *cis*-product (Figure 5.6.1.3). The identity of the trans ligand has particular importance in the outcome of square planar substitutions (discussed further in the next sections). We will designate the trans ligand generally with the symbol T to indicate its position (Figure 5.6.1.3), the leaving group as X, and the entering group as Y. The spectator ligands (ligands that are cis to X) will be desginated L and L'. For the discussion that follows, the plane of the metal complex will be designated as the xy plane, while the z axis is perpendicular to the plane (Figure 5.6.1.3). The x and y axes will run colinear to the bond axes, with the x axis running colinear to the T-M-X bonds (Figure 5.6.1.3).

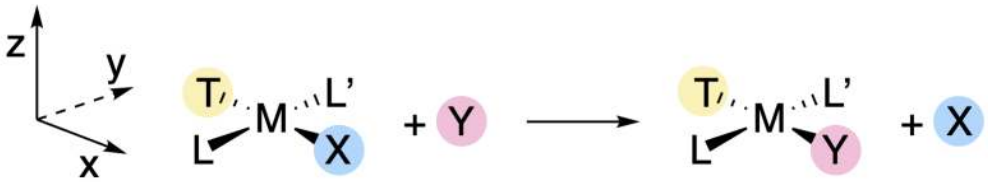


Figure 5.6.1.3: Stereochemistry is strictly retained in the reactions of square planar complexes. By convention, the plane of the metal complex is the xy plane, with the x axis colinear with the T-M-X bonds. M = metal ion | X = leaving group ligand | Y = entering group ligand | T = ligand trans to the leaving/entering group. (CC-BY-SA; Kathryn Haas)

The retention of stereochemistry, and the fact that X, Y, and T can influence the rate of reaction provide hints at the nature of intermediates and/or transition states involved in these reactions. The existence of five-coordinate square pyramidal structures, like those of $[\mathrm{Ni(CN)_5}]^{3-}$ and $[\mathrm{Pt(SnCl_3)_5}]^{3-}$, suggests that five-coordinate intermediates are possible. However the substitutions of square planar complexes are generally classified as associative interchange mechanisms (I_a) because isolation of a true intermediate is rarely accomplished. In any case, the retention of stereochemistry is explained by a five-coordinate trigonal bipyramidal transition state in which X, Y, and T are each in the trigonal plane (along with the metal center). As the M-X bond is breaking, the M-Y bond is forming and Y replaces X in the position trans to T. Because T, Y and X are in the trigonal plane in the transition state, all three ligands are able to interact with the same d orbitals of the central metal ion. Thus the identities of X, Y,

and T should influence the ability of the M-X bond to break and the M-Y bond to form. On the other hand, L and L' are in a perpendicular plane, and would interact with different orbitals than X and Y. This explains why spectator ligands L and L' have little effect on the reaction rate, as they are interacting with different orbitals than those involved in bond breaking and bond making.

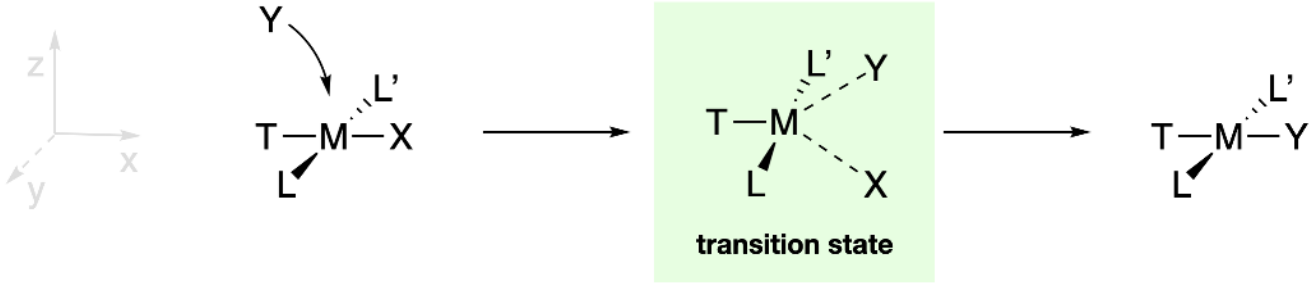


Figure 5.6.1.4: Mechanism for simple I_a substitution. The structure of the transition state is trigonal bipyramidal, with T, X, and Y in the trigonal plane with M. The spectator ligands, L and L', are in a perpendicular plane and are coplanar with T and M. (CC-BY-SA; Kathryn Haas)

The solvent-assisted pathway can occur through similar transition states and mechanistic steps, except that there are additional steps involving solvent association and displacement.

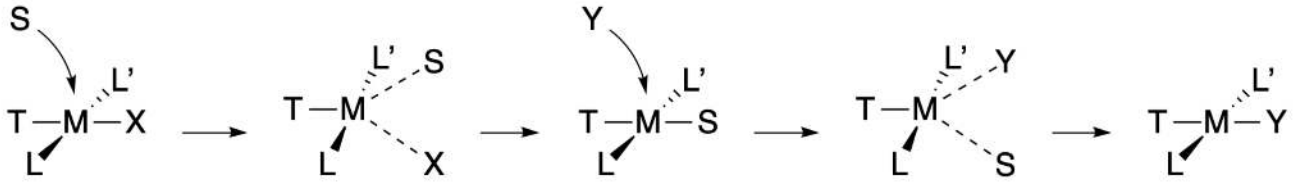


Figure 5.6.1.5: Solvent-assisted I_a substitution. Compare to Figure 5.6.1.4. S is solvent. (CC-BY-SA; Kathryn Haas)

Although there is general consensus that square planar complexes react through associative pathways, the characterization of intermediates and/or transition states has remained elusive, and there is still debate as to the intricate details of the reaction mechanisms involving square planar complexes. For example, there are arguments that a six-coordinate transition state may exist in the solvent-assistant pathway.

This page titled 5.6.1: Kinetics and Stereochemistry of Square Planar Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.6.2: Evidence for Associative Reactions

The reactions of Pt(II) complexes have been thoroughly investigated, and there are several lines of experimental evidence that have lead to the general conclusion that square planar complexes react through associative mechanisms. The experimental evidence is presented here.

The entering group

In the reaction of $\mathrm{trans}-[\mathrm{PtL_2Cl_2}]$, the rate of reaction depends on the identity of the incoming ligand Y.



Figure 5.6.2.1: Substitution reaction of $\mathrm{trans}-[\mathrm{PtL_2Cl_2}]$. (CC-BY-SA; KAthryn Haas)

For example, the rate of the reaction shown above depends heavily on the ligand, Y, as follows:

$$\text{most kinetically labile } \mathrm{PR_3} > \mathrm{CN^-} > \mathrm{SCN^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{N_3^-} > \mathrm{NO_2^-} > \text{py} > \mathrm{NH_3}\ \mathrm{Cl^-} > \mathrm{CH_3OH}\ \text{most kinetically inert}$$

In general, ligands that would form the strongest bonds with Pt(II) due to their soft character or π-binding ability react fastest. The rate constants in the above series range by nearly ten orders of magnitude. This huge range of rate constants as a factor of Y demonstrates suggests that M-Y bond formation is part of the rate limiting step. This is evidence for rate-determining association A or I_a.

The leaving group

Since the leaving group occupies a similar position in the transition state as the entering group, we should expect the leaving group to have a similar effect on the rate constants as was found for Y. In fact, this is true. For the reaction of $[\mathrm{Pt(diene)X}]^+$ with pyridine, the follow trend was observed by varying the leaving group, X:

$$\text{most kinetically labile } \mathrm{NO_3^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-} > \mathrm{N_3^-} > \mathrm{SCN^-} > \mathrm{NO_2^-} > \mathrm{CN^-}\ \text{most kinetically inert}$$

The rate of reaction follows an order that is nearly opposite as that observed for Y: The softer the ligand, the slower the dissociation. The rate constants in this series span a range of approximately five orders of magnitude, illustrating that breaking of the M-X bond is part of the rate-determining step. This is evidence for a mechanism involving associative interchange character (I_a or I_d. The importance of the leaving group somewhat depends on the identity of the entering group, and vice-versus.

The trans ligand

The trans ligand also occupies a similar position to X and Y in the transition state. So, as you might expect, it too has influence on the rate of reaction. In general, the rate of substitution of X in Pt(II) complexes general follows the order given below when T is varied as:

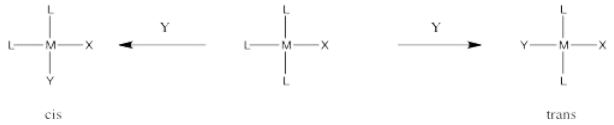
$$\text{M-X most kinetically labile } \mathrm{CN^-}\ \mathrm{CO}\ \mathrm{C_2H_4} > \mathrm{PH_3}\ \mathrm{SH_2} > \mathrm{NO_2^-} > \mathrm{I^-} > \mathrm{Br^-} > \text{py}\ \mathrm{NH_3} > \mathrm{OH^-} > \mathrm{H_2O}\ \text{M-X most kinetically inert}$$

The effect of the trans ligand deserves a more through discussion, and will be addressed in the next section. It is mentioned here because it is evidence for the trigonal bipyramidal intermediate that was described earlier for associative substitution in square planar metal complexes.

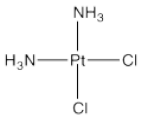
This page titled 5.6.2: Evidence for Associative Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.7: The Trans Effect

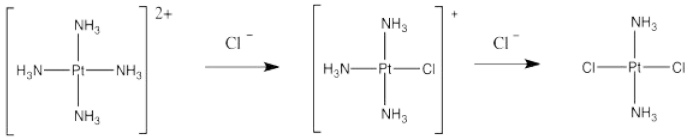
Occasionally in ligand substitution there is a situation in which there are two identical ligands that could be replaced, but two different products would result depending on which ligand left. This situation often happens in square planar complexes, for example. Replacement of one ligand would lead to a *cis* product. Replacement of the other one would lead to a *trans* product.



An important example of this issue is in the synthesis of cis-platin, an antitumour medication frequently used to treat ovarian and testicular cancer.

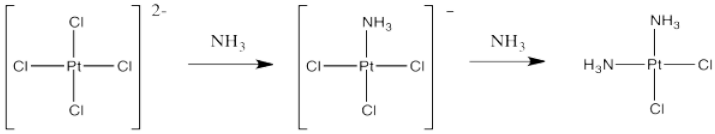


Cis-platin could be made from treatment of tetraammineplatinum(II) with chloride salts. The chloride ion could replace two of the ammonia ligands.



But that doesn't work. That synthesis results in the formation of *trans*-platin, a compound that has all of the nasty side effects of the *cis* isomer but with none of the therapeautic benefit.

If instead you were to start with tetrachloroplatinate salts and treat them with ammonia, you could replace two of the chloride ligands. That works really well, and it provides *cis*-platin, not *trans*-platin.



? Exercise 5.7.1

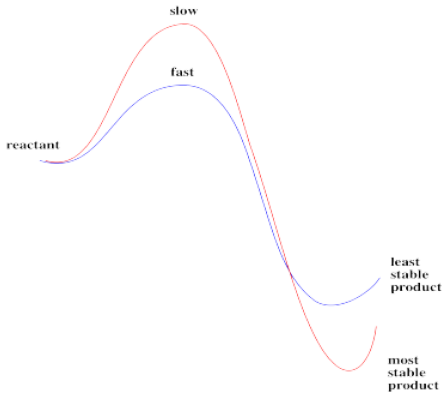
What do you think is the mechanism of substitution of the two reactions above? Why?

Answer

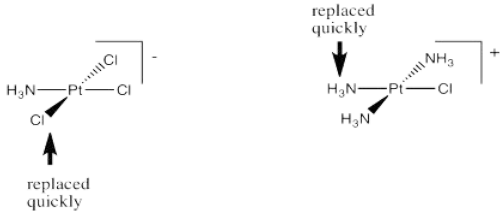
This is probably an associative mechanism because of the square planar geometry.

This reaction, if run under these conditions, is clearly not always under thermodynamic control. Two different products result, depending on how the reaction is done. One of those isomers is probably more stable than the other; if thermodynamics were in charge, it would form the same thing both times.

Instead, there may be an element of kinetic control for at least one of the pathways. A given product might be made, not because it is more stable, but simply because it forms more quickly than the other one.



Take another look at those two reactions. One of the things that they have in common is that the ligand that gets replaced is *trans* to a chloride. It is not *trans* to an ammonia. Maybe the other ligands in the complex can influence how quickly one ligand can leave.



Specifically, the "*trans* effect" is the role of *trans*-ligands in influencing substitution rates in square planar complexes.

The following kinetic data were obtained for substitutions on square planar platinum complexes, in the reaction:

$$trans-(PEt_3)_2PtLCl+py \rightarrow trans-(PEt_3)_2PtLpy^+ + Cl^-$$

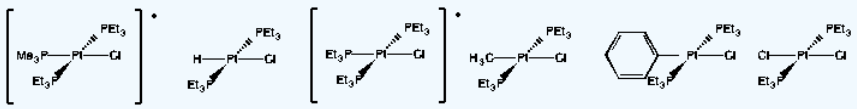
L	k_{obs} (s^{-1})	T, °C
PMe_3	0.20	0
H^-	0.047	0
PEt_3	0.041	0
CH_3^-	6.0 x 10^{-4}	25
$C_6H_5^-$	1.2 x 10^{-4}	25
Cl^-	3.5 x 10^{-6}	25

Ref: Cooper Langford & Harry Gray, *Ligand Substitution Processes*, W.A. Benjamin, NY, 1965, p. 25.

? Exercise 5.7.2

Draw structures for each of the complexes listed in the table.

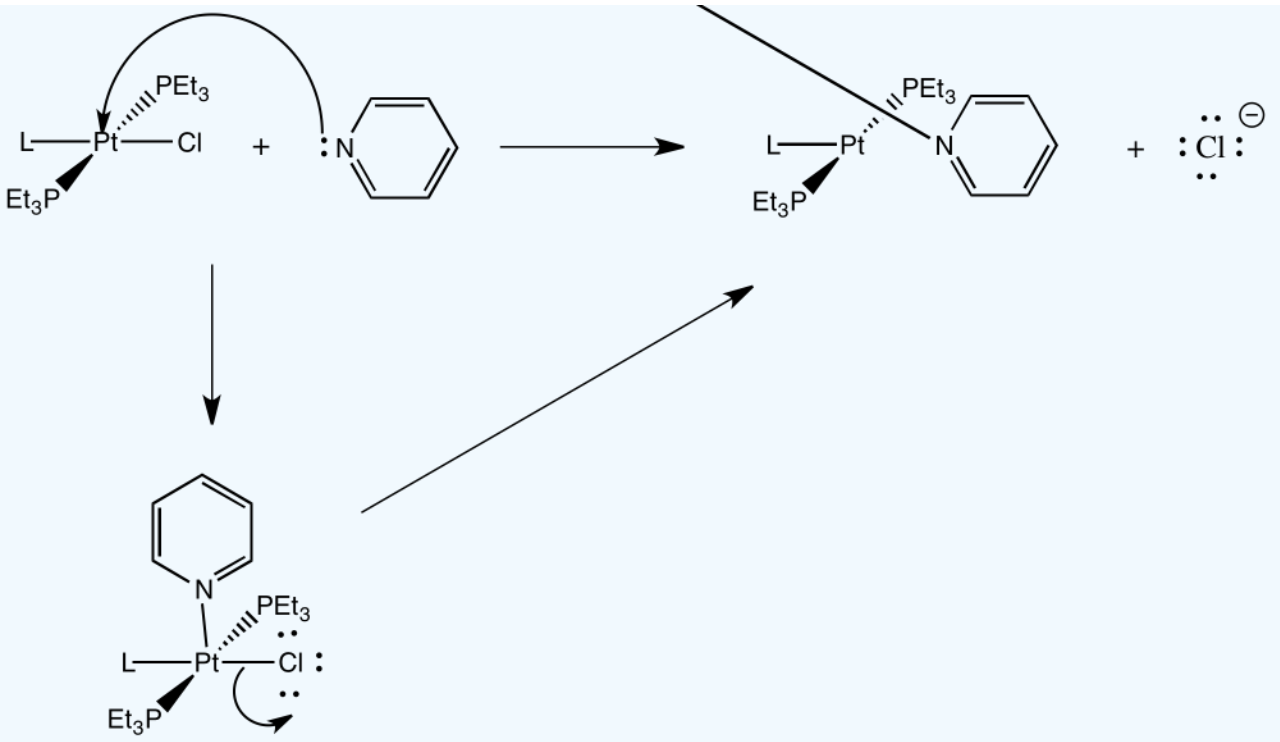
Answer



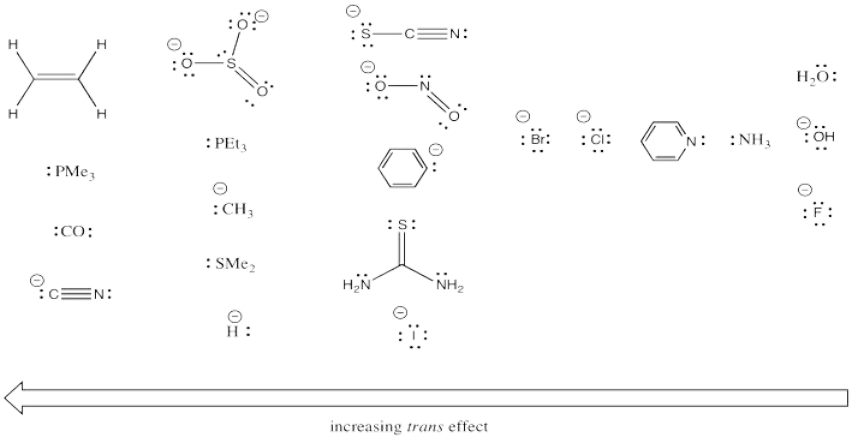
? Exercise 5.7.3

Provide a mechanism with arrows for the reaction studied in the table.

Answer



Clearly that *trans* ligand has a dramatic effect on how quickly the chloride can be substituted in the above study. Additional studies like this one have led to some general trends. Below, the ligands on the left have strong *trans*-effects. Ligands *trans* to them are substituted very quickly. The ligands on the right have very modest *trans* effects. Ligands *trans* to them are substituted only slowly.



Exercise 5.7.4

Look for empirical trends in the series of ligands above. Without trying to explain exactly why, find chemically relevant factors that may be responsible for these reactivity trends.

Answer

There is an electronegativity trend: the less electronegative, the greater the *trans* effect (see the halogens, as well as the series O,N,C and also the orders within several pairings: S,P; O,S and N,P).

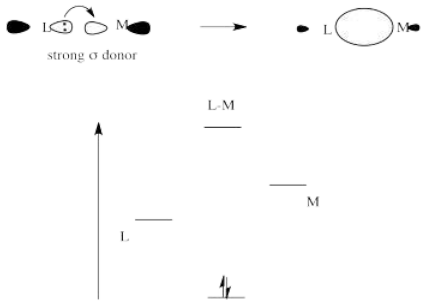
Alternatively, some of the above could be described by a polarizability trend: more polarizable atom, greater *trans* effect (for example, the halogens).

Most of the ligands containing π-bonds have strong *trans* influence (but not all).

Most of the π-donors have a weaker *trans* influence. However, these ligand cover a very broad range in this series.

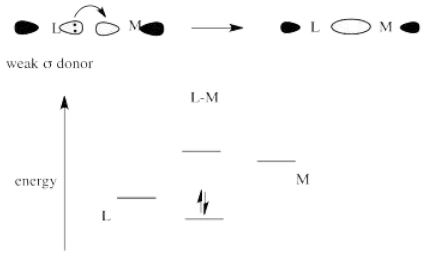
In general, explanations of the trans effect have focused on two separate types of ligands. These are strong sigma donors and strong pi acceptors.

Strong sigma donors donate electrons very effectively to the metal via a sigma bond. Because the ligand trans to this donor would be bonding via donation to the same metal p orbital, there is a competition. The metal p orbital bonds more favorably with the strong sigma donor, and the ligand trans to it is left with a weaker bond.



The strong sigma donor gets good overlap with the metal orbital and the resulting interaction goes down low in energy.

The weak sigma donor gets poorer overlap with the metal orbital and only weak stabilization of the donor electrons.



Place these two choices together, and the metal orbital will engage in a strong bonding interaction with the strong σ-donor. Doing so lowers the electronic energy significantly. It won't interact very much with the weak σ-donor, because doing that won't result in as much lowering of electronic energy. The result is a strong bond on one side of the metal and a weak bond on the other. That weak bond will break easily and that ligand will be replaced easily.



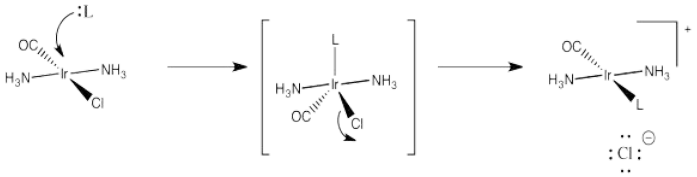
Exercise 5.7.5

Which of the ligands in the *trans* effect series are probably strong σ-donors? Why?

Answer

The strongest σ-donors are typically those with more polarizable donor atoms (such as S, P, I) as well as those with less electronegative donor ions such as C^- and H^-.

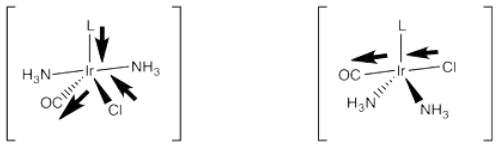
Strong pi acceptors exert their trans effect in a different way. They are thought to stabilize a particular geometry of the five-coordinate intermediate in substitution of square planar complexes. We haven't worried too much about the geometry of that intermediate, but it is probably trigonal bipyramidal. It would have three ligands in an equatorial plane and two more directly opposite each other, in the axial positions.



https://chem.libretexts.org/@go/page/429288

Essentially, the incoming ligand pushes two of the ligands down from the square plane to form this trigonal bipyramid. When it comes time for a ligand to leave, it is probably going to be one of these ligands that is already on the move. They are already on a trajectory out of the square plane, anyway.

A strong pi acceptor like CO exerts its *trans* effect by making sure it, along with the ligand opposite it, gets into that equatorial plane. It does that by a stabilizing delocalization that happens when the π-acceptor is in the electron-rich equatorial plane. In that position, it can draw electron density via π-donation from two different donors. If it were in an axial position, it could still delocalize electrons this way, but it would draw most effectively from just one donor rather than two.



So which of those two ligands is going to keep moving and leave the complex? It certainly won't be the one that is exerting a stabilizing, delocalizing effect on the complex via its strong bonding interactions. It will be the unlucky *trans* ligand that got dragged along with it.

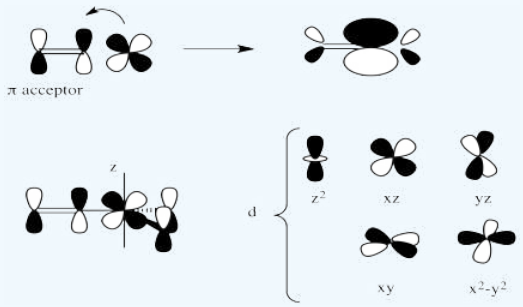
Exercise 5.7.6

Which of the ligands in the *trans*-effect series are probably strong π-acceptors? Show why.

Exercise 5.7.7

Draw an orbital picture showing the -delocalization described in the trigonal bipyramidal intermediate. Label the orbitals, assuming the z axis is along the axis of the trigonal bipyramid (i.e. the equatorial plane is the xy plane).

Answer



Exercise 5.7.8

Substitution of trans ligands in μ-oxo-bis(μ-acetato)diruthenium complexes: Synthesis and kinetic studies. Hussain, Bhatt, Kumar, Thorat, Padhiyar and Shukla, *Inorganica Chemica Acta*, **2009**, *362*, 1101-1108.

Given the structure $[Ru_2O(L)_6(acetate)_2](PF_6)_2$, in which L is a neutral donor,

a) Draw the structure of the counterion, PF_6^-.

b) Provide an account of the valence electron count in the ruthenium coordination complex.

Valence electrons on metal	
Total charge on ligands	
Charge on the metal	
Revised count on metal	

Electrons donated by ligands	
Total electrons on metal in complex	

Data shows that the ligands L are *trans* to the bridging oxo ligand are labile.

c) Use orbital cartoons and words to provide an explanation for this effect.

When water is added to an acetone solution of $[Ru_2O(pyridine)_4(L)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$ is formed.

d) Draw the product of this reaction.

When pyridine is added to $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_6(acetate)_2](PF_6)_2$ is formed. The following rate constants were observed for this reaction.

[pyridine] mol L^{-1}	k_{obs} s^{-1} (x 10^{-3})
0.005	1.75
0.012	2.53
0.025	9.7
0.049	16.7
0.100	35.2

e) Use the data from this table to determine the order in pyridine. Provide an explanation for your conclusion.

f) Draw a mechanism for the reaction, consistent with the data.

g) Write a rate law for the reaction.

h) The authors studies the same reaction with different ligands instead of pyridine. They observed an increase in rate constants with increasing basicity of the incoming ligands. Provide an explanation for this observation.

Answer a



5 valence electrons - 6 bonds - 0 nonbonding = -1

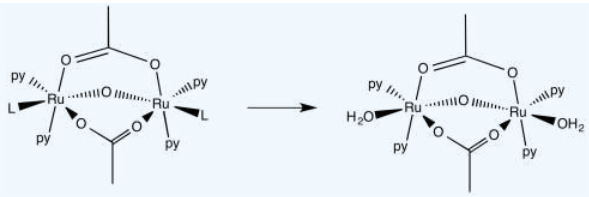
Answer b

Valence electrons on metal	8
Total charge on ligands	-4 (-2 per Ru)
Charge on the metal	+2
Revised count on metal	6
Electrons donated by ligands	12
Total electrons on metal in complex	18

Answer c

The oxo is a strong sigma donor and hogs the orbital with the metal thus leaving very little room for orbital bonding trans to the sigma donor.

Answer d



Answer e

First order. Although there is some amount of error in the data, doubling the pyridine concentration generally results in a doubling of the rate.

Answer f

The mechanism you draw would have to involve a first associative step; because the complex is already 18 electrons, associative interchange is likely.

Answer g

$$Rate = k[ML_n][py]$$

Answer h

Basic ligands have stronger attraction to the metal thus accelerating the reaction.

This page titled 5.7: The Trans Effect is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.7: The Trans Effect** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

5.8: Redox Mechanisms

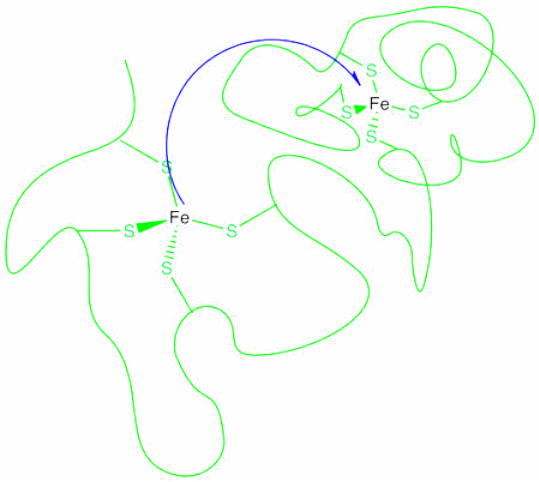
The oxidation state of a metal ion can be changed by **red**uction/**ox**idation (redox) reactions in which electrons are transferred between a metal center and another species. The other species could be another metal ion or some other redox partner. In the case of metal complexes, the electron transfer often occurs at the metal center, changing the oxidation state of the metal ion(s) involved. This section will focus on the redox reactions involving change in metal ion oxidation state.

There are two general mechanisms by which electrons can be transferred to or from a metal center. The definition of these two mechanisms depends on whether the redox partner is bound within the metal ion's inner sphere (bound directly to the metal ion), or whether it is just nearby the metal complex (in the metal ion's outer sphere). If the redox partner is bound to the metal ion itself, it is called an **inner-sphere electron transfer**. Electrons can also be transferred between two species that are close in proximity, but not bound to one another. When electrons are transferred to or from a metal through close proximity, but not through direct bonds to the metal center, it is an **outer-sphere electron transfer**.

This page titled 5.8: Redox Mechanisms is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.8.1: Outer Sphere Electron Transfer

How does an electron get from one metal to another? This might be a more difficult task than it seems. In biochemistry, an electron may need to be transfered a considerable distance. Often, when the transfer occurs between two metals, the metal ions may be constrained in particular binding sites within a protein, or even in two different proteins.



That means the electron must travel through space to reach its destination. Its ability to do so is generally limited to just a few Angstroms (remember, an Angstrom is roughly the distance of a bond). Still, it can react with something a few bond lengths away. Most things need to actually bump into a partner before they can react with it.

This long distance hop is called an outer sphere electron transfer. The two metals react without ever contacting each other, without getting into each others' coordination spheres. Of course, there are limitations to the distance involved, and the further away the metals, the less likely the reaction. But an outer sphere electron transfer seems a little magical.

Barrier to Reaction: A Qualitative Picture of Marcus Theory

So, what holds the electron back? What is the barrier to the reaction? Rudy Marcus at Caltech has developed a mathematical approach to understanding the kinetics of electron transfer, in work he did beginning in the late 1950's. We will take a very qualitative look at some of the ideas in what is referred to as "Marcus Theory". An electron is small and very fast. All those big, heavy atoms involved in the picture are lumbering and slow. The barrier to the reaction has little to do with the electron's ability to whiz around, although even that is limited by distance. Instead, it has everything to do with all of those things that are barely moving compared to the electron.

Imagine an iron(II) ion is passing an electron to an iron(III) ion. After the electron transfer, they have switched identities; the first has become an iron(III) and the second has become an iron(II) ion.

Nothing could be simpler. The trouble is, there are big differences between an iron(II) ion and an iron(III) ion. For example, in a coordination complex, they have very different bond distances. Why is that a problem? Because when the electron hops, the two iron atoms find themselves in sub-optimal coordination environments.

? Exercise 5.8.1.1

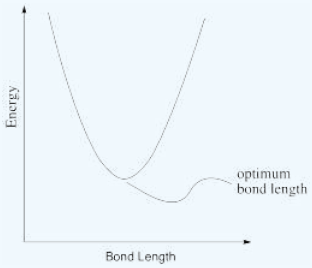
Suppose an electron is transferred from an Fe(II) to a Cu(II) ion. Describe how the bond lengths might change in each case, and why. Don't worry about what the specific ligands are.

Answer

The bonds to iron would contract because the increased charge on the iron would attract the ligand donor electrons more strongly. The bonds to copper would lengthen because of the lower charge on the copper.

Exercise 5.8.1.2

In reality, a bond length is not static. If there is a little energy around, the bond can lengthen and shorten a little bit, or vibrate. A typical graph of molecular energy vs. bond length is shown below.



a. Why do you think energy increases when the bond gets shorter than optimal?
b. Why do you think energy increases when the bond gets longer than optimal?
c. In the following drawings, energy is being added as we go from left to right. Describe what is happening to the bond length as available energy increases.

Answer a

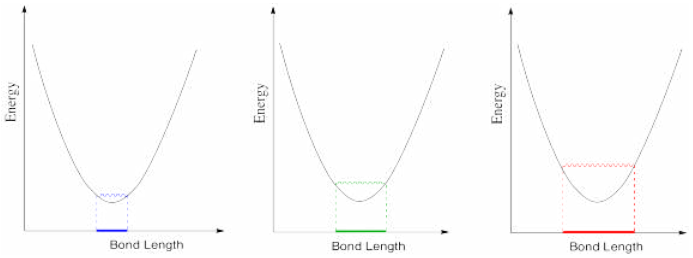
a) Most likely there are repulsive forces between ligands if the bonds get too short.

Answer b

b) Insufficient overlap between metal and ligand orbitals would weaken the bond and raise the energy.

Answer c

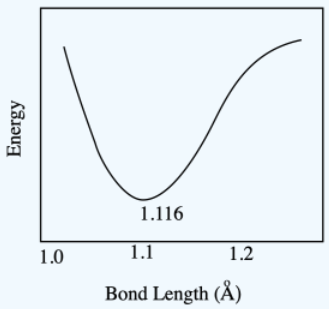
c) The range of possible bond lengths gets broader as energy is increased. The bond has more latitude, with both longer and shorter bonds allowed at higher energy.



Exercise 5.8.1.3

The optimum C-O bond length in a carbon dioxide molecule is 1.116 Å. Draw a graph of what happens to internal energy when this bond length varies between 1.10 Å and 1.20 Å. Don't worry about quantitative labels on the energy axis.

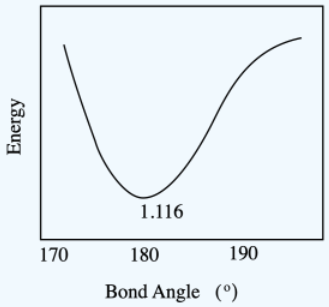
Answer



Exercise 5.8.1.4

The optimum O-C-O bond angle in a carbon dioxide molecule is 180 °. Draw a graph of what happens to internal energy when this bond angle varies between 170 ° and 190 °. Don't worry about quantitative labels on the energy axis.

Answer



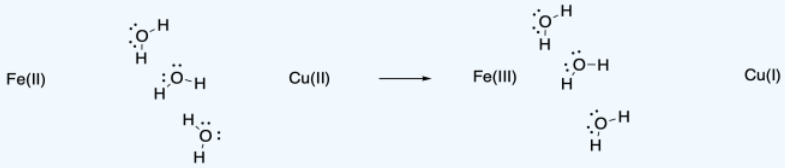
The barrier to electron transfer has to do with reorganizations of all those big atoms before the electron makes the jump. In terms of the coordination sphere, those reorganizations involve bond vibrations, and bond vibrations cost energy. Outside the coordination sphere, solvent molecules have to reorganize, too. Remember, ion stability is highly influenced by the surrounding medium.

Exercise 5.8.1.5

Draw a Fe(II) ion and a Cu(II) ion with three water molecules located somewhere in between them. Don't worry about the ligands on the iron or copper. Show how the water molecules might change position or orientation if an electron is transferred from iron to copper.

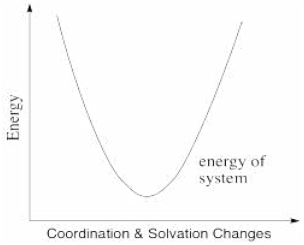
Answer

The water molecules may pivot toward the more highly charged Fe(III), or they may shift closer to it because of the attraction between the ion and the dipole of the water molecule.



Keep in mind that such adjustments would happen in non-polar solvents, too, although they would involve weaker IMFs such as ion - induced dipole interactions.

Thus, the energetic changes needed before electron transfer can occur involve a variety of changes, including bond lengths of several ligands, bond angles, solvent molecules, and so on. The whole system, involving both metals, has some optimum set of positions of minimum energy. Any deviations from those positions requires added energy. In the following energy diagram, the x axis no longer defines one particular parameter. Now it lumps all changes in the system onto one axis. This picture is a little more abstract than when we are just looking at one bond length or one bond angle, but the concept is similar: there is an optimum set of positions for the atoms in this system, and it would require an input of energy in order to move any of them move away from their optimum position.

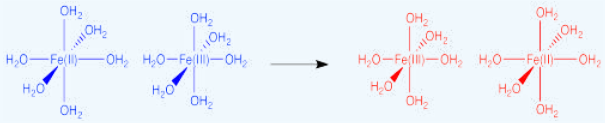


It is thought that these kinds of reorganizations -- involving solvent molecules, bond lengths, coordination geometry and so on -- actually occur prior to electron transfer. They happen via random motions of the molecules involved. However, once they have happened, there is nothing to hold the electron back. Its motion is so rapid that it can immediately find itself on the other atom before anything has a chance to move again.

Consequently, the barrier to electron transfer is just the amount of energy needed for all of those heavy atoms to get to some set of coordinates that would be accessible in the first state, before the electron is transferred, but that would also be accessible in the second state, after the electron is transfered.

? Exercise 5.8.1.6

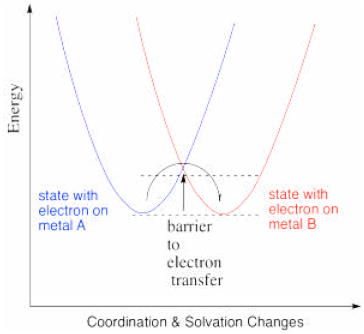
Describe some of the changes that contribute to the barrier to electron transfer in the following case.



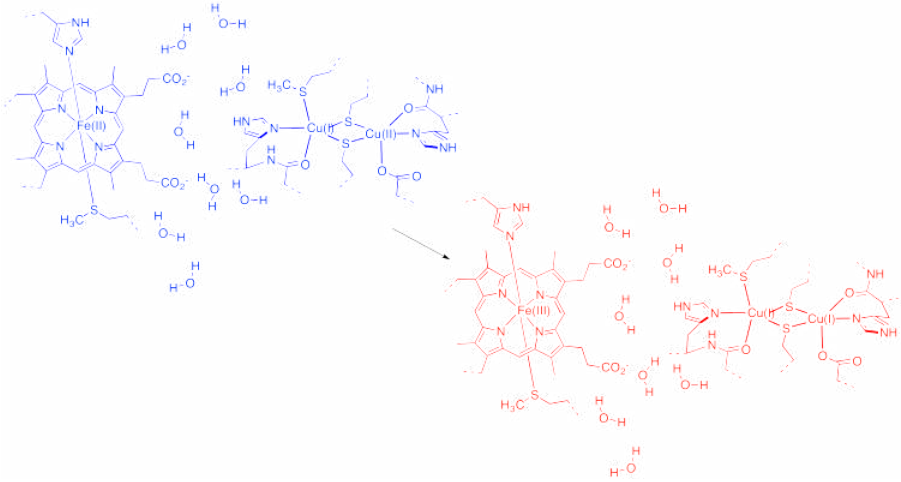
Answer

The reactants and products are very similar in this case. However, the Fe(III) complex has shorter bonds than the Fe(II) complex because of greater electrostatic interaction between the metal ion and the ligands. These changes in bond length needed in order to get ready to change from Fe(III) to Fe(II) (or the reverse) pose a major barrier to the reaction.

In the drawing below, an electron is transferred from one metal to another metal of the same kind, so the two are just switching oxidation states. For example, it could be an iron(II) and an iron(III), as pictured in the problem above. In the blue state, one iron has the extra electron, and in the red state it is the other iron that has the extra electron. The energy of the two states are the same, and the reduction potential involved in this transfer is zero. However, there would be some atomic reorganizations needed to get the coordination and solvation environments adjusted to the electron transfer. The ligand atoms and solvent molecules have shifted in the change from one state to another, and so our energy surfaces have shifted along the x axis to reflect that reorganization.



That example isn't very interesting, because we don't form anything new on the product side. Instead, let's picture an electron transfer from one metal to a very different one. For example, maybe the electron is transferred from cytochrome c to the "copper A" center in cytochrome c oxidase, an important protein involved in respiratory electron transfer.



? Exercise 5.8.1.7

In the drawing above, some water molecules are included between the two metal centres.

a. Explain what happens to the water molecules in order to allow electron transfer to occur, and why.
b. Suppose there were a different solvent, other than water, between the complexes. How might that affect the barrier to the reaction?

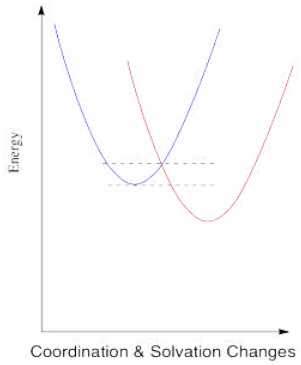
Answer a

a) The drawing is an oversimplification, but in general the water molecules are shown reorienting after the electron transfer because of ion-dipole interactions. In this case, the waters are shown orienting to present their negative ends to the more positive iron atom after the electron transfer. In reality, in a protein there are lots of other charges (including charges on the ligand) that may take part in additional ion-dipole interactions.

Answer b

b) Because electron transfer is so fast, atomic and molecular reorganisations are actually thought to happen before the electron transfer. The water molecules would happen to shift into a position that would provide the greatest possible stabilisation for the ions and then the electron would be transferred. A less polar solvent than water would be less able to stabilize ions and the electron would be slower to transfer as a result. In addition, a less polar solvent than water would be a poor medium to transmit an electron, which is charged and therefore stabilized by interactions with polar solvents.

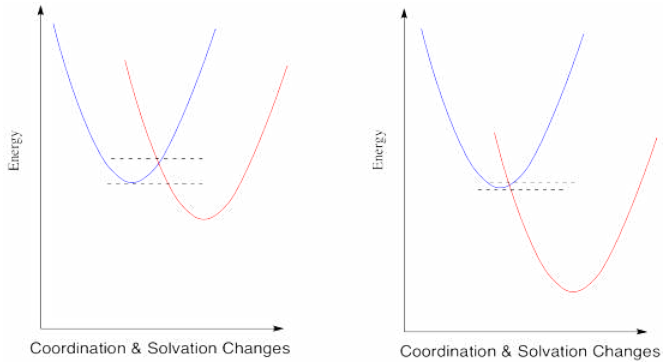
The energy diagram for the case involving two different metals is very similar, except that now there is a difference in energy between the two states. The reduction potential is no longer zero. We'll assume the reduction potential is positive, and so the free energy change is negative. Energy goes down upon electron transfer.



Compare this picture to the one for the degenerate case, when the electron is just transferred to a new metal of the same type. A positive reduction potential (or a negative free energy change) has the effect of sliding the energy surface for the red state

downwards. As a result, the intersection point between the two surfaces also slides downwards. Since that is the point at which the electron can slide from one state to the other, the barrier to the reaction decreases.

What would happen if the reduction potential were even more positive? Let's see in the picture below.



The trend continues. According to this interpretation of the kinetics of electron transfer, the more exothermic the reaction, the lower its barrier will be. It isn't always the case that kinetics tracks along with thermodynamics, but this might be one of them.

But is all of this really true? We should take a look at some experimental data and see whether it truly works this way.

Oxidant	E°	k ($M^{-1}s^{-1}$) (margin of error shown in parentheses)
$Co(diene)(NH_3)_2^{3+}$	0.12	3.0(4)
$Co(diene)H_2O)NCS^{2+}$	0.38	11(1)
$Co(diene)(H_2O)_2^{3+}$	0.53	800(100)
Co(EDTA)	0.60	6000(1000)

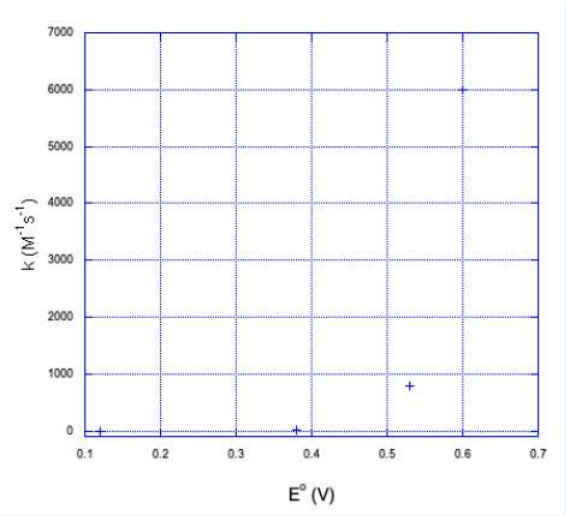
As the reduction potential becomes more positive, free energy gets more negative, and the rate of the reaction dramatically increases. So far, Marcus theory seems to get things right.

? Exercise 5.8.1.8

a. Plot the data in the above table.
b. How would you describe the relationship? Is it linear? Is it exponential? Is it direct? Is it inverse?
c. Plot rate constant versus free energy change. How does this graph compare to the first one?

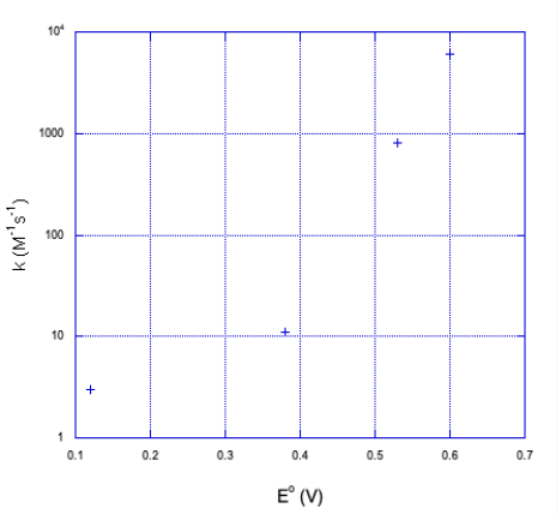
Answer a

a) Here is a plot of the data.



Answer b

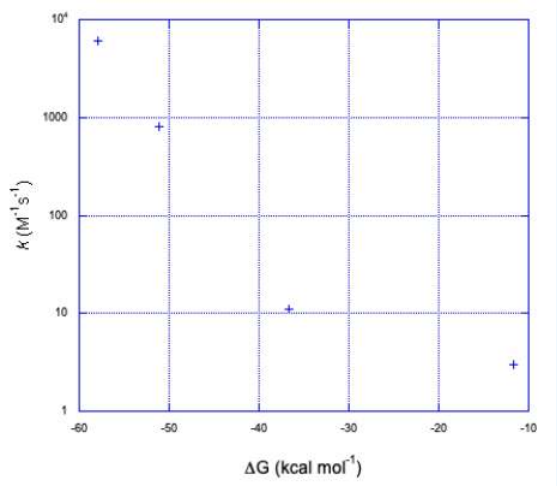
b) It doesn't look linear. If we plot the y axis on a log scale, things become a little more linear.



It looks closer to a logarithmic relationship than a linear one.

Answer c

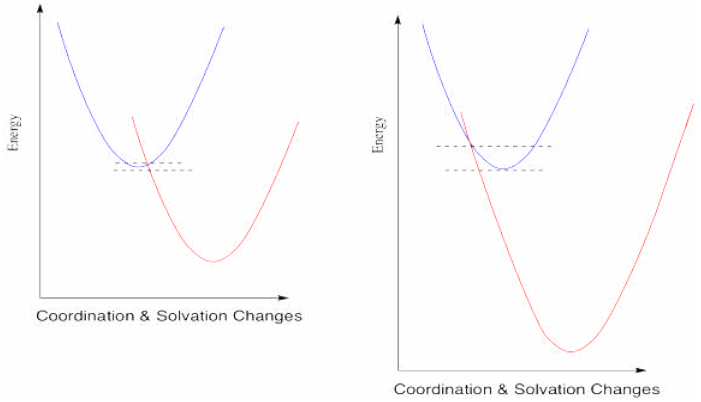
c) Assuming one electron transfer:



The graph takes the same form but in the opposite direction along the x axis.

Marcus Inverted Region

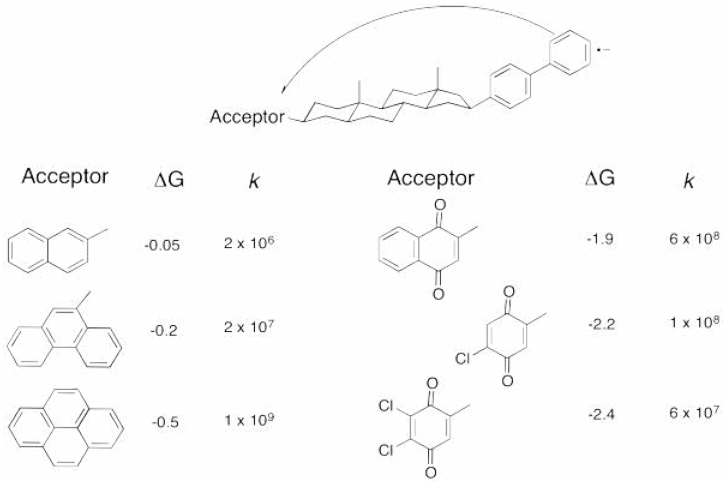
When you look a little closer at Marcus theory, though, things get a little strange. Suppose we make one more change and see what happens when the reduction potential becomes *even more* positive.



So, if Marcus is correct, at some point as the reduction potential continues to get more positive, reactions start to slow down again. They don't just reach a maximum rate and hold steady at that plateau; the barrier gets higher and higher and the reactions get slower and slower. If you feel a little skeptical about that, you're in good company.

Marcus always maintained that this phenomenon was a valid aspect of the theory, and not just some aberration that should be ignored. The fact that nobody had ever actually observed such a trend didn't bother him. The reason we didn't see this kind of thing, he said, was that we just hadn't developed technology that was good enough to measure these kind of rates accurately.

But technology did catch up. Just take a look at the following data (from Miller, *J. Am.Chem. Soc.* **1984**, *3047*).



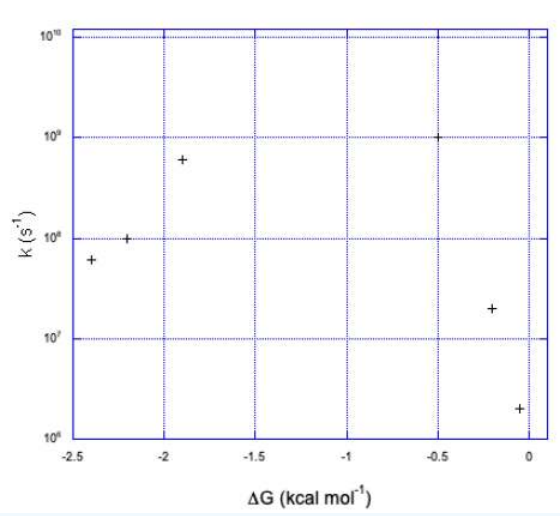
Don't worry that there are no metals involved anymore. An electron transfer is an electron transfer. Here, an electron is sent from the aromatic substructure on the right to the substructure on the left. By varying the part on the left, we can adjust the reduction potential (or the free energy change, as reported here.

? Exercise 5.8.1.9

a. Plot the data in the above table.
b. How would you describe the relationship?

Answer a

a)



Answer b

b) We can see two sides of an inverted curve. The reaction gets much faster as the free energy becomes more negative, but at some point the rate begins to decrease again.

As the reaction becomes more exergonic, the rate increases, but then it hits a maximum and decreases again. Data like this means that the "Marcus Inverted Region" is a real phenomenon. Are you convinced? So were other people. In 1992, Marcus was awarded the Nobel Prize in Chemistry for this work.

? Exercise 5.8.1.10

Take a look at the donor/acceptor molecule used in Williams' study, above. a) Why do you suppose the free energy change is pretty small for the first three compounds in the table? b) Why does the free energy change continue to get bigger over the last three compounds in the table?

Answer

The acceptor compound becomes an anion when it accepts an electron. The first three compounds do not appear to be strongly electrophilic; they can accept electrons simply because of resonance stability of the resulting anion. The last three have electron withdrawing groups (chlorines and oxygens) that would stabilize the anion even further.

? Exercise 5.8.1.11

The rates of electron transfer between cobalt complexes of the bidentate bipyridyl ligand, $Co(bipy)_3^{n+}$, are strongly dependent upon oxidation state in the redox pair. Electron transfer between Co(I)/Co(II) occurs with a rate constant of about 10^9 $M^{-1}s^{-1}$, whereas the reaction between Co(II)/Co(III) species proceeds with k = 18 $M^{-1}s^{-1}$.

a. What geometry is adopted by these complexes?
b. Are these species high spin or low spin?
c. Draw d orbital splitting diagrams for each complex.
d. Explain why electron transfer is so much more facile for the Co(I)/Co(II) pair than for the Co(II)/Co(III) pair.

Answer a

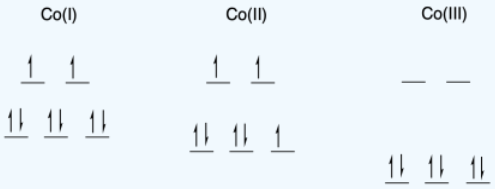
a) octahedral; bpy is a bidentate ligand.

Answer b

b) Co is first row; Co(I) and Co(II) have relatively low charge. Usually we would expect them to be high spin. Co(III) is at a cut-off point in the first row; it is just electronegative enough that it is usually low spin.

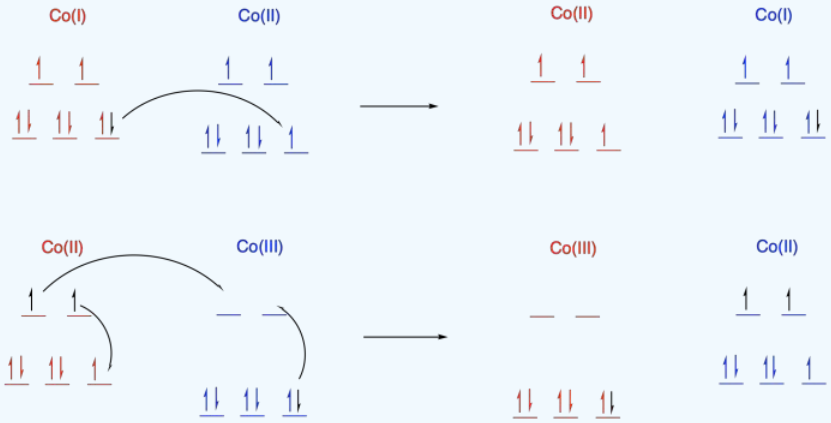
Answer c

c)



Answer d

d) In a transfer from Co(II) to Co(III), there is additional reorganization needed because the metal changes between high and low spin. Not only does one electron have to move from one metal to another metal, but additional electrons have to shuffle from one orbital to another on the same metal to accommodate the change. These reorganizations have a barrier, slowing the reaction.



This page titled 5.8.1: Outer Sphere Electron Transfer is shared under a CC BY-NC license and was authored, remixed, and/or curated by Kathryn Haas.

- **1.9: Outer Sphere Electron Transfer** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI3.htm.

5.8.2: Inner Sphere Electron Transfer

In some cases, electron transfers occur much more quickly in the presence of certain ligands. For example, compare the rate constants for the following two electron transfer reactions, involving almost exactly the same complexes:

$$Co(NH_3)_6^{3+} + Cr^{2+} \longrightarrow Co^{2+} + Cr^{3+} + 6\,NH_3 \quad k = 10^{-4}\,M^{-1}\,s^{-1}$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \longrightarrow Co^{2+} + CrCl^{2+} + 6\,NH_3 \quad k = 6 \times 10^{5}\,M^{-1}\,s^{-1}$$

(Note: aqua ligands are omitted for simplicity. Ions, unless noted otherwise, are aqua complexes.)

Notice two things: first, when there is a chloride ligand involved, the reaction is much faster. Second, after the reaction, the chloride ligand has been transferred to the chromium ion. Possibly, those two events are part of the same phenomenon.

Similar rate enhancements have been reported for reactions in which other halide ligands are involved in the coordination sphere of one of the metals.

In the 1960's, Henry Taube of Stanford University proposed that halides (and other ligands) may promote electron transfer via bridging effects. What he meant was that the chloride ion could use one of its additional lone pairs to bind to the chromium ion. It would then be bound to both metals at the same time, forming a bridge between them. Perhaps the chloride could act as a conduit for electron transfer. The chloride might then remain attached to the chromium, to which it had already formed a bond, leaving the cobalt behind.

Electron transfers that occur via ligands shared by the two metals undergoing oxidation and reduction are termed "inner sphere" electron transfers. Taube was awarded the Nobel Prize in chemistry in 1983; the award was based on his work on the mechanism of electron transfer reactions.

? Exercise 5.8.2.1

Take another look at the two electron transfer reactions involving the cobalt and chromium ion, above.

a. What geometry is adopted by these complexes?
b. Are these species high spin or low spin?
c. Draw d orbital splitting diagrams for each complex.
d. Explain why electron transfer is accompanied by loss of the ammonia ligands from the cobalt complex.
e. The chloride is lost from the cobalt complex after electron transfer. Why does it remain on the chromium?

Answer a

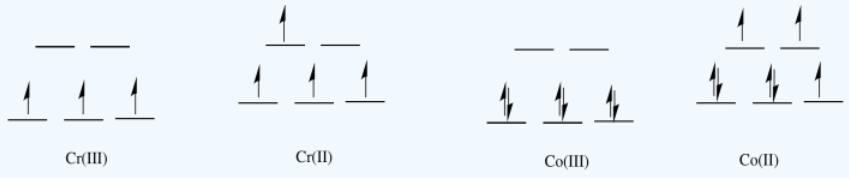
a) octahedral

Answer b

b) In the first row, 2^+ complexes are almost always high spin. However, 3^+ complexes are sometimes low spin.

Answer c

c)



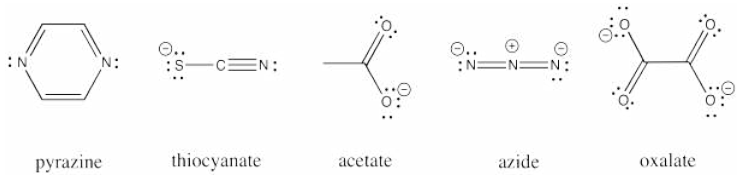
Answer d

d) The Co(II) complex is high spin and labile. The ligands are easily replaced by water.

Answer e

e) The Cr(III) complex is only d^3; it is inert.

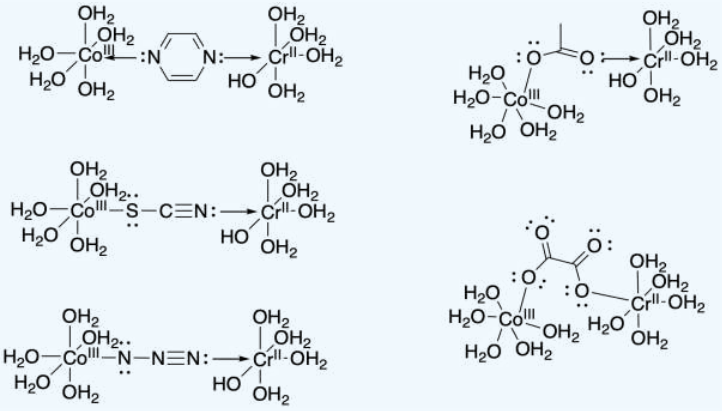
Other ligands can be involved in inner sphere electron transfers. These ligands include carboxylates, oxalate, azide, thiocyanate, and pyrazine ligands. All of these ligands have additional lone pairs with which to bind a second metal ion.



Exercise 5.8.2.2

Draw an example of each of the ligands listed above bridging between a cobalt(III) and chromium(II) aqua complex.

Answer

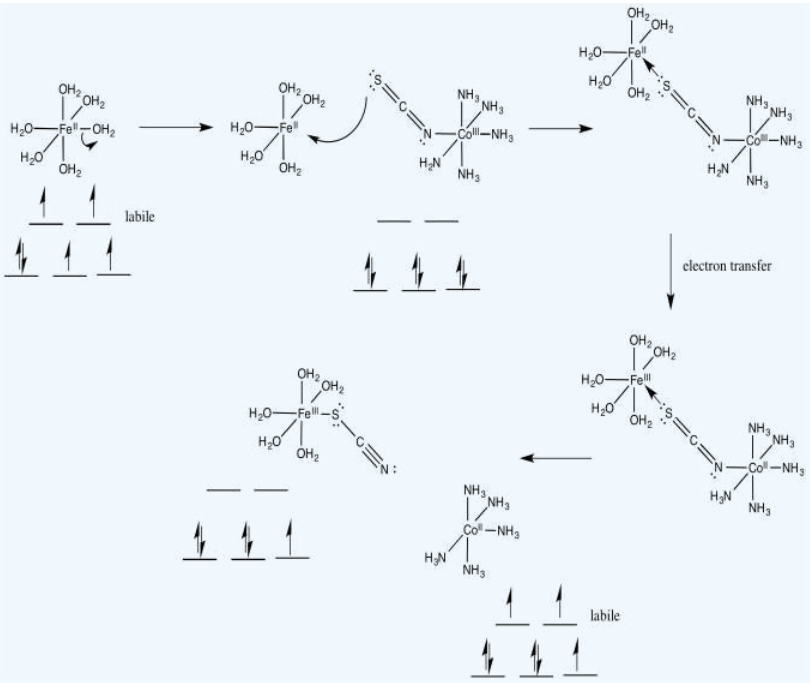


Exercise 5.8.2.3

Explain, with structures and d orbital splitting diagrams, how the products are formed in the following reaction, in aqueous solution.

$$Fe(OH_2)_6^{2+} + (SCN)Co(NH_3)_5^{2+} \longrightarrow (NCS)Fe(OH_2)_5^{2+} + Co(OH_2)_6^{2+} + 5\,NH_3$$

Answer



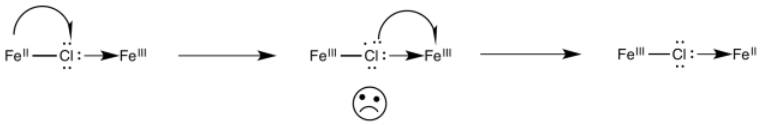
How does the electron travel over the bridge?

Once the bridge is in place, the electron transfer may take place via either of two mechanisms. Suppose the bridging ligand is a chloride. The first step might actually involve an electron transfer from chlorine to the metal; that is, the chloride could donate one electron from one of its idle lone pairs. This electron could subsequently be replaced by an electron transfer from metal to chlorine.



Sometimes, we talk about the place where an electron *used to be*, describing it as a "hole". In this mechanism, the electron donated from the bridging chloride ligand leaves behind a hole. The hole is then filled with an electron donated from the other metal.

Alternatively, an electron might first be transferred from metal to chlorine, which subsequently passes an electron along to the other metal. In the case of chlorine, this idea may be unsatisfactory, because chlorine already has a full octet. Nevertheless, some of the other bridging ligands may have low-lying unoccupied molecular orbitals that could be populated by this extra electron, temporarily.

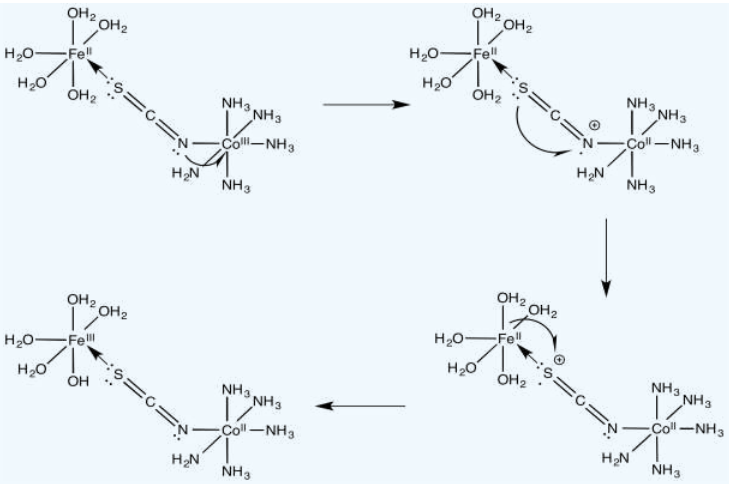


? Exercise 5.8.2.4

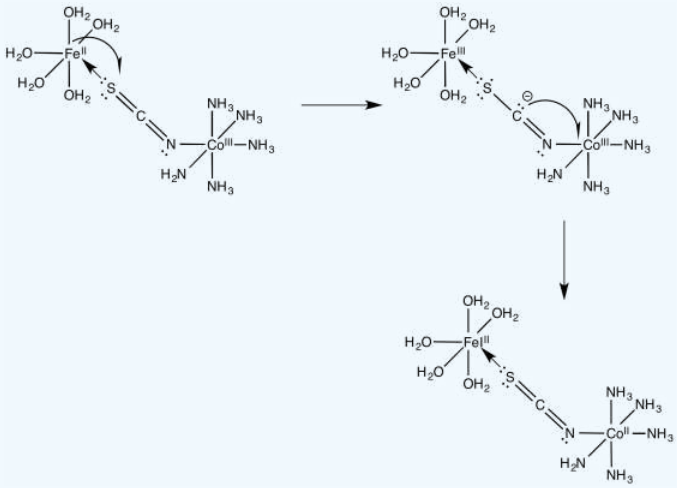
For the iron / cobalt electron transfer in problem Exercise 5.8.2.3(RO9.3.), show

a. an electron transfer mechanism via a hole migration along the bridge
b. an electron transfer mechanism via an electron migration along the bridge

Answer a



Answer b



Exercise 5.8.2.5

One of the many contributions to the barrier for electron transfer between metal ions is internal electronic reorganization.

a) Draw d orbital splitting diagrams for each of the following metal ions in an octahedral environment.

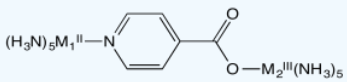
Ru(II) or Os(II)

Ru(III) or Os(III)

Co(II)

Co(III)

Flash photolysis is a method in which an electron can be moved instantly "uphill" from one metal to another (e.g. from M_2^{II} to M_1^{III}, below); the electron transfer rate can then be measured as the electron "drops" back from M_1^{II} to M_2^{III}.



b) Explain the relative rates of electron transfer reaction in this system, as measured by flash photolysis in the table below.

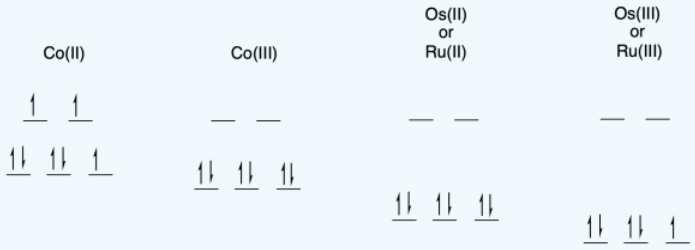
M_1^{II}	M_2^{III}	k_{obs} s^{-1}
Os	Ru	> 5 x 10^9

Os	Co	1.9 x 10^5

c) Does the reaction above probably occur via an inner sphere or by an outer sphere pathway? Why?

Answer a

a)



Answer b

b) The electron transfer between Os(II) and Ru(III) will not involve any electron reorganization because both are low spin to begin with. However, the electron transfer between Os(II) and Co(III) will result in cobalt changing from low spin to high spin. The need to move electrons between different d orbitals on the cobalt will add to the barrier, slowing down the reaction.

Answer c

c) The pathway is probably inner sphere because of the bridging ligand. Furthermore, the conjugation in the bridging ligand would help in conducting an electron from one end of the ligand to the other, either through an electron mechanism or a hole mechanism.

? Exercise 5.8.2.6

Outer sphere electron transfer rates depend on the free energy change of the reaction (ΔG°) and the distance between oxidant and reductant (d) according to the relation

Rate constant = $k = Ae^{(-\Delta G)}e^{-d}$

a) What happens to the rate of the reaction as distance increases between reactants?

One potential problem in measuring rates of intramolecular electron transfer (i.e. *within* a molecule) is competition from intermolecular electron transfer (*between* molecules).

b) What would you do in the flash photolysis experiment above to discourage intermolecular electron transfer?

c) How could you confirm whether you were successful in discouraging intermolecular reaction?

Answer a

a) The rate decreases exponentially as distance increases.

Answer b

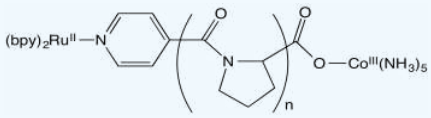
b) You might keep the concentration low in order to increase the distance between molecules, reducing the likely hood of an outer-sphere electron transfer.

Answer c

c) If you ran the experiment at a series of dilutions, intramolecular electron transfer would be unaffected but outer sphere electron transfer would not. If the rates were the same across a number of different concentrations, the reaction would probably be intramolecular.

Exercise 5.8.2.7

Stephan Isied and coworkers at Rutgers measured the following electron transfer rates between metal centers separated by a peptide. (*Chem Rev* **1992**, *92*, 381-394)



a. The proline repeating unit is crucial in ensuring a steady increase in distance between metal centers with increased repeat units, n. Why?
b. An inner sphere pathway in this case is expected to be somewhat slow because of the lack of conjugation in the polyproline bridge. Explain why.
c. Plot the data below, with log*k* on the y axis (range from 4-9) and d on the x axis (12-24 Angstroms).

n	d (Å)	k_{obs} (s^{-1})
1	12.2	5×10^{8}
2	14.8	1.6×10^{7}
3	18.1	2.3×10^{5}
4	21.3	5.1×10^{4}
5	24.1	1.8×10^{4}

d) A linear relationship is in agreement with Marcus theory; log*k* = - c x d. Is your plot linear?

Isied offers a number of possible explanations for the data, all of which involve two competing reaction pathways.

e) Suggest one explanation for the data.

Answer a

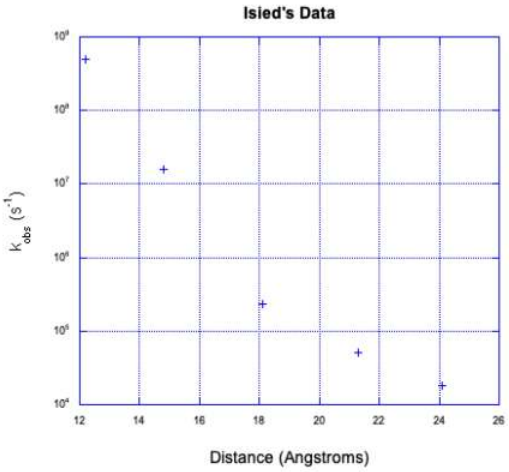
a) Rings are frequently used to introduce conformational rigidity (or decrease conformational flexibility), limiting the range of potential shapes a molecule could adopt. If the molecule can't wiggle around as much, then the distance between the ends of the molecule should be more constant.

Answer b

b) Although the ligand is bridging, it would be difficult to picture either an electron or hole mechanism of inner sphere electron transfer. There are few pi bonds or lone pairs to use as places to put electrons or temporarily remove electrons from, shuttling the electrons from place to place along the ligand. A conjugated system would be much more likely to carry out inner sphere electron transfer.

Answer c

c)



Answer d

d) The data is not linear.

Answer e

e) The data appear to show two lines that cross. That's a classic symptom of two competing mechanisms. The faster mechanism, to the left, is probably an intramolecular electron transfer. The slower mechanism, to the right, may be an intermolecular electron transfer.

This page titled 5.8.2: Inner Sphere Electron Transfer is shared under a CC BY-NC license and was authored, remixed, and/or curated by Kathryn Haas.

- **1.10: Inner Sphere Electron Transfer** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI3.htm.

5.9: Reactions of Coordinated Ligands

So far, our coverage of the reactions of metal complexes has focused only on the reactions that occur at the metal center. However, there are also reactions that can occur to the ligands bound at the metal center. When a ligand binds to an electropositive metal center, bonds within the ligand can be polarized in new ways, leading to new or enhanced reactivity. Some of these reactions are covered in the chapters on organometallic chemistry, and there are many examples of how biology employs metal ions at enzyme active sites to catalyze biological transformations. This section will briefly describe some of the most common types of reactions that can be catalyzed by metal ion binding.

This page titled 5.9: Reactions of Coordinated Ligands is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.9.1: Metal-catalyzed Hydrolysis

Transition metal ions (but not alkali metal ions) act as Lewis acids in metal-ligand interactions. As a consequence of the metal ion interacting with the ligand, the electronic structure of the ligand is altered. In some cases, the metal-ligand interaction causes changes in the strength and reactivity of other bonds within the ligand itself. For example, when a ligand has an acidic proton, interactions with a metal ion will make that acidic proton more acidic. In other words, interaction with the metal ion can cause a decrease in the ligand's pK_a. The metal-ligand complex itself can act as a stronger Bronsted acid (giving off a proton) compared to the "free" ligand. We can see this type of alteration in the pK_a of water when it is "free" compared to when it is bound to a metal ion.

Example: Water meets a transition metal ion[1]

In biology, the solvent is water. Water is also a ligand that binds to metal ions, according to the equation shown below.

$$\mathrm{nH_2O + M^{x^+} \rightleftharpoons [M(H_2O)_n]^{x^+}}$$

There is a LOT of water around in biological systems. Consequently, the reaction shown above is shifted far to the right (toward the aquo metal complex, $\mathrm{[M(H_2O)_n]^{x^+}}$) in aqueous solution. Consequently, when metals are dissolved in aqueous solution, the "free" ion does not exist, and rather the metal is in complex with water. This is generally true unless there are other ligands present that have stronger affinity for the metal ion.

Consider the two equilibrium reactions shown below. The autoionization of water is shown on the left. This reaction has a very small equilibrium constant ($K_W = 10^{-14}$) and thus the pK_a for dissociation of a proton from water is $pK_a = 14$. On the left is the dissociation of a proton from a water molecule bound to $\mathrm{Zn^{2+}}$ ion (other water ligands are not drawn for simplicity). The bond between $\mathrm{H_2O}$ and Zn is considered to be covalent.

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-} \qquad \text{vs.} \qquad \mathrm{[Zn(H_2O)]^{2+} \rightleftharpoons H^+ + [Zn(OH)]^+}$$

? Exercise 5.9.1.1

Predict which reaction above is more favorable. In other words, in which case is water a better acid; when water is "free", or when it is bound to a transition metal ion like $\mathrm{Zn^{2+}}$? Defend your prediction.[1]

Hint

Consider these two things:

(1) In which case is the hydroxide ion more stable: when it is a free ion or when it is bound to Zn? How will this effect one case relative to the other?

(2) Consider separation of charge in each equilibrium. Is the localization of positive and negative charge more energetically favorable in the reactands or in the products in each case? How will this effect one case relative to the other?

Answer

Water is a better acid when it has a covalent bond to a metal ion. The metal-ligand interaction weakens the H-O bond and stabilizes the conjugate base that forms after deprotonation.

? Exercise 5.9.1.2

Water has a pK_a of 14. When water is bound to a $\mathrm{Zn^{2+}}$ ion in aqueous solution, its pK_a is lowered to 10. Calculate the pH of pure water and the pH of a solution of 0.1 M $\mathrm{ZnSO_4}$.

Hint

You will need the chemical equations above and you will need to recall the definitions of K_a and pK_a, as well as pH to complete this task. Recall that $pK_a = -\log K_a$ and $pH = -\log[H^+]$. The K_a is the equilibrium constant for the

chemical equation. Use an I.C.E. table to calculate the amount of hydrogen ion at equilibrium.

Answer

The pH of pure water is 7. The pH of 0.1 M $ZnSO_4$ depends only on the concentration of the Zn aquo complex that forms after dissociation of $ZnSO_4$ to Zn^{2+} and SO_4^{2-}. We can use the I.C.E method to determine that the concentration of hydrogen ion at equilibrium is approximately 3.2×10^{-6} after 0.1M Zn^{2+} is initially added to water. This gives approximately $pH = 5.5$.

? Exercise 5.9.1.3

Transition metals dramatically decrease solution pH compared to pure water. On the other hand, alkali metals do not significantly affect pH.

a) Based on this information, what can you conclude about the relative covalent nature of water's interactions with transition metals compared to alkali metals?

b) Rationalize this based on the element's position on the periodic table and their consequent electron configurations.

Answer

a) transition metals form more covalent bonds with water, while alkali metal's interactions are more electrostatic in character.

b) transition metals have partially-filled d subshells, while alkali metals have the electron configurations of the nobel gases. Perhaps the nobel gas electron configuration makes covalent bonding unfavorable, while partially filled d-orbitals enables productive bonding interactions with ligands.

? Exercise 5.9.1.4

When a transition metal binds to a Cys side chain, it usually binds to the thiolate anion form of this side chain. Explain why the Cys loses its proton when a metal ion binds. Use drawings to describe what happens to the pK_a of the thiol hydrogen.

Hint

A cystein side chain has a thiol (R-SH) group. Recall that thiols behave similarly to alcohols, but thiols are more acidic than alcohols.

Answer

Bonding of a cystein S to a metal ion would weaken the S-H bond and increase the acidity of that proton (it's pKa would decrease). In bilogical conditions, near neutral pH, this bonding could decrease the pKa of the thiol group so much that the H is lost to give the conjugate base thiolate bound to the metal.

Biological hydrolysis[2]

Above you learned how metals can act as Lewis Acids to increase the acidity of a bound water molecule (or other ligand). This modulation of water's pK_a can be really useful to catalyze reactions in which hydroxide ion is a reactant. The enzyme **carbonic anhydrase (CA)** is a prime example of how biology uses this property to catalyze an important biological acid/base reaction. CA is the enzyme that converts CO_2 into bicarbonate (HCO_3^-) very quickly. This is important in the blood to get to CO_2 to the lungs to be exhaled. Conversion of CO_2 to bicarbonate is also important in production of the aqueous fluid of eye and other secretions; and CA is an important drug target for treatment of glaucoma.

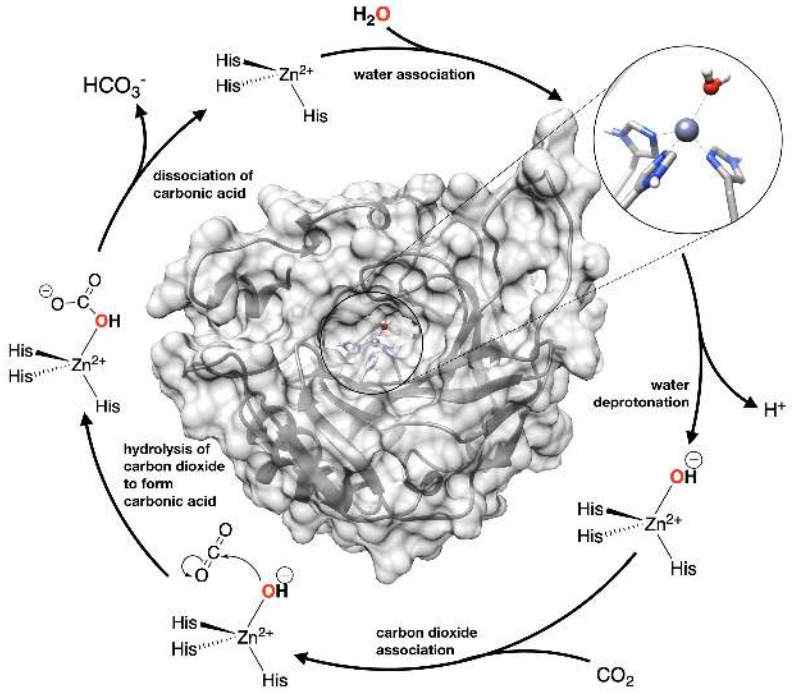


Figure 5.9.1.4: Formation of carbonic acid from carbon dioxide catalyzed by human carbonic anhydraze IV. The structure of protein and acitve site were created from PDB 1znc. (CC-BY-SA; Kathryn Haas)

The figure shows the structure of human carbonic anhydrase IV (from PDB 1znc), with a blow up of the Zn active site where Zn is bound to 3 histidine side chains (His). The mechanism for this enzyme is shown in the chemical equations circling the structure in Figure 5.9.1.4 As we discused above, binding water to a metal ion can change its pK_a, and make its protons more acidic by stabilizing the hydroxide ion. When hydroxide is needed to carry out hydrolysis reactions, acidic metal ions, like Zn^{2+} are often used to stabilize the hydroxide nucleophile in order to catalyze the reaction (lower the activation energy). The pK_a of “free” water is 14. For water in $[Zn(H_2O)_6]^{2+}$ in aqueous solution, the pK_a is 10. But, in the active site of carbonic anhydrase, the pK_a of water is lowered even more, to 7, by the protein environment around the Zn active site. The active site of this protein has the "power" to lower the pKa of water even more than in the case of aqueous Zn as a virtue of the hydrophobic pocket of the active site that makes charge separation more unstable compared to bulk water where charges can be better solubilize by bulk water.

Look carefully at the catalytic cycle shown in Figure 5.9.1.4and identify the step in which water looses a proton (the step labeled "water deprotonation". This step would be nearly impossible under biological conditions at pH 7.4. In other words, it would happen too infrequently to be useful in biological systems. But, when the pKa is lowered to 7, which is below the pH, that step becomes so favorable, that it would happen spontaneously in solution.

Carbonic anhydrase is just one example of how metal ions can be useful for catalyzing hydrolysis reactions. There are several more examples of catalytic enzymes and small molecule metal complexes that use metals (Cu, Co, Ni, Mn, Ca, and Mg) to catalyze hydrolysis of esters (eg hydrolysis of fats), amides (eg hydrolysis of peptide bonds with water), phosphate esters (eg hydrolysis of DNA and RNA) using mechanisms simlar to that shown above for hydrolysis of carbon dioxide.

Sources

1. Inspired by or taken directly from *Metals in Acid Base Chemistry*, an in-class activity created by Sheila Smith, University of Michigan- Dearborn (sheilars@umd.umich.edu) and posted on VIPEr (www.ionicviper.org) on October 17, 2009. Copyright Sheila Smith 2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License. To view a copy of this license visit http://creativecommons.org/about/license/.

2. From *Metals in Biological Systems - Who? How? and Why?*, a 5 slides about learning object created by Adam R. Johnson, Harvey Mudd College (adam_johnson@hmc.edu), Hilary Eppley, DePauw Univeristy (), and Sheila Smith, University of Michigan- Dearborn (sheilars@umd.umich.edu) and posted on VIPEr (www.ionicviper.org) on January 20, 2010. Copyright Sheila

Smith 2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License. To view a copy of this license visit http://creativecommons.org/about/license/.

This page titled 5.9.1: Metal-catalyzed Hydrolysis is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.9.2: Template Reactions

A template reaction is one in which a metal ion acts as a template to bring reactive sites in close proximity. In the absence of the metal ion, the same reaction would proceed to form a different product. An example of the template effect is the dialykation of nickel dithiolate (Figure 5.9.2.1). The same dialkylation in the absence of the Ni template creates a polymer.

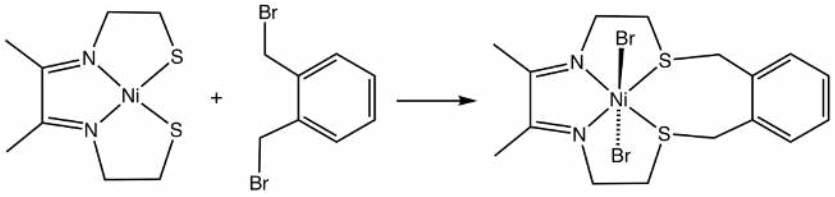


Figure 5.9.2.1: The Dialkylation of nickle dithiolate. (Public Domain; Smokefoot)

Another example of a template reaction is in the synthesis of crown ethers from dialkylations that are templated by metal ions. Again, the same reaction carried out without the template metal would form a polymer.

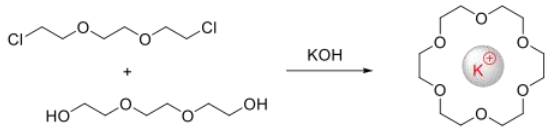


Figure 5.9.2.1: 18-Corwn-6 can be synthesized by the Williamson ether synthesis using potassium ion as the template cation. (Carolineneil, 18-crown-6 was synthesized using potassium ion as the template cation, CC BY-SA 4.0)

This page titled 5.9.2: Template Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

5.9.3: Electrophilic Substitutions

We have seen how metal ion binding can alter the pKa of a bound ligand by polarizing bonds. In a similar fashion, binding of a ligand to a metal ion can alter the location of electron density so that positions on the ligand take on new reactivity. This can be seen in the case of acetylacetone (acac) complexes (most recently discussed in section 12.5.3). The metal coordination to the acac ligand induces enol tautomerization, placing electron density at the central alpha carbon and causing it to become a potent nucleophile. Reactions occur at that nucleophilic carbon in similar manner to the electrophilic aromatic substitution reactions that you may have learned about in an Organic Chemistry course.

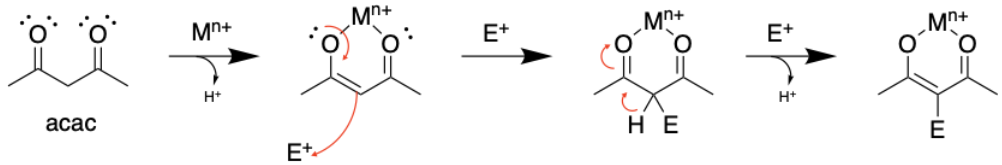


Figure 5.9.3.1: Electrophilic substitution of the acac ligand. E^+ = electrophile. (CC-BY-SA; Kathryn Haas)

This page titled 5.9.3: Electrophilic Substitutions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

CHAPTER OVERVIEW

6: Catalysis

6.1: Introduction to Organometallic Chemistry
6.2: Nomenclature, Ligands, and Classification
6.3: Electron Counting in Organometallic Complexes
6.3.1: The 18 Electron Rule
6.3.2: Simplifying the Organometallic Complex by Deconstruction
6.4: Survey of Organometallic Ligands
6.4.1: Carbon Monoxide (Carbonyl Complexes)
6.4.2: Ligands similar to CO
6.4.3: Hydrides and Dihydrogen Complexes
6.5: Bonding between Metal Atoms and Organic Pi Systems
6.5.1: Linear π Systems
6.5.2: Cyclic π systems
6.5.3: Odd-numbered π Systems
6.5.4: Fullerene Complexes
6.6: Metal-Carbon Bonds
6.6.1: Metal Alkyls
6.6.2: Carbenes
6.6.3: Carbyne (Alkylidyne) Complexes
6.6.4: Carbido and Cumulene Complexes
6.6.5: Carbon Wires- Polyyne and Polyene Bridges
6.7: Characterization of Organometallic Complexes

This page titled 6: Catalysis is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

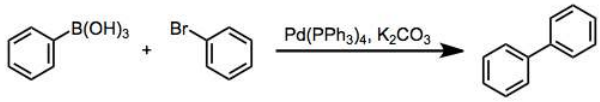
6.1: Introduction to Organometallic Chemistry

What is Organometallic Chemistry?

This chapter will introduce a subfield of inorganic coordination chemistry; organometallic chemistry. Let's begin with a few simple questions: what is organometallic chemistry? What, after studying organometallic chemistry, will we know about the world that we didn't know before? Why is the subject worth studying? And what kinds of problems is the subject meant to address? The purpose of this introduction is twofold: (1) to help motivate us as we move forward (that is, to remind us that there is a point to all this!); and (2) to illustrate the kinds of problems we'll be able to address using concepts from the field. You might be surprised by the spine-chilling power you feel after learning about the behavior of organometallic compounds and reactions!

Put most bluntly, **organometallic chemistry is the study of compounds containing, and reactions involving, metal-carbon bonds**. The metal-carbon bond may be transient or temporary, but if one exists during a reaction or in a compound of interest, we're squarely in the domain of organometallic chemistry. Despite the denotational importance of the M-C bond, bonds between metals and the other common elements of organic chemistry also appear in organometallic chemistry: metal-nitrogen, metal-oxygen, metal-halogen, and even metal-hydrogen bonds all play a role. Metals cover a vast swath of the periodic table and include the alkali metals (group 1), alkali earth metals (group 2), transition metals (groups 3-12), the main group metals (groups 13-15, "under the stairs"), and the lanthanides and actinides. We will focus most prominently on the behavior of the transition metals, so called because they cover the transition between the electropositive group 2 elements and the more electron-rich main group elements.

Why is organometallic chemistry worth studying? Well, for me, it mostly comes down to synthetic flexibility. There's a reason the "organo" comes first in "organometallic chemistry"—our goal is usually the creation of new bonds in *organic* compounds. The metals tend to just be along for the ride (although their influence, obviously, is essential). And the fact is that you can do things with organometallic chemistry that you cannot do using straight-up organic chemistry. Case in point:



The venerable Suzuki reaction...unthinkable without palladium!

The establishment of the bond between the phenyl rings through a means other than dumb luck seems unthinkable to the organic chemist, but it's natural for the palladium-equipped metal-organicker. Bromobenzene looks like a potential electrophile at the bromine-bearing carbon, and if you're familiar with hydroboration you might see phenylboronic acid as a potential nucleophile at the boron-bearing carbon. Catalytic palladium makes it all happen! Organometallic chemistry is full of these mind-bending transformations, and can expand the synthetic toolbox of the organic chemist considerably.

To throw another motive into the mix for the non-specialist (or the synthesis-spurning chemist), organometallic chemistry is full of intriguing stories of scientific inquiry and discovery. Exploring how researchers take a new organometallic reaction from "ooh pretty" to strong predictive power is instructive for anyone interested in "how science works," in a practical sense. We'll examine a number of classical experiments in organometallic chemistry, both for their value to the field and their contributions to the general nature of scientific inquiry.

What kinds of problems should we be able to address as we move forward? Here's a bulleted list of the most commonly encountered types of problems in an organometallic chemistry course:

- Describe the structure of an organometallic complex…
- Predict the product of the given reaction conditions…
- Draw a reasonable mechanism based on evidence…
- Devise a synthetic route to synthesize a target organometallic compound…
- Explain the observation(s)…
- Predict the results of a series of experiments…

The first four are pretty standard organic-esque problems, but it's the last two, more general classes that really make organometallic chemistry compelling. Just imagine putting yourself in the shoes of the pioneers and making the same predictions they did!

There you have it, a short introduction to organometallic chemistry and why it's worth studying. The rest of this chapter will describe what organometallic chemistry really is…it will be helpful to keep these motives in mind as you study. Keep a thirst for predictive power, and it's hard to go wrong with organometallic chemistry!

Resources for learning organometallic chemistry

For the penny-pinching student or layman, there are several good resources for organometallic chemistry on the Web. Nothing as exhaustive as Reusch's Virtual Textbook of Organic Chemistry exists for organometallic chemistry, but the base of resources available on the Web is growing. Rob Toreki's Organometallic HyperTextBook could use a CSS refresh, but contains some nice introductions to different organometallic concepts and reactions. Try the electron-counting quiz!

VIPER is a collection of electronic resources for teaching and learning inorganic chemistry, and includes a nice section on organometallic chemistry featuring laboratory assignments, lecture notes, and classroom activities. Awesome public lecture notes are available from Budzelaar at the University of Manitoba and Shaughnessy at Alabama (Roll Tide?). For practice problems, check out Fu's OpenCourseWare material from MIT and Shaughnessy's problem sets.

Historical Background and Introduction to Metallocenes

Definition: Organometallic Complex

Organometallic Complex: A complex with bonding interactions between a metal atom and one or more carbon atoms of an organic group or molecule.

An **organometallic complex** is defined as a complex with bonding interactions between one or more carbon atoms of an organic group or molecule and at least one metal atom. It is important to understand that *just the presence of an organic ligand is not sufficient to define an organometallic compound*. If there are organic ligands present, but no metal-carbon bonds, the complex is said to be "**metal-organic**". There must be interactions between a carbon and a metal for the complex to be considered organometallic.

Example 6.1.1

Which of the molecules below is an organometallic complex?

$$[\mathrm{Sn(Me)_4}] \qquad \mathrm{Sn(OMe)_4} \qquad \mathrm{cis{-}[PtCl_2(NH_3)_2]} \tag{6.1.1}$$

Solution

The tetramethyl tin ($\mathrm{Sn(Me)_4}$) has metal-carbon bonds, and thus it is an organometallic complex.

Tetramethoxy tin ($\mathrm{Sn(OMe)_4}$) has metal-oxygen bonds. It lacks metal-carbon bonds, but it does contain organic ligands; thus it is a "metal-organic" complex rather than organometallic.

Cisplatinum ($\mathrm{cis{-}[PtCl_2(NH_3)_2]}$) contains no carbon and thus it is neither organometallic or metal-organic; it is just a coordination compound.

Industrial Importance of Organometallic Compounds

Organometallic compounds are a very important class of compounds in industry. For example, tens of thousand of tons of aluminum and tin alkyl compounds are produced each year for industrial purposes. The use of organometallic compounds as catalysts to produce other compounds is even more important. Organometallic catalysts are used for a range of industrial syntheses from manufacture of commodity polymers like polypropylene and polyethylene to production of simple organic molecules like acetaldehyde and acetic acid. These compounds are produced at a scale in the order of millions of tons per year.

History of Organometallic Chemistry

Let us take a historical approach to organometallic chemistry and see how the field has evolved. Arguably, the first organometallic compound was kakodyl oxide, an organo-arsenic compound (Figure 6.1.2). It was accidentally produced by the French chemist Louis Cadet in 1760 when he was working on inks. He heated arsenic oxide and potassium acetate and obtained a red-brown oily liquid, known as Cadet's fuming liquid. It consists mostly of cacodyl and cacodyl oxide (Figure 6.1.2). In cacodyl, there is an As-As bond and two methyl groups attached to each As atom. In the other product, cacodyl oxide, there is an O atom bridging the two

As atoms, and each As is bound to two methyl groups. The names of these two compounds come from the greek word “kakodes”, meaning "bad smell". Indeed, they have a very intense, garlic-like smell. The reaction can be used to identify arsenic in samples. For instance, if you suspected your food was poisoned with arsenic, you could heat a sample together with potassium acetate. If a bad, garlic-like smell evolved, this would indicate that there is arsenic in your sample.

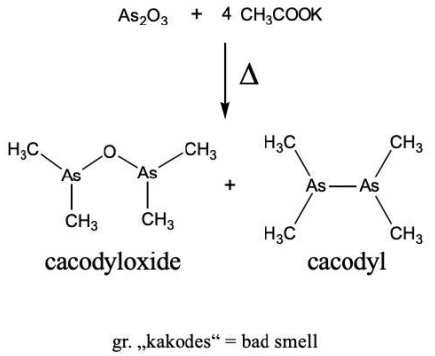


Figure 6.1.2: Cacodyl and cacodyl oxide

Another important milestone in coordination chemistry was the discovery of Zeise’s salt by the Danish chemist William Zeise in 1827 (Figure 6.1.3). Zeise’s salt was the first olefin complex in which an olefin was bound side-on to a metal using its π-electrons for σ-bonding. Zeise observed that when sodium hexachloroplatinate (2-) was heated in ethanol, a compound with the composition $Na[PtCl_3(C_2H_4)]$ could be isolated. The chemical composition of the compound suggested that there was a C_2H_4 organic fragment bonded to the platinum, but it was not clear how.

This question was only answered more than 100 years later in 1969 with the crystal structure analysis of Zeise’s salt. The crystal structure revealed that an ethylene molecule was bound side-on to the platinum (Figure 6.1.3). The two carbon atoms had about the same distance to the Pt arguing that they were equally strongly involved in the bonding with Pt. The first C had a distance of 216 pm while the second carbon had a distance of 215 pm. The ethylene molecule was oriented perpendicular to the plane made of the three chloro ligands and the platinum atom. The Cl-Pt-Cl bond angles were near 90°. Overall, the structure could be described as a structure derived from a square planar structure with the ethylene as the fourth ligand that would stand perpendicular to the plane in order to minimize steric repulsion with the chloro ligands.

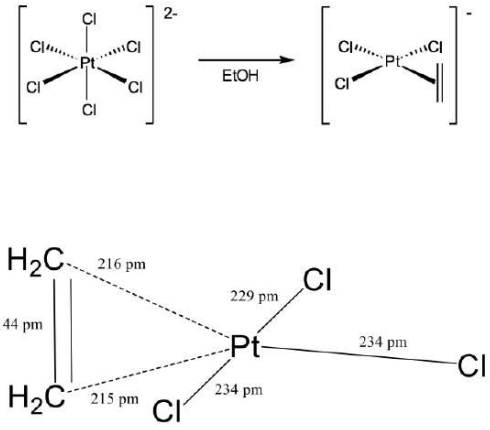


Figure 6.1.3: Zeise's salt: Synthesis and crystal structure.

An important question was how to describe the bonding in the compound. It was noteworthy that the C-C bond length in Zeise’s salt was significantly longer (144 pm) than that in a free ethylene molecule (134 pm). Based on the bond-strength bond-length concept this argued that the bond was weaker than a regular C=C double bond, and that the bond order was smaller than 2. What could explain this lower bond order and the side-on coordination of the ethylene in Zeise’s salt?

The answer is that the ethylene molecule uses its π-electrons for σ-bonding with a metal d-orbital (Figure 6.1.4). You can see above that the lobe of a $d_{x^2-y^2}$ orbital has the correct orientation to overlap with the bonding π-orbitals of the ethylene ligand in a σ-fashion. Through this interaction electron density gets donated from the bonding ligand π-orbital into the metal-d-orbital. This results in a lower electron density for π-bonding within the ligand, and thus the bond order is decreased. In addition, there is

another effect that lowers the bond order. A metal d-orbital can interact with the π*-orbitals in π-fashion. In this process, electron density can be donated from the metal d-orbital into the empty π-orbitals of the ligand. The increased electron density in the π-orbitals further decreases the bond order.

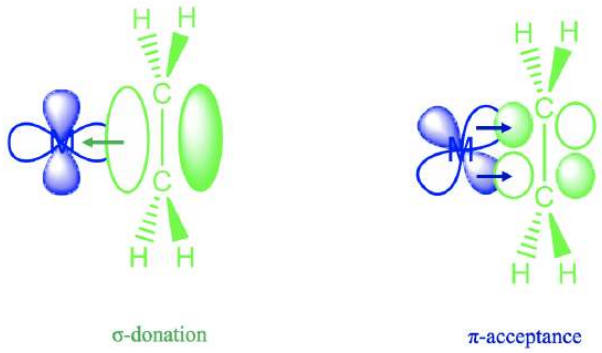


Figure 6.1.4: An orbital view of bonding in Zeise's salt

In 1890, a further milestone in organometallic chemistry was reached with the synthesis of the first carbonyl complex, the nickel tetracarbonyl. Nickel tetracarbonyl is a colorless liquid that boils at 43°C. The compound was prepared by the German chemist Ludwig Mond. Nickel tetracarbonyl forms spontaneously from nickel metal and carbon monoxide at room temperature. The reaction is the basis of the Mond-process that is used up to date in order to purify nickel (Figure 6.1.5). Carbon monoxide gas can be streamed over impure Ni metal at temperatures of 50-60°C to form $Ni(CO)_4$ in gaseous form. Impurities are left behind in solid form. Then, the nickel tetracarbonyl is thermally decomposed at ca. 220° to form nickel and carbon monoxide. The process can be varied to produce nickel in powder form, as spheres (Figure 6.1.5), and as coatings. The Mond process is still used despite the very high toxicity of nickel tetracarbonyl.

$$\mathrm{Ni_{(s,\ impure)} + 4\,CO_{(g)} \longrightarrow Ni(CO)_{4(g)}} \qquad 50-60^{\circ}\mathrm{C\ (also\ spontaneous\ at\ room\ temp)}$$

$$\mathrm{Ni(CO)_{4(g)} \longrightarrow Ni_{(s,\ purified)} + 4\,CO} \qquad 220-250^{\circ}\mathrm{C\ (Ni\ is\ purified)}$$



Figure 6.1.5: Purified Ni spheres prepared through the Mond process (René Rausch, Nickel kugeln, CC BY-SA 3.0 DE)

In 1900 the first Grignard reagents were discovered. Victor Grignard (Figure 6.1.9) was an enthusiastic young French chemist who discovered how to make organomagnesium halides (RMgX) while working for his Ph.D.. His supervisor, Sabatier, had been trying this chemistry for some time, but Victor was the genius who solved the problem. Organomagnesium halides form from magnesium and organic halides in ethers. This discovery in 1900 changed the course of organic chemistry and won Grignard and Sabatier the Nobel Prize in 1912.

$$\boxed{\text{The Grignard Reaction:} \quad \ce{Mg_{(s)}} + \text{R-X} \ce{->[ether]} \text{R-Mg-X}}$$

In 1917, the first lithium alkyls were prepared by Wilhelm Schlenk. Like Grignard reagents, lithium alkyls are very valuable reactants in synthetic organic chemistry. Lithium alkyls are very air-sensitive compounds, and some even self-ignite in air (for example tert-butyl lithium is explosive when exposed to air). Therefore, they need to be handled carefully under inert gas. So that the reactions could be carried out under air0free conditions, Wilhelm Schlenk made an important invention: The Schlenk-lines (Figure 6.1.6). The Schlenk lines allows a chemist to remove all gas (air) from a reaction flasks and back-fill the flask with an inert gas. A Schlenk line has a dual manifold with several ports. One manifold is connected to a source of purified inert gas, while the other is connected to a vacuum pump. The inert-gas line is vented through an oil bubbler, while solvent vapors and gaseous reaction products are prevented from contaminating the vacuum pump by a liquid nitrogen or dry ice/acetone cold trap. Special stopcocks or Teflon taps allow vacuum or inert gas to be selected without the need for placing the sample on a separate line.



Figure 6.1.6: A Schlenk-line (Polimerek, Double vac line front view, CC BY-SA 3.0)

Discovery of Metallocenes

The discoveries discussed above were important milestones in the development of organometallic chemistry. But the field expanded more rapidly with the discovery of the first metallocene: ferrocene. Like often in science, ferrocene was discovered through an accident. In 1951 Peter Pauson and Thomas Kealy attempted to synthesize the organic compound fulvalene through oxidative coupling of cyclopentadienyl magnesium chloride with iron (III) chloride. However, instead of obtaining fulvalene they observed the formation hydrofulvalene together with an orange powder with “remarkable stability”. Analysis of the powder showed that the chemical compound contained two cyclopentadienyl rings and one iron atom. According to the knowledge on bonding in organometallic compounds that was known at the time Kealy and Pauson suggested a structure for the molecule in which two cyclopentadienyl group were bound to a single Fe atom via two Fe-C bonds (Figure 6.1.7).

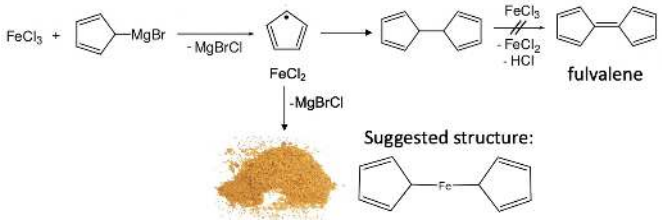
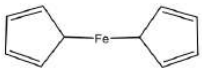


Figure 6.1.7: Synthesis of ferrocene (Attribution: T.J. Kealy, P.L. Pauson, Nature 1951, 168, 1039.)

However, the remarkable stability of the compound was in contradiction to the proposed structure. The structure would be a 10 electron complex which would be highly coordinatively unsaturated. This would be inconsistent with the observed stability. We can briefly practice our electron counting skills again in order to prove that there are only 10 electrons (Figure 6.1.8). (Electron counting will be discussed in more depth later in this chapter)



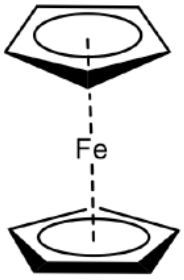
Structure is coordinatively unsaturated and has 10 valence electrons.

Fe:	8e
Ox-State (+2):	-2e
Ligands:	2x2e = 4e
Sum:	10e

Figure 6.1.8: Electron counting in the wrong structure for $Fe(Cp)_2$

The compound was stable in air, and could be sublimed without decomposition. Further, the double-bonds in the cyclopentadienyl rings resisted hydrogenation. In addition, the structure was inconsistent with spectroscopic observations. Only one C-H stretch vibration was observed in the IR and only one signal was observed in the ^1H NMR. Kealy and Pauson’s structure would have been consistent with three C-H stretch vibrations and three NMR resonances. For these reasons, Kealy’s and Pausons structure was soon questioned. Ernst Otto Fischer at University of Munich and Sir Geoffrey Wilkinson at Harvard University (Figure 6.1.9) suggested an alternative structure that was very different from all known organometallic structures. The bonding in this structure was completely different from all bonding concepts considered thus far for organometallics. What structure did they propose? They proposed a sandwich structure in which the two aromatic cyclopentadienyl anions would sandwich an Fe^{2+} ion. What would be the

bonding in this structure? The cylopentadienyl anion would donate its six π-electrons into the valence orbitals of the metal. Thus, all five carbon atoms would be equally involved in the bonding, the ligand would act as a η^5-ligand. Because of the donation of π-electrons in the cycopentadiene unit, the structure was called “ferrocene”. The ferrocene structure would explain the stability and low reactivity of the compound.



Ferrocene

Figure 6.1.9: The sandwich structure of ferrocene

Electron-counting gives an 18 electron complex (Figure 6.1.10). Let us verify this using the oxidation state method. Fe would contribute eight electrons in the neutral state. The ligands would be considered as cyclopendienyl anions with a 1- charge. This would give an oxidation state of +2 for Fe reducing the number of electrons from eight to six. The two ligands would contribute six electrons each giving twelve electrons. 12+6=18. Hence, the structure fulfills the 18 electron rule. The structure is also consistent with the spectroscopic observation of one NMR resonance and one C-H stretch vibration. All these were excellent arguments to support the ferrocene sandwich structure, however they were not an absolute proof. The proof finally came with the X-ray crystal structure determination which unambiguously confirmed the sandwich structure.

Fe:	8e
Ox-State (+2):	-2e
Ligands:	2x6e = 12e
Sum:	18e

Figure 6.1.10: Electron counting in ferrocene using the oxidation state method

---

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 6.1: Introduction to Organometallic Chemistry is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **1.2: What is Organometallic Chemistry?** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **1.1: Resources for Organometallic Chemistry** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **10.1: Historical Background and Introduction into Metallocenes** by Kai Landskron is licensed CC BY 4.0.

6.2: Nomenclature, Ligands, and Classification

The nomenclature of coordination compounds was described in an earlier section (Section 9.2). Organometallic compounds are named using this same system, so it may be helpful to review before proceeding. Here, we will point out some of the symbols and terminology that are used heavily in naming organometallic complexes.

Hapticity

The eta (η) symbol is used to indicate the variable **hapticity** of ligands with conjugated π systems. For example, the cyclopentadiene anion (Cp, C_5H_5) ligand has the capability to coordinate a metal ion in several ways due to its cyclic conjugated π system. The hapticity (the number of atoms involved in the metal bonding interaction) must be indicated in the formula with the η^n notation, and in the name with the appropriate prefix. Figure 6.2.1 illustrates three different hapticities, and the relevant formula symbols and names.

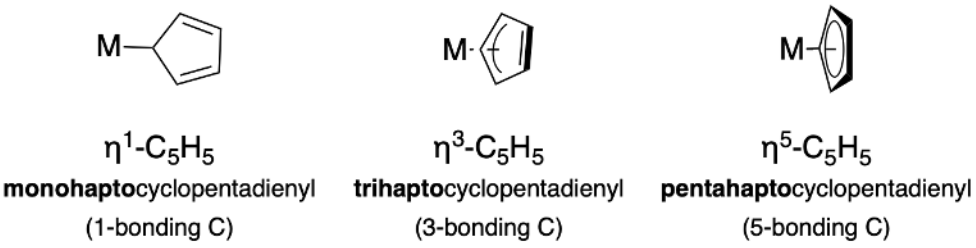


Figure 6.2.1: The cyclopentadiene anion is shown coordinating to a metal ion (M) using three different coordination modes: On the left, Cp as a monohapto ligand. In the center, Cp is shown bonding to a metal in a trihapto fashion where the metal interacts with three carbons. On the right, Cp is shown bonding in a pentahapto fashion, where the five ligand carbons interact equally through the π system . (CC-BY-SA 4.0; Kathryn Haas)

Another common ligand is the π-allyl anion (C_3H_3), which can coordinate in either an η^1 or η^3 fashion, as illustrated below (Figure 6.2.2).

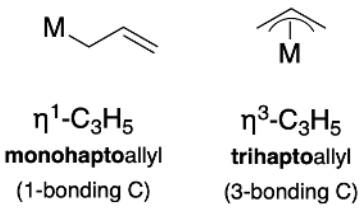


Figure 6.2.2: The allyl anion is shown coordinating in a η^1 and eta^3 modes. (CC-BY-SA 4.0; Kathryn Haas)

Bridging ligands

Ligands that bridge two or more metal ions are indicated using the symbol, mu (μ). For a ligand that bridges n metal ions, the symbol is written as μ_n. However the subscript is often ommitted when $n = 2$. Some examples of the carbonyl ligand are given below. More specific rules for naming are found in Section 9.2.

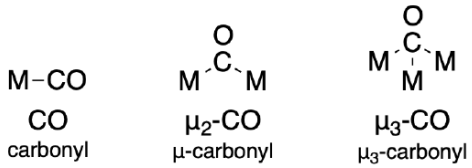
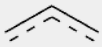
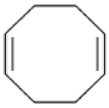


Figure 6.2.3: The carbonyl ligand is shown as a terminal ligand (with no μ necessary), bridging two metals (μ_2), and bridging three metals μ_3). (CC-BY-SA 4.0; Kathryn Haas)

Common Ligands and Classifications

Some common organic ligands found in organometallic compounds are listed below with their names and structures.

Name	Structure	CBC description
Alkyl		X
Carbonyl		L
Carbene (alkylidene)		X_2
Carbyne (alkylidyne)		X_3
Ethylene		L
Acteylene		L
Acyl		X
π-allyl ($C_3H_5^-$)		X for η^1 LX for η^3
Cyclopropenyl (cyclo-C_3H_3)		X for η^1 LX for η^3
Cyclobutadiene (cyclo-C_4H_4)		L_2 for η^4
Cyclopentadienyl (cyclo-C_5H_5, Cp)		X for η^1 LX for η^3 L_2X for η^5
Benzene		L_3 for η^6
1,5-cyclooctadiene (1,5-COD)		L_2 for η^4

Covalent Bond Classification Method (CBC)

Later in this chapter, you will learn to count electrons. The way in which you count depends on what counting scheme you choose to use. But in any case, the way in which we "count" the electrons from ligands depends on the ligand type. The covalent bond classification method (CBC) has been in use since the late 1990's to classify ligands in organometallic complexes. This method classifies ligands into three main types as follows. (see Application of the Covalent Bond Classification Method for the Teaching of Inorganic Chemistry. Malcolm L. H. Green and Gerard Parkin, Journal of Chemical Education 2014 91 (6), 807-816, DOI: 10.1021/ed400504f.)

CBC Ligand Class/Type	Examples	Use in neutral Ligand Method of Electron Counting	Use in Donor Pair Method of Electron Counting
X-type	$H-$, $Cl-$, H_3C^-	Considered neutral Donates 1 electron to the metal	Considered anionic Donates 2 electrons to the metal
L-type	CO, NH_3, H_2O	Considered neutral Donates 2 electrons to the metal	Considered neutral Donates 2 electrons to the metal

CBC Ligand Class/Type	Examples	Use in neutral Ligand Method of Electron Counting	Use in Donor Pair Method of Electron Counting
Z-type (rarely used)	BR_3, Lewis acids	Considered neutral Accepts 2 electrons	Considered cationic Donates 0 electrons

This page titled 6.2: Nomenclature, Ligands, and Classification is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

6.3: Electron Counting in Organometallic Complexes

In this section we will learn how to **count valence electrons in coordination compounds**. Electron counting is important because the number of electrons in a complex can be used to predict the compound's stability and reactivity. There are two different methods that are commonly used, and each is described below. Each of the two methods will lead to the same result if done correctly. Which method you prefer is “personal taste”, but each method is about equally common in the literature, so it is good to be familiar with both of them.

This page titled 6.3: Electron Counting in Organometallic Complexes is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **Chapter 6.1: The 18 Electron Rule** by Kai Landskron is licensed CC BY 4.0.

6.3.1: The 18 Electron Rule

Method A for counting electrons: The Donor Pair Method

The donor pair method consider ligands to donate pairs of electrons to the metal. Each ligand-metal bond is considered a pair of electrons donated to the metal by the ligand. The method consists of the steps described in the box below.

How to count with the DONOR PAIR METHOD

1. **Determine the oxidation state of the metal center.** This step can be done by first deconstructing the complex so that each ligand "keeps" its bonded electrons (See Figure 6.3.1.2). by considering the overall charge of the complex and the charge of each ligand, the oxidation state of the metal center can be determined. An alternative to deconstruction is to consider each ligand's class according to the Covalent Bond Classification (CBC) method discussed earlier.
2. **Determine the number of metal ion valence electrons**. The number of valence electrons can be determined from the metal's group on the periodic table and its oxidation state. If the oxidation state is positive we subtract electrons from the group number, if it is negative, which is rare, then we add electrons.
3. **Determine the number of bonded electrons derived from ligands**. Each ligand single bond provides two electrons, double bonds provide four electrons, etc.
4. **Add** the number of electrons from the metal ion valence (step 2) to the number of bonded electrons from the ligands to get the total valence electron count for the complex.

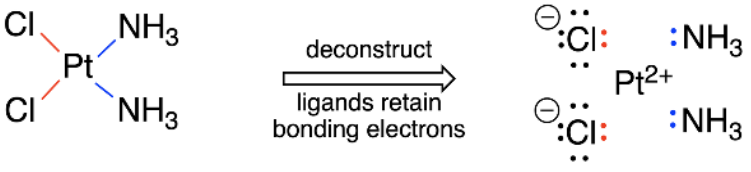
Below is an example of using the donor pair method to count electrons in the chemotherapy drug cis$-[PtCl_2(NH_3)_2]$, also called *cis*-platinum (Figure 6.3.1.1). This compound is neutral in charge.

Step 1: Deconstruction of the complex using the donor pair method would convert each metal-ligand bond to a pair of electrons on the ligand. Without consulting the Covalent Bond Classification (CBC) method, we can determine the charge on each ligand using the simple Lewis dot diagrams that result. The ligands consist of two neutral ammines and two negatively charged chlorides. The ligands account for a total negative charge of -2. Since the metal complex is neutral, there must be a +2 change on the metal. Thus, the metal oxidation state is +2.

Step 2: With the knowledge that the Pt has an oxidation state of +2, and is in group 10 of the periodic table, we can determine the number of valence electrons on Pt(II). Subtract the oxidation state from the group number to get 8 valence electrons on the Pt(II) ion.

Step 3: Each of the ligands had one bond to Pt, thus each is a 2-electron donor. The ligands combined contribute a total of 8 electrons.

Step 4: Adding the 8 electrons from Pt(II) and the 8 electrons from the ligands gives a total electron count of 16.



Fragment	Electron Count
Pt(II)	8
2x Cl^-	4
2x NH_3	4
Total	**16**

Figure 6.3.1.1: Example of the oxidation state method

Method B for counting electrons: The Neutral Atom Method (aka Neutral Ligand Method)

The “neutral atom method”, is sometimes called "the neutral ligand method". In this method, each ligand is considered to donate the number of electrons that it would *if the ligand were neutral*. The neutral atom method is carried out according to the steps described below.

How to count using the NEUTRAL LIGAND/ATOM METHOD

1. Determine the number of valence electrons on the metal center, as if it were a neutral atom. Add those electrons to the total count.
   Hint: The number valence electrons is the same as the group number of the transition metal in the periodic table (groups 3-12 for the transition metals).
2. Account for the ionic charge on the entire coordination complex. If the charge is neutral, you can ignore this step. If the complex has a positive charge, you subtract that many electrons from the total count. If the complex is an anion, you add the anionic charge to the total electron count.
3. Determine how many electrons are contributed by each ligand. (This is the most complicated step)
   - Deconstruct the metal ion (break its M-L bonds) so that each resulting ligand fragment and the central metal are neutral.
   - Then count the number of electrons from each ligand that contributed to the bond. Add the sum of those electrons from all the ligands to the total count.
     (Remeber you've already accounted for the electrons from the neutral atom in step #1)
4. Add the metal ion valence electrons (step 1), the total ligand electrons (step 3), and accounting for the charge of the complex (step 2). The total sum is the total valence electron count for the metal complex.

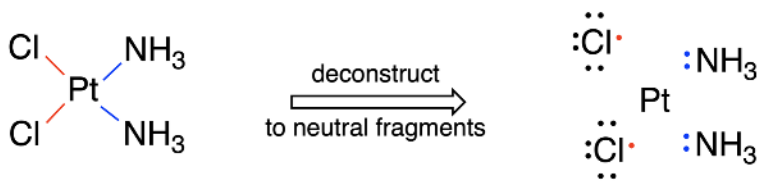
Below is an example of applying the neutral atom method to count electrons in the *cis*-platinum complex ($[\mathrm{Pt(Cl)_2(NH_3)_2}]$ (Figure \(\PageIndex{2}\)).

Step 1: The metal is platinum which is located in group 10 of the periodic table. Therefore, a neutral platinum atom has ten valence electrons.

Step 2: The complex is neutral, this we can ignore this step.

Step 3: Each Cl is considered to donate 1 electron and each ammine ligand is considered to donate two electrons. The Cl's donate a total of two electrons, and the ammines donate a total of four electrons to give a total of 6 from all ligands.

Step 4: Ten electrons from Pt and six electrons from the ligands combine to give a total electron count of 16.



Neutral fragment	Electron Count
Pt	10
2x Cl	2
2x NH_3	4
Total	**16**

Figure 6.3.1.2: Example of applying the neutral fragment method to count the total valence electrons in $[\mathrm{Pt(Cl)_2(NH_3)_2}]$.

There are pros and cons to each of the methods presented above. The neutral atom method has the advantage that we do not have to calculate charges of ligands or the metal oxidation states to reach the final answer. However, the disadvantage is that we must think about how to cleave bonds to create neutral fragments. We may need to cleave bonds in an way that is contrary to the real donor-acceptor nature of a coordination compound. The donor-pair method does account for the donor-acceptor nature of a coordination compound because the bonds are considered dative bonds, and the electrons are assigned to the ligands and metals accordingly. And advantage to the donor-pari method is that we do not need to think how to cleave bonds in artificial ways because we cleave the bonds always heteroleptically. However, the disadvantage is that it requires us to calcuate charges at the ligands to determine metal oxidation states, which is an additional, non-trivial step.

The 18 Electron Rule

Electron counting is a critical step in the context of an important rule in coordination chemistry: The 18 electron rule. **The 18 electron rule states that transition metal complexes are *normally* most stable when they have a total count of 18 electrons in the valence shell**. In other words, for d-block metal complexes, a valence configuration that fills all valence orbitals ($ns^2\ (n-1)d^{10}\ np^6$) is most stable; it is equivalent to a nobel-gas configuration for the metal atom, and is analogous to the "octet rule" for the main-group elements. Complexes that have 18 electrons in their count are considered to be **coordinatively saturated**. In general, coordinatively saturated compounds are considered to be relatively stable, and when they react they usually undergo

dissociation or oxidation reactions that decrease the electron count. If the there are less than 18 electrons, the species is **coordinatively unsaturated**, and considered less stable than a species with 18 electrons. In general, coordinatively unsaturated complexes tend to react in ways that can increase the electron count. They tend to undergo reactions involving associations to add more electrons to the system and/or tend to gain electrons through redox reactions (the metal becomes reduced). If a species has more than 18 electrons it is **coordinatively oversaturated** and tends to lose ligands. It is usually easily oxidized. Both loss of ligands and oxidation reduces to the number of electrons to or at least closer to 18.

Definitions:

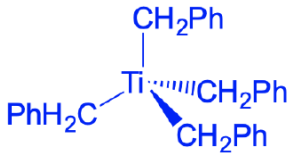
Coordinatively saturated: when the complex has an electron count =18 electrons. These complexes are considered most stable.

Coordinatively unsaturated: when the complex has an electron count <18 electrons. These complexes tend to add more ligands, and to become reduced.

Coordinatively oversaturated: when the complex has an electron count >18 electrons. These complexes tend to lose ligands and become oxidized.

Exceptions to the 18-electron rule:

The 18 electron rule has many exceptions, and therefore needs to be applied with caution. In particular, group 3, 4, and 10 complexes deviate often from the 18 electron rule.



Contribution metal:	4e
Oxidation state: +4	-4e
Electrons contributed by ligands:	4x2e=8e
Sum:	**8e**

Figure 6.3.1.3: Example of counting electrons in the tetrahedral tetrabenzyltitanium(0) complex using the oxidation state method

For illustration purposes, let us count the number of electrons of the tetrahedral tetrabenzyltitanium(0) complex by the oxidation state method. We could also use the neutral atom method, which would give the same results. This complex is a group 4 complex because titanium is in group 4. How many electrons will the titanium contribute? Because the number of electrons is always the same as the group number, it will contribute four electrons. Next, what is oxidation state of Ti? To determine it we must determine the charge at the ligands. To do that we cleave the bonds heteroleptically. This will give benzylate anions with -1 charge. There are four of these ions, and therefore there will be four negative charges overall. The complex is charge-neutral, and thus the oxidation state is +4 because -4+4=0. Therefore, we need to subtract four electrons. Because we cleaved the bond heteroleptically, each ligand contributes two electrons, giving overall eight electrons coming from the four ligands. This means that we have overall eight electrons, or an 8-electron complex. This is far, far away from 18 electrons. Nonetheless, the complex is stable. How can we explain this? The answer is that in order to achieve 18 electrons it would need to add five additional ligands if each ligand is considered a 2-electron donor. This would increase the coordination number to 9 which is too high to produce a stable complex. In order to reduce the complex to an 18 electron complex, 10 electrons would need to be added. This would produce a complex with a -10 charge which is way to high to be stable. The arguments are generalizable for group 3 and group 4 complexes. Because these elements only have a few d electrons, the ligands would need to contribute a lot of electrons to produce an 18 electron complex. This would require just too many ligands to add. The coordination numbers would get too high. If electrons are added instead of ligands, the negative charge at the complex would be to high to be stable based on electron-electron repulsion arguments.



Contribution metal:	10e
Charge:	0e
Electrons contributed by Cl ligands:	2x1e=2e
Electrons contributed by NH_3 ligands:	2x2e=4e
Sum:	**16e**

Figure 6.3.1.4: Counting electrons in the diamminedichloro palladium complex using the neutral atom method.

These arguments cannot be applied for group 10 elements, because these elements have many d electrons. The explanation in this case is that these elements like to make square planar complexes when in the oxidation number is +2. Square planar complexes prefer 16 instead of 18 electrons. We will learn later, when we discuss bonding in coordination compounds, why this is. You can see that the square planar diamminedichloro palladium complex shown is square planar and has sixteen electrons. There are 10 electrons coming from Pd. If we use the neutral atom method, no electrons need to be added or subtracted due to the charge at the complex. The complex is charge-neutral. To assess how many electrons come from the ligands we need to cleave the bonds so that neutral ligands are produced. The Pd-Cl bonds need to be cleave homoleptically, the Pd-N bonds need to be cleave heteroleptically. Therefore, the two chloro ligands are 1e donors, and the two ammine ligands are 2e donors. This gives 10+4+2=16 electrons.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 6.3.1: The 18 Electron Rule is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **Chapter 6.1: The 18 Electron Rule** by Kai Landskron is licensed CC BY 4.0.

6.3.2: Simplifying the Organometallic Complex by Deconstruction

Organometallic complexes, which consist of centrally located metals and peripheral organic compounds called ligands, are the workhorses of organometallic chemistry. Just like organic intermediates, understanding something about the structure of these molecules tells us a great deal about their expected reactivity. Some we would expect to be stable, and others definitely not! A big part of our early explorations will involve describing, systematically, the principles that govern the stability of organometallic complexes. From the outset, I will say that these principles are not set in stone and are best applied to well controlled comparisons. Nonetheless the principles are definitely worth talking about, because they form the foundation of everything else we'll discuss. Let's begin by exploring the general characteristics of organometallic complexes and identifying three key classes of organic ligands.

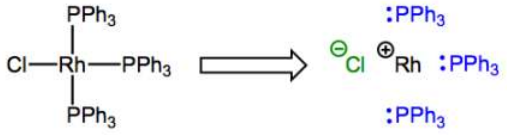
When we think of metals we usually think of electropositive atoms or even positively charged ions, and many of the metals of OM chemistry fit this mold. In general, it is useful to imagine organic ligands as electron donors and metals as electron acceptors. When looking at a pair of electrons shared between a transition metal and main-group atom (or hydrogen), I imagine the cationic metal center and anionic main-group atom racing toward one another from oblivion like star-crossed lovers. In the opposite direction (with an important caveat that we'll address soon), we can imagine ripping apart metal–R covalent bonds and giving both electrons of the bond to the organic atom. This heterolytic bond cleavage method reproduces the starting charges on the metal and ligand. Unsurprisingly, the metal is positive and the ligand negative.

FYI, you might see the blue bipyridine referred to as an L2 ligand elsewhere; this just means that a single bipyridine molecule possesses two L-type binding points. Ligands with multiple binding points are also known as chelating or polydentate ligands. Chelating ligands may feature mixed binding modes; for instance, the allyl ligand is of the LX-type. Chelating ligands can also bind to two different metal centers; when they act in this way, they're called bridging ligands. But don't let all this jargon throw you! Deconstruct complexes one binding point at a time, and you cannot go wrong.

Next, we'll take a closer look at the metal center and expand on the purpose of the deconstruction process described here.

"Bookkeeping" through deconstruction of organometallic complexes

Now it's time to turn our attention to the metal center, and focus on what the deconstruction process can tell us about the nature of the metal in organometallic complexes. Let's turn our attention now to a new complex. I've gone ahead and deconstructed it for us.



Say hello to rhodium (Rh)! Don't fret; it's just a group 9 element.

The complex possesses one X-type and three L-type ligands, so the rhodium atom ends up with a formal charge of +1. The formal charge on the metal center after deconstruction has a very special name that you will definitely want to commit to memory: it's called the oxidation state. It's usually indicated with a roman numeral next to the atomic symbol of the metal (the "+" is implied). In the complex shown above, rhodium is in the Rh(I) or +1 oxidation state. Oxidation state is most useful because changes in oxidation state indicate changes in electron density at the metal center, and this can be a favorable or unfavorable occurrence depending on the other ligands around. We will see this principle in action many, many times! Get used to changes in oxidation state as everyday events in organometallic reaction mechanisms. Unlike carbon (with the exception of carbene…what's its oxidation state?!) and other second-row elements, the transition metals commonly exhibit multiple different oxidation states. More on that later, though. For now, training yourself to rapidly identify the oxidation state of a complexed metal is most important. Please note that when a complex possesses an overall charge, the oxidation state is affected by this charge!

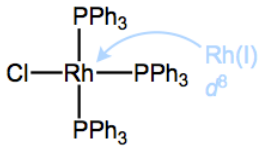
oxidation state = number of X-type ligands bound to metal + overall charge of complex

What of this number of d electrons concept? A very useful way to think about "number of d electrons" is as the "number of non-bonding electrons on the metal center," and you're probably familiar with identifying non-bonding electrons from organic chemistry. The numbers of valence electrons of each organic element are set in stone: carbon has four, nitrogen has five, et cetera. Furthermore, using this knowledge, it's straightforward to determine the number of lone pair electrons associated with an atom by subtracting its number of covalent bonds from its total number of valence electrons. E.g., for a neutral nitrogen atom in an amine

NR3, 5 – 3 = 2 lone pair electrons, typically. The extension to organometallic chemistry is natural! We can analyze complexed metal centers in the same way, but they tend to have a lot more non-bonding electrons than organic atoms, and the number depends on the metal's oxidation state. For instance, the deconstructed rhodium atom in the figure above has 8 d electrons: 9 valence electrons minus 1 used for bonding to Cl. Dative bonds don't affect d electron count since both electrons in the bond come from the ligand.

number of non-bonding electrons = number of d electrons = metal's group number – oxidation state

Drawing all the non-bonding d electrons out as lone pairs would clutter things up, so they are never drawn…but we must remember that they're around! Why? Because the number of d electrons profoundly affects a complex's geometry. We will return to this soon, but the key idea is that the ligands muck up the energies of the d orbitals as they approach the metal (recall the "star-crossed lovers" idea), and the most favorable way to do so depends on the number of non-bonding electrons on the metal center.



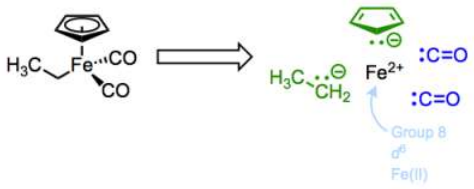
Oxidation state and d electron count: two tools the OM chemist can't live without!

This post introduced us to two important bookkeeping tools, oxidation state and number of d electrons. In the final installment of the "Simplifying the Organometallic Complex" series, we'll bring everything together and discuss total electron count. We'll see that total electron count may be used to draw a variety of insightful conclusions about organometallic complexes.

Apply deconstruction to gain insight

So far, we've seen how deconstruction can reveal useful "bookkeeping" properties of organometallic complexes: number of electrons donated by ligands, coordination number, oxidation state, and d electron count (to name a few). Now, let's bring everything together and discuss total electron count, the sum of non-bonding and bonding electrons associated with the metal center. Like oxidation state, total electron count can reveal the likely reactivity of OM complexes—in fact, it is often more powerful than oxidation state for making predictions. We'll see that there is a definite norm for total electron count, and when a complex deviates from that norm, reactions are likely to happen.

Let's begin with yet another new complex. This molecule features the common and important cyclopentadienyl and carbon monoxide ligands, along with an X-type ethyl ligand.



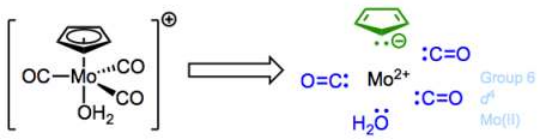
What is the total electron count of this Fe(II) complex?

The Cp or cyclopentadienyl ligand is a polydentate, six-electron L2X ligand. The two pi bonds of the free anion are dative, L-type ligands, which we'll see again in a future post on ligands bound through pi bonds. Think of the electrons of the pi bond as the source of a dative bond to the metal. Since both electrons come from the ligand, the pi bonds are L-type binders. The anionic carbon in Cp is a fairly standard, anionic X-type binder. The carbon monoxide ligands are interesting examples of two-electron L-type ligands—notice that the free ligands are neutral, so these are considered L-type! Carbon monoxide is an intriguing ligand that can teach us a great deal about metal-ligand bonding in OM complexes…but more on that later.

After deconstruction, we see that the Fe(II) center possesses 6 non-bonding d electrons. The total electron count is just the d electron count plus the number of electrons donated by the ligands. Since the d electron count already takes overall charge into account, we need not worry about it as long as we've followed the deconstruction procedure correctly.

total electron count = number of d electrons + electrons donated by ligands

For the Fe(II) complex above, the total electron count is thus 6 + (6 + 2 + 2 + 2) = 18. Let's work through another example: the complex below features an overall charge of +1. Water is a dative ligand—that "2″ is very important!

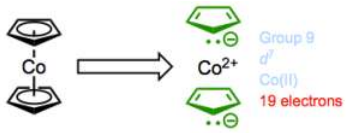


Note that the overall charge is lumped into the oxidation state and d electron count of Mo.

The oxidation state of molybdenum is +2 here…remember that the overall charge factors in to that. When everything is said and done, the total electron count is 4 + (6 + 2 + 2 + 2 + 2) = 18.

What's up with 18?! As it turns out, 18 electrons is a very common number for stable organometallic complexes. So common that the number got its own rule—the 18-electron rule—which states that stable transition-metal complexes possess 18 or fewer electrons. The rule is analogous to organic chemistry's octet rule. The typical explanation for the 18-electron rule points out that there are 9 valence orbitals (1 s, 3 p, 5 d) available to metals, and using all of these for bonding seems to produce the most stable complexes. Of course, as soon as the rule left the lips of some order-craving chemist, researchers set out to find counterexamples to it, and a number of counterexamples are known. Hartwig describes the rule as an "empirical guideline" with little theoretical support. In fact, theoretical studies have shown that the participation of p orbitals in complex MOs is unlikely. I know that's not what you want to hear—but hang with me! The 18-electron rule is still a very useful guideline. It's most interesting, in fact, when it is not satisfied.

One last example…how would you expect the complex below to react?



Cobaltocene: jonesing for chemical change.

If we assume that the 18-electron rule is true, then cobaltocene has a real problem. It possesses 7 + (6 + 6) = 19 total valence electrons! Yet, we can also reason that this complex will probably react to relieve the strain of not having 18 electrons by giving up an electron. Guess what? In practice, cobaltocene is a great one-electron reducing agent, and can be used to prepare anionic complexes through electron transfer.

$$CoCp_2 + ML_n \rightarrow [CoCp_2] + [ML_n]^- \tag{6.3.2.1}$$

This post described how to calculate total electron count and introduced the power of the 18-electron rule for predicting whether a complex will donate or accept electrons. We will definitely see these ideas again! But what happens when the electron counts of two complexes we're interested in comparing are the same? We'll need more information. In the next post, we'll explore the periodic trends of the transition series. Our goal will be to make meaningful comparisons between complexes of different metals.

Contributors and Attributions

- Dr. Michael Evans (Georgia Tech)

This page titled 6.3.2: Simplifying the Organometallic Complex by Deconstruction is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **3.5: Simplifying the Organometallic Complex (Part 1)** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **3.6: Simplifying the Organometallic Complex (Part 2)** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **3.7: Simplifying the Organometallic Complex (Part 3)** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.4: Survey of Organometallic Ligands

Organometallic chemistry may be taught in many ways. Some textbooks spend a significant chunk of time discussing ligands, while others forego ligand surveys to dive right in to reactions and mechanisms. I like the ligand survey approach because it allows you to get a grip on expected behaviour for each type of ligand before you see them pop up as intermediates in reaction cycles. With the general principles in hand, it becomes easier to generate explanations for observed each ligan's effect on a reactions. Instead of generalizing from complex, specific examples in the context of reaction mechanisms, we'll look at general trends first and apply these to reaction intermediates and mechanisms later. This section will kick off with carbon monoxide, a simple but fascinating ligand.

This section begins a survey of some of the most common or most interesting ligands in organometallic complexes. We will begin with a survey of ligands that participate in "dative" bonding to metal ions in this section (6.4.), followed by ligands that interact with metal ions through their π electrons, and those that have multiple metal-carbon bonds in the following sections.

This page titled 6.4: Survey of Organometallic Ligands is shared under a not declared license and was authored, remixed, and/or curated by Michael Evans.

- **2.2: Carbon Monoxide** by Michael Evans has no license indicated.

6.4.1: Carbon Monoxide (Carbonyl Complexes)

Introduction into Carbonyl Complexes

In this chapter we will look closer at carbonyl complexes, often just called carbonyls. Why? They are interesting for a number of reasons. Firstly, they are a quite extensive class of compounds with a diverse coordination chemistry. We will learn that the CO ligand can bind to a metal in various, sometimes non-obvious ways. Further, carbonyls are frequently used as starting materials for other coordination compounds. This is because the carbonyl ligand has no charge and carbon monoxide is a gas. Because of that a ligand substitution reaction can be easily driven to the right side by purging CO out of the reaction vessel. CO is a C_1 unit, and this is frequently used in catalysis with carbonyls. Carbonyls are often intermediates in reactions that add a single carbon atom to a hydrocarbon chain. A fascinating fundamental property of carbonyls is that its π-accepting properties stabilize metals in low, sometimes even negative oxidation numbers.

Bonding in CO

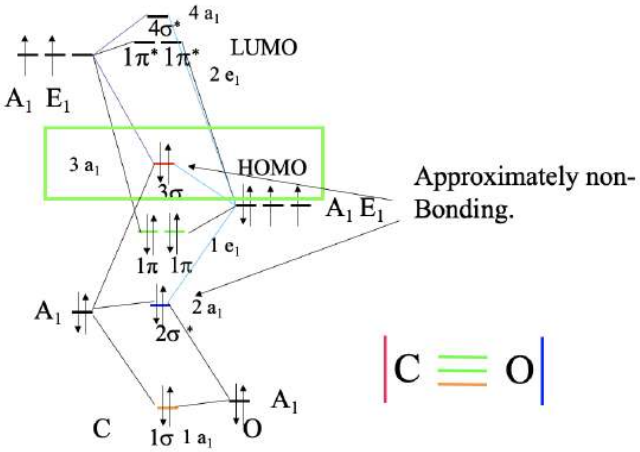


Figure 6.4.1.1: Bonding in the CO molecule. MO diagram (left), and corresponding valence bond structure (right). For more explaination click here.

The carbon in the CO molecule is the more reactive end, and thus CO prefers to bind with the carbon to a metal, and not with oxygen. This is not obvious because the carbon is less electronegative than oxygen. The reason is that the HOMO of the CO molecule is an approximately non-bonding orbital which is primarily localized at the carbon (Figure 6.4.1.1). In the valence bond picture it is resembled by the electron-lone pair at the carbon atom. The electron lone pair at the oxygen is resembled by the $2a_1$ molecular orbital which has a significantly lower energy, therefore it is rarely used in bonding. Both the π and π*-orbitals are relatively close in energy to the HOMO, and thus these orbitals can also be used for bonding in carbonyls. This explains the diverse coordination chemistry of carbonyls.

σ-binding Modes of The Carbonyl Ligand

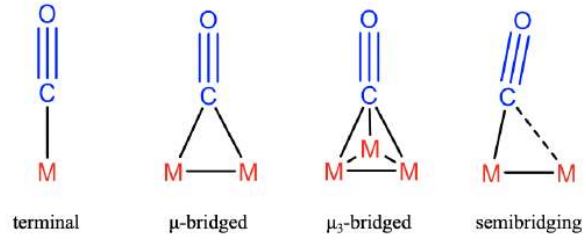


Figure 6.4.1.2: σ-binding modes of the carbonyl ligand. Attribution: W. Petz

In the most simple case the CO uses its electron lone pair at the carbon to bind to single metal atom M (Figure 6.4.1.2). In this case we call CO a terminal carbonyl ligand. In addition, it is possible that the electron lone pair is shared between two or even three metals that are interconnected via metal-metal bonds. In these cases, we say that the CO acts as a μ-bridged, and μ_3-brigded ligand, respectively. If two metals held together by a metal-metal bond are different, then the interaction of CO with one metal may be

stronger than with the other. In this case the CO ligand acts as a semibridging ligand. In all these cases CO acts as a 2-electron donor because it donates its two electrons in the electron lone pair in the carbon atom.

In addition to the electron lone pair at the carbon the CO ligand can also use its binding π-orbitals for electron-donation into metal orbitals (Figure 6.4.1.3). However, these electrons can only be used in conjunction with the electron lone pair at C because the electron pair has a higher energy than the π-electrons, and electrons of higher energy are always used first. For steric reasons the electron lone pair and the π-electrons are always donated to different metals that are held together by metal-metal bonds.

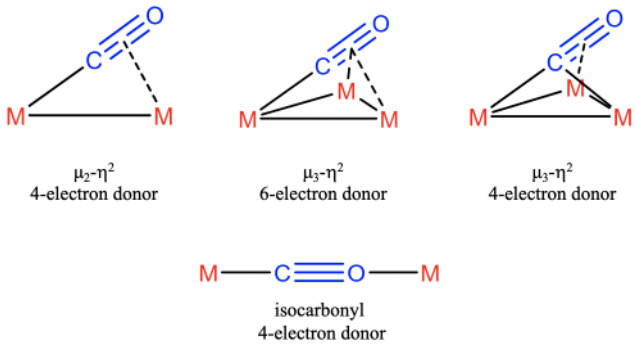


Figure 6.4.1.3: Binding in π-orbitals for electron-donation into metal orbitals. Attribution: W. Petz

In the most simple case the CO ligand binds in μ_2-η_2-mode which implies that the electron lone pair binds to one metal and two π-electrons bind to another. In this this case the CO ligand acts as a 4-electron donor. In addition, it is possible that all four π-electrons are involved involved in the bonding in addition to the electron lone pair. In this case three metal atoms are involved. The first one interacts with the electron-lone pair, the second one with the two π-electrons, and the third one with the other two π-electrons. Because three metals are bridged and both atoms of the ligand are involved in the bonding with the metal we can say that CO binds in μ_3-η_2-fashion and acts as a 6-electron donor. It is also possible that the electron-lone pair is being shared between two metals, and two π-electrons are donated to the third metal. Also in this case the ligand binds in μ_3-η_2-fashion, but acts as a 4-electron donor. Another way the CO ligand can act as 4-electron donor is when it acts as an isocarbonyl ligand. In this case it uses its electron pairs at both the C and the O-atoms. This is only possible when steric circumstances favor the utilization of the O-electron lone pair over the energetically higher π-electrons. This is rare.

π-binding Modes of The Carbonyl Ligand

The carbonyl ligand can use its π*-orbitals for bonding with metal d-orbitals in π-fashion. The ligand acts as a π-acceptor. There are two possibilities for the binding (Figure 6.4.1.4).

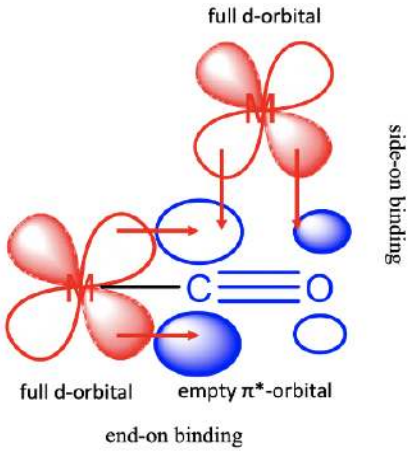


Figure 6.4.1.4: π-binding modes of the carbonyl ligand

The first one occurs when the CO-ligand acts as a terminal ligand binding end-on. In this case the two lobes of the π*-orbitals at the carbon interact with the the lobes of a metal d-orbital. Also the bonding π-orbitals have the right symmetry to overlap with the metal d-orbital in this mode, but their energies are much further away from those of the d-orbitals, so that these interactions can be neglected. The second possibility is that the CO binds side-on to the a metal-d-orbital. In this case one lobe at C and one lobe at O

interacts with the metal d-orbital. These interactions are less strong compared to the end-on interactions because the orbital overlap is less efficient due to the unequal size of the lobes of the π*-orbital. The π*-orbital is mostly localized at the carbon-atom because the carbon atom is the more electropositive atom. Note that the bonding π-orbitals do not have the right symmetry to overlap with a metal-d orbital in π-fashion, they can only overlap in σ-fashion when the binding is side-on.

The Dewar-Chatt-Duncanson model

The σ-donor and the π-acceptor interactions in carbonyl complexes synergistically reinforce each other. This synergistic effect is called the Dewar-Chatt-Duncanson model for carbonyls. How can we understand the synergistic interactions. Let us consider a carbonyl ligand that binds end-on to a metal.

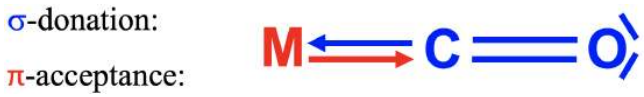


Figure 6.4.1.5: σ-donor and the π-acceptor interactions in carbonyl complexes.

Let us first look at the σ-donor interactions. The electron lone pair at the carbon donates electron density into empty metal d-orbitals and a dative bond is formed between the metal and the carbon. The donated electron density enhances the energy of the metal d-electrons due to increased electron-electron repulsion. Because of their increased energy the d-electrons get more easily accepted by the carbonyl ligand through the π-acceptor interactions. The π-acceptor interactions increase the bond order between the metal and the carbon bond. At the same time the bond order between carbon and oxygen gets decreases because electron density has been transferred from the metal into the π*-orbitals (Figure 6.4.1.5).

The strength of the π-acceptor interactions can differ significantly in carbonyls. One can draw three different structures for weak, intermediate, and strong π-acceptor interactions (Figure 6.4.1.6 to 6.4.1.8).



Figure 6.4.1.6: Weak π-acceptor interactions

When only weak interactions are present we can represent the M-C bond as a single bond, and the C-O bond as a triple bond.



Figure 6.4.1.7: Intermediate π-acceptor interactions

When the interactions have intermediate strength we can represent both the M-C bond and the C-O bond as a double-bonds.



Figure 6.4.1.8: Strong π-acceptor interactions

When the π-acceptor interactions are strong then the M-C bond becomes a triple bond and the C-O bond becomes a single bond.

On what does the strength of the π-acceptor interactions depend? It depends mostly on the charge on the carbonyl. Carbonyl cations with a charge of +2 or higher tend to have weak π-acceptor interactions. Neutral carbonyls or carbonyls with a +1 or -1 charge have intermediate π-acceptor interactions. and those with a negative charge of 2- or higher have strong π-acceptor interactions. One can see from this that the smaller the positive charge and the higher the negative charge, the higher the metal-carbon bond-order, and the stronger the metal-carbon bond. As a consequence negative charges tend to stabilize carbonyls, while positive charges destabilize them. Therefore, carbonylate anions tend to be more stable compared to carbonyl cations. The stability of neutral carbonyls is intermediate.

Homoleptic Carbonyls of The Transition Metals

After having understood the principles of the bonding in carbonyls let us next think about what structures transition metal carbonyls make. The structures follow mostly the 18 electron rule. For the most simple homoleptic carbonyls, in which the carbonyl ligand binds end-on to the transition metal acting as a two-electron donor, we would just assemble as many ligands as needed until we have 18 electrons. This would give us the coordination number in the carbonyl from which we could deduct the structure. This works well for transition metals with an even number of valence electrons.

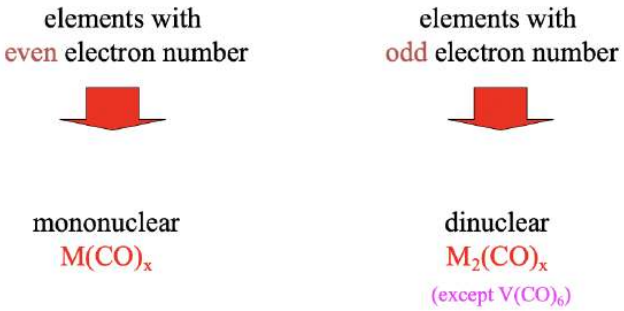


Figure 6.4.1.9: Mononuclear carbonyls vs dinuclear carbonyls. Attribution: W. Petz

In this case the number of ligands x is just 18 minus the number of metal electrons divided by 2. We would therefore expect a mononuclear carbonyl of the type $M(CO)_x$ (Figure 6.4.1.9). For metals with an odd number of electrons, the situation is more complicated because an odd number times two multiplied with an integer number never gives 18. In this case, as many ligands x as needed to make a 17 valence electron complex are added to the metal, and then the 17 valence electron complex dimerizes to form a dinuclear carbonyl of the composition $M_2(CO)_x$. An exception is the vanadium. It makes a 17 valence electron vanadium hexacarbonyl that does not dimerize because a coordination number of 7 is not favorable.

Homoleptic carbonyls of the 6th group (M = Cr, Mo, W)

Now let us look closer at the carbonyls with metals with an even number of electrons. We can start out with group 6 which contains the elements chromium, molybdenum, and tungsten. Our task is to determine the composition and structure of the carbonyls.

sum:	18e
metal electrons:	6e
charge:	0 e
# ligand electrons needed:	18-6=12e
# of ligands needed:	12/2=6

$M(CO)_6$
(octahedral)

Figure 6.4.1.10: Determining the composition and structure of carbonyls via electron counting

According to the 18 electron rule we need 18 electrons overall. How many are contributed by the metal? Because the metals are in group 6, they all have six electrons. The carbonyls carry no charge, so there are no electrons to be subtracted or added. How many ligand electrons do we need to get to 18? Well, that is 18-6=12 electrons. How many carbonyl ligands are needed then? Because each ligand is considered a two electron donor, we need 12/2=6 ligands. The composition of the carbonyl will therefore be $M(CO)_6$. The carbonyl adopts octahedral shape in order to maximize the distance of the ligands from each other. The group 6 carbonyls are colorless, crystalline, and sublimable solids.

Charged Octahedral Carbonyls with 18 Electrons

	ν(CO)/cm^{-1}		ν(CO)/cm^{-1}		ν(CO)/cm^{-1}
$[Co(CO)_6]^{3+}$		$[Rh(CO)_6]^{3+}$		$[Ir(CO)_6]^{3+}$	2254
$[Fe(CO)_6]^{2+}$	2204	$[Ru(CO)_6]^{2+}$	2199	$[Os(CO)_6]^{2+}$	2190
$[Mn(CO)_6]^{+}$	2100	$[Tc(CO)_6]^{+}$	not reported	$[Re(CO)_6]^{+}$	2085
$Cr(CO)_6$	1986	$Mo(CO)_6$	1986	$W(CO)_6$	1977
$[V(CO)_6]^{-}$	1847	$[Nb(CO)_6]^{-}$	1850	$[Ta(CO)_6]^{-}$	1850
$[Ti(CO)_6]^{2-}$	1750	$[Zr(CO)_6]^{2-}$	1757	$[Hf(CO)_6]^{2-}$	1757

Figure 6.4.1.11 Charged octahedral 18 electron carbonyls and the wave number of their C-O stretch vibrations. Green: Known charged carbonyls, Red: Unknown charged carbonyls.

Are there also other 18 e carbonyls of the type $M(CO)_6$ with other metals but group 6 metals? Yes, but the charge at the carbonyl needs to be adjusted so that the complex has 18 electrons. For instance, we can replace Cr by V, but then the we need a 1- charge which results in a carbonylate of the formula $V(CO)_6^-$. Why? The vanadium is in group 5 and has one electron less than chromium. For that reason, we must add an electron which gives the complex a 1- charge. Also the higher homologues $Nb(CO)_6^-$ and $Ta(CO)_6^-$ are known. What if we go further to the left in the periodic table? Titanium is left to the vanadium, and has four valence electrons. Therefore, the 18 valence electron hexacarbonyl of titanium has a 2- charge, and the formula is $Ti(CO)_6^{2-}$. Again, the higher homologues of $Ti(CO)_6^{2-}$, the $Zr(CO)_6^{2-}$ and the $Hf(CO)_6^{2-}$ are also known. Can we also go to the right in the periodic table? Manganese sits to the right of the chromium. The manganese has one electron more than the chromium, therefore the 18 electron hexacarbonyl of manganese must be a carbonyl cation with a 1+ charge, and the formula is $Mn(CO)_6^{2+}$. Of the higher homologues, both the $Tc(CO)_6^+$ and the $Re(CO)_6^+$ are known, too. To the right of the Mn, there is the Fe which has 8 valence electrons. Therefore the 18 electron iron hexacarbonyl must have a 2+ charge, and the formula is $Fe(CO)_6^{2+}$. The higher homologues $Ru(CO)_6^{2+}$ and $Os(CO)_6^{2+}$ are also known. Can we go even further to the left, to the Co? The expected formula for Co carbonyl would be $Co(CO)_6^{3+}$, but it is not known, and neither is the higher homologue, the $Rh(CO)_6^{3+}$. Only the $Ir(CO)_6^{3+}$ has been isolated. This reflects a general trend in carbonyl chemistry. Positive charges destabilize the carbonyl, and carbonyls with high positive charges are frequently not stable. On the other hand, negative charges stabilize a carbonyl and even carbonylates with high negative charges are stable. We can easily explain this by the fact that the bond order between the metal and the carbon decreases with increasing positive charge, and increases with increasing negative charge. Increasing bond order strengthens the stability of the carbonyl. We see from this that the π-acceptor properties are quite important for the stability of carbonyls. We also see that in carbonylates the oxidation numbers of the metals are negative. Negative oxidation numbers are quite unusual for metals. We conclude that the carbonyl ligand has the unusual property to stabilize the metal in negative oxidation states.

Is there a way to easily measure the bond order of an M-C bond? We can do this indirectly by measuring the IR-spectrum of the carbonyl. Because the bond order of the C-O bond decreases with increasing bond order for the M-C bond, the wavenumber for the C-O stretch vibration can be used as a measure for the M-C bond order. The lower the wavenumber, the lower the C-O bond order, and the higher the M-C bond order. When we look at the numbers for the different carbonyls within a period we see that as

expected the wavenumbers increase with increasing group number indicating a decreasing bond order. We can also look down the groups. We see that in this case, the numbers hardly change, meaning that the bond order is hardly affected by the period of the metal.

Homoleptic Carbonyls of the 8th Group (Fe, Ru, Os)

What charge-neutral carbonyls would we expect for the group 8 elements Fe, Ru, and Os?

sum:	18e
metal electrons:	8e
charge:	0 e
# ligand electrons needed:	18-8=10e
# of ligands needed:	10/2=5

$M(CO)_5$
(trigonal-bibyramidal)

Figure 6.4.1.12: Carbonyls for the group 8 elements

Overall, these carbonyl need to have 18 electrons. In this case the metals have 8 electrons. The charge is 0. This means that we would have 18-8=10 electrons that would need to come from the ligand. The number of ligands needed would therefore be 10/2=5. Thus, we would expect pentacarbonyls of the composition $M(CO)_5$ (Figure 6.4.1.12). These carbonyls adopt the trigonal-bipyramidal shape. The group 8 carbonyls are all liquids. The iron pentacarbonyl has a light-orange color while the ruthenium and the osmium carbonyls are colorless.

Charged Trigonal-Bipyramidal Carbonyls with 18 electrons

$[Ni(CO)_5]^{2+}$	$[Pd(CO)_5]^{2+}$	$[Pt(CO)_5]^{2+}$
$[Co(CO)_5]^{+}$	$[Rh(CO)_5]^{+}$	$[Ir(CO)_5]^{+}$
$Fe(CO)_5$	$Ru(CO)_5$	$Os(CO)_5$
$[Mn(CO)_5]^{-}$	$[Tc(CO)_5]^{-}$	$[Re(CO)_5]^{-}$
$[Cr(CO)_5]^{2-}$	$[Mo(CO)_5]^{2-}$	$[W(CO)_5]^{2-}$
$[V(CO)_5]^{3-}$	$[Nb(CO)_5]^{3-}$	$[Ta(CO)_5]^{3-}$

Figure 6.4.1.13: 18 Charged trigonal-bipyramidal carbonyls with 18 electrons. Green: Known charged carbonyls, Red: unknown charged carbonyls.

We can again ask if there are charged isosteric pentacarbonyls with 18 e of metals other than group 8 metals. The answer is yes. The manganese is left to the iron in the periodic table and has one electron less. Therefore its pentacarbonyl needs to have a 1- charge and the composition is $Mn(CO)_5^-$. Also the higher homologues, the $Tc(CO)_5^-$ and the $Re(CO)_5^-$ exist. The Cr has one electron less than than the Mn, therefore its pentacarbonyl has a 2- charge and the formula is $Cr(CO)_5^{2-}$. $Mo(CO)_5^{2-}$ and $W(CO)_5^{2-}$ are also known. The vanadium has another electron less because it is in the 5th group, therefore its pentacarbonyl has a 3- charge, and the formula is $V(CO)_5^{3-}$. Again, the higher homologues, the $Nb(CO)_5^{3-}$ and the $Ta(CO)_5^{3-}$ are also stable. Also for the pentacarbonylates high negative charges are no problem for the stability of the complexes due to the stabilizing effect of the π-acceptor interactions. What about carbonyl cations with trigonal bipyramidal shape? As we go from Fe to Co, we need a 1+ charge at the carbonyl to achieve 18 electrons. The respective $Co(CO)_5^+$ cation is stable, and so are their higher homologues, the $Rh(CO)_5^+$ and the $Ir(CO)_5^+$. However, the group 10 pentacarbonyl cations $Ni(CO)_5^{2+}$, $Pd(CO)_5^{2+}$, and $Pt(CO)_5^{2+}$ are not stable. The 2+ positive charge weakens the metal-carbon bond too much. This behavior is consistent with the weakening of the M-C bond with increasing positive charge due to weaker π-acceptor effects.

Homoleptic carbonyls of group 10 (Ni, Pd, Pt)

What about the group 10 carbonyls?

sum:	18e
metal electrons:	10e
charge:	0 e
# ligand electrons needed:	18-10=8e
# of ligands needed:	8/2=4

$M(CO)_4$
(tetrahedral)

Figure 6.4.1.14: Carbonyls for the group 10 elements

In this case the metals have 10 electrons. There is no charge. The number of ligand electrons needed is 18-10 = 8 electrons. Thus, the number of ligands is 8/2=4. Therefore, the composition is $M(CO)_4$ (Figure 6.4.1.14). The shape is tetrahedral because we have an 18 and not a 16 valence electron complex. Nickel tetracarbonyl is a volatile, colorless liquid. The higher homologues, the $Pd(CO)_4$ and the $Pt(CO)_4$ are not stable. We can explain this when remembering that the π-orbital overlap in tetrahedral complexes is generally weak. Therefore, the M-C carbon bond is less effectively stabilized by the π-acceptor interactions compared to octahedral and trigonal-bipyramidal carbonyls. This effect is even more pronounced for the Pd and Pt carbonyls because they have larger orbitals that can overlap even less effectively with the relatively small π^*-orbitals of the CO ligand. In this case the π-acceptor interactions are so weak so that the entire molecule is no longer stable.

Charged Tetrahedral Carbonyls with 18 electrons

$[Cu(CO)_4]^+$	$[Ag(CO)_4]^+$	$[Au(CO)_4]^+$
$Ni(CO)_4$	$Pd(CO)_4$	$Pt(CO)_4$
$[Co(CO)_4]^-$	$[Rh(CO)_4]^-$	$[Ir(CO)_4]^-$
$[Fe(CO)_4]^{2-}$	$[Ru(CO)_4]^{2-}$	$[Os(CO)_4]^{2-}$
$[Mn(CO)_4]^{3-}$	$[Tc(CO)_4]^{3-}$	$[Re(CO)_4]^{3-}$
$[Cr(CO)_4]^{4-}$	$[Mo(CO)_4]^{4-}$	$[W(CO)_4]^{4-}$

Figure 6.4.1.15: Charged tetrahedral carbonyls with 18 electrons. Green: Known carbonyls. Red: Unknown carbonyls.

What about charged 18 electron tetrahedral carbonyls with other metals? Again, negatively charged carbonylates are stable, even with high negative charges. $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Mn(CO)_4^{3-}$, and $Cr(CO)_4^{4-}$ are all stable and so are their higher homologues. The $Cu(CO))_4^+$ which has a 1+ positive charge is also known, but its higher homologues, the $Ag(CO)_4^+$ and the $Au(CO)_4^+$ are not.

Overall Stability Trends

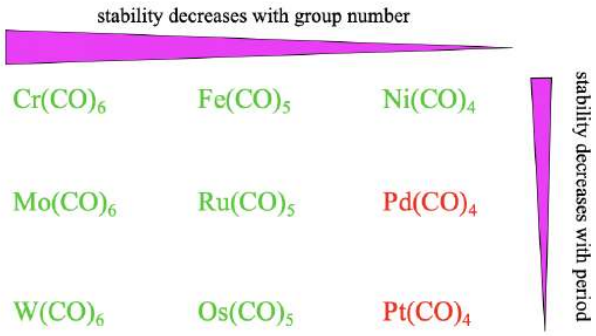


Figure 6.4.1.16: Stability trends. Attribution: W. Petz

Overall the stability of carbonyls tends to decrease from group 6 to group 8 to group 10 (Figure 6.4.1.16). This trend is because the octahedral shape allows for the best orbital overlap for π-acceptor interactions, followed by the trigonal bipyramidal, followed by the tetrahedral shape. The stability also tends to decline from the 4th to the 6th period. This trend can be explained by less efficient orbital overlap due to increasingly different orbital size between the ligand and the metal orbitals. These effects are sufficiently large for $Pd(CO)_4$ and $Pt(CO)_4$ to make them instable.

Group 4 and Group 12 Carbonyls (non-existing)

We have discussed group 6, 8, and 10 carbonyls, but not group 4 and group 12. Why? Because no carbonyls of these groups are stable. What is the reason? For group 4 carbonyls, we would need seven carbonyl ligands. This would lead to a coordination number of seven which is unacceptably high for carbonyls. For group 12 carbonyls, we would only need three carbonyl ligands. This would lead to an unacceptably low coordination number of 3.

Homoleptic carbonyls of the 7th group (M = Mn, Tc, Re)

Now let us think about what structures the homoleptic carbonyls with metals having an odd number of electrons form. Let us start with the 7th group which consists of the metals Mn, Tc, and Re. Our approach is to see how many ligands we need to produce a 17 valence electron fragment, and then dimerize that fragment.

sum:	17e
metal electrons:	7e
charge:	0 e
# ligand electrons needed:	17-7=10e
# of ligands needed:	10/2=5

$(CO)_5M\text{-}M(CO)_5 = M_2(CO)_{10}$

(derived from octahedral $M(CO)_5L$ (L=$M(CO)_5$))

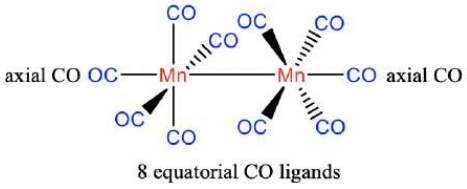


Figure 6.4.1.17: Homoleptic carbonyls with group 7 metals. Attribution: W. Petz.

The group 7 metals have seven valence electrons. Again, we will assume that there is no charge on the carbonyl. The number of ligand electrons to produce the 17 valence electrons fragment will therefore be 17-7 = 10. The number of ligands needed is therefore 10/2=5 assuming that the carbonyl ligand is a 2-electron donor binding end-on to the metal. This gives an $M(CO)_5$ fragment that dimerizes to form an $M_2(CO)_{10}$ carbonyl with a metal-metal bond. The structure can be thought to be derived from an octahedral structure in which each metal is surrounded octahedrally by five CO ligands and an $M(CO)_5$ fragment acting as the sixth ligand. Each $M(CO)_5$ unit has one axial ligand and four equatorial ligands, whereby the axial ligand is co-directional with the metal-metal bond. The four equatorial ligands of the first metal are in staggered conformation relative to the four equatorial ligands of the second metal due to steric repulsion arguments.

Charged Isoelectronic Carbonyls of the Type $M_2(CO)_{10}$

Can we make charged isoelectronic carbonyls of the type $M_2(CO)_{10}$ with other metals? The answer is yes, but only carbonylate anions with low negative charge, and no carbonyl cations. The formation of carbonyl cations is prohibited because of the weakening of the π-acceptor interactions that result from the positive charge. High negative charges are not possible because too many negative charges on the metal atoms lead to electrostatic repulsion and the destabilization of the metal-metal bonds.

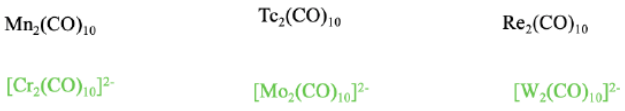


Figure 6.4.1.18: Charged isoelectronic carbonyls of the type $M_2(CO)_{10}$

There are therefore only $Cr_2(CO)_{10}^{2-}$, and the higher homologues $Mo_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$, but no other M_2CO_{10} type carbonyl ions.

Homoleptic carbonyls of the 9th group (M = Co, Rh, Ir)

What are the expected structures for the homoleptic carbonyls of group 9?

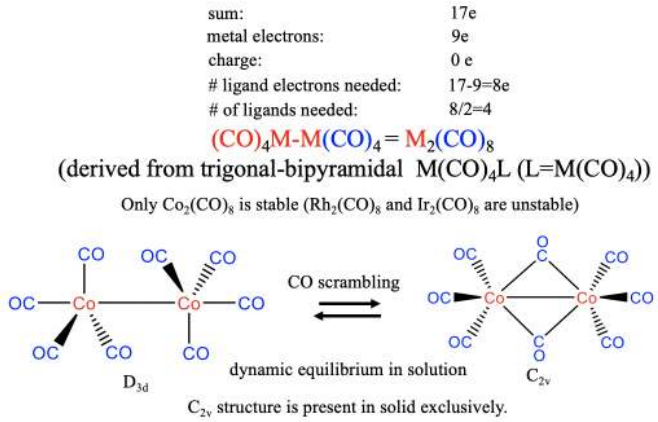


Figure 6.4.1.19: Homoleptic carbonyls of the group 9 metals. Attribution: W. Petz.

In this case, the metal contributes 9 electrons, and this means that 17-9=8 electrons need to come from the carbonyl ligand. We therefore need 8/2=4 CO molecules to produce an $M(CO)_4$ 17 valence electron fragment. Two of the fragments then dimerize to form a dinuclear carbonyl of the composition M_2CO_8. In nature, however, only the Co-carbonyl is realized, the Rh and the Ir analogs are unstable. The structure of the $Co_2(CO)_8$ carbonyl can be derived from an $M(CO)_4L$ trigonal-pyramid, whereby L is the second $M(CO)_4$ unit (Fig. 10.2.19). According to that, the coordination number is 5. There are two axial and six equatorial ligands whereby the equatorial ligands are oriented in a staggered conformation. In solution this structure is in dynamic equilibrium with a second structure with C_{2v} symmetry in which two CO ligands are bridging. Due to this equilibrium there is constant ligand scrambling, meaning that the CO ligands constantly move from axial to equatorial positions, and migrate from one metal atom to the other. In solid state the C_{2v}-type structure is present exclusively indicating that it is slightly more stable.

Charged Isoelectronic Carbonyls of the Type $M_2(CO)_8$

The charged, isoelectronic carbonyls of the type $M_2(CO)_8$ behave similarly to that of the type $M_2(CO)_{10}$. There are no highly charged binuclear carbonylate anions, and no carbonyl cations.

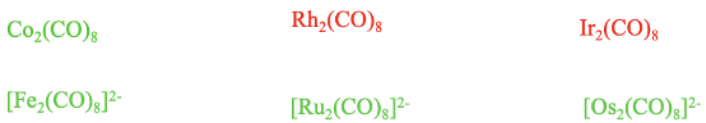


Figure 6.4.1.20: Charged isoelectronic carbonyls of the type $M_2(CO)_8$ (green: stable carbonyl. red: unstable carbonyl)

There are only the weakly negatively charged $[Fe_2(CO)_8]^{2-}$, $[Ru_2(CO)_8]^{2-}$, and $[Os_2(CO)_8]^{2-}$. The weakly negative charge stabilizes the metal-carbon bond without destabilizing the metal-metal bond too much. We can further see from this that a weakly negative charge is better for the stability of the species than no charge at all.

Homoleptic Carbonyls of the 11th Group (M = Cu, Ag, Au)

The group 11 metals Cu, Ag, and Au have eleven valence electrons.

sum:	17e
metal electrons:	11e
charge:	0 e
# ligand electrons needed:	17-11=6e
# of ligands needed:	6/2=3

$(CO)_3M\text{-}M(CO)_3 = M_2(CO)_6$

(derived from tetrahedral $M(CO)_3L$ ($L=M(CO)_3$))

$Cu_2(CO)_6$, $Ag_2(CO)_3$, and $Au_2(CO)_3$ are not known. but....

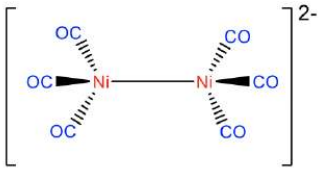


Figure 6.4.1.21: Homoleptic carbonyls of the 11th group metals (Attribution: W. Petz)

Therefore, six ligand electrons are needed to achieve 17 electrons (Figure 6.4.1.21). This means that 6/2=3 CO ligands are required to produce the 17 valence electron fragment. The dimer of it has the composition $M_2(CO)_6$ and its structure can be derived from a tetrahedral $M(CO)_3L$ structure in which L is the second $M(CO)_3$ fragment. Neither the Cu, nor the Ag, nor the Au carbonyl are known due to the weak π-overlap in tetrahedral coordination. However, the weakly negatively $[Ni_2(CO)_6]^{2-}$ ion is known which may be explained by the stabilizing effect of one negative charge on the M-C bond.

Overall Stability Trends

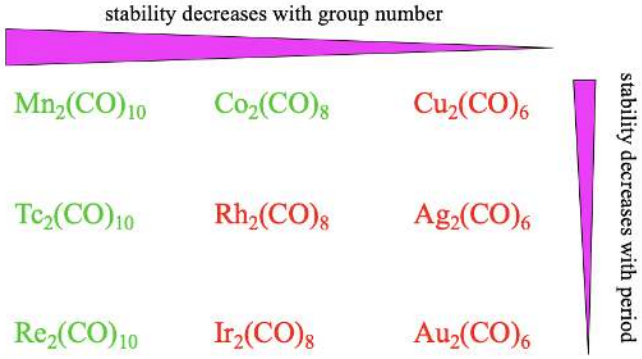


Figure 6.4.1.22: Overall stability trends for dinuclear carbonyls. Green: stable. Red: Unstable.

Overall, we see the same stability trends for the dinuclear carbonyls as compared to the mononuclear ones. The stability decreases with the group number because π-overlap becomes smaller with smaller coordination numbers. Also, we see that the stability decreases with the period because of decreasing match of orbital sizes.

Homoleptic carbonyls of the 5th group (M = V, Nb, Ta)

The 17 valence electron fragment of the carbonyl of vanadium has the composition $V(CO)_6$. It does not dimerize because the coordination number of 6 is much more favorable compared to the coordination number 7. $V(CO)_6$ is a dark violet radical of octahedral shape. The radical electron is sterically inactive. $V(CO)_6$ can be used as an oxidant because it can be reduced easily to the 18 valence electron species $V(CO)_6^-$. The higher homologues $Nb(CO)_6$ and $Ta(CO)_6$ are not known. This may be explained by the weaker orbital overlap between the relatively small π^*-orbitals of the carbonyl ligand and the large metal d-orbitals of Nb and Ta.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

Synthesis

Metal carbonyl complexes containing only CO ligands abound, but most cannot be synthesized by the method we all wish worked, bathing the elemental metal in an atmosphere of carbon monoxide (entropy is a problem, as we already discussed for $W(CO)_6$). This method does work for nickel(0) and iron(0) carbonyls, however.

$M + n\ CO \rightarrow M(CO)_n$ [M = Fe, n = 5; M = Ni, n = 4]

Other metal carbonyl complexes can be prepared by **reductive carbonylation**, the treatment of a high-oxidation-state complex with CO. These methods usually require significant heat and pressure. One example:

$WCl_6 + CO + \text{heat, pressure} \rightarrow W(CO)_6$

Still other methods employ **deinsertion** from organic carbonyl compounds like dimethylformamide. These methods are particularly useful for preparing mixed carbonyl complexes in the presence of reducing ligands like phosphines.

$IrCl_3(H_2O)_3 + 3\ PPh_3 + HCONMe_2 + PhNH_2 \rightarrow IrCl(CO)(PPh_3)_2 + (Me_2NH_2)Cl + OPPh_3 + (PhNH_3)Cl + 2\ H_2O$

The key thing to notice about the reaction above is that the CO ligand is derived from dimethylformamide (DMF).

This page titled 6.4.1: Carbon Monoxide (Carbonyl Complexes) is shared under a not declared license and was authored, remixed, and/or curated by Kai Landskron.

- **10.2: Principles of carbonyl complexes** by Kai Landskron is licensed CC BY 4.0.
- **2.2: Carbon Monoxide** by Michael Evans has no license indicated.

6.4.2: Ligands similar to CO

Now let us leave the CO ligand, consider a number of related ligands, and discuss similarities and differences compared to the CO ligand.

The cyano ligand (CN^-)

Let us start with the cyano ligand CN^-. This ligand is isoelectronic to the CO ligand. The N atom has one electron less than O, but the negative charge at the cyanide ligand compensates for that. One question we can ask is: What is the reactive end? The answer is: In analogy to the carbonyl ligand the reactive end is the carbon atom. We can explain this by the fact that the MO diagram is similar to that of CO, only the differences in atomic orbital energies are smaller due to the smaller electronegativity difference between C and N compared to C and O. Therefore, like in CO, the HOMO is represented by the electron lone pair at the C, which makes C the more reactive end. Due to the smaller electronegativity difference, the difference in energy between the lone pair at C and the lone pair at N is smaller, therefore, in contrast to CO, the cyano ligand acts far more often as a bridging ligand between two metals using both of its electron lone pairs.

Would we expect the cyano ligand to be a stronger or weaker σ-donor compared to the CO ligand? Think about it for a moment. The answer is: It is a stronger σ-donor because of its negative charge. The negative charge at the ligand increases electrostatic repulsion between the electrons, and this increases the orbital energies. Therefore, there is a stronger tendency to donate the electrons. Our next question is: Is the CN^- ligand a stronger or weaker π-acceptor than CO? The energy of the π^*-orbitals is higher compared to CO because of the negative charge at the ligand. Because of that, electrons from the metal cannot be as easily accepted by the ligand. Therefore, the cyano ligand is a weaker π-acceptor than the carbonyl ligand. Our last question is: Are cyano complexes more stable with metals in high or low oxidation states. Because of electrostatic arguments a cyanide anion interacts more strongly with a metal cation rather than a metal in a zero or negative oxidation state. Therefore, unlike CO, CN^- does not stabilize metals in low oxidation states. It prefers to make complexes with metal in high, positive oxidation numbers.

The Nitrosyl Ligand NO

The nitrosyl ligand NO is another ligand similar to CO. It has one more electron that CO because N has one more electron than C. The additional electron makes NO an "odd" molecule with a radical electron. Like in CO and CN^-, the more electropositive element is the reactive end. In the case of NO it is the N atom. The radical electron is the most reactive electron that can be most easily donated, however the electron lone pair at N may be donated in addition. In the former case, the NO is a 1-electron donor, in the latter it is a 3-electron donor. How can we tell if one or three electrons have been donated? When only one electron is donated, the electron lone pair at the nitrogen is sterically active and leads to a bent structure (Fig. 6.4.2.1).

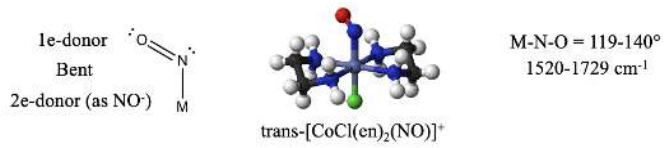


Figure 6.4.2.1: The Trans-bis-(ethylenediamine)chloronitrosyl cobalt (1+) cation as an example of an NO complex with NO as 1e donor.

An example is the trans-bis-(ethylenediamine)chloronitrosyl cobalt (1+) cation. Generally, the O−N−M bond angle in nitrosyl complexes with NO as a 1e-donor can vary between 119 and 140°. We can also identify a bent nitrosyl ligand in the IR spectrum. Typical wave numbers are 1520-1729 cm^{-1}.

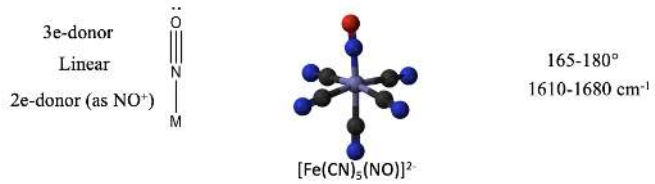


Figure 6.4.2.2: THe Nitroprusside anion as an example of a complex with NO as a 3e donor. (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...l-3D-balls.png)

When the nitrosyl ligand donates all three electrons, then it binds to the metal in a linear fashion (Fig. 6.4.2.2). The electron lone pair is no longer sterically active because it is involved in the bonding. An example is the nitroprusside anion $[Fe(CN)_5(NO)]^{2-}$.

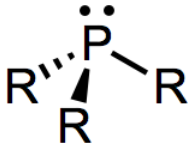
It is used as a medication for the treatment of high blood pressure. The bond angles in complexes with NO as the 3-electron donor are often not exactly 180°, but vary between 165 and 180°. It can also be identified in the IR because it has a characteristic band between 1610-1680 cm^{-1}.

There is a also a different view on nitrosyl complexes with linear and bent structures. In bent structures we can also consider the ligand as an NO^- anion that donates two electrons. The NO^- anion has two electron lone pairs at N. When it donates two electrons then one sterically active electron lone pair remains at the nitrogen atom. In linear structures we can regard the ligand also as an NO^+ cation that donates two electrons. An NO^+ cation has one electron lone pair at N, and when it donates that lone pair then there is no sterically active electron at the nitrogen left, and thus the ligand binds in a linear fashion.

We could also ask: What can neutral NO not be a 2-electron donor with the radical electron left at N? The answer is: The radical electron is the highest energy electron, and is always used first in interactions with a metal.

Phosphine Ligands

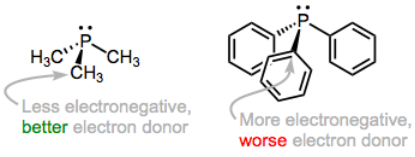
Phosphines are most notable for their remarkable electronic and steric tunability and their "innocence"—they tend to avoid participating directly in organometallic reactions, but have the ability to profoundly modulate the electronic properties of the metal center to which they're bound. Furthermore, because the energy barrier to umbrella flipping of phosphines is quite high, "chiral-at-phosphorus" ligands can be isolated in enantioenriched form and introduced to metal centers, bringing asymmetry just about as close to the metal as it can get in chiral complexes. Phosphorus NMR is a technique that Just Works (thanks, nature). Soft phosphines match up very well with the soft low-valent transition metals. Electron-poor phosphines are even good π-acids!



Like CO, phosphines are dative, L-type ligands that formally contribute two electrons to the metal center. Unlike CO, most phosphines are not small enough to form more than four bonds to a single metal center (and for large R, the number is even smaller). Steric hindrance becomes a problem when five or more PR_3 ligands try to make their way into the space around the metal. An interesting consequence of this fact is that many phosphine-containing complexes do not possess 18 valence electrons. Examples include $Pt(PCy_3)_2$, $Pd[P(t\text{-}Bu)_3]_2$, and $[Rh(PPh_3)_3]^+$. Doesn't that just drive you crazy? It drives the complexes crazy as well—and most of these coordinatively unsaturated compounds are wonderful catalysts.

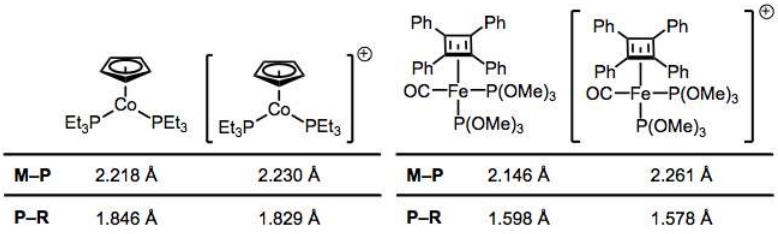
Bridging by phosphines is extremely rare, but ligands containing multiple phosphine donors that bind in an L_n (n > 1) fashion to a single metal center are all over the place. These ligands are called chelating or polydentate to indicate that they latch on to metal centers through multiple binding sites. For entropic reasons, chelating ligands bind to a single metal center at multiple points if possible, instead of attaching to two different metal centers (the aptly named chelate effect). An important characteristic of chelating phosphines is bite angle, defined as the predominant P–M–P angle in known complexes of the ligand. We'll get into the interesting effects of bite angle later, but for now, we might imagine how "unhappy" a ligand with a preferred bite angle of 120° would be in the square planar geometry. It would much rather prefer to be part of a trigonal bipyramidal complex, for instance.

The predominant orbital interaction contributing to phosphine binding is the one we expect, a lone pair on phosphorus interacting with an empty metallic d orbital. The electronic nature of the R groups influences the electron-donating ability of the phosphorus atom. For instance, alkylphosphines, which possess P–Csp^3 bonds, tend to be better electron donors than arylphosphines, which possess P–Csp^2 bonds. The rationale here is the greater electronegativity of the sp^2 hybrid orbital versus the sp3 hybrid, which causes the phosphorus atom to hold more tightly to its lone pair when bound to an sp^2 carbon. The same idea applies when electron-withdrawing and -donating groups are incorporated into R: the electron density on P is low when R contains electron-withdrawing groups and high when R contains electron-donating groups. Ligands (and associated metals) in the former class are called electron poor, while those in the latter class are electron rich.



As we add electronegative R groups, the phosphorus atom (and the metal to which it's bound) become more electron poor.

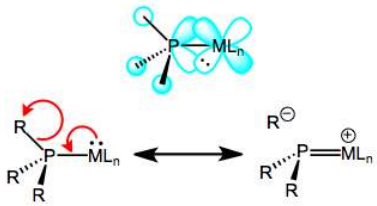
Like CO, phosphines participate in backbonding to a certain degree; however, the phenomenon here is of a fundamentally different nature than CO backbonding. For one thing, phosphines lack a π* orbital. In the days of yore, chemists attributed backbonding in phosphine complexes to an interaction between a metallic dπ orbital and an empty 3d orbital on phosphorus. However, this idea has elegantly been proven bogus, and a much more organicker-friendly explanation has taken its place (no d orbitals on P required!). In an illuminating series of experiments, M–P and P–R bond lengths were measured via crystallography for several redox pairs of complexes. I've chosen two illustrative examples, although the linked reference is chock full of other pairs. The question is: how do we explain the changes in bond length upon oxidation?



M–P	2.218 Å	2.230 Å	**M–P**	2.146 Å	2.261 Å
P–R	1.846 Å	1.829 Å	**P–R**	1.598 Å	1.578 Å

Upon oxidation, M–P bond lengths increase and and P–R bond lengths decrease. Why?

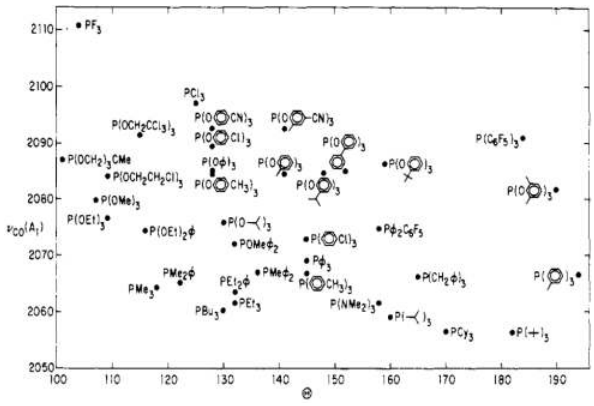
Oxidation decreases the ability of the metal to backbond, because it removes electron density from the metal. This explains the increases in M–P bond length—just imagine a decrease the M–P bond order due to worse backbonding. And the decrease in P–R bond length? It's important to see that invoking only the phosphorus 3d orbitals would not explain changes in the P–R bond lengths, as the 3d atomic orbitals are most definitely localized on phosphorus. Instead, we must invoke the participation of σ*P–R orbitals in phosphine backbonding to account for the P–R length decreases. When all is said and done, the LUMO of the free phosphine has mostly P–R antibonding character, with some 3d thrown into the mix. The figure below depicts one of the interactions involved in M–P backbonding, a dπ → σ* interaction (an orthogonal dπ → σ* interaction also plays a role). As with CO, a resonance structure depicting an M=P double bond is a useful heuristic! Naturally, R groups that are better able to stabilize negative charge—that is, electron-withdrawing groups—facilitate backbonding in phosphines. Electron-rich metals help too.



Backbonding in phosphines, a sigma-bond-breaking affair.

The steric and electronic properties of phosphines vary enormously. Tolman devised some intriguing parameters that characterize the steric and electronic properties of this class of ligands. To address sterics, he developed the idea of cone angle—the apex angle of a cone formed by a point 2.28 Å from the phosphorus atom (an idealized M–P bond length), and the outermost edges of atoms in the R groups, when the R groups are folded back as much as possible. Wider cone angles, Tolman reasoned, indicate greater steric congestion around the phosphorus atom. To address electronics, Tolman used a not-so-old friend of ours—the CO stretching frequency (νCO) of mixed phosphine-carbonyl complexes. Specifically, he used Ni(CO)3L complexes, where L is a tertiary phosphine, as his standard. Can you anticipate Tolman's logic? How should νCO change as the electron-donating ability of the phosphine ligands increases?

Tolman's logic went as follows: more strongly electron-donating phosphines are associated with more electron-rich metals, which are better at CO backbonding (due fundamentally to higher orbital energies). Better CO backbonding corresponds to a lower νCO due to decreased C–O bond order. Thus, better donor ligands should be associated with lower νCO values (and vice versa for electron-withdrawing ligands). Was he correct? Exhibit A…



Tolman's map of the steric and electronic properties of phosphine ligands.

Notice the poor ligand trifluorophosphine stuck in the “very small, very withdrawing” corner, and its utter opposite, the gargantuan tri(tert-butyl)phosphine in the “extremely bulky, very donating” corner. Intriguing! One can learn a great deal just by studying this chart.

Dr. Michael Evans (Georgia Tech)

Bonding in Phosphine Complexes

Let us have a look at the MO diagram of the PH_3 molecule and compare it with the NH_3 molecule. As one would expect, the MOs are overall similar, but there is one important difference. While the LUMO in NH_3 is the anti-bonding $3a_1$ orbital, the LUMOs in the PH_3 molecule are the anti-bonding 2e orbitals. The relative energies of the $3a_1$ and 2e orbitals in the PH_3 and NH_3 molecules are swapped up. This can be attributed to the fact that the the P atom uses the 3s and the 3p orbitals as valence orbitals, while N uses the 2s and 2p orbitals. The 3s and the 3p orbitals are larger and overlap less effectively with the small 1s orbitals of the hydrogen. They also have a higher energy making the P-H bonds less polar than the N-H bonds. The energy of the PH_3 HOMO is higher than that of the NH_3 HOMO. Both the HOMO and the LUMO of PH_3 are more diffuse and polarizable than the respective orbitals in NH_3.

The higher energy of the HOMO in PH_3 makes it a better donor than NH_3. In addition, the PH_3 has π-acceptor properties because the 2e LUMO are relatively low-lying anti-bonding 2e orbitals and have suitable shape for π-overlap with metal d-orbitals. NH_3 does not have these π-acceptor properties because its LUMO is the $3a_1$ orbital, and not the 2e orbitals. The 2e orbitals in NH_3 are energetically too high in order to allow for significant π-acceptor interactions.

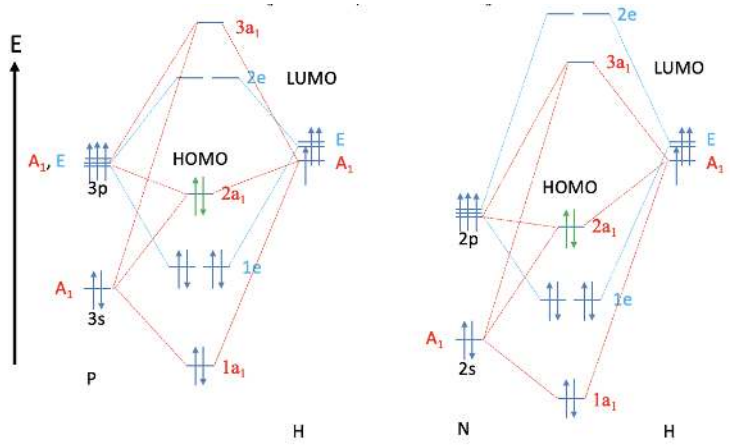


Figure 6.4.2.3: MO diagrams of PH_3 and NH_3

The σ-donor and π-acceptor properties of the phosphine ligand can be modified by substituting H by other groups. Generally, more electron donating groups increase the energy of the HOMO and the LUMO. This strengthens the σ-donor and reduces the π-acceptor properties. Vice versa, more electron withdrawing groups decrease the energy of the HOMO and the LUMO. As a consequence, the ligand becomes a weaker σ-donor and a stronger π-acceptor (Fig. 6.4.2.4).

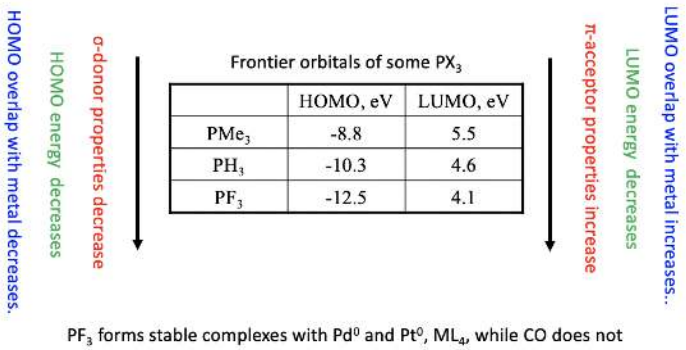


Figure 6.4.2.4: HOMO and LUMO energies of three phosphines

The table above shows the HOMO and LUMO energies of three phosphines. As expected the HOMO and LUMO energies decrease from PMe_3 to PH_3 to PF_3 due to the increasingly electron-withdrawing nature of the substituent. As a consequence, the σ-donor properties weaken and the π-acceptor properties strengthen from to PMe_3 to PH_3 to PF_3.

Not only the energies, but also the orbital overlap is important for the strength of the π-acceptor properties of the phosphine ligands. The more strongly electron-withdrawing the group is the more the anti-bonding e-type LUMO orbitals are located at the P atom. The more these orbitals are localized at P, the better they can overlap with the ligand. Vice versa the localization of the HOMO shifts toward the group as the group becomes more electron-withdrawing, thereby weakening the σ-donor properties.

Phosphine ligands with strongly electron withdrawing groups such as PF_3 have π-acceptor properties strong enough to stabilize metals in low oxidation numbers, similar to CO. For example, the PF_3 ligand forms stable complexes with Pd and Pt atoms in the oxidation number 0, while the respective Pd and Pt carbonyls are not known.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

6.4.2: Ligands similar to CO is shared under a CC BY license and was authored, remixed, and/or curated by LibreTexts.

- **10.3: The Concept of Isolobality, Carbonyl Clusters, and Ligands Related to CO** by Kai Landskron is licensed CC BY 4.0.
- **2.9: Phosphines** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.4.3: Hydrides and Dihydrogen Complexes

Ligands can, shockingly enough, bind through the electrons in their own σ bonds in an L-type fashion. This binding mode depends as much on the metal center as it does on the ligand itself—to see why, we need only recognize that σ complexes look like intermediates in concerted oxidative additions. With a slight reorganization of electrons and geometry, an L-type σ ligand can become two X-type ligands. Why, then, are σ complexes stable? How can we control the ratio of σ complex to X_2 complex in a given situation? How does complexation of a σ bond change the ligand's properties? We'll address these questions and more in this post.

General Properties

The first thing to realize about σ complexes is that they are highly sensitive to steric bulk. Any old σ bond won't do; hydrogen at one end of the binding bond or the other (or both) is necessary. The best studied σ complexes involve dihydrogen (H_2), so let's start there.

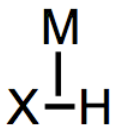


Figure 6.4.3.1: A bonding interaction between a metal ion and the σ bond of a generic $X-H$ ligand.

Mildly backbonding metals may bind dihydrogen "side on." Like side-on binding in π complexes, there are two important orbital interactions at play here: The first is a sigma bonding interaction ($\sigma H-H \rightarrow d\sigma$), as pictured on the left in Figure 6.4.3.2; the second is a π bonding interaction ($d\pi \rightarrow \sigma^* H-H$), as pictured on the right in Figure 6.4.3.2 Dihydrogen complexes can "tautomerize" to hydride $(H)_2$ isomers through cleavage of the $H-H$ bond to the metal (this is an oxidative addition reaction, as discussed in the chapter on organometallic reactions).

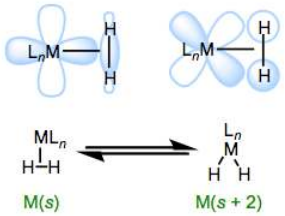


Figure 6.4.3.2: Orbital interactions and $L-X_2$ equilibrium in σ complexes.

H_2 binding in an L-type fashion massively acidifies the ligand. Changes in of over thirty pKa units have been observed upon metal binding! Analogous acidifications of X–H bonds, rarely exhibit ΔpKa > 5. What's causing the different behavior of X–H and H–H ligands? The key is to consider the conjugate base of the ligand—in particular, how much it's stabilized by a metal center relative to the corresponding free anion. The principle here is analogous to the famous dictum of organic chemistry: consider charged species when making acid/base comparisons. Stabilization of the unhindered anion H^- by a metal is much greater than stabilization of larger, more electronegative anions like HO^- and NH_2^- by a metal. As a result, it's more favorable to remove a proton from metal-complexed H_2 than from larger, more electronegative X–H ligands.

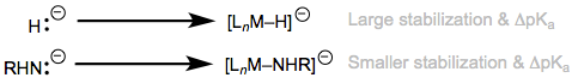


Figure 6.4.3.3: When the conjugate base is stabilized, the pKa of the acid is decreased. The metal ion has a more important stabilizing effect on H^- compared to any other conjugate base (X^-).

Remarkably large stabilization by an acidic metal fragment, without any counterbalancing from steric factors, explains the extreme acidification of dihydrogen upon metal binding.

The electronic nature of the metal center has two important effects on σ complexes. The first concerns the acidity of H_2 upon metal binding. The principle here is consistent with what we've hammered into the ground so far. In the same way cationic organic acids are stronger than their neutral counterparts, σ complexes of electron-poor metals—including (and especially) cations—are stronger acids than related complexes of electron-rich metals. The second concerns the ratio of L-type to X_2-type binding. We should expect more electron-rich metal centers to favor the X2 isomer, since these should donate more strongly into the σ*H–H orbital. This idea

was masterfully demonstrated in a study by Morris, in which he showed that H_2 complexes of π-basic metal centers show all the signs of X2 complexes, rather than L complexes. More generally, metal centers in σ complexes need a good balance of π basicity and σ acidity (I like to call this the “Goldilocks effect”). Because of the need for balance, σ complexes are most common for centrally located metals (groups 6-9).

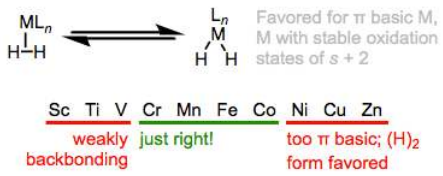


Figure 6.4.3.4: Oxidative addition of H_2 is important for electron-rich, π-basic metal centers. Groups 6-9 hit the "Goldilocks" spot.

The M–H bond in hydride complexes is a good base—anyone who’s ever quenched lithium aluminum hydride can attest to this! Intriguingly, because it’s a good base, the M–H bond can participate in hydrogen bonding with an acidic X–H bond, where X is a heteroatom. This kind of bonding, called dihydrogen bonding (since two hydrogen atoms are involved), is best described as a sort of σM–H→σ*X–H orbital interaction. Think of it as analogous to a traditional hydrogen bond, but using a σ bond instead of a lone pair. Crazy, right?!

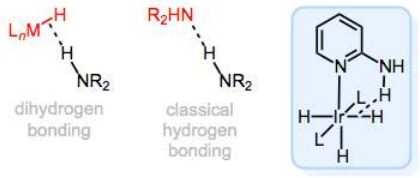


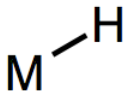
Figure 6.4.3.1:

Dihydrogen bonding in metal hydrides: a sort of "interrupted protonation" of M–H.

Other kinds of σ complexes are known, but these are rarer than H–H complexes. One class that we’ve seen before involve agostic interactions of C–H bonds in alkyl ligands. σ Complexes of inorganic ligands like silanes and stannanes may involve complex bonding patterns, but we won’t concern ourselves with those here.

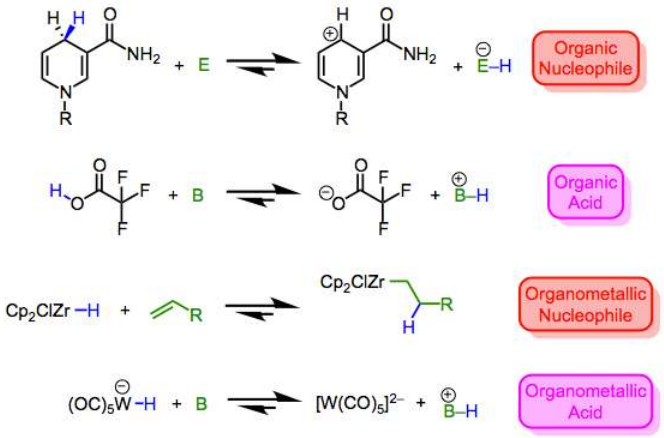
Hydride Complexes

Metal-hydrogen bonds, also known (misleadingly) as **metal hydrides**, are ubiquitous X-type ligands in organometallic chemistry. There is much more than meets the eye to most M-H bonds: although they’re simple to draw, they vary enormously in polarization and pKa. They may be acidic or hydridic or both, depending on the nature of the metal center and the reaction conditions. In this post, we’ll develop some heuristics for predicting the behavior of M-H bonds so that later, we can discuss their major modes of reactivity (acidity, radical reactions, migratory insertion, etc.).



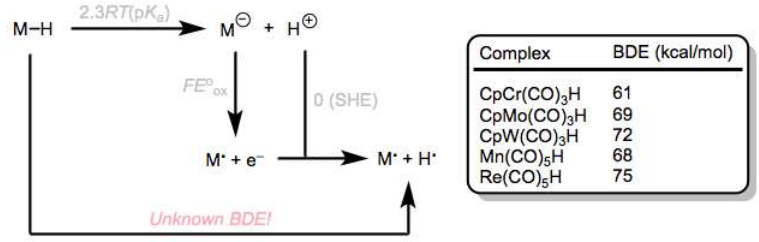
General Properties

Metal hydrides run the gamut from nucleophilic/basic to electrophilic/acidic. Then again, the same can be said of X–H bonds in organic chemistry, which may vary from mildly nucleophilic (consider Hantzsch esters and NADH) to extremely electrophilic (consider triflic acid). As hydrogen is what it is in both cases, it’s clear that the nature of the X fragment—more specifically, the stability of the charged fragments X+ and X−—dictate the character of the X–H bond. Compare the four equilibria outlined below—the stabilities of the ions dictate the position of each equilibrium. By now we shouldn’t find it surprising that the highly π-acidic W(CO)5 fragment is good at stabilizing negative charge; for a similar reason, the ZrCp2Cl fragment can stabilize positive charge.*



Metal-hydrogen bonds may be either hydridic (nucleophilic) or acidic (electrophilic). The nature of other ligands and the reaction conditions are keys to making predictions.

Let's turn our attention now to *homolytic* M–H bond strength. A convenient thermodynamic cycle allows us to use the acidity of M–H and the oxidation potential of its conjugate base in order to determine bond strength. This clever method, employed by Tilset and inspired by the inimitable Bordwell, uses the cycle in the figure below. BDE values for some complexes are provided as well. From the examples provided, we can see that bond strength increases down a group in the periodic table. This trend, and the idea that bridging hydrides have larger BDEs than terminal M–H bonds, are just about the only observable trends in M–H BDE.

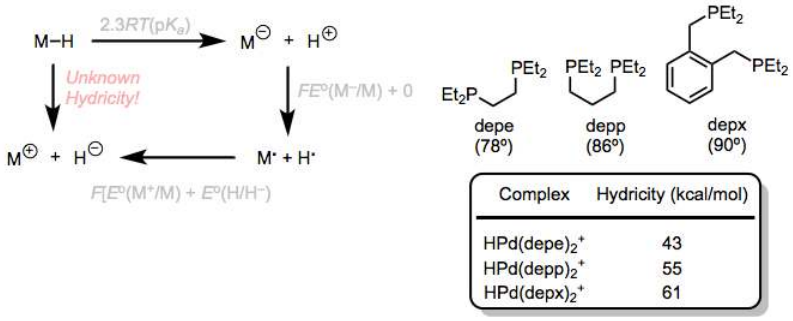


Complex	BDE (kcal/mol)
$CpCr(CO)_3H$	61
$CpMo(CO)_3H$	69
$CpW(CO)_3H$	72
$Mn(CO)_5H$	68
$Re(CO)_5H$	75

A clever cycle for determining BDEs from other known quantities, with select BDE values. I've left out solvation terms from the thermodynamic cycle. For more details, see the Tilset link above.

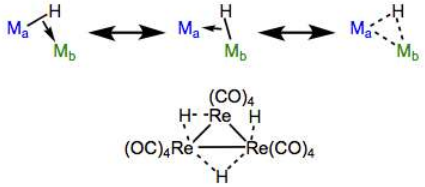
Why is knowing M-H BDEs useful? For one thing, the relative BDEs of M-C and M-H bonds determine the thermodynamics of β-hydride elimination, which results in the replacement of a covalent M-C bond with an M-H bond. Secondly, complexes containing weak M-H bonds are often good hydrogen transfer agents and may react with organic radicals and double bonds, channeling stannane and silane reductants from organic chemistry.

Hydricity refers to the tendency of a hydride ligand to depart as H–. A similar thermodynamic cycle relates the energetics of losing H– to the oxidation potentials of the conjugate base and the oxidized conjugate base; however, this method is complicated by the fact that hydride loss establishes an open coordination site. I've provided an abridged version of the cycle below. Hydricities are somewhat predictable from the electronic and steric properties of the metal center: inclusion of electron-donating ligands tends to increase hydricity, while electron-withdrawing or acidic ligands tend to decrease it. For five-coordinate hydrides that form 16-electron, square planar complexes upon loss of hydride, the bite angle of chelating phosphines plays an interesting role. As bite angle increases, hydricity does as well.



A thermodynamic cycle for hydricity, with some examples. Hydricity and bite angle are well correlated in five-coordinate palladium hydrides.

Bridging hydrides are an intriguing class of ligands. A question to ponder: how can a ligand associated with only two electrons possibly bridge two metal centers? How can two electrons hold three atoms together? Enter the magic of three-center, two-electron bonding. We can envision the M–H sigma bond as an electron donor itself! With this in mind, we can imagine that hydrides are able to bind end-on to one metal (like a standard X-type ligand) and side-on to another (like an L-type π system ligand, but using sigma electrons instead). Slick, no? We'll see more side-on bonding of sigma electrons in a future post on sigma complexes.



Resonance forms of bridging hydrides, with an example. Sigma complexes like these show up in other contexts, too!

Consistent with the idea that bridging is the result of "end-on + side-on" bonding, bond angles of bridging hydrides are never 180°.

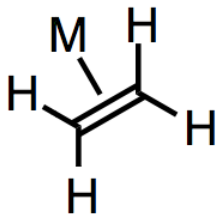
Dr. Michael Evans (Georgia Tech)

This page titled 6.4.3: Hydrides and Dihydrogen Complexes is shared under a not declared license and was authored, remixed, and/or curated by Michael Evans.

- **2.3: σ Complexes** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **2.6: Metal Hydrides** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.5: Bonding between Metal Atoms and Organic Pi Systems

With this section, we finally reach our first class of dative **actor** ligands, **π systems**. In contrast to the **spectator** L-type ligands we've seen so far, π systems most often play an important role in the reactivity of the OM complexes of which they are a part (since they act in reactions, they're called "actors"). π Systems do useful chemistry, not just with the metal center, but also with other ligands and external reagents. Thus, in addition to thinking about how π systems affect the steric and electronic properties of the metal center, we need to start considering the metal's effect on the ligand and how we might expect the ligand to behave as an active participant in reactions. To the extent that structure determines reactivity—a commonly repeated, and extremely powerful maxim in organic chemistry—we can think about possibilities for chemical change without knowing the elementary steps of organometallic chemistry in detail yet.



This page titled 6.5: Bonding between Metal Atoms and Organic Pi Systems is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

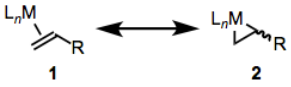
- **2.10: π Systems** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.5.1: Linear π Systems

General Properties

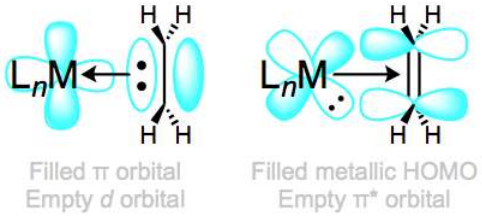
The π bonding orbitals of alkenes, alkynes, carbonyls, and other unsaturated compounds may overlap with dσ orbitals on metal centers. This is the classic ligand HOMO → metal LUMO interaction that we've beaten into the ground over the last few posts. Because of this electron donation from the π system to the metal center, coordinated π systems often act electrophilic, even if the starting alkene was nucleophilic (the **Wacker oxidation** is a classic example; water attacks a palladium-coordinated alkene). The π → dσ orbital interaction is central to the structure and reactivity of π-system complexes.

Then again, a theme of the last three posts has been the importance of orbital interactions with the opposite sense: metal HOMO → ligand LUMO. Like CO, phosphines, and NHCs, π systems are often subject to important backbonding interactions. We'll focus on alkenes here, but these same ideas apply to carbonyls, alkynes, and other unsaturated ligands bound through their π clouds. For alkene ligands, the relative importance of "normal" bonding and backbonding is nicely captured by the relative importance of the two resonance structures in the figure below.



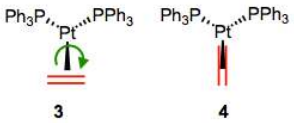
Resonance forms of alkene ligands.

Complexes of weakly backbonding metals, such as the electronegative late metals, are best represented by the traditional dative resonance structure **1**. But complexes of strong backbonders, such as electropositive Ti(II), are often best drawn in the **metallacyclopropane** form **2**. Organic hardliners may have a tough time believing that **1** and **2** are truly resonance forms, but several studies—e.g. of the Kulinkovich cyclopropanation—have shown that independent synthetic routes to metallacyclopropanes and alkene complexes containing the same atoms result in the same compound. Furthermore, bond lengths and angles in the alkene change substantially upon coordination to a strongly backbonding metal. We see an elongation of the C=C bond (consistent with decreased bond order) and some pyramidalization of the alkene carbons (consistent with a change in hybridization from sp2 to sp3). A complete orbital picture of "normal" bonding and backbonding in alkenes is shown in the figure below.



Normal bonding and backbonding in alkene complexes.

Here's an interesting question with stereochemical implications: what is the orientation of the alkene relative to the other ligands? From what we've discussed so far, we can surmise that one face of the alkene must point toward the metal center. Put differently, the bonding axis must be normal to the plane of the alkene. However, this restriction says nothing about rotation about the bonding axis, which spins the alkene ligand like a pinwheel. Is a particular orientation preferred, or can we think about the alkene as a circular smudge over time? The figure below depicts two possible orientations of the alkene ligand in a trigonal planar complex. Other orientations make less sense because they would involve inefficient orbital overlap with the metal's orthogonal d orbitals. Which one is favored?



Two limiting cases for alkene orientation in a trigonal planar complex.

First of all, we need to notice that these two complexes are **diastereomeric**. They have different energies as a result, so one must be favored over the other. Naive steric considerations suggest that complex **4** ought to be more stable (in most complexes, steric

factors dictate alkene orientation). To dig a little deeper, let's consider any electronic factors that may influence the preferred geometry. We've already seen that electronic factors can overcome steric considerations when it comes to complex geometry! To begin, we need to consider the crystal field orbitals of the complex as a whole. Verify on your own that in this d10, Pt(0) complex, the crystal-field HOMOs are the dxy and dx2–y2 orbitals. Where are these orbitals located in space? In the xy-plane! Only the alkene in **3** can engage in efficient backbonding with the metal center. In cases when the metal is electron rich and/or the alkene is electron poor, complexes like **3** can sometimes be favored in spite of sterics. The thought process here is very similar to the one developed in an earlier post on geometry. However, please note that this situation is fairly rare—steric considerations often either match or dominate electronics where alkenes are concerned.

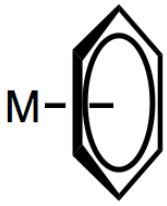
Dr. Michael Evans (Georgia Tech)

This page titled 6.5.1: Linear π Systems is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.10: π Systems** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.5.2: Cyclic π systems

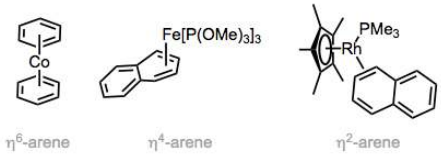
Arene or **aromatic ligands** are the subject of this post, the second in our series on π-system ligands. Arenes are dative, L-type ligands that may serve either as actors or spectators. Arenes commonly bind to metals through more than two atoms, although η2-arene ligands are known. Structurally, most η6-arenes tend to remain planar after binding to metals. Both "normal" bonding and backbonding are possible for arene ligands; however, arenes are stronger electron donors than CO and backbonding is less important for these ligands. The reactivity of arenes changes dramatically upon metal binding, along lines that we would expect for strongly electron-donating ligands. After coordinating to a transition metal, the arene usually becomes a better electrophile (particularly when the metal is electron poor). Thus, metal coordination can enable otherwise difficult **nucleophilic aromatic substitution** reactions.



General Properties

The coordination of an aromatic compound to a metal center through its aromatic π MOs removes electron density from the ring. I'm going to forego an in-depth orbital analysis in this post, because it's honestly not very useful (and overly complex) for arene ligands. π → dσ (normal bonding) and dπ → π* (backbonding) orbital interactions are possible for arene ligands, with the former being much more important, typically. To simplify drawings, you often see chemists draw "toilet-bowl" arenes involving a circle and single central line to represent the π → dσ orbital interaction. Despite the single line, it is often useful to think about arenes as L3-type ligands. For instance, we think of η6-arenes as six-electron donors.

Multiple coordination modes are possible for arene ligands. When all six atoms of a benzene ring are bound to the metal (η6-mode), the ring is flat and C–C bond lengths are slightly longer than those in the free arene. The ring is bent and non-aromatic in η4-mode, so that the four atoms bound to the metal are coplanar while the other π bond is out of the plane. η4-Arene ligands show up in both stable complexes (see the figure below) and reactive intermediates that possess an open coordination site. To generate the latter, the corresponding η6-arene ligand undergoes **ring slippage**—one of the π bonds "slips" off of the metal to create an open coordination site. We'll see ring slippage again in discussions of the aromatic cyclopentadienyl and indenyl ligands.



Arene ligands exhibit multiple coordination modes.

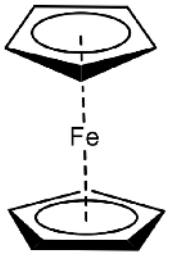
Even η2-arene ligands bound through one double bond are known. Coordination of one π bond results in **dearomatization** and makes η2-benzene behave more like butadiene, and furan act more like a vinyl ether. With naphthalene as ligand, there are multiple η2 isomers that could form; the isomer observed is the one that retains aromaticity in the free portion of the ligand. In fact, this result is general for polycyclic aromatic hydrocarbons: binding maximizes aromaticity in the free portion of the ligand. In the linked reference, the authors even observed the coordination of two different rhodium centers to naphthalene—a bridging arene ligand! Other bridging modes include σ, π-binding (the arene is an LX-type ligand, and one C–M bond is covalent, not dative) and L2-type bridging through two distinct π systems (as in biphenyl).

Arene ligands are usually hydrocarbons, not heterocycles. Why? Aromatic heterocycles, such as pyridine, more commonly bind using their basic lone pairs. That said, a few heterocycles form important π complexes. Thiophene is perhaps the most heavily studied, as the desulfurization of thiophene from fossil fuels is an industrially useful process.

Dr. Michael Evans (Georgia Tech)

Bonding in Ferrocene

Ferrocene was the first metallocene to be discovered and characterized. The structure of ferrocene is shown below.



Ferrocene

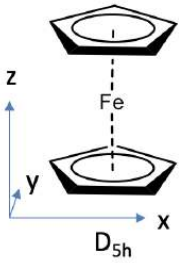
Figure 6.5.2.9: The sandwich structure of ferrocene

Can the stability of the ferrocene structure also be explained by molecular orbital theory? Let us check! First, we need to decide on the point group. We will make the simplification that the two C_p cyclopentadienyl rings are in eclipsed formation, and then the point group is D_{5h}. Actually, the rings are in staggered confirmation and the point group is D_{5d}, but the energy difference is minimal, and there is a very small activation barrier between the two conformers.

$\mathbf{D_{5h}}$	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^2$	$5\sigma_h$	$h=20$	
A_1'	1	1	1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2'	1	1	1	−1	1	1	1	−1	R_z	
E_1'	2	$2cos(72^\circ)$	$2cos(144^\circ)$	0	2	$2cos(72^\circ)$	$2cos(144^\circ)$	0	$(x,\ y)$	
E_2'	2	$2cos(144^\circ)$	$2cos(72^\circ)$	0	2	$2cos(144^\circ)$	$2cos(72^\circ)$	0		$(x^2-y^2,\ xy)$
A_1"	1	1	1	1	−1	−1	−1	−1		
A_2"	1	1	1	−1	−1	−1	−1	1	z	
E_1"	2	$2cos(72^\circ)$	$2cos(144^\circ)$	0	−2	$-2cos(72^\circ)$	$-2cos(144^\circ)$	0	$(R_x,\ R_y)$	$(xz,\ yz)$
E_2"	2	$2cos(144^\circ)$	$2cos(72^\circ)$	0	−2	$-2cos(144^\circ)$	$-2cos(72^\circ)$	0		

(6.5.2.1)

We can define the z-axis standing perpendicular to the Cp rings, and the xy plane to be coplanar with the Cp rings.



$3d_{yz}$, $3d_{xz}$	E_1''
$3d_{x2-y2}$, $3d_{xy}$	E_2'
$3d_{z2}$	A_1'
4s	A_1'
$4p_x$, $4p_y$	E_1'
$4p_z$	A_2''

Figure 6.5.2.18: The coordinate system for ferrocene, Fe valence orbitals, and their symmetry types.

The Fe 3d, 4s and 4p orbitals will be our frontier orbitals and we can read their symmetry types from the character table of D_{5h}. The $3d_{xz}$ and $3d_{yz}$ have E_1'' symmetry, the $3d_{x^2-y^2}$ and the $3d_{xy}$ have E_2' symmetry, the $3d_{z^2}$ has A_1' symmetry, the 4s has A_1' symmetry, and the $4p_x$ and the $4p_y$ orbitals have E_1' symmetry, and the $4p_z$ has A_2'' symmetry.

Next, we need to determine the ligand group orbitals. We know that the π-ligand molecular orbitals are the ones that donate the electrons into the metal-orbitals, thus we have to have a closer look at these orbitals. The π-MOs of the ligand are made from the five $2p_z$ orbitals of the carbon atoms that stand perpendicular to the ring. This means that there are 5 MOs to consider.

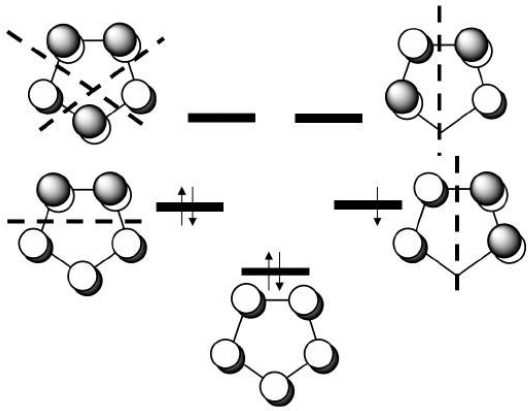


Figure 6.5.2.19: MOs of the cyclopentadienyl ligand and their relative energy

You can see the five MOs and their relative energy above. One is strongly bonding and has no node. Then, there are two double-generate weakly bonding ones that have one node, and finally there are two anti-bonding ones that have two nodes. Because the cyclopentadienyl anion has six π electrons, the bonding MO and the two weakly bonding MOs are full, the anti-bonding MOs are empty.

Because we have two Cp^- anions to consider we have overall 10 MOs to combine. We would therefore expect ten ligand group orbitals (LGOs). We can determine their symmetry type by determining the reducible and irreducible representations. The results are shown below.

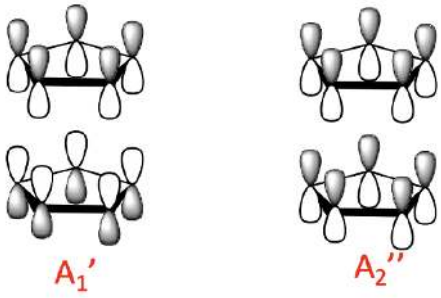


Figure 6.5.2.20: 0-node LGOs

We can generally divide the LGOs into three groups with a different number of nodes. There are two 0-node LGOs with A_1' and A_2'' symmetry. They are made from the 0-node MOs of the ligand. There is a bonding an anti-bonding combination possible. In the bonding combination the 0–node ligand MOs have the lobes with the same algebraic sign pointing toward each other. The anti-bonding combination has the lobes with opposite algebraic sign pointing toward each other.

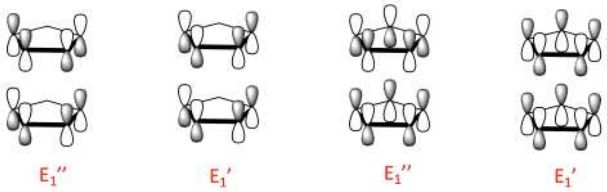


Figure 6.5.2.21: 1-node LGOs

There are four 1-node LGOs with E_1' and E_1'' symmetry. They are constructed from the two 1-node ligand MOs. Like for the 0-node orbitals, there is a bonding and an anti-bonding combination possible.

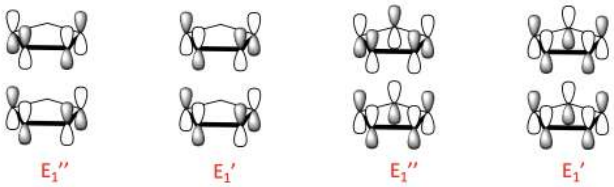


Figure 6.5.2.22: 2-node LGOs

Finally, there are four 2-node LGOs with E_2' and E_2'' symmetry. They are made from the 2-node ligand MOs and there is also a bonding and an anti-bonding combination possible.

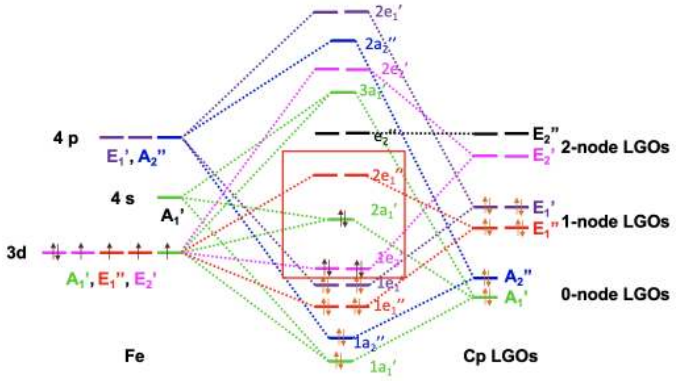


Figure 6.5.2.23: MO diagram of ferrocene

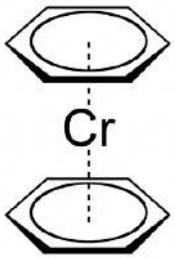
Now we have all the information to draw the molecular orbital diagram of ferrocene. As usual we plot the metal frontier orbitals on the left and label their symmetry. We plot the Cp LGOs on the right and also label the symmetry. We can order the LGOs according to energy with the 0-node LGOs having the lowest energy and the 2-node LGOs having the highest energy. Then, we can start to combine orbitals of the same symmetry type to form MOs. There are two metal AOs of the A_1' type and one A_1' LGO giving three MOs of this symmetry type, one bonding, one approximately non-bonding, and third one anti-bonding. We can connect AOs, LGOs, and MOs with dotted lines. Next, we can combine the A_2'' AO and the A_2'' LGO to form a bonding and an anti-bonding MO. We again connect the AOs, LGOs, and MOs with dotted lines. Then, we can produce two bonding e_1'' and two anti-bonding e_1'' MOs from the E_1'' metal AOs and the E_1'' LGOs and connect the orbitals with dotted lines. There are two E_1' LGOs and two E_1' AOs that can be combined to two bonding $1e_1$' and two anti-bonding $2e_1$' MOs and we again connect the orbitals with dotted lines. The two E_2' LGOs can be combined with the two E_2' d-orbitals to form a pair of bonding $1e_2$' and anti-bonding $2e_2$' molecular orbitals. Lastly, we notice that the E_2'' LGOs do not find a partner, and we have to write them as non-bonding with the same energy into the MO diagram.

Now we need to fill the electrons into the orbitals. The ligands have twelve electrons overall. They can be filled into the six orbitals of the lowest energy. This fills the $1a_1$', the $1a_2$'', the $1e_1$'', the and $1e_1$' orbitals. We notice that all MOs are bonding which supports the stability of the molecule. We still need to consider the metal d-orbitals. We have an Fe^{2+} ion and thus six metal d-electrons. They would go into the $1e_2$' orbital which is bonding and the $2a_1$' orbital which is weakly bonding. The $2a_1$ is the HOMO, and the next higher $2e_1$'' is the LUMO. We can see that we can fill all metal electrons into bonding MOs. The LUMO is an anti-bonding orbital, and thus overall all bonding MOs are filled, and no non-bonding and anti-bonding orbitals need to be filled. This is the ideal situation for a stable molecule. We can also see that the MO diagram explains the 18 electron rule. All 18 electrons are in bonding MOs.

We can consider the $1e_2$', the $2a_1$', and the $2e_1$'' metal d-orbitals in the ligand field produced by the Cp-ligands as these 5 orbitals can hold the maximum possible number of 10 d-electrons, have similar energy then the d-orbitals, and have contributions from them.

Metallocenes with other cyclic π-ligands

Is it possible to make metallocenes with other π-conjugated rings but the cylopentadienyl anion?



Bis-(benzene) chromium (0)

Figure 6.5.2.24: Bis-(benzene) chromium

The answer is yes, for instance benzene is known to act as a ligand bis-(benzene) chromium (0). In this case the ligand acts as a η^6-ligand because all six carbon atoms are involved in the bonding. Why does chromium give stable metallocene complex with benzene? We can explain this again with the 18 electron rule. In bis-(benzene) chromium (0), chromium is in the oxidation state 0 because the benzene ligand has no charge. Thus, chromium contributes six electrons. Adding the 12 π-electrons from the two benzene ligands gives 18 electrons.

Other cyclic π-ligands

Also cyclobutadiene can act as a cylic π-ligand in complexes. The cyclobutadiene is is different from the cyclopentadienyl anion and the benzene ligand in two ways. Firstly, it has much more ring strain then the previous two, and secondly it is not an aromatic, but an anti-aromatic ligand. Remember, we have an aromatic ring when there are 4n+2 π-electrons, whereby n is an inter number. This means that rings with two (n=0), six (n=1), and ten (n=2) π-electrons are aromatic. Anti-aromatic rings are those that have 4n electrons, such as four (n=1), eight (n=2) and so forth. Cyclobutadiene has four electrons, and thus it is anti-aromatic. Anti-aromatic rings are less stable than aromatic ones because not all π-electrons are in bonding molecular orbitals. Let us illustrate this by constructing the MO diagram for the π-system of the cyclobutadiene molecule (Figure 6.5.2.25)

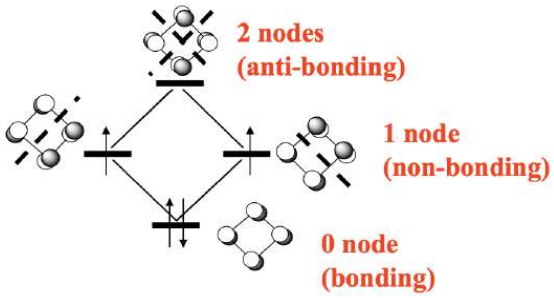


Figure 6.5.2.25: MO diagram for the π-system of the cyclobutadiene molecule

The π-system is made of four carbon atoms contributing a half-filled $2p_z$ orbital each (if we define the plane of the molecule as the xy plane). That makes four p-orbitals with four electrons that give four molecular orbitals. There is a bonding MO with no node, two doubly-degenerate non-bonding ones with one node, and one anti-bonding one with two nodes (Figure 6.5.2.25). There are four electrons. We can fill two electrons into the bonding MO, but the other two must go into the two non-bonding ones under obedience of Hund's rule.

Jahn-Teller distortion in cyclobutadiene

One may think that the cyclobutadiene is a square planar molecule because of complete delocalization of the π-electrons, but that is actually not the case. There are two shorter double-bonds and two longer single-bonds, and the shape of the molecules is a rectangle. This means that the two double bond are localized. We can view this effect as a Jahn-Teller distortion.

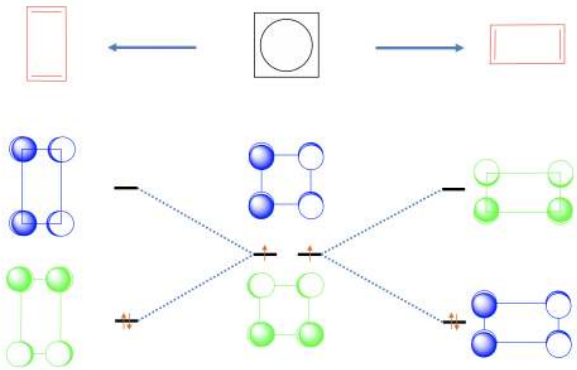


Figure 6.5.2.26: Jahn-Teller distortion in cyclobutadiene

The distortion of the square to form a rectangle is energetically favorable because it lowers the energy of the two non-bonding electrons. Why? Let us look at the non-bonding orbital 1 first and elongate in x-direction, and squeeze in y-direction (Figure 6.5.2.26). We can see that we bring the p-orbitals with bonding interactions further apart, and bring those with anti-bonding interactions closer together. This means that the energy of this orbital goes up and the orbital becomes anti-bonding. Let us do the same with non-bonding orbital 2. We see that the opposite happens. The bonding interactions are enhanced and the anti-bonding interactions are weakened. Therefore, this orbital becomes bonding and the energy goes down. We can now fill the two electrons into the bonding MO. We see that we have lowered the energy of the electrons through the distortion.

We could also have squeezed in x-direction and elongated in y-direction. In this case orbital 1 would have become bonding and orbital 2 anti-bonding. However, this distortion is symmetry-equivalent to the previous one, and does not produce a new molecule. Both molecules can be superposed by a simple 90° rotation.

Cyclobutadiene as η^4-ligand

Cyclobutadiene (Cb) in its free form is not stable because of the high ring strain and the anti-aromaticity, but complexes with cyclobutadiene as a ligand are stable. We would expect that 18 electron complexes are most stable.

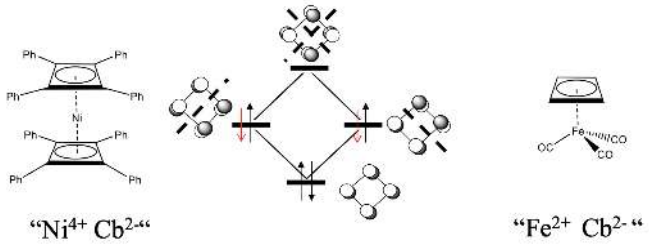


Figure 6.5.2.27: Complexes with cyclobutadiene

What would be an 18 electron sandwich complex with two cyclobutadiene ligands? Because each cyclobutadiene contributes four electrons, ten electrons would need to come from the metal, and we would expect a nickel cyclobutadienyl complex $Ni(Cb)_2$. This complex is not known, but derivatives are. For example a Ni complex with two tetraphenyl butadiene ligands are known (Figure 6.5.2.27). Another example is the butadienyl tricarbonyl iron (0) complex. Interestingly, when cyclobutadiene acts as a η^4-ligand, then it is not distorted, but square planar. An explanation is that we can formally treat the cyclobutadiene ligand as an Cb^{2-} ligand binding to a metal cation. For instance in $FeCb(CO)_3$ the Fe would be an Fe^{2+}, in the nickel complex, the nickel would be a Ni^{4+}. The Cb^{2-} anion would formally aromatic because it has 4n+2=6 electrons. The additional two electrons would be in the non-bonding orbitals. Because the two non-bonding orbitals are completely filled now, there would be no longer a driving force for the distortion. Note though that is is a formal view only, and there are arguments that speak against this view. One is that the addition of the two electrons to the ligand should further destabilize the ring because the added electrons are non-bonding. Aromaticity would rather be achieved by removing two electrons to form a Cb^{2+} cation that would have only two electrons in the bonding orbital.

Cyclooctetraene (cot) as a ligand

Also metallocenes with cyclooctatetraene (cot) acting as η^8-ligand is known. However, because of the large ring size only metals with large atomic radii, can make metallocenes with this ligand. For example uranium makes a uranocenes with two cyclooctatetraene ligands (Figure 6.5.2.28).

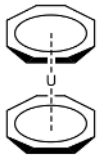


Figure 6.5.2.28: Aromatic Cot^{2-} ligand

Like cyclobutadiene, cyclooctatetraene is an anti-aromatic ligand with 4n=8 π-electrons (n=2). In the free cyclooctatetraene molecule is non-planar and the π-electrons are localized (Figure 6.5.2.29).



Figure 6.5.2.29: Free cyclooctatraene is non-planar, thus π electrons are localized.

In metallocenes however, the ring becomes planar (Figure 6.5.2.28). One can again formally explain that by assuming an aromatic cot^{2-} ligand that binds to a metal 2+ cation, however one should keep in mind again that this is a formal view and not necessarily reflects the bonding situation in the compound.

Metals having smaller atomic radius can bind to *cot* in η^2, η^4, and less commonly in η^6-mode. The 18 electron rule holds in most cases. For instance, *cot* can make a η^4-complex in tricarbonyl cyclooctatetraene ruthenium (0) (Figure 6.5.2.30).

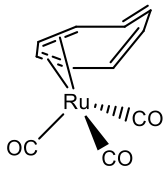


Figure 6.5.2.30: tricarbonyl cyclooctatetraene ruthenium (0)

Also two metals can bind to a single *cot*-ligand. This is for instance realize in μ-cyclooctetraene bis(tricarbonyl ruthenium (0) (Figure 6.5.2.31).

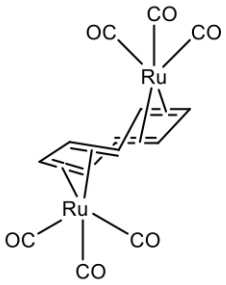


Figure 6.5.2.31: bis(tricarbonyl) cyclooctetraene ruthenium (0)

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

6.5.2: Cyclic π systems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **2.10: π Systems** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **10.1: Historical Background and Introduction into Metallocenes** by Kai Landskron is licensed CC BY 4.0.

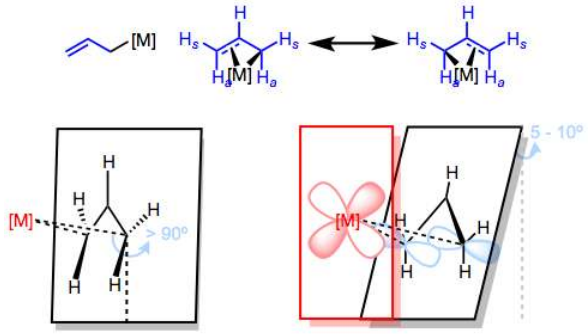
6.5.3: Odd-numbered π Systems

Odd-numbered π systems—most notably, the allyl and cyclopentadienyl ligands—are formally LnX-type ligands bound covalently through one atom (the “odd man out”) and datively through the others. This formal description is incomplete, however, as resonance structures reveal that multiple atoms within three- and five-atom π systems can be considered as covalently bound to the metal. To illustrate the plurality of equally important resonance structures for this class of ligands, we often just draw a curved line from one end of the π system to the other. Yet, even this form is not perfect, as it obscures the possibility that the datively bound atoms may dissociate from the metal center, forming σ-allyl or ring-slipped ligands. What do the odd-numbered π systems really look like, and how do they really behave?



General Properties

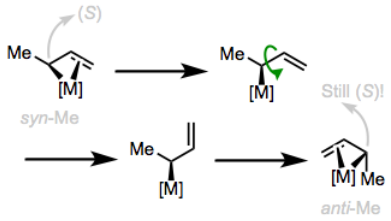
Allyls are often actor ligands, most famously in allylic substitution reactions. The allyl ligand is an interesting beast because it may bind to metals in two ways. When its double bond does not become involved in binding to the metal, allyl is a simple X-type ligand bound covalently through one carbon—basically, a monodentate alkyl! Alternatively, allyl can act as a bidentate LX-type ligand, bound to the metal through all three conjugated atoms. The LX or “trihapto” form can be represented using one of two resonance forms, or (more common) the “toilet-bowl” form seen in the general figure above. I don’t like the toilet-bowl form despite its ubiquity, as it tends to obscure the important dynamic possibilities of the allyl ligand.



Can we use FMO theory to explain the wonky geometry of the allyl ligand?

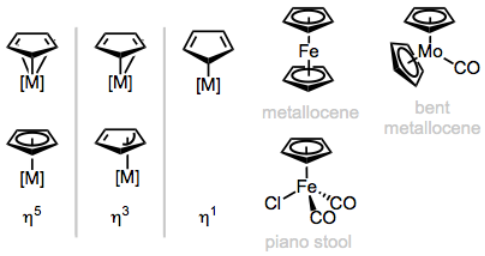
The lower half of the figure above illustrates the slightly weird character of the geometry of allyl ligands. In a previous post on even-numbered π systems, we investigated the orientation of the ligand with respect to the metal and came to some logical conclusions by invoking FMO theory and backbonding. A similar treatment of the allyl ligand leads us to similar conclusions: the plane of the allyl ligand should be parallel to the xy-plane of the metal center and normal to the z-axis. In reality, the allyl plane is slightly canted to optimize orbital overlap—but we can see at the right of the figure above that π2–dxy orbital overlap is key. Also note the rotation of the anti hydrogens (anti to the central C–H, that is) toward the metal center to improve orbital overlap.

Exchange of the syn and anti substituents can occur through σ,π-isomerization followed by bond rotation and formation of the isomerized trihapto form. Notice that the configuration of the stereocenter bearing the methyl group is unaffected by the isomerization! It should be noted that 1,3-disubstituted allyl complexes almost exclusively adopt a syn,syn configuration without danger of isomerization.



The methylene and central C–H simply change places!

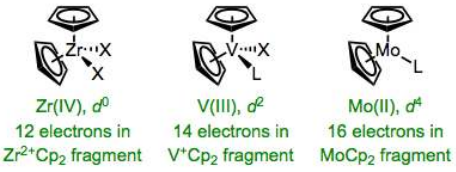
Upon deconstruction, the cyclopentadienyl (Cp) ligand yields the aromatic cyclopentadienyl anion, an L2X-type ligand. Cp is normally an η5-ligand, but η3 (LX) and η1 (X) forms are known in cases where the other ligands on the metal center are tightly bound. η1-Cyclopentadienyl ligands can sometimes be fluxional—the metal has the ability to "jump" from atom to atom. Variations on the Cp theme include Cp* (C5Me5) and the monomethyl version (C5H4Me). Cp may be found as a loner alongside other ligands (in "half-sandwich" or "piano-stool" complexes), or paired up with a second Cp ligand in metallocenes. The piano-stool and bent metallocene complexes are most interesting for us, since these have potential for open coordination sites—plain vanilla metallocenes tend to be relatively stable and boring.



Binding modes of Cp and general classes of Cp complexes.

Research for this post has made me appreciate the remarkable electron-donating ability of the cyclopentadienyl (Cp) ligand, which renders its associated metal center electron rich. The LUMO of Cp is high in energy, so the ligand is a weak π-acid and is, first and foremost, a σ-donor. This effect is apparent in the strong backbonding displayed by Cp carbonyl complexes. Despite its strong donating ability, Cp is rarely an actor ligand unless another ligand shakes things up—check out the nucleophilic reactivity of doubly jazzed-up ferrocene for a nice example.

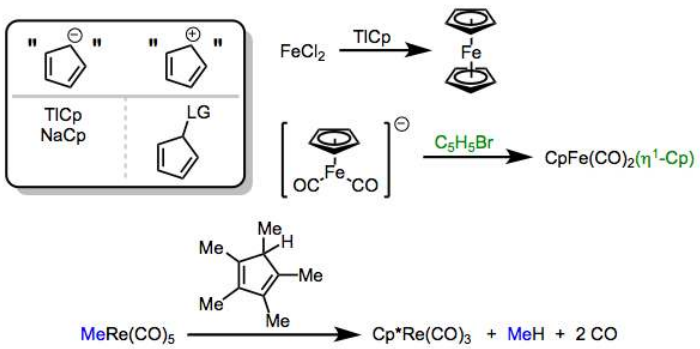
It's critical to recognize that η5-Cp is a six-electron ligand (!). Because Cp piles on electrons, the numbers of ligands bound to the metal in Cp complexes tend to be lower than we might be used to, especially in bent metallocenes containing two Cp's. Still, the number of ligands we'd expect on the metal center in these complexes is perfectly predictable. We just need to keep in mind that the resulting complexes are likely to contain 16 or 18 total electrons.



By considering the MCp2 fragment, we can predict the nature of ancillary ligands in bent metallocenes.

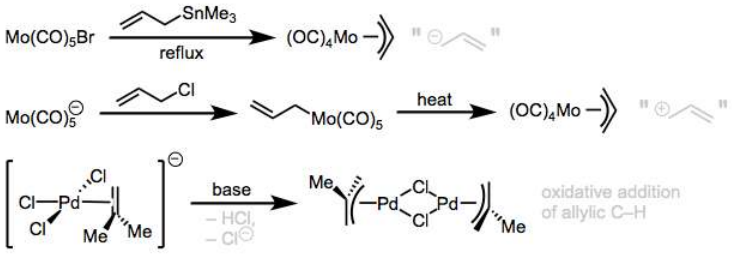
Synthesis

Crabtree cleanly divides methods for the synthesis of Cp complexes into those employing Cp+ equivalents, Cp– equivalents, and the neutral diene. Naturally, the first class of reagents are appropriate for electron-rich, nucleophilic complexes, while the second class are best used in conjunction with electron-poor, electrophilic complexes. The figure below provides a few examples.



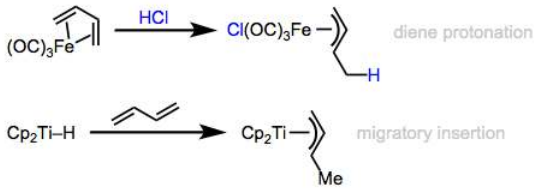
Methods for the synthesis of Cp complexes. The possibilities are exhausted by anionic, cationic, and neutral Cp equivalents!

Methods for synthesizing allyl complexes can also be classified according to whether the allyl donor is a cationic, anionic, or neutral allyl equivalent. In metal-catalyzed allylic substitution reactions, the allyl donor is usually a good electrophile bearing a leaving group displaced by the metal (an allyl cation equivalent). However, similar complexes may be obtained through oxidative addition of an allylic C–H bond to the metal, as in the synthesis of methallyl palladium chloride dimer below. Transmetalation of nucleophilic allyls from one metal to another, which we can imagine as nucleophilic attacks of an anionic allyl group, are useful when the metal is electron-poor.



Nucleophilic, electrophilic, and neutral allyl donors.

Complexes containing conjugated dienes are also viable precursors to allyl complexes. Migratory insertion of a diene into the M–H bond is a nice route to methyl-substituted allyl complexes, for example. Interestingly, analogous insertions of fulvenes do not appear to lead to Cp complexes, but some funky reductive couplings that yield ansa-metallocenes are known. External electrophilic attack (e.g., protonation) and nucleophilic attack on coordinated dienes also result in allyl complexes. In essence, one double bond of the diene becomes a part of the allyl ligand in the product; the other is used as a “handle” to establish the key covalent bond to the allyl ligand.

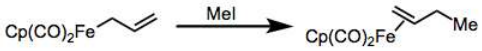


Dienes: brave crusaders in the quest for allyl complexes.

Reactions

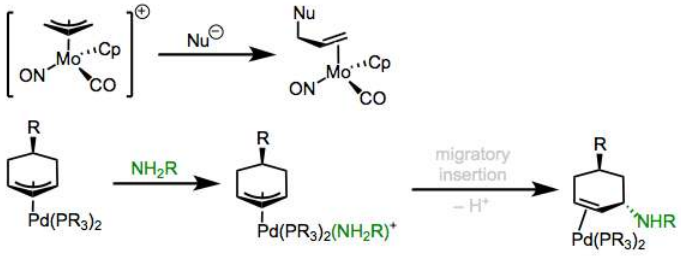
Since the Cp ligand is typically a spectator, we’ll focus in this section on the reactivity of allyl ligands. As usual, the behavior of the allyl ligand depends profoundly on the nature of its coordinated metal center, which depends in turn on the metal’s ancillary ligands. Avoid “tunnel vision” as you study the examples below—depending on the issue at hand, the ancillary ligands may be as important as (or more important than) the actor ligand.

Nucleophilic allyl complexes react with electrophiles like H+, MeI, X+, and acylium ions to yield cationic alkene complexes.



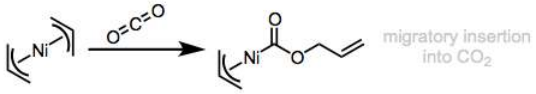
Attack of electrophiles on nucleophilic allyl complexes. Notice the donating Cp ligand!

In a conceptually related process, nucleophiles can attack allyl ligands bound to electrophilic metals. This process is key in allylic substitution reactions. In some cases, the nucleophile is known to bind to the metal first, then transfer to the allyl ligand through reductive elimination. Alternatively, direct attack on the allyl ligand may occur on the face opposite the metal. The figure below illustrates both possibilities.



External and internal attack of nucleophiles on coordinated allyl ligands.

Migratory insertion of allyl ligands is known, and is analogous to insertions involving alkyl ligands (see the figure below). Movement of the allyl ligand toward the coordination site of the dative ligand is assumed. Of course if oxidative addition to form allyl complexes is possible, reductive elimination of allyl ligands with other X-type ligands is also possible. We'll hit on these process in more detail in their dedicated posts.



Like alkyl ligands, allyls can migrate onto dative ligands like CO and π bonds.

One final post on σ-complexes will bring this series to a temporary close. In the next post, we'll look at ligands that, rather surprisingly, bind through their σ-electrons. These "non-classical" ligands behave like other dative ligands we've seen before, but are important for many reactions that involve main-group single bonds, such as oxidative addition. Before their discovery, the relevance of σ-ligands for reaction mechanisms went unappreciated by organometallic chemists.

This page titled 6.5.3: Odd-numbered π Systems is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.8: Odd-numbered π Systems** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.5.4: Fullerene Complexes

The π systems of fullerenes (eg buckmisterfullerene, C_{60}) also act as ligands for metal complexes. Most transition metal-fullerene complexes are derived from C_{60}. The structure of $C_{60}[IrCl(CO)(PMe_3)_2]_2$ is shown in Figure 6.5.4.1.



Figure 6.5.4.1: Structure of $C_{60}[IrCl(CO)(PMe_3)_2]_2$. doi=10.1021/ic00101a015. (Smokefoot, YEMVOB, CC BY-SA 4.0)

As ligands, fullerenes behave similarly to electron-deficient alkenes, and they prefer coordination to electron-rich metal centers (metal ions with softer character like those of the 4d and 5d transition metals). They almost always coordinate in a dihapto (η^2) fashion. The η^2 metal binding most often occurs on the junction of two 6-membered rings, as shown for $[[Ph_3P]_2Pt]_6(\eta^2-C_{60})$ on the left of Figure 6.5.4.2 In (\ce{Ru3(CO)9(C60)}\), the fullerene binds to the triangular face of the cluster as shown on the right in Figure 6.5.4.2

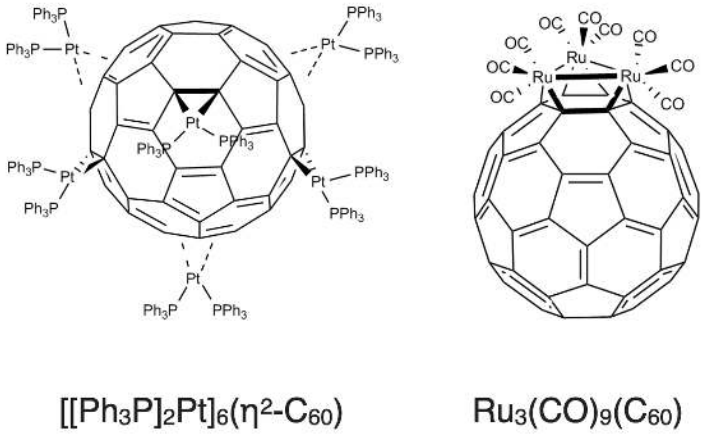


Figure 6.5.4.2: Structures of two η^2 fullerene complexes. Left, $[[Ph_3P]_2Pt]_6(\eta^2-C_{60})$. Right, $Ru_3(CO)_9(C_{60})$. (CMSherwood, Fullerene 4 and Fullerene 2, CC BY-SA 3.0)

Hexahapto and pentahato binding is possible, but is less common that dihapto coordination. Modification of the fullerene with phynyl substituents makes the fullerene a more electron rich ligand so that penta- and hexahapto coordination is more favorable. For example, the pentaphenyl anion, $C_{60}Ph_5^-$, binds to Fe in a pentahpto (η^5) fashion, similar to the interactions in ferrocene (Left, Figure 6.5.4.3).

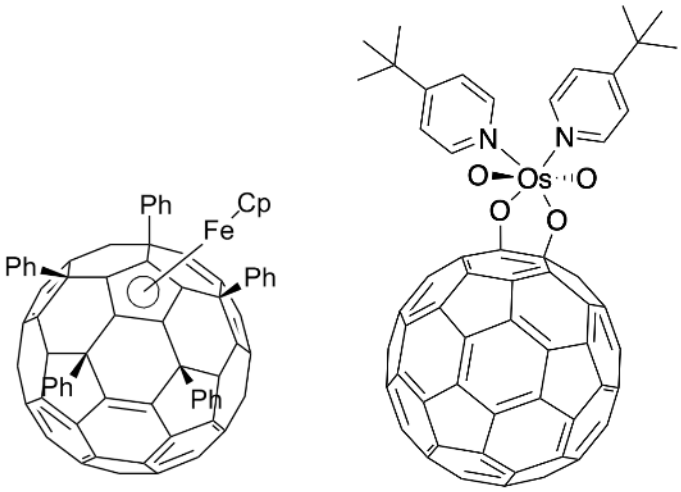


Figure 6.5.4.3: Structures of two modified fullerenes. Left, a ferrocene-like complex of the pentaphynyl bucknisterfullerene anion (CMSherwood, Fullerene 3, CC BY-SA 3.0). Right, the structure of \(\ce{C60(OsO4)(4-*t*-butylpyridine)2}\), which was important for the original determination of the structure for C_{60} (CC-BY-SA; Kathryn Haas).

The first X-ray structure that gave insight into the spherical structure of fullerenes was derived from an oxygen adduct of osmium tetroxide (Right, Figure 6.5.4.3).

6.5.4: Fullerene Complexes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

6.6: Metal-Carbon Bonds

6.6.1: Metal Alkyls

6.6.2: Carbenes

6.6.3: Carbyne (Alkylidyne) Complexes

6.6.4: Carbido and Cumulene Complexes

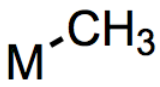
6.6.5: Carbon Wires- Polyyne and Polyene Bridges

This page titled 6.6: Metal-Carbon Bonds is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

6.6.1: Metal Alkyls

Part 1:

With this post we finally reach the defining ligands of organometallic chemistry, alkyls. Metal alkyls feature a metal-carbon σ bond and are usually actor ligands, although some alkyl ligands behave as spectators. Our aim will be to understand the general dependence of the behavior of alkyl ligands on the metal center and the ligand's substituents. Using this knowledge, we can make meaningful comparisons between related metal alkyl complexes and educated predictions about their likely behavior. Because alkyl ligands are central to organometallic chemistry, I've decided to spread this discussion across multiple posts. We'll deal first with the general properties of metal alkyls.



In the Simplifying the Organometallic Complex series, we decomposed the M–C bond into a positively charged metal and negatively charged carbon. This deconstruction procedure is consistent with the relative electronegativities of carbon and the transition metals. It can be very useful for us to imagine metal alkyls essentially as stabilized carbanions—but it's also important to understand that M–C bonds run the gamut from extremely ionic and salt-like ($NaCH_3$) to essentially covalent ($[HgCH_3]^+$). The reactivity of the alkyl ligand is inversely related to the electronegativity of the metal center.

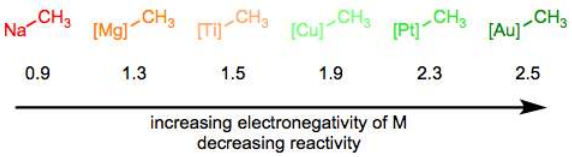


Figure 6.6.1.1: Reactivity decreases as the metal's electronegativity increases. Values given are Pauling electronegativities. (Michael Evans)

The hybridization of the carbon atom is also important, and the trend here follows the trend in nucleophilicity as a function of hybridization in organic chemistry. *sp*-Hybridized ligands are the least nucleophilic, followed by sp^2 and sp^3 ligands respectively.

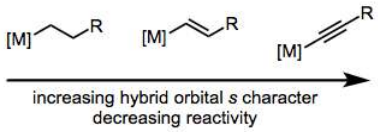
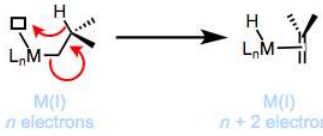


Figure 6.6.1.1: Note that this trend is similar to the nucleophilicity of carbanions as a function of hybridization. (Michael Evans)

The history of transition metal alkyls is an intriguing example of an incorrect scientific paradigm. After several unsuccessful attempts to isolate stable metal alkyls, organometallic chemists in the 1920s got the idea that metal-carbon bonds were weak in general. However, later studies showed that it was *kinetic instability*, not thermodynamic, that was to blame for our inability to isolate metal alkyls. In other words, most metal alkyls are susceptible to decomposition pathways with low activation barriers—the instability of the M–C bond *per se* is not to blame. Crabtree cites typical values of 30-65 kcal/mol for M–C bond strengths.

What are the major decomposition pathways of metal alkyl complexes? **β-hydride elimination** is the most common. Thermodynamically, the ubiquity of β-hydride elimination makes sense—M–C bonds run 30-65 kcal/mol, while M–H bonds tend to be stronger. The figure below summarizes the accepted mechanism and requirements of β-hydride elimination. We'll revisit this fundamental reaction of organometallic complexes in a future post.



1. The β-carbon must bear a hydrogen.
2. M–C and C–H must be *syn coplanar*.
3a. The metal must possess a vacant coordination site and an accessible empty orbital.
3b. The metal must possess 16 or fewer total electrons.
4. For rapid elimination, the metal must be at least d^2.

Figure 6.6.1.1: What kinds of metal alkyl complexes violate the requirements for beta-hydride elimination? (Copyright; author via source)

Kinetically stable metal alkyl complexes violate one of the requirements for β-hydride elimination. Methyl and neopentyl complexes lack β-hydrogens, violating requirement 1. Tightly binding, chelating ligands may be used to prevent the formation of an empty coordination site, violating requirements 3a and 3b. Titanium complexes are known that violate requirement 4 and eliminate only very slowly—back-donation from the metal to the σ^*_{C-H} is required for rapid elimination (see below).

Reductive elimination is a second common decomposition pathway. The alkyl ligand hooks up with a second X-type ligand on the metal, and the metal is reduced by two units with a decrease in the total electron count by two units. I've omitted curved arrows here because different mechanisms of reductive elimination are known. We'll discuss the requirements of reductive elimination in detail in a future post; for now, it's important to note that the thermodynamic stability of C–X versus that of (M–X + M–C) is a critical driving force for the reaction.

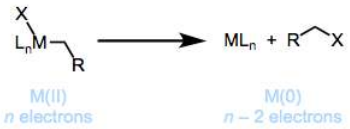


Figure 6.6.1.1: The thermodynamics of reductive elimination can present problems for some alkyl complexes. (Copyright; author via source)

When X = H, reductive elimination is nearly always thermodynamically favorable; thus, isolable alkyl hydride complexes are rare. This behavior is a feature, not a bug, when we consider that hydrogenation chemistry depends on it! On the other hand, when X = halogen reductive elimination is usually disfavored. Reductive elimination of C–C (X = C) can be favored thermodynamically, but is usually slower than the corresponding C–H elimination.

Complexes that cannot undergo β-hydride elimination are sometimes susceptible to **α-elimination**, a mechanistically similar process that forms a metal carbene. This process is particularly facile when the α-position is activated by an adjacent electron donor (Fischer carbenes are the result).

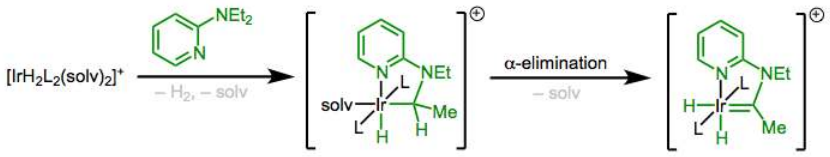


Figure 6.6.1.1: Oxidative addition followed by alpha-elimination, forming a Fischer carbene from an alkyl complex. (Copyright; author via source)

In some metal alkyl complexes, C–H bonds at the α, β, or even farther positions can serve as electron donors to the metal center. This idea is supported by crystallographic evidence and NMR chemical shifts (the donating hydrogens shift to high field). Such interactions are called **agostic interactions**, and they resemble an "interrupted" transition state for hydride elimination. Alkyl complexes that cannot undergo β-hydride elimination for electronic reasons (high oxidation state, d^0 metals) and vinyl complexes commonly exhibit this phenomenon. The fact that β-hydride elimination is slow for d^0 metals—agostic interactions are seen instead—suggests that back-donation from a filled metal orbital to the σ^*_{C-H} is important for β-hydride elimination. Here's an interesting, recent-ish review of agostic interactions.

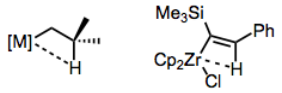


Figure 6.6.1.1: Copy and Paste Caption here. (Copyright; author via source)

In the next post in this series, we'll explore the synthesis of metal alkyl complexes in more detail, particularly clarifying the question: how can we conquer β-hydride elimination?

Part 2:

In this post, we'll explore the most common synthetic methods for the synthesis of alkyl complexes. In addition to enumerating the reactions that produce alkyl complexes, this post will also describe strategies for getting around β-hydride elimination when isolable alkyl complexes are the goal. Here we go!

Properties of Stable Alkyl Complexes

Stable alkyl complexes must be resistant to β-hydride elimination. In the last post we identified four key conditions necessary for elimination to occur:

1. The β-carbon must bear a hydrogen.
2. The M–C and C–H bonds must be able to achieve a *syn* coplanar orientation (pointing in the same direction in parallel planes).
3. The metal must bear 16 total electrons or fewer and possess an open coordination site.
4. The metal must be at least d^2.

Stable alkyl complexes must violate at least one of these conditions. For example, titanium(IV) complexes lacking *d* electrons β-eliminate very slowly. The complex below likely also benefits from chelation (see below).

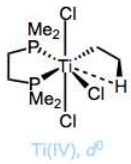


Figure 6.6.1.1: No d electrons here! (Michael Evans)

Complexes have been devised that are unable to achieve the *syn* coplanar orientation required for elimination, or that lack β-hydrogens outright. A few examples are provided below—one has to admire the cleverness of the researchers who devised these complexes. The metallacyclobutane is particularly striking!

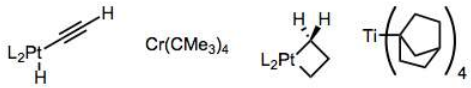


Figure 6.6.1.1: Complexes whose beta-C–H bonds cannot align in a syn coplanar manner with the M–C bond. (Copyright; author via source)

Using tightly binding, chelating ligands or a directing group on the substrate, the formation of 16-electron complexes susceptible to β-hydride elimination can be discouraged. Notice how the hyrdrogen-bonding L_2 ligands in the central complex below hold the metal center in a death grip.

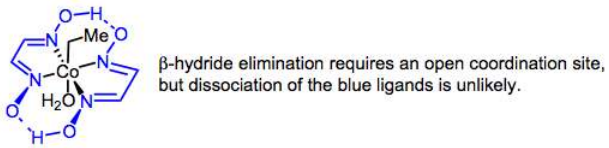


Figure 6.6.1.1: Tightly chelating ligands prevent the opening of a coordination site. (Copyright; author via source)

Finally, it's worth noting that complexes with an open coordination site—such as 16-electron, square-planar complexes of Ni, Pd, and Pt important for cross-coupling—are susceptible to reactions with solvent or other species at the open site. Bulky alkyl ligands help prevent these side reactions. In the example below, the methyl groups of the *o*-tolyl ligands extend into the space above and below the square plane, discouraging the approach of solvent molecules perpendicular to the plane.

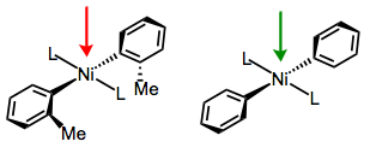


Figure 6.6.1.1: The approach of solvent perpendicular to the square plane is slowed by methyl groups on the aryl ligand. (Copyright; author via source)

Many transition metal complexes catalyze (*E*)/(*Z*) isomerization and the isomerization of terminal alkenes (α-olefins) to internal isomers via β-hydride elimination. This is a testament to the importance of this process for alkyl complexes. Of course, transient alkyl complexes may *appear* to be susceptible to β-hydride elimination, but if other processes are faster, elimination will not occur. Thus, the optimization of many reactions involving alkyl complexes as intermediates has involved speeding up other processes at the expense of β-hydride elimination—hydrocyanation is a good example.

Synthesis of Alkyl Complexes

The dominant synthetic methods for alkyl complexes are based on nucleophilic attack, electrophilic attack, oxidative addition, and migratory insertion. The first two methods should be intuitive to the organic chemist; the second two are based on more esoteric (but no less important) reactions of organometallic complexes.

Metals bearing good leaving groups are analogous to organic electrophiles, and are susceptible to **nucleophilic attack** by organolithiums, Grignard reagents, and other polarized organometallics. These reactions can be viewed as a kind of **transmetalation**, as the alkyl ligand moves from one metal to another. Electron-withdrawing X-type ligands like –Cl and –Br should jump out as good leaving groups. On the other hand, clean substitution of L-type ligands by anionic nucleophiles is much more rare (anionic complexes would result).



Figure 6.6.1.1: Simple and straightforward: nucleophile attacks electrophilic metal. (Copyright; author via source)

Many anionic metal complexes are nucleophilic enough to attack electrophilic sources of carbon such as alkyl and acyl halides in an **electrophilic attack** mode. An available lone pair on the metal and open coordination site are prerequisites for this chemistry. The charge on the complex increases by one unit (in effect, negative charge is transferred to the electrophile's leaving group). We can classify these as oxidative ligation reactions—notice that the oxidation state of the metal increases by two units.



Figure 6.6.1.1: Oxidative ligation for the synthesis of alkyl complexes. Total electron count does not change. (Copyright; author via source)

Oxidative addition results in the cleavage of a W–Z bond and placement of two new X-type ligands (–W and –Z) on the metal center, with an increase in the oxidation state of the metal and the total electron count by two units. Organic halides are extremely common substrates for this reaction, the first step in the mechanism of cross-coupling reactions. The oxidized metal complex containing new alkyl and halide ligands is the final product. Notice that *two* open coordination sites are required (not necessarily simultaneously), the metal center must be amenable to two-electron oxidation, and the number of total electrons of the complex increases by two. In essence, the electrons of the W–Z bond join the complex's party. Take note that there are many known mechanisms for oxidative addition! We'll explore these different mechanisms in detail in a future post.

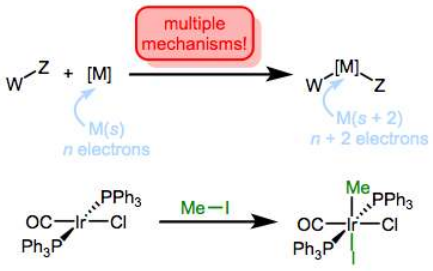


Figure 6.6.1.1: Oxidative addition, with a representative example, for the synthesis of metal alkyl complexes. (Copyright; author via source)

Finally, **migratory insertion** of unsaturated organic compounds is an important method for the synthesis of certain alkyl complexes, and an important step of organometallic reactions that result in addition across π bonds. Migratory insertion is the microscopic reverse of β-hydride elimination. The clever among you may notice that the use of migratory insertion to synthesize alkyl complexes seems inconsistent with our observation that its reverse is ubiquitous for metal alkyls—shouldn't equilibrium favor the olefin hydride complex? In many cases this is the case; however, there are some notable exceptions. For example, perfluoroalkyl complexes are exceptionally stable (why?), so the insertion of fluoroalkenes is often favored over elimination.

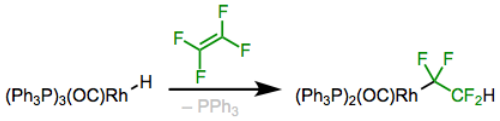


Figure 6.6.1.1: Why does this work? Thank fluorine! (Copyright; author via source)

As we noted above, we can still invoke kinetically stable alkyl complexes as *intermediates* in reactions provided subsequent steps are faster. In the next post, we'll examine the general classes of reactions in which alkyl complexes find themselves the major players, focusing on the specific mechanistic steps that involve the alkyl complex (reductive elimination, transmetalation, migratory insertion, and [naturally] β-hydride elimination).

Part 3:

In this last post on alkyl ligands, we'll explore the major modes of reactivity of metal alkyls. We've discussed β-hydride elimination in detail, but other fates of metal alkyls include reductive elimination, transmetallation, and migratory insertion into the M–C bond. In a similar manner to our studies of other ligands, we'd like to relate the steric and electronic properties of the metal alkyl complex to its propensity to undergo these reactions. This kind of thinking is particularly important when we're interested in controlling the relative rates and/or extents of two different, competing reaction pathways.

Reactions of Metal Alkyl Complexes

Recall that **β-hydride elimination** is an extremely common—and sometimes problematic—transformation of metal alkyls. Then again, there are reactions for which β-hydride elimination is desirable, such as the Heck reaction. Structural modifications that strengthen the M–H bond relative to the M–C bond encourage β-hydride elimination; the step can also be driven by trapping of the metal hydride product with a base (the Heck reaction uses this idea).

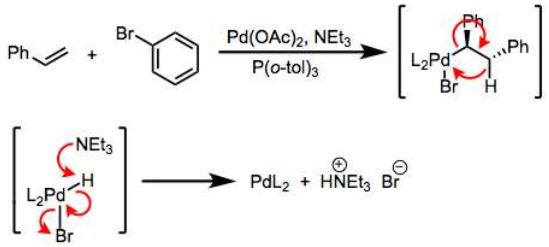


Figure 6.6.1.1: During the Heck reaction, beta-hydride elimination is driven by a base. (Copyright; author via source)

On the flip side, stabilization of the M–C bond discourages elimination and encourages its reverse: migratory insertion of olefins into M–H. Previously we saw the example of perfluoroalkyl ligands, which possess exceptionally stable M–C bonds. The fundamental idea here—that electron-withdrawing groups on the alkyl ligand stabilize the M–C bond—is quite general. Hartwig describes an increase in the "ionic character" of the M–C bond upon the addition of electron-withdrawing groups to the alkyl ligand (thereby strengthening the M–C bond, since ionic bonds are stronger than covalent bonds). Bond energies from organic chemistry bear out this idea to an extent; for instance, see the relative BDEs of Me–Me, Me–Ph, and Me–CCH in this reference. I still find this explanation a little "hand-wavy," but it serves our purpose, I suppose.

Metal alkyls are subject to **reductive elimination**, the microscopic reverse of oxidative addition. The metal loses two covalent ligands, its formal oxidation state decreases by two units, total electron count decreases by two units, and an R–X bond forms. Reductive elimination is favorable when the R–X bond in the organic product is more stable than the M–R and M–X bonds in the starting complex (a thermodynamic issue). It should be noted, however, that the kinetics of reductive elimination depend substantially on the steric bulk of the eliminating ligands. Concerted reductive elimination of R–H usually possesses a lower activation energy than R–R elimination.

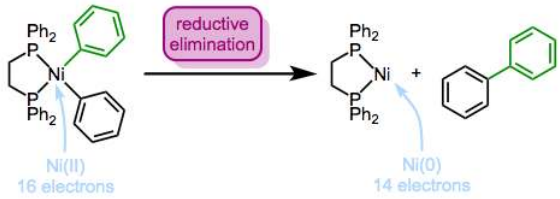


Figure 6.6.1.1: An example of reductive elimination. Intuitively, the electron density at the metal center increases as this step proceeds. (Copyright; author via source)

Transmetalation involves the transfer of an alkyl ligand from one metal to the other. An interesting problem concerns the relative reactivity of metal alkyls toward transmetalation. Assuming similar, uncomplicated ligand sets, which of two metal centers is more likely to hold on to an alkyl ligand? Consider the two situations below.

$$\mathrm{MR} + \mathrm{M'} \rightleftharpoons \mathrm{M} + \mathrm{M'R}$$

$$\mathrm{MR} + \mathrm{M'R'} \rightleftharpoons \mathrm{MR'} + \mathrm{M'R}$$

The first is a *bona fide* transmetalation; the second is really a double replacement reaction. The distinction is rarely drawn in practice, but it's important! The difference is that in the first case, a single-electron transfer of sorts must take place, while in the second case, no redox chemistry is necessary. Favorability in the first case is governed by the relative reduction potentials of M and M' (the reaction goes forward when M' is more easily oxidized than M); in the second case, the relative electropositivities of the metals is key, and other factors like lattice energies may be important. The distinction between transmetalation *per se* and double replacement explains the paradoxical synthetic sequence in the figure below. In practice, both are called "transmetalation." See these slides (page 6) for a summarizing reference.

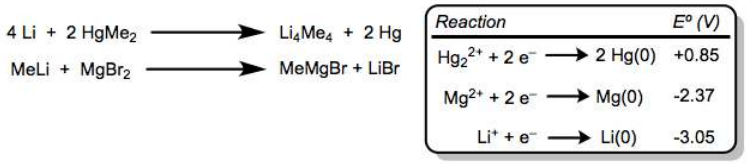


Figure 6.6.1.1: How are both of these reactions favorable? The first is a true transmetalation; the second is a double replacement. (Copyright; author via source)

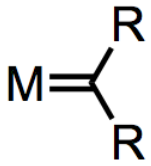
This brings our extended look at metal alkyl complexes to a temporary close. Of course, metal alkyls are *everywhere* in organometallic chemistry…so seeing them again is pretty much inevitable! The next installment in the Epic Ligand Survey series concerns allyl, cyclopentadienyl, and other odd-membered pi systems. These L_nX-type ligands can, like arenes, pile as many as six electrons on the metal center at once.

This page titled 6.6.1: Metal Alkyls is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.5: Metal Alkyls** by Michael Evans is licensed CC BY-NC-SA 4.0.

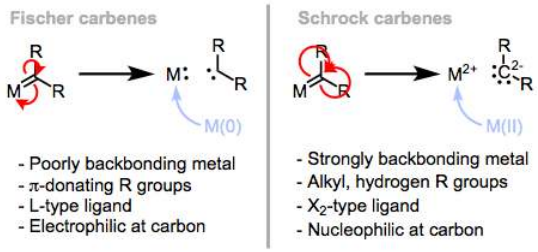
6.6.2: Carbenes

In a previous post, we were introduced to the N-heterocyclic carbenes, a special class of carbene best envisioned as an L-type ligand. In this post, we'll investigate other classes of carbenes, which are all characterized by a metal-carbon double bond. Fischer carbenes, Shrock carbenes, and vinylidenes are usually actor ligands, but they may be either nucleophilic or electrophilic, depending on the nature of the R groups and metal. In addition, these ligands present some interesting synthetic problems: because free carbenes are quite unstable, ligand substitution does not cut the mustard for metal carbene synthesis.



General Properties

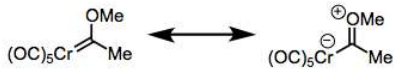
Metal carbenes all possess a metal-carbon double bond. That's kind of a given. What's interesting for us about this double bond is that there are multiple ways to deconstruct it to determine the metal's oxidation state and number of d electrons. We could give one pair of electrons to the metal center and one to the ligand, as we did for the NHCs. This procedure nicely illustrates why compounds containing M=C bonds are called "metal carbenoids"—the deconstructed ligand is an L-type carbenoid. Alternatively, we could give both pairs of electrons to the ligand and think of it as an X2-type ligand. The appropriate procedure depends on the ligand's substituents and the electronic nature of the metal. The figure below summarizes the two deconstruction procedures.



The proper method of deconstruction depends on the electronic nature of the ligand and metal.

When the metal possesses π-acidic ligands and the R groups are π-basic, the complex is best described as an L-type Fischer carbene and the oxidation state of the metal is unaffected by the carbene ligand. When the ligands are "neutral" (R = H, alkyl) and the metal is a good backbonder—that is, in the absence of π-acidic ligands and electronegative late metals—the complex is best described as an X2-type Schrock carbene. Notice that the oxidation state of the metal depends on our deconstruction method! Thus, we see that even the oxidation state formalism isn't perfect.

Deconstruction reveals the typical behavior of the methylene carbon in each class of complex. The methylene carbon of Schrock carbenes, on which electron density is piled through backbonding, is nucleophilic (the 2– charge screams nucleophilic!). On the other hand, the methylene carbon of Fischer carbons is electrophilic, because backbonding is weak and does not compensate for σ-donation from the ligand to the metal. To spot a Fischer carbene, be on the lookout for reasonable zwitterionic resonance structures like the one at right below.

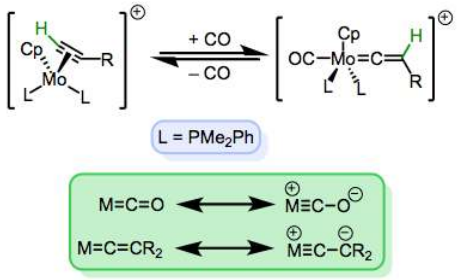


Thanks to the pi-accepting CO ligands, the metal handles the negative charge well. This is a Fischer carbene.

The clever reader may notice that we haven't mentioned π-acidic R groups, such as carbonyls. Complexes of this type are best described as Fischer carbenes as well, as the ligand is still electrophilic. However, complexes of this type are difficult to handle and crazy reactive (see below) without a π-basic substituent to hold them in check.

Vinylidenes are the organometallic analogues of allenes, and are best described as intermediate in behavior between Fischer and Schrock carbenes. They are electrophilic at the α carbon and nucleophilic at the β carbon—in fact, a nice analogy can be made

between vinylidenes and carbon monoxide. Tautomerization to form alkyne π-complexes is common, as the vinylidene and alkyne complexes are often comparable in stability.



Vinylidene tautomerization, and an analogy between vinylidenes and CO.

Take care when diagnosing the behavior of metal carbenes. In these complexes, there is often a subtle interplay between the R groups on the carbene and other ligands on the metal. In practice, many carbenes are intermediate between the Fischer and Schrock ideals.

Synthesis

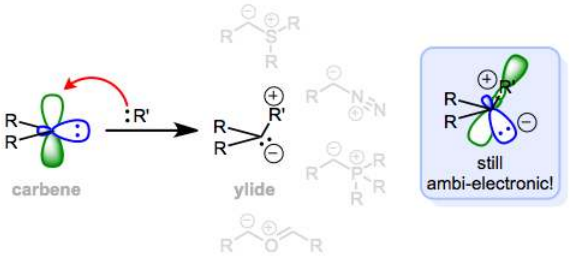
Metal carbenes present a fascinating synthetic problem. A cursory look at the deconstruction procedures above reveals that these complexes cannot be made using ligand substitution reactions, because the free ligands are far too unstable. Although the synthetic methods introduced here will be new for us, the attuned organic chemist will find them familiar. The conceptual foundations of metal carbene synthesis are similar to methods for the synthesis of alkenes in organic chemistry.

In the post on NHCs, we saw that the free carbene is both nucleophilic (via the lone pair in its σ system) and electrophilic (via its empty 2pz orbital). Organic precursors to metal carbenes and alkenes also possess this property—they can act both as nucleophiles and electrophiles. Fundamentally, this “ambi-electronic” behavior is useful for the creation of double bonds. One bond comes from “forward flow,” and the other from “reverse flow.” Naturally, the other reacting partner also needs to be ambi-electronic for this method to work.



A fundamental paradigm for double bond synthesis: ambi-electronic compounds doing what they do.

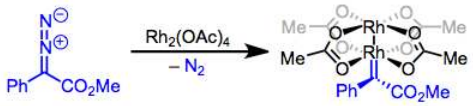
What sets carbene precursors apart from free carbenes? What other kinds of molecules may act as both nucleophiles and electrophiles at the same atom? Watch what happens when we tack a third group onto the free carbene…the figure below shows the result in general and a few specific examples in gray.



A "dative ligand" R' is the difference between a carbene and an ylide. Both are ambi-electronic.

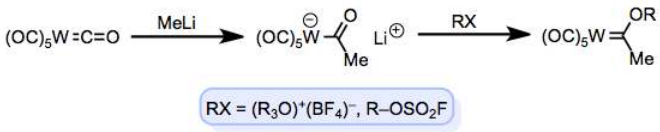
An ylide, which contains adjacent positive and negative charges, results from this purely hypothetical process. Ylides (diazo compounds, specifically) are the most common precursors to metal carbene complexes. Like free carbenes, ylides are ambi-electronic. The electrophilic frontier orbital of an ylide is just the σ* orbital of the bond connecting the charged atoms, which makes sense if we consider the positively charged fragment as a good leaving group (it always is). The lone pair is still nucleophilic. The figure above depicts some of the most famous ylides of organic chemistry, including those used for alkene synthesis (Corey-Chaykovsky and Wittig) and cycloaddition reactions (the carbonyl ylide).

Although diazo compounds are most commonly drawn with charges on the two nitrogen atoms, the diazo carbon is a good nucleophile and can attack electrophilic metal centers to initiate metal carbene formation. A slick 15N kinetic isotope effect study showed that C–N bond cleavage is the rate-limiting step of the reaction below. Visualize the carbanionic resonance structure to kick off the mechanism! Don't think too hard about the structure of rhodium(II) acetate here. Rhodium, copper, ruthenium, and iridium all form carbene complexes with diazo compounds in a similar way.



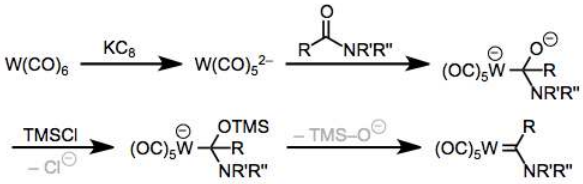
After association of the nucleophilic carbon to Rh, elimination with loss of nitrogen gas is the slow step of this reaction.

Diazo compounds work well for metal carbene formation when they possess an electron-withdrawing group, which stabilizes the ylide through conjugation. What about Fischer carbenes, which possess electron-donating groups on the carbene carbon? An interesting method that still involves a "push-and-pull" of electron flow (but not ylides) employs metal-CO complexes. Upon addition of a strong nucleophile ("forward flow") to the carbonyl carbon, a metalloenolate of sorts is produced. Treatment with an electrophile RX that prefers oxygen over the metal ("reverse flow") results in an OR-substituted Fischer carbene. Reactions reminiscent of transesterification trade out the OR group for an –SR group (using a thiol) or an –NR2 group (using a secondary amine).



Fischer's classical route to L-type carbenes.

As counterintuitive as it may seem, it's possible to use metal dianions for the synthesis of Fischer carbenes via a method pioneered by Hegedus and Semmelhack. Potassium intercalated in graphite—the mysterious "KC8"—reduces group 6 metal carbonyl complexes to the corresponding dianions, which subsequently unleash a deluge of electrons on a poor, unsuspecting amide to afford NR2-substituted Fischer carbenes after treatment with trimethylsilyl chloride.

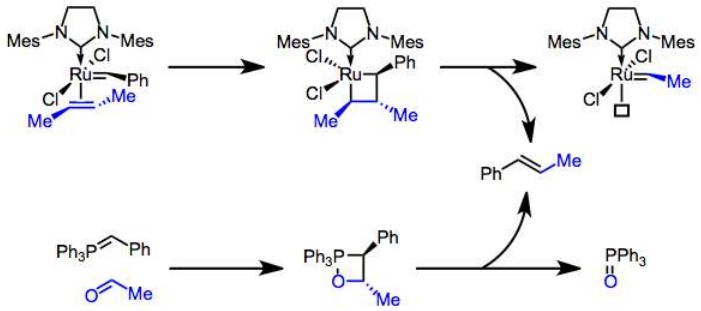


One-directional electron flow for Fischer carbene synthesis: the Hegedus-Semmelhack approach.

For other methods for the synthesis of Fischer carbenes, check out this nice review from the Baran group.

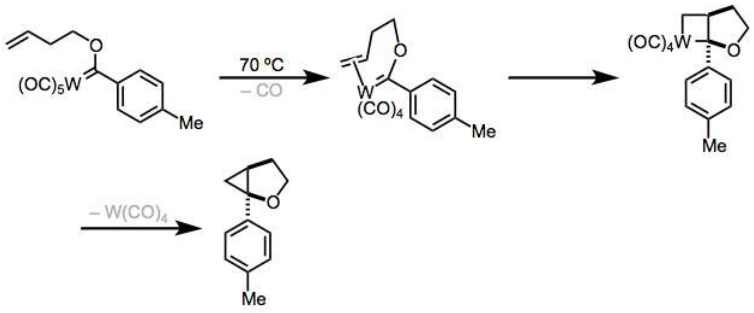
Reactions

In many ways, the reactivity of metal carbenes parallels that of ylides. Olefin metathesis catapulted metal carbenes to international stardom, but in many ways, metathesis is conceptually similar to the Wittig reaction, which employs phosphorus ylides. During both mechanisms, an ylide/carbene hooks up with another doubly bound molecule to form a four-membered ring. This step is followed by what we might call "orthogonal breakdown" to yield two new double bonds.



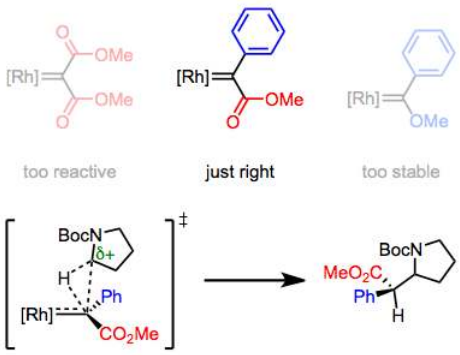
Wittig, Grubbs, and Schrock: Lords of the Chemical Dance. Ambi-electronic molecules are the dancers!

In my opinion, bond insertion reactions are the most interesting processes in which carbenes regularly engage. Bond insertions may be subdivided into cyclopropanation (π-bond insertion) and σ-bond insertion. Evidence suggests that most cyclopropanations take place by a mechanism that overlaps with metathesis—instead of orthogonal breakdown, reductive elimination occurs to release the three carbon atoms as a cyclopropane.



The metallacyclobutane mechanism of cyclopropanation.

σ-Bond insertion involves electron-rich C–H bonds most prominently, suggesting that electrophilic Fischer carbenes should be best for this chemistry. Fischer carbenes incorporating electron-withdrawing groups love to dimerize to form olefins and/or cyclopropanate olefins—how might we put the brakes on this behavior? If we simply tack a π-basic substituent onto the carbene carbon, the reactivity of these complexes is “just right” for C–H insertion. Notably, no covalent organometallic intermediates are involved; the electrophilic carbene carbon snuggles in between C and H in a single step. The transition state of this step resembles the transfer of a hydride from the organic substrate to the carbene, with “rebound” of electron density toward the partial positive charge.



Donor-acceptor carbenoids are the "Goldilocks complexes" of C–H insertion.

Let’s end with a nod to the similarity between Fischer carbenes and carboxylic acid derivatives (esters and amides). Transesterification-type reactions allow the chemist to swap out heteroatomic substituents on the carbene carbon at will (see above). Alkyl substitutents can even be deprotonated at the α carbon, just like esters! When we see the electronic similarities between the M=C bond of a Fischer carbene and the O=C bond of carboxylic acid derivatives, the similar behavior is only natural.

This page titled 6.6.2: Carbenes is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **2.1: Carbenes** by Michael Evans is licensed CC BY-NC-SA 4.0.

6.6.3: Carbyne (Alkylidyne) Complexes

Learning Objectives

In this lecture you will learn the following

- The metal−ligand multiple bonding and their relevance in.
- The Fischer type carbyne complexes.
- The Schrock type carbyne complexes.

The metal−ligand multiply bonded systems even extended beyond the doubly bonded Fischer and the Schrock carbenes to the triply bonded $L_nM{\equiv}CR$ type Fischer carbyne and the Schrock carbyne complexes. Similar to carbene that exists in a singlet and a triplet spin state, the carbyne also exists in two other spin states *i.e* in a doublet and a quartet form.

Upon binding to the metal in its doublet spin state as in the Fischer carbene system, the carbyne moiety donates two electrons *via* its *sp* hybridized lone pair containing orbital to an empty metal *d* orbital to yield a $L_nM{\leftarrow}CR$ type ligand to metal dative bond. It also makes a covalent π−bond through one of its singly occupied p_z orbital with one of the metal *d* orbitals. The carbyne−metal interaction consist of two ligand to metal interactions namely a dative one and a covalent one that together makes the carbyne moiety a LX type of a ligand. In addition to these two types of ligand to metal bonding interactions, there remains an empty p_y orbital on the carbyne−C atom that can accommodate electron donation from a filled metal *d* orbital to give a metal to ligand π−back bonding interaction (Figure 6.6.3.1).

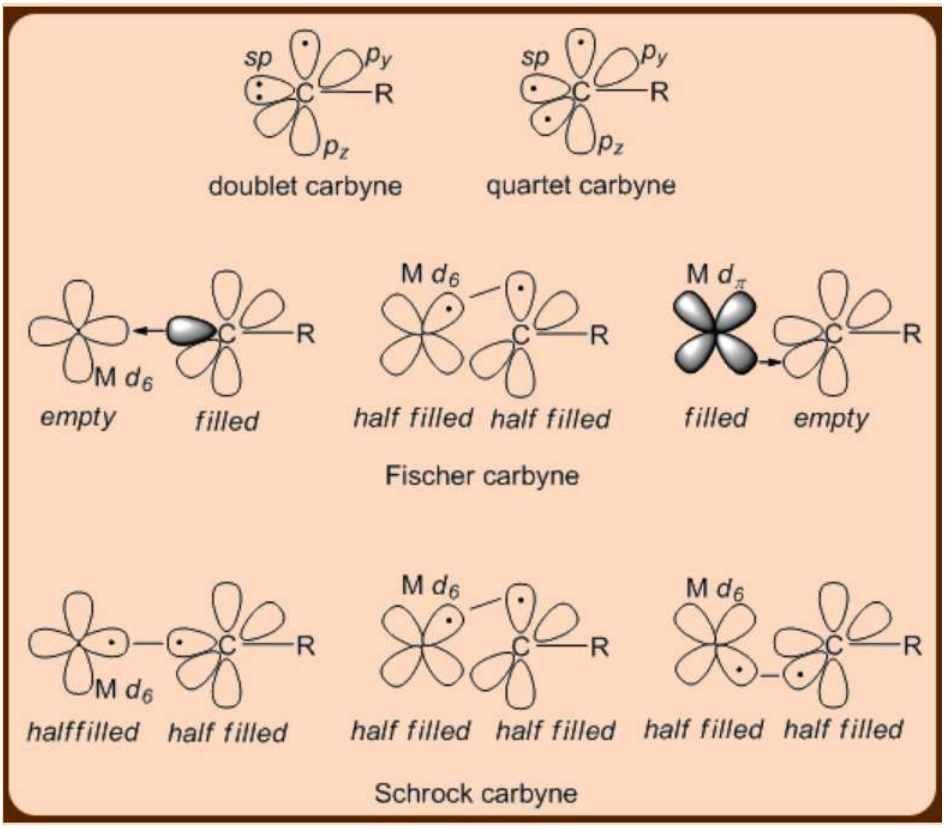


Figure 6.6.3.1: Metal−ligand multiple bonding in the Fischer and Schrock carbyne system

Analogously, in the quartet carbyne spin state in the Schrock carbyne systems three covalent bonds occur between the singly occupied *sp*, $p_y$and p_z orbitals of carbyne−C moiety with the respective singly occupied metal *d* orbitals (Figure 6.6.3.1).

Similar to what has been observed earlier in the case of the Fischer carbenes and Schrock carbenes, the Fischer carbyne complexes are formed with metal centers in lower oxidation states for *e.g.* as in $Br(CO)_4W{\equiv}CMe$, while the Schrock carbyne complexes are formed with metals in higher oxidation state, *e.g.* as in $(t{-}BuO)_3W{\equiv}Ct{-}Bu$.

Carbyne complexes can be prepared by the following methods.

i. The Fischer carbyne complexes can be prepared by the electrophilic abstraction of a methoxy group from a methoxy methyl substituted Fischer carbene complex.

$$\mathrm{L(CO)_4M{=}C(OMe)Me + 2\,BX_3 \longrightarrow [L(CO)_4M \equiv CMe]^+BX_4^- + BX_2(OMe) \longrightarrow X(CO)_4M \equiv CMe}$$

ii. Schrock carbynes can be prepared by the deprotonation of a α−CH bond of a metal−carbene complex.

$$\mathrm{CPCl_2Ta{=}CHR \xrightarrow[(ii)\,Ph3P{=}CH2]{(i)\,PMe3} Cp(PMe_3)ClTa \equiv CR}$$

iii. by an α−elimination reaction on a metal−carbene complex

$$\mathrm{Cp \cdot Br_2Ta{=}CHt{-}Bu \xrightarrow[(ii)\,Na/Hg]{(i)\,dmpe} Cp \cdot (dmpe)HTa \equiv Ct{-}Bu}$$

iv. by metathesis reaction

$$\mathrm{(t{-}BuO)_3W \equiv W(Ot{-}Bu)_3 + t{-}BuC \equiv Ct{-}Bu \longrightarrow 2\,(t{-}BuO)_3W \equiv Ct{-}Bu}$$

The reactivities of Fischer and the Schrock carbynes mirror that of the Fischer and Schrock carbenes. For example, the Fischer carbyne undergo nucleophilic attack at the carbyne−C atom while the Schrock carbyne undergo electrophilic attack at the carbyne−C atom.

Summary

The theme of metal−ligand multiple bonding extends beyond the doubly bonded Fischer and the Schrock carbene systems to even triply bonded Fischer and the Schrock carbyne systems. The carbyne moieties in these Fischer and the Schrock carbyne systems respectively exist in a doublet and a quartet spin state. The carbyne complexes are generally prepared from the respective carbene analogues by the abstraction of alkoxy (OR), proton (H^+), hydride (H^-) moieties, the α−elimination reactions and the metathesis reactions. The reactivity of the Fischer and the Schrock carbyne complexes parallel the corresponding Fischer and the Schrock carbene counterparts with regard to their reactivities toward electrophiles and nucleophiles.

This page titled 6.6.3: Carbyne (Alkylidyne) Complexes is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **13.2: Metal-Carbynes** by M. S. Balakrishna & Prasenjit Ghosh is licensed CC BY-NC-SA 4.0. Original source: https://nptel.ac.in/courses/104101006.

6.6.4: Carbido and Cumulene Complexes

Carbido ligand: One single carbon

A metal carbido (aka carbide, or simply carbon) complex is a metal complex that contains the ligand, carbon (C). Most molecular carbido complexes are clusters, usually featuring carbide as a six-fold bridging ligand. Examples include $[Rh_6C(CO)_{15}]^{2-}$, and $[Ru_6C(CO)_{16}]^{2-}$. The iron carbonyl carbides exist not only in the encapsulated carbon ($[Fe_6C(CO)_{16}]^{2-}$) but also with exposed carbon centres as in $Fe_5C(CO)_{15}$ and $Fe_4C(CO)_{13}$.



Figure 6.6.4.1: Structure of $Fe_5C(CO)_{15}$ containing a carbido bridging five iron centers. (Public domain)

In rare cases, carbido ligands are terminal ligands (Figure 6.6.4.2, left). Although it is tempting to extend the model of metal-carbon bonds from the alkyl (M−C), carbene (M=C, and carbyne (M≡C) ligands and evoke the idea of a quadruple bond between metal and carbon in the case of a carbido, experimental data is more consistent with a triple bonded to a metal ion (($M{\equiv}C_1$)). For example, the metal-carbon bond in the $RuC(PCy_3)_2Cl_2$ complex is similar to the bond length of other complexes with C??M (Figure 6.6.4.2).

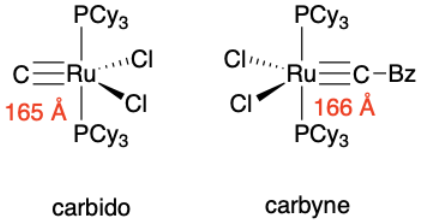


Figure 6.6.4.2: Carbido-metal bonds are similar in length to the C??M of metal carbynes. Cy = cyclohexane, Bz = benzyl. (CC-BY-SA; Kathryn Haas)

Source: https://en.Wikipedia.org/wiki/Metal_carbido_complex

Cumulene ligands: Chains of carbon atoms with consecutive double bonds

Chains of carbon atoms that have consecutive (cumulated) double bonds are intriguing ligands for metal complexes due to their potential utility as molecular wires in nano or optical devices. The first reported complex containing a vinylidene ligand was $Ph_2C_2Fe_2(CO)_8$. The first monometallic vinylidene complex was $(C_5H_5)Mo(P(C_6H_5)_3)(CO)_2[C{=}C(CN)_2]Cl$ Just as in the case of conjugated pi systems, the longer the length of a cumulated diene, the closer the HOMO/LUMO gap, and thus the more conductive. To date, the longest cumulenylidene ligand reported is heptahexaenylidene (Figure 6.6.4.3).

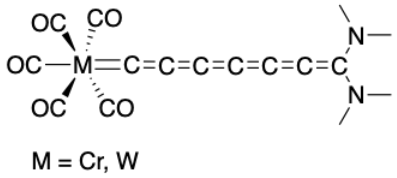


Figure 6.6.4.3: Structure of a metal complex with a heptahexaenylidene ligand. (CC-BY-SA; Kathryn Haas)

Source: https://en.Wikipedia.org/wiki/Cumule...ply%20cumulene.

This page titled 6.6.4: Carbido and Cumulene Complexes is shared under a CC BY-SA license and was authored, remixed, and/or curated by Kathryn Haas.

6.6.5: Carbon Wires- Polyyne and Polyene Bridges

Organic molecules with conjugated π systems are known to have interesting optical and electronic properties. When ligands with conjugated π systems are used to bridge two metal centers, the two metals can behave in a cooperative way because the electronic state of one metal ion is conjugated to the other. The most intensely investigated complexes are bimetallic metal complexes (two metal ions) that are bridged by long carbon chains with alternating single and double bonds. Some examples are given below. (This topic is reviewed in Aguirre-Etcheverry D. O'Hare, *Chem. Rev.*, **2010**, *110*, 4839, doi: 10.1021/cr9003852)

Polyene

Polyenes are organic molecules with alternating double and single bonds. In other words, they contain a series of consecutive \ce{(-C= C-)_{n)} with $n > 1$. Aromatic and cyclic polyenes were discussed in a previous section. One of the longest ligands reported as of 2010 was a $\mathrm{Ru{-}(CH)_{14}{-}Ru}$ complex (shown in Figure 6.6.5.1).

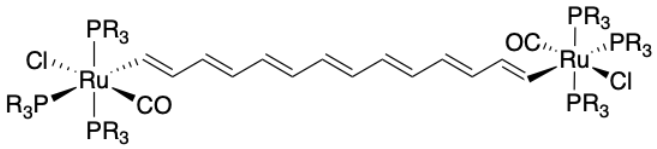


Figure 6.6.5.1: Structure of linear polyene complex of Ru with and 14-carbon polyene. (CC-BY-SA; Kathryn Haas)

Source: Aguirre-Etcheverry D. O'Hare, *Chem. Rev.*, **2010**, *110*, 4839, doi: 10.1021/cr9003852

Polyyne ligands

Polyynes are organic molecules with alternating single and double bonds. In other words, they contain a series of consecutive $(-\mathrm{C}{\equiv}\mathrm{C}-)\mathrm{n}$ with $n > 1$.

Organometallic polyynes capped with metal complexes are well characterized. As of the mid-2010s, the most intense research had concerned rhenium (ReC_nRe, n=6-20), ruthenium ($RuRuC_nRuRu$, n = 8–20), iron ($FeC_{12}CFe$), platinum (PtC_nPt, n = 16–28), palladium (ArC_nPd, n = 6–10), and cobalt ($Co_3C_nCo_3$, n = 14–26) complexes (Figure 6.6.5.1).

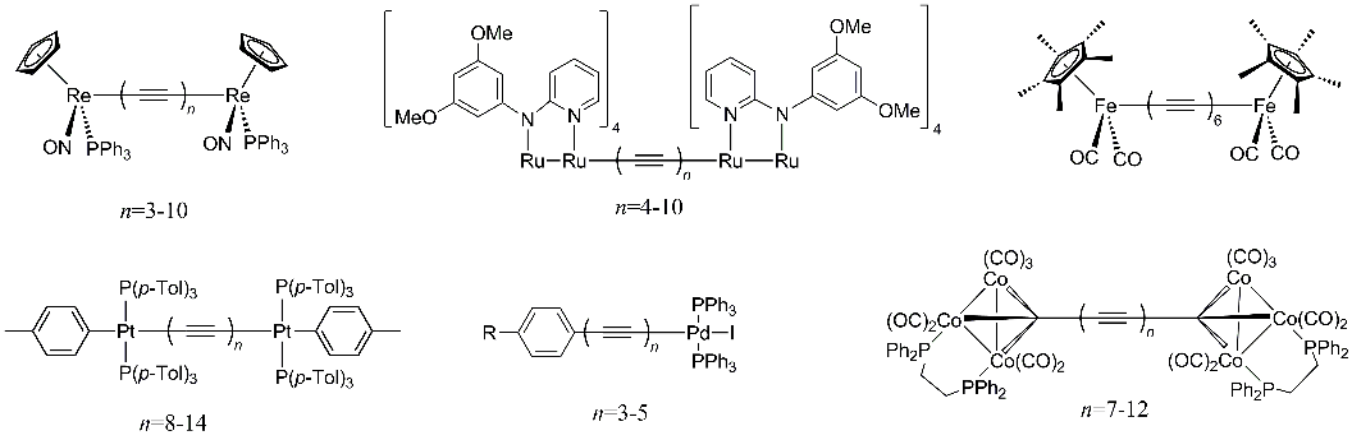


Figure 6.6.5.1: Examples of known polyyne organometallic complexes. (Pigulski, Organometallic polyynes, CC BY-SA 4.0)

Source: https://en.Wikipedia.org/wiki/Polyyne

This page titled 6.6.5: Carbon Wires- Polyyne and Polyene Bridges is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

6.7: Characterization of Organometallic Complexes

Learning Objectives

In this lecture you will learn the following

- The characterization techniques of organometallic compounds.
- The NMR analysis of these compounds.
- The IR analysis of these compounds.
- The X-ray single crystal diffraction studies of these compounds.

The characterization of an organometallic complex involves obtaining a complete understanding of the same right from its identification to the assessment of its purity content, to even elucidation of its stereochemical features. Detailed structural understanding of the organometallic compounds is critical for obtaining an insight on its properties and which is achieved based on the structure-property paradigm.

Synthesis and isolation

Synthesis and isolation are two very important experimental protocols in the overall scheme of things of organometallic chemistry and thus these needs to be performed carefully. The isolation of the organometallic compounds is essential for their characterization and reactivity studies. Fortunately, many of the methods of organic chemistry can be used in organometallic chemistry as the organometallic compounds are mostly nonvolatile crystalline solids at room temperature and atmospheric pressure though a few examples of these compounds are known to exist in the liquid [$(CH_3C_5H_4Mn(CO)_3$] and even in the vapor [$Ni(CO)_4$] states. The organometallic compounds are comparatively more sensitive to aerial oxygen and moisture, and because of which the manipulation of these compounds requires stringent experimental skills to constantly provide them with anaerobic environment for their protection. All of these necessities led to the development of the so-called special Schlenk techniques, requiring special glasswares and which in conjunction with a high vacuum line and a dry box allow the lab bench-top manipulation of these compounds. Successful isolation of organometallic compounds naturally points to the need for various spectroscopic techniques for their characterizations and some of the important ones are discussed below.

1H NMR spectroscopy

The ^1H NMR spectroscopy is among the extensively used techniques for the characterization of organometallic compounds. Of particular interest is the application of ^1H NMR spectroscopy in the characterization of the metal hydride complexes, for which the metal hydride moiety appear at a distinct chemical shift range between 0 ppm to −40 ppm to the high field of tetramethyl silane (TMS). This upfield shift of the metal hydride moiety is attributed to a shielding by metal *d*−electrons and the extent of the upfield shift increases with higher the d^n configuration. Chemical shifts, peak intensities as well as coupling constants from the through-bond couplings between adjacent nuclei like that of the observation of $J_{P\text{-}H}$, if a phosphorous nucleus is present within the coupling range of a proton nucleus, are often used for the analysis of these compounds. The ^1H NMR spectroscopy is often successfully employed in studying more complex issues like fluxionality and diastereotopy in organometallic molecules (Figure 6.7.1).

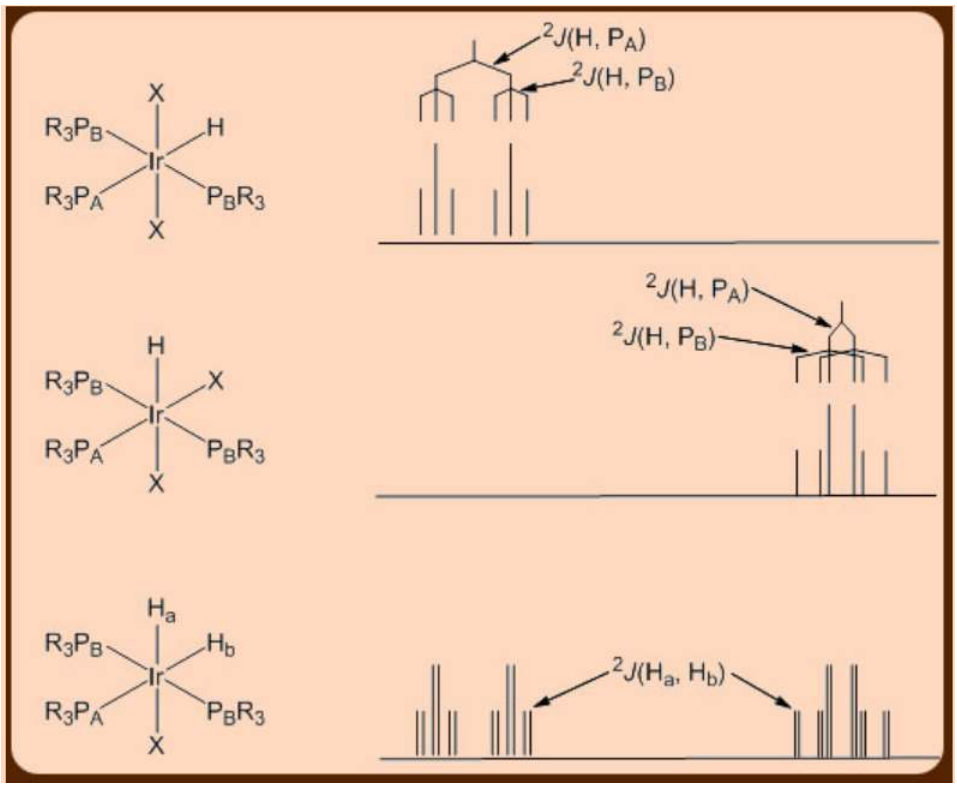


Figure 6.7.1: Different phosphorous-proton coupling patterns in various iridium hydride complexes.

The paramagnetic organometallic complexes show a large range of chemical shifts, for example, $(\eta^6{-}C_6H_6)_2V$ exhibits proton resonances that extend even up to 290 ppm.

13C NMR spectroscopy

Although the natural abundance of NMR active ^{13}C (I = ½) nuclei is only 1 %, it is possible to obtain a proton decoupled $^{13}C\{^1H\}$ NMR spectra for most of the organometallic complexes. In addition, the off−resonance ^1H decoupled ^{13}C experiments yield $^1J_{C\text{-}H}$ coupling constants, which contain vital structural information, and hence are very critical to the ^{13}C NMR spectral analysis. For example, the $^1J_{C\text{-}H}$ coupling constants directly correlate with the hybridization of the C−H bonds with *sp* center exhibiting a $^1J_{C\text{-}H}$ coupling constant of ~250 Hz, a sp^2 center of 160 Hz and a sp^3 center of 125 Hz. Similar to what is seen in ^1H NMR, a phosphorous−carbon coupling is also observed in a ^{13}C NMR spectrum with the *trans* coupling (~100 Hz) being larger than the *cis* coupling (~10 Hz).

^{31}P NMR spectroscopy

The ^{31}P NMR spectroscopy, which in conjunction with ^1H and ^{13}C NMR spectroscopies, is a useful technique in studying the phosphine containing organometallic complexes. The ^{31}P NMR experiments are routinely run under ^1H decoupled conditions for simplification of the spectral features that allow convenience in spectral analysis. Thus, for this very reason, many mechanistic studies on catalytic cycle are conveniently undertaken by ^{31}P NMR spectroscopy whenever applicable.

IR spectroscopy

Qualitative to semi-quantitative analysis of organometallic compounds using IR spectroscopy are performed whenever possible. In general the signature stretching vibrations for chemical bonds are more conveniently looked at in these studies. The frequency (ν) of a stretching vibration of a covalent bond is directly proportional to the strength of the bond, usually given by the force constant (k) and inversely proportional to the reduced mass of the system, which relates to the masses of the individual atoms.

$$\nu = \frac{1}{2\pi C}\sqrt{\frac{k}{m_r}}$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

The organometallic compounds containing carbonyl groups are regularly studied using IR spectroscopy, and in which the CO peaks appear in the range between 2100−1700 cm^{-1} as distinctly intense peaks.

Crystallography

The solid state structure elucidation using single crystal diffraction studies are extremely useful techniques for the characterization of the organometallic compounds and for which the X-ray diffraction and neutron diffraction studies are often undertaken. As these methods give a three dimensional structural rendition at a molecular level, they are of significant importance among the various available characterization methods. The X-ray diffraction technique is founded on Bragg's law that explains the diffraction pattern arising out of a repetitive arrangement of the atoms located at the crystal lattices.

$$2d\sin\theta = n\lambda$$

A major limitation of the X-ray diffraction is that the technique is not sensitive enough to detect the hydrogen atoms, which appear as weak peaks as opposed to intense peaks arising out of the more electron rich metal atoms, and hence are not very useful for metal hydride compounds. Neutron diffraction studies can detect hydrogens more accurately and thus are good for the analysis of the metal hydride complexes.

Summary

Along with the synthesis, the isolation and the characterization protocols are also integral part of the experimental organometallic chemistry. Because of their air and moisture sensitivities, specialized experimental techniques that succeed in performing the synthesis, isolation and storage of these compounds in an air and moisture-free environment are often used. The organometallic compounds are characterized by various spectroscopic techniques including the ^{1}H NMR, ^{13}C NMR and IR spectroscopies and the X-ray and the neutron diffraction studies.

This page titled 6.7: Characterization of Organometallic Complexes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by M. S. Balakrishna & Prasenjit Ghosh via source content that was edited to the style and standards of the LibreTexts platform.

- **12.1: Characterization of Organometallic Complexes** by M. S. Balakrishna & Prasenjit Ghosh is licensed CC BY-NC-SA 4.0. Original source: https://nptel.ac.in/courses/104101006.

CHAPTER OVERVIEW

7: Organometallic Reactions and Catalysis

Introduction

This chapter is a survey of common organometallic reactions and catalytic cycles. The reactions of organometallic complexes are divided into two main categories: (1) Reactions that involve gain or loss of ligands, and (2) Reactions involving modification of ligands.

7.1: Reactions Involving Gain or Loss of Ligands
- 7.1.1: Ligand Dissociation and Substitution
- 7.1.2: Oxidative Addition
- 7.1.3: Reductive Elimination
- 7.1.4: Sigma Bond Metathasis
- 7.1.5: Application of Pincer Ligands

7.2: Reactions Invloving Modification of Unsaturated Ligands
- 7.2.1: Introduction to Insertion
- 7.2.2: CO Insertions (Alkyl Migration)
- 7.2.3: Migratory Insertion-1,2-Insertions
- 7.2.4: β-Elimination Reactions
- 7.2.5: Abstraction and Addition

7.3: Organometallic Catalysts
- 7.3.1: Catalytic Deuteration
- 7.3.2: Hydroformylation
- 7.3.3: Monsanto Acetic Acid Process
- 7.3.4: Wacker (Smidt) Process
- 7.3.5: Hydrogenation by Wilkinson's Catalyst
- 7.3.6: Olefin Metathesis

7.4: Heterogeneous Catalysts
- 7.4.1: Ziegler-Natta Polymerizations
- 7.4.2: Water-Gas Shift Reaction

7.5: Problems
- 7.5.1: Concept Review Questions Chapter 12
- 7.5.2: Homework Problems Chapter 12

This page titled 7: Organometallic Reactions and Catalysis is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

SECTION OVERVIEW

7.1: Reactions Involving Gain or Loss of Ligands

Many reactions of organometallic complexes involve change in coordination number. In a dissociation reaction, one or more ligands are eliminated from the complex and the coordination number decreases. In an association, one or more ligands are added to the complex and the coordination number increases. If the coordination number changes while the metal oxidation state remains constant, the reactions are considered **association/addition** reactions or **dissociation** reactions. Reactions can also occur where the coordination number changes while the metal oxidation state also changes. These reactions are considered **reductive eliminations** or **oxidative additions** (or a combination of these).

Types of reactions involving gain or loss of ligands

- **Association or Addition Reaction**: a reaction in which the coordination number increases; metal oxidation state is unchanged.
- **Dissociation Reaction**: a reaction in which the coordination number decreases; metal oxidation state is unchanged.
- **Oxidative Addition**: a reaction in which coordination number increases while metal oxidation state increases.
- **Reductive Elimination**: a reaction in which coordination number decreases while metal oxidation state decreases.

7.1.1: Ligand Dissociation and Substitution

7.1.2: Oxidative Addition

7.1.3: Reductive Elimination

7.1.4: Sigma Bond Metathasis

7.1.5: Application of Pincer Ligands

This page titled 7.1: Reactions Involving Gain or Loss of Ligands is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.1.1: Ligand Dissociation and Substitution

As discussed in Chapter 13, ligand substitution is characterized by a continuum of mechanisms bound by associative (A) and dissociative (D) extremes. At the associative extreme, the first step is an Associative reaction; the incoming ligand forms a bond to the metal and creates an intermediate of higher coordination number. Then the departing ligand takes its lone pair and leaves. At the dissociative extreme, the fist step is a Dissociative reaction and the order of events is opposite; a ligand departs and a new complex with lower coordination number forms. Then, a new ligand associates with the complex in the second step. Sometimes, instead of reacting, the "intermediate" is simply a stable complex with a different coordination number than the reactant.

The most common reactions that are used to create new complexes are Dissociations and Substitutions (involving both Dissociation and Association steps). Associative substitution is common for 16-electron complexes (like d^8 complexes of Ni, Pd, and Pt), while both Dissociation and Dissociative Substitution are the norm for 18-electron complexes. Then again, reality is often more complicated than these extremes. In some cases, evidence is available for interchange (I_a or I_d).

In this subsection, we'll explore ligand substitution reactions and mechanisms in the context of organometallic chemistry. We'd like to be able to (a) predict whether a mechanism is likely to be associative or dissociative; (b) propose a reasonable mechanism from given experimental data; and (c) describe the results we'd expect given a particular mechanism. Keep these goals in mind as you learn the theoretical and experimental nuts and bolts of substitution reactions.

Dissociation

Carbonyl compounds are known to undergo dissociation reactions upon heating or irradiation with light. For example, upon heating, the the cyclopentadienylmolybdenum tricarbonyl dimer ($Cp_2Mo_2(CO)_6$), where Cp is the cyclopentadienyl ligand) loses a CO ligand from each Mo ion, and a triple bond between the Mo ions is formed (Top, Figure 7.1.1.1). An example of a photoactivated dissociation of CO is the case of neutral iron pentacarbonyl, $Fe(CO)_5$. Irradiation of $Fe(CO)_5$ with UV produces $Fe(CO)_4$ (Bottom, Figure 7.1.1.1).

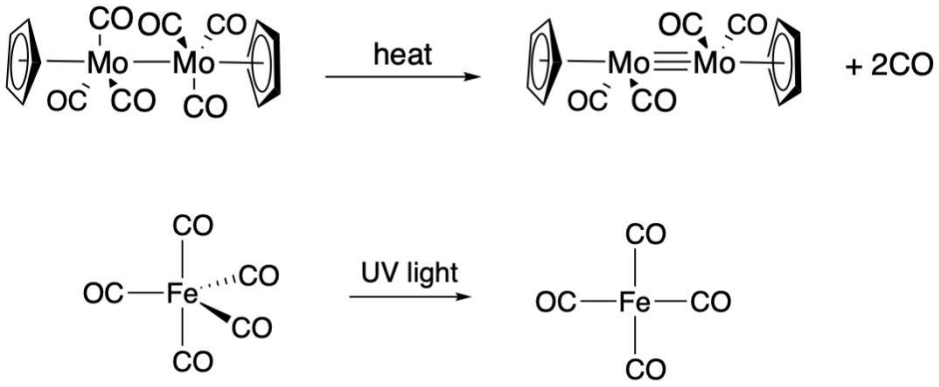


Figure 7.1.1.1: Dissociation reactions: Top, the thermally-activated dissociation of CO from cyclopentadienylmolybdenum tricarbonyl dimer. Bottom, the photochemically-activated dissociation of CO from ironpentacarbonyl. (CC-BY-SA; Kathryn Haas)

However, in each of the cases shown above, the product complex is reactive toward ligand association, usually resulting in an overall substitution. The cyclopentadienylmolybdenum dicarbonyl dimer shown on the top of Figure 7.1.1.1 binds a variety of substrates across the metal-metal triple bond. And the iron tetracarbonyl complex shown on the bottom in Figure 7.1.1.1 readily captures a variety of ligands to result in an overall substitution (example given below); when a ligand doe not associate with it, $Fe_2(CO)_9$ is produced.

Sources: Iron Pentacarbonyl and Cyclopentadienylmolybdenum tricarbonyl dimer articles from Wikipedia.

Dissociative Substitution

Associative substitution is unlikely for saturated, 18-electron complexes—coordination of another ligand would produce a 20-electron intermediate. For 18-electron complexes, dissociative substitution mechanisms involving 16-electron intermediates are more likely. In a slow step with positive entropy of activation, the departing ligand leaves, generating a coordinatively unsaturated

intermediate. The incoming ligand then enters the coordination sphere of the metal to generate the product. For the remainder of this post, we'll focus on the kinetics of the reaction and the nature of the unsaturated intermediate (which influences the stereochemistry of the reaction). The reverse of the first step, re-coordination of the departing ligand (rate constant k–1), is often competitive with dissociation.

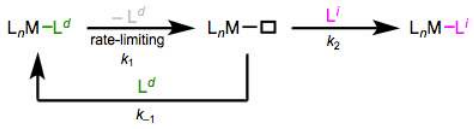


Figure 7.1.1.7: A general scheme for dissociative ligand substitution. There's more to the intermediate than meets the eye! (Michael Evans)

Reaction Kinetics

Let's begin with the general situation in which k_1 and k_{-1} are similar in magnitude. Since k_1 is rate limiting, k_2 is assumed to be much larger than k_1 and k_{-1}. Most importantly, we need to assume that variation in the concentration of the unsaturated intermediate is essentially zero. This is called the steady state approximation, and it allows us to set up an equation that relates reaction rate to observable concentrations Hold onto that for a second; first, we can use step 2 to establish a preliminary rate expression.

$$\text{rate} = k_2[L_nM\text{–}\lozenge][Li] \tag{1}$$

Of course, the unsaturated complex is present in very small concentration and is unmeasurable, so this equation doesn't help us much. We need to remove the concentration of the unmeasurable intermediate from (1), and the steady state approximation helps us do this. We can express variation in the concentration of the unsaturated intermediate as (processes that make it) minus (processes that destroy it), multiplying by an arbitrary time length to make the units work out. All of that equals zero, according to the SS approximation. The painful math is almost over! Since Δt must not be zero, the other factor, the collection of terms, must equal zero.

$$\Delta[L_nM\text{–}\lozenge] = 0 = (k1[L_nM\text{–}L^d]\text{–}k\text{–}1[L_nM\text{–}\lozenge][L^d]\text{–}k_2[L_nM\text{–}\lozenge][Li])\Delta t \tag{2}$$

$$0 = k_1[L_nM\text{–}Ld]\text{–}k_{-1}[L_nM\text{–}\lozenge][Ld]\text{–}k_2[L_nM\text{–}\lozenge][Li] \tag{3}$$

Rearranging to solve for $[L_nM\text{–}\lozenge]$, we arrive at the following.

$$[L_nM\text{–}\lozenge] = k_1\frac{[L_nM\text{–}L_d]}{(k_{-1}[L_d] + k_2[Li]} \tag{4}$$

Finally, substituting into equation (1) we reach a verifiable rate equation.

$$\text{rate} = k_2k_1\frac{[L_nM\text{–}Ld][Li]}{(k_{-1}[L_d] + k_2[Li]} \tag{5}$$

When k_{-1} is negligibly small, (5) reduces to the familiar equation (6), typical of dissociative reactions like S_N1.

$$\text{rate} = k_1[L_nM\text{–}L_d] \tag{6}$$

Unlike the associative rate law, this rate does not depend on the concentration of incoming ligand. For reactions that are better described by (5), we can drown the reaction in incoming ligand to make $k_2[Li]$ far greater than $k_{-1}[Ld]$, essentially forcing the reaction to fit equation (6).

The Unsaturated Intermediate & Stereochemistry

Dissociation of a ligand from an octahedral complex generates an usaturated ML5 intermediate. When all five of the remaining ligands are L-type, as in Cr(CO)5, the metal has 6 d electrons for a total electron count of 16. The trigonal bipyramidal geometry presents electronic problems (unpaired electrons) for 6 d electrons, as the figure below shows. The orbital energy levels come from crystal field theory. Distortion to a square pyramid or a distorted TBP geometry removes the electronic issue, and so five-coordinate d6 complexes typically have square pyramidal or distorted TBP geometries. This is just the geometry prediction process in action!

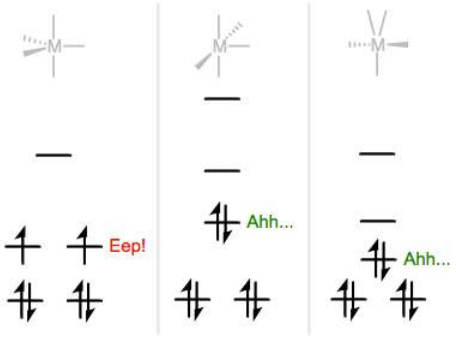


Figure 7.1.1.8: TBP geometry is electronically disfavored for d6 metals. Distorted TBP and SP geometries are favored. (Michael Evans)

When the intermediate adopts square pyramidal geometry (favored for good π-acceptors and σ-donors…why?), the incoming ligand can simply approach where the departing ligand left, resulting in retention of stereochemistry. Inversion is more likely when the intermediate is a distorted trigonal bipyramid (favored for good π-donors). As we've already seen for associative substitution, fluxionality in the five-coordinate intermediate can complicate the stereochemistry of the reaction.

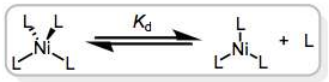
Encouraging Dissocative Substitution

In general, introducing structural features that either stabilize the unsaturated intermediate or destabilize the starting complex can encourage dissociative substitution. Both of these strategies lower the activation barrier for the reaction. Other, quirky ways to encourage dissociation include photochemical methods, oxidation/reduction, and ligand abstraction.

Let's begin with features that stabilize the unsaturated intermediate. Electronically, the intermediate loves it when its d electron count is nicely matched to its crystal field orbitals. As you study organometallic chemistry, you'll learn that there are certain "natural" d electron counts for particular geometries that fit well with the metal-centered orbitals predicted by crystal field theory. Octahedral geometry is great for six d electrons, for example, and square planar geometry loves eight d electrons. Complexes with "natural" d electron counts—but bearing one extra ligand—are ripe for dissociative substitution. The classic examples are d8 TBP complexes, which become d8 square planar complexes (think Pt(II) and Pd(II)) upon dissociation. Similar factors actually stabilize starting 18-electron complexes, making them less reactive in dissociative substitution reactions. d6 octahedral complexes are particularly happy, and react most slowly in dissociative substitutions. The three most common types of 18-electron complexes, from fastest to slowest at dissociative substitution, are:

$$d^8 \text{ TBP} > d^10 \text{ tetrahedral} > d^6 \text{ octahedral}$$

Destabilization of the starting complex is commonly accomplished by adding steric bulk to its ligands. Naturally, dissociation relieves steric congestion in the starting complex. Chelation has the opposite effect, and tends to steel the starting complex against dissociation.



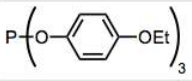
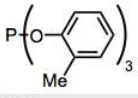
L	Cone Angle	K_d
$P(OEt)_3$	109	$< 10^{-10}$
	128	$6 * 10^{-10}$
$P(Oi\text{-}Pr)_3$	130	$2.7 * 10^{-5}$
	141	$4 * 10^{-2}$
PPh_3	145	huge

Figure 7.1.1.9: As steric bulk on the ligand increases, dissociation becomes more favorable. (Michael Evans)

I plan to cover the "quirky" methods in a post of their own, but these include strategies like N-oxides for CO removal, photochemical cleavage of the metal–departing ligand bond, and the use of silver cation to abstract halide ligands. Oxidation and

reduction can also be used to encourage substitution: 17- and 19-electron complexes are much more reactive toward substitution than their 18-electron analogues.

Associative Substitutions

Despite the sanctity of the 18-electron rule in organometallic chemistry, a wide variety of stable complexes possess fewer than 18 total electrons at the metal center. Perhaps the most famous examples of these complexes are 14- and 16-electron complexes of group 10 metals (Ni, Pt, Pd). Ligand substitution in complexes of this class typically occurs via an associative mechanism, involving approach of the incoming ligand to the complex before departure of the leaving group. If we keep this principle in mind, it seems easy enough to predict when ligand substitution is likely to be associative. But how can we spot an associative mechanism in experimental data, and what are some of the consequences of this mechanism?

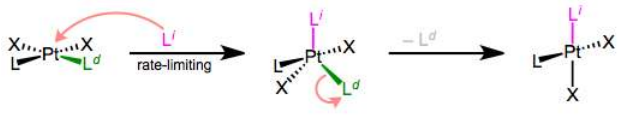


Figure 7.1.1.2: Associative substitution. (Michael Evans)

The prototypical mechanism of associative ligand substitution. The first step is rate-determining. A typical mechanism for associative ligand substitution is shown above. It should be noted that square pyramidal geometry is also possible for the intermediate, but is less common. Let's begin with the kinetics of the reaction.

Reaction Kinetics for Associative Reactions

Reaction kinetics are commonly used to elucidate organometallic reaction mechanisms, and ligand substitution is no exception. Different mechanisms of substitution may follow different rate laws, so plotting the dependence of reaction rate on concentration often allows us to distinguish mechanisms. Associative substitution's rate law is analogous to that of the S_N2 reaction—rate depends on the concentrations of both starting materials.

$$L_nM\text{–}L^d + L_i \rightarrow L_nM\text{–}L_i + L^d \tag{7.1.1.1}$$

$$\frac{d[L_nM\text{–}L^i]}{dt} = rate = k_1[L_nM\text{–}L^d][L^i] \tag{7.1.1.2}$$

The easiest way to determine this rate law is to use pseudo-first-order conditions. Although the rate law is second order overall, if we could somehow render the concentration of the incoming ligand unchanging, the reaction would appear first order. The observed rate constant under these conditions reflects the constancy of the incoming ligand's concentration ($k_{obs} = k_1[L^i]$, where both k_1 and $[Li]$ are constants). How can we make the concentration of the incoming ligand invariant, you ask? We can drown the reaction in ligand to achieve this. The teensy weensy bit actually used up in the reaction has a negligible effect on the concentration of the "sea" of starting ligand we began with. The observed rate is equal to $k_{obs}[L_nM\text{–}L^d]$, as shown by the purple trace below. By determining k_{obs} at a variety of $[L^i]$ values, we can finally isolate k_1, the rate constant for the slow step. The red trace below at right shows the idea.

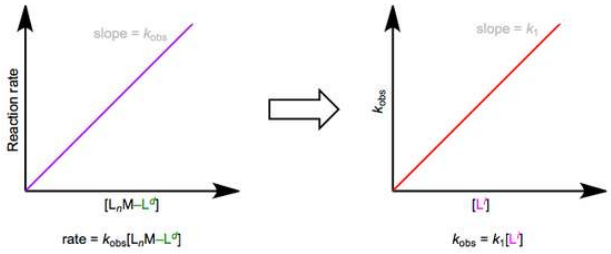


Figure 7.1.1.3: Associative substitution under pseudo-first-order conditions. The reaction is "swamped out" with incoming ligand. (Michael Evans)

In many cases, the red trace ends up with a non-zero y-intercept…curious, if we limit ourselves to the simple mechanism shown in the first figure of this post. A non-zero intercept suggests a more complex mechanism. We need to add a new term (called k_s for reasons to become clear shortly) to our first set of equations:

$$rate = (k_1[L_i] + k_s)[L_nM\text{–}L^d] \tag{7.1.1.3}$$

$$k_{obs} = k_1[L_i] + k_s \tag{7.1.1.4}$$

The full rate law suggests that some other step (with rate ks[LnM–Ld]) independent of incoming ligand is involved in the mechanism. To explain this observation, we can invoke the solvent as a reactant. Solvent can associate with the complex first in a slow step, then incoming ligand can displace the solvent in a fast step. Solvent concentration doesn't enter the rate law because, well, it's drowning the reactants and its concentration undergoes negligible change! An example of this mechanism in the context of Pt(II) chemistry is shown below.

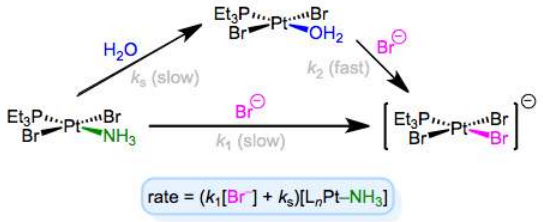


Figure 7.1.1.4: Associative substitution with solvent participation—a head-scratching mechanism for many an organometallic grad student! (Michael Evans)

As an aside, it's worth mentioning that the entropy of activation of associative substitution is typically negative. Entropy decreases as the incoming ligand and complex come together in the rate-determining step. Dissociative substitution shows the opposite behavior: loss of the departing ligand in the RDS increases entropy, resulting in positive entropy of activation.

Stereochemistry of Associative Substitution

As we saw in discussions of the trans effect, the entering and departing ligands both occupy equatorial positions in the trigonal bipyramidal intermediate. Microscopic reversibility is to blame: the mechanism of the forward substitution (displacement of the leaving by the incoming ligand) must be the same as the mechanism of the reverse reaction (displacement of the incoming by the leaving ligand). This can be a confusing point, so let's examine an alternative mechanism that violates microscopic reversibility.

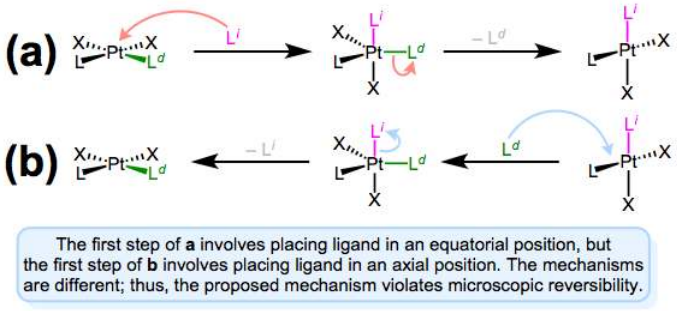


Figure 7.1.1.5: A mechanism involving approach to an axial position and departure from an equatorial position violates microscopic reversibility. Forward and reverse reactions a and b differ! (Michael Evans)

The figure above shows why a mechanism involving axial approach and equatorial departure (or vice versa) is not possible. The forward and reverse reactions differ, in fact, in both steps. In forward mechanism a, the incoming ligand enters an axial site. But in the reverse reaction, the incoming ligand (viz., the departing ligand in mechanism a) sits on an equatorial site. The second steps of each mechanism differ too—a involves loss of an equatorial ligand, while b involves loss of an axial ligand. Long story short, this mechanism violates microscopic reversibility. And what about a mechanism involving axial approach and axial departure? Such a mechanism is unlikely on electronic grounds. The equatorial sites are more electron rich than the axial sites, and σ bonding to the axial d_{z^2} orbital is expected to be strong. Intuitively, then, loss of ligand from an axial site is less favorable than loss from an equatorial site.

I know what you're thinking: what the heck does all of this have to do with stereochemistry? Notice that, in the equatorial-equatorial mechanism (first figure of this post), the axial ligands don't move at all. The configuration of the starting complex is thus retained in the product. Although retention is "normal," complications often arise because five-coordinate TBP complexes—like other odd-coordinate organometallic complexes—are often fluxional. Axial and equatorial ligands can rapidly exchange through a process called Berry pseudorotation, which resembles the axial ligands "cutting through" a pair of equatorial ligands like scissors (animation!). Fluxionality means that all stereochemical bets are off, since any ligand can feasibly occupy an equatorial site. In the example below, the departing ligand starts out cis to L, but the incoming ligand ends up trans to L.

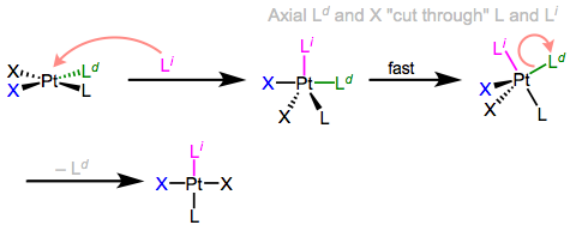


Figure 7.1.1.6: Berry pseudorotation in the midst of associative ligand substitution. (Michael Evans)

Associative Substitution in 18-electron Complexes?

Associative substitution can occur in 18-electron complexes if it's preceded by the dissociation of a ligand. For example, changes in the hapticity of cyclopentadienyl or indenyl ligands may open up a coordination site, which can be occupied by a new ligand to kick off associative substitution. An allyl ligand may convert from its π to σ form, leaving an open coordination site where the π bond left. A particularly interesting case is the **nitrosyl ligand**—conversion from its linear to bent form opens up a site for coordination of an external ligand.

Summary of Associative Substitution

Associative ligand substitution is common for complexes with 16 total electrons or fewer. The reaction is characterized by a second-order rate law, the possibility of solvent participation, and a trigonal bipyramidal intermediate that is often fluxional. An open coordination site is essential for associative substitution, but such sites are often hidden in the dynamism of 18-electron complexes with labile ligands.

Dr. Michael Evans (Georgia Tech)

Quirky Substitutions

Over the years, a variety of "quirky" substitution methods have been developed. All of these have the common goal of facilitating substitution in complexes that would otherwise be inert. It's an age-old challenge: how can we turn a stable complex into something unstable enough to react? Photochemical excitation, oxidation/reduction, and radical chains all do the job, and have all been well studied. We'll look at a few examples in this post—remember these methods when simple associative or dissociative substitution won't get the job done.

Photochemical Substitution

Substitution reactions of dative ligands—most famously, CO—may be facilitated by photochemical excitation. We just discussed the photochemically-activated dissociation of CO from ironpentacarbonyl above; that reaction is often used to accomplish substitution of a CO ligand. Other CO complexes also undergo photochemically-activated CO substitution reactions. Two examples are shown below. The first reaction yields only monosubstituted product without ultraviolet light, even in the presence of a strongly donating phosphine.

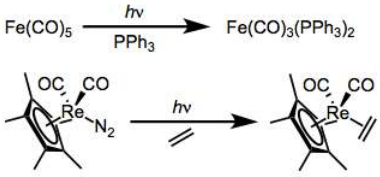


Figure 7.1.1.10:Dissociative photochemical substitutions of CO and dinitrogen. (Michael Evans)

All signs point to dissociative mechanisms for these reactions (the starting complexes have 18 total electrons each). Excitation, then, must increase the M–L antibonding character of the complex's electrons; exactly how this increase in antibonding character happens has been a matter of some debate. Originally, the prevailing explanation was that the LUMO bears M–L antibonding character, and excitation kicks an electron up from the HOMO to the LUMO, encouraging cleavage of the M–L bond. A more recent, more subtle explanation backed by calculations supports the involvement of a metal-to-ligand charge-transfer state along with the "classical" ligand-field excited state.

Oxidation/Reduction

Imagine a screaming baby without her pacifier—that's a nice analogy for an odd-electron organometallic complex. Complexes bearing 17 and 19 total electrons are much more reactive toward substitution than their even-electron counterparts. Single-electron oxidation and reduction ("popping out the pacifier," if you will) can thus be used to efficiently turn on substitution. As you might expect, oxidation and reduction work best on electron-rich and electron-poor complexes, respectively. The Mn complex in the oxidative example below, for instance, includes a strongly donating MeCp group (not shown).

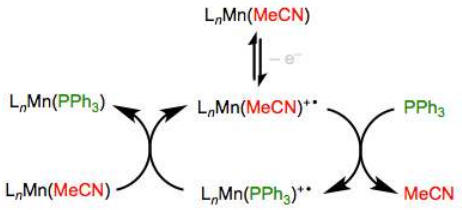


Figure 7.1.1.11: Oxidation accelerates substitution in electron-rich complexes through a chain process. (Michael Evans)

Reduction works well for electron-poor metal carbonyl complexes, which are happy to accept an additional electron.

There is a two-electron oxidation method that's also worth knowing: the oxidation of CO with amine oxides. This nifty little method releases carbon dioxide, amine, and an unsaturated complex that may be quenched by a ligand hanging around. The trick is addition to the CO ligand followed by elimination of the unsaturated complex. As the oxidized CO2 and reduced amine float away, the metal complex finds another ligand.

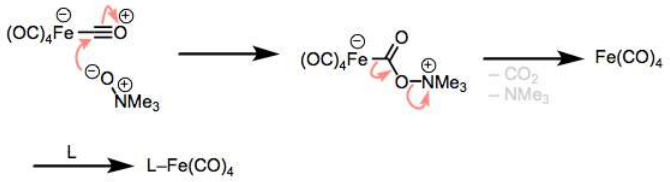


Figure 7.1.1.12: Oxidation of CO with amine oxides. A fun method for dissociative substitution of metal carbonyls! (Michael Evans)

Radical Chain Processes

Atom abstraction from 18-electron complexes produces neutral 17-electron intermediates, which are susceptible to ligand substitution via radical chain mechanisms. The fact that the intermediates are neutral distinguishes these methods from oxidation-based methods. First-row metal hydrides are great for these reactions, owing to their relatively weak M–H bonds. One example is shown below.

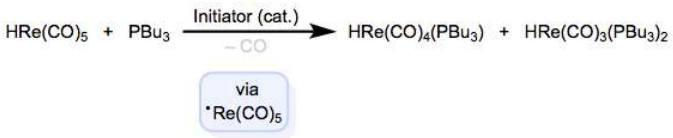


Figure 7.1.1.13: Radical-chain substitution involving atom abstraction. (Michael Evans)

After abstraction of the hydrogen atom by initiator, substitution is rapid and may occur multiple times. Propagation begins anew when the substituted radical abstracts hydrogen from the starting material to regenerate the propagating radical and form the product. These quirky methods are nice to have in your back pocket when you're backed into a synthetic corner—sometimes, conventional associative and dissociative substitution just won't do the job. In the next post, we'll press on to oxidative addition.

Template:Evans

This page titled 7.1.1: Ligand Dissociation and Substitution is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **4.4: Ligand substitution** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **4.3: Dissociative Ligand Substitution Reactions** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **4.2: Associative Ligand Substitution** by Michael Evans is licensed CC BY-NC-SA 4.0.
- **4.10: Quirky Ligand Substitutions** by Michael Evans is licensed CC BY-NC-SA 4.0.

7.1.2: Oxidative Addition

An **oxidative addition** is a reaction in which the coordination number and the oxidation state of the metal ion both increase by 2. In other words, the metal becomes oxidized by two electrons as the coordination number increases by 2 ligands. The microscopic reverse of oxidative addition is reductive elimination (discussed in the next section).

Oxidative addition can occur in a cis- or trans-fashion. A cis-addition means that two ligands are added so that they have cis-orientation to each other after the reaction is complete. A trans-addition implies that two new ligands are in opposite, trans-position after they have been added. We can further distinguish between mononuclear and dinuclear additions. Mononuclear addition involves a complex with a single metal. Dinuclear additions are additions to a metal-metal bond. The addition cleaves the metal-metal bond and adds one ligand to each fragment.

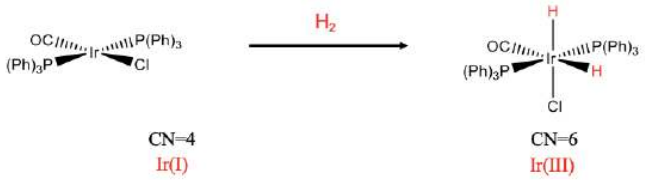


Figure 7.1.2.1: Mononuclear oxidative cis-addition (Attribution: A. Vedernikov, U Maryland (modified))

Let's explore a few examples. The first example is a mononuclear cis-addition (Fig. 7.1.2.1). In the reaction we add dihydrogen to a square planar iridium complex. After the reaction there are two additional hydrido ligands, and the coordination number has increased from 4 to 6. We can see that the two hydrido ligands are oriented in cis-fashion relative to each other. We can verify that the addition of the hydrido ligands oxidized the metal by determining the oxidation number of the metal before and after the reaction. There are three neutral ligands and one negatively charged chloro ligand. There is no overall charge at the complex. This means that the oxidation number of Ir is +1. After the reaction, there are the two hydrido ligands that have both a -1 charge. Remember, we get the charge at a ligand by cleaving the metal-ligand bond so that all electrons in the bond get assigned to the ligand. This means the oxidation number must be increased by +2, and is +3 after the reaction.

We can rationalize why the addition occurs in cis-fashion and not in trans-fashion. The two hydrido ligands are the smallest ligands, therefore, steric repulsion is minimized in the complex is minimized when the two hydrido ligands are in cis-position.

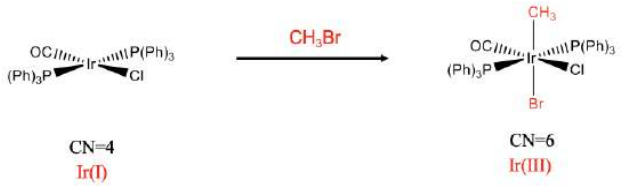


Figure 7.1.2.2: Mononuclear oxidative trans-addition (Attribution: A. Vedernikov, U Maryland (modified))

The second example is a mononuclear trans-addition (Fig. 7.1.2.2). In this reaction CH_3Br is added to the iridium complex. In this case the two new ligands, a CH_3 and the Br group are in opposite position. Again, the coordination number increases from four to six. We can again verify that an oxidation has occurred by analyzing the oxidation number of Ir. As previously determined, the oxidation number of iridium in the reactant complex is +1. Let us analyze the product complex. The chloro ligand and the bromo ligand have a 1- charge. In addition to that also the CH_3 ligand has a 1- charge assuming that we treat the Ir-C bond as a dative bond. Thus, the oxidation number of Ir must be +3 to give a neutral complex.

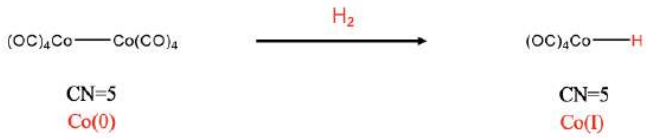


Figure 7.1.2.3: Dinuclear addition (Attribution: A. Vedernikov, U Maryland (modified))

The third example is a dinuclear addition (Fig. 7.1.2.3). This addition is neither cis nor trans because it cleaves a metal-metal bond, and the one new ligand is added to each fragment. In the example the Co-Co bond of the dicobalt octacarbonyl gets cleaved upon the reaction with dihydrogen, and two $HCo(CO)_4$ complexes with Co-H bonds form. In this case the coordination number does not

increase. Both the reactant and the products have the coordination number 5. We can see that an oxidation of Co has occurred by comparing the oxidation numbers. In the reactant the oxidation number of Co is zero because all CO ligands are neutral and the complex is overall neutral. In the carbonyl hydride product, Co has the oxidation number +1, because the hydrido ligand has a 1- charge.

Oxidative Additions with Intact Ligands

In the previous examples, the ligands that reacted with the complexes lost their integrity. The H-H bond in the H_2 molecule cleaved to form the hydrido ligands, and the C-Br bond in CH_3Br was cleaved to form separate Br and methyl ligands. Not all ligands lose their integrity upon their addition, in particular when they contain multiple bonds. These ligands are called intact ligands. In these cases the bond order *between two atoms in the ligand* is decreased, but the bond order is still at least 1. For example, the alkyne ligand shown belo decreases from a carbon-carbon bond order of three to a bond order of two after it binds to Pt.

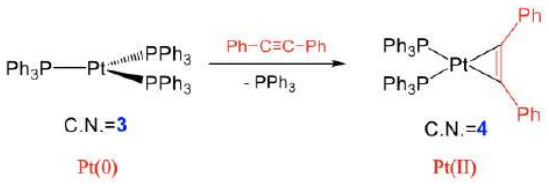


Figure 7.1.2.4: Oxidative addition with intact ligands (Attribution: A. Vedernikov, U Maryland (modified))

Examples for intact ligands are are alkenes, alkynes, O_2, etc. In an oxidative addition with an alkyne for example, the alkyne binds side-on to the transition metal under the formation of two metal-C single bonds, and the reduction of the bond order within the alkyne from 3 to 2 (Fig. 7.1.2.4). In the shown reaction, a diphenyl ethine molecule adds to tris(triphenyl phosphine) platinum under the formation of two Pt-C single bonds. The C-C triple bond in the ligand becomes a double bond. This reaction occurs under loss of one of the three triphenyl phosphine ligands. The coordination number at the metal increases from 3 to 4. We can again show that the reaction is oxidative by comparing the oxidation numbers of the metal. In the reactant, Pt has the oxidation number 0 because the three triphenyl phosphine ligands have no charge and the complex has overall no charge. After the reaction, the oxidation number of Pt is +2. This is because when we assign the four electrons of the two Pt-C single bonds to the ligand, the ligand becomes a $(Ph\text{-}C{=}C\text{-}Ph)^{2-}$ ligand with each C atom carrying a 1- charge. Because the product complex is overall neutral, the oxidation number of Pt is +2.

Nucleophilic Displacement Reactions

Another important reaction is the nucleophilic displacement reaction. This type of reaction can be classified as an oxidative addition although it does not strictly meet the definnition. In these reactions a metal complex (typically an anion) acts as a nucleophile. A ligand is added, but no electrons are added to the complex. The reactions can be extremely useful for the synthesis of organic compounds. The utility results mostly from the fact that an organic electrophile is turned into a nucleophile.

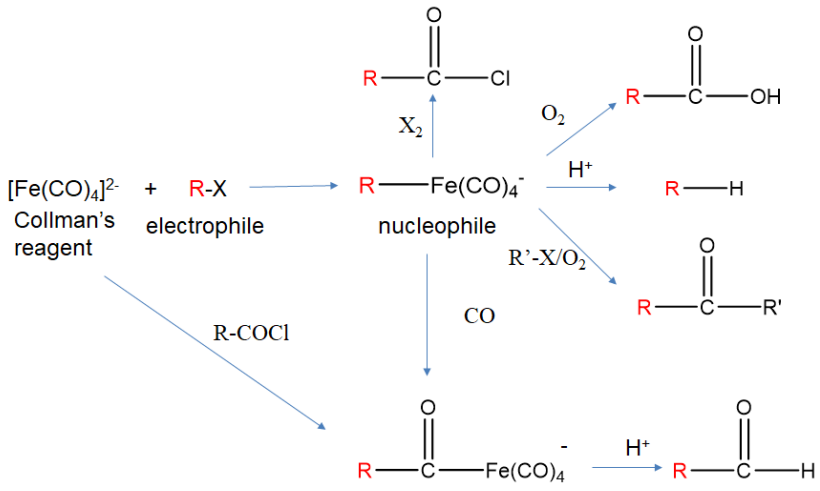


Figure 7.1.2.5: Mononuclear oxidative trans-addition (Attribution: A. Vedernikov, U Maryland (modified)): Examples of nucleophilic displacement reactions

For example, tetracarbonyl ferrate (2-), also known as Collman's reagent reacts with alkyl halides to form alkyl tetracarbonyl ferrate (-) (Fig. 7.1.2.5). We can check that the addition of the alkyl group did not add any electrons by counting the electrons before and after the reaction. The $Fe(CO)_4^{2-}$ anion is an 18e complex. Applying the neutral atom method to the electron counting in $[R\text{-}Fe(CO)_4]^-$ means that Fe contributes 8e, the 1- charge adds 1e, the CO ligands 4x2=8 electrons and the alkyl ligand 1e. This gives 8+1+8+1=18 electrons. Also the oxidation number of Fe has not changed upon the addition of the ligand. It is -2 before and after the reaction.

In the alkyltetracarbonyl ferrate (1-) anion, the group R which was formerly an electrophile in R-X, can now act as a nucleophile due to the fact that the Fe-C bond is polarized toward the C-atom. As a nucleophile it can for instance react with protons to form an alkane. It can also react with oxygen to form a carboxylic acid. In the presence of another alkyl halide R'-X it can form a ketone R-C(O)-R'. It can also insert CO into the Fe-C bonding in a so-called migratory insertion reaction, and the reaction product can react with acid to form an aldehyde. With dihalogens X_2 it can form acyl chloride. Collman's reagent cannot only add alkyl halides by also acyl halides to form acyl tetracarbonyl ferrates (-).

This page titled 7.1.2: Oxidative Addition is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.1: Organometallic reactions** by Kai Landskron is licensed CC BY 4.0.

7.1.3: Reductive Elimination

Reductive Elimination Reactions

Reductive elimination is the microscopic reverse of oxidative addition. The reductive elimination can only occur when the two ligands to be eliminated are in cis-position.

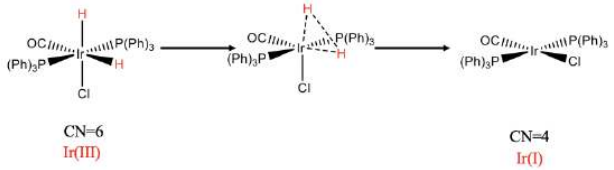


Figure 7.1.3.1: Reductive elimination (Attribution: A. Vedernikov, U Maryland.)

For instance the previously discussed oxidative cis-addition of H_2 to the iridium complex is reversible, and the reverse is called the reductive elimination (Fig. 7.1.3.1). The cis-orientation of the two hydrido ligands is necessary to form an H-H bond. The reaction can be thought of going along a reaction path in which the Ir-H bonds become gradually larger and and the H-H distance gradually smaller until the H_2 molecule is eliminated from the complex.

During reductive elimination, the electrons in the M–X bond head toward ligand Y, and the electrons in M–Y head to the metal. The eliminating ligands are always X-type! On the whole, the oxidation state of the metal decreases by two units, two new open coordination sites become available, and an X–Y bond forms. What does the change in oxidation state suggest about changes in electron density at the metal? As suggested by the name “reductive,” the metal gains electrons. The ligands lose electrons as the new X–Y bond cannot possibly be polarized to both X and Y, as the original M–X and M–Y bonds were. Using these ideas, you may already be thinking about reactivity trends in reductive elimination…hold that thought.

It’s been observed in a number of cases that a ligand dissociates from octahedral complexes before concerted reductive elimination occurs. Presumably, dissociation to form a distorted TBP geometry brings the eliminating groups closer to one another to facilitate elimination.

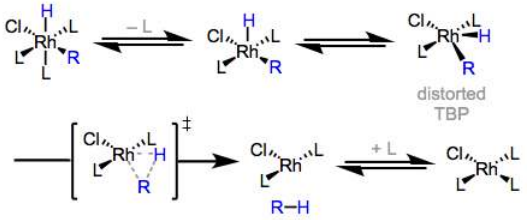


Figure 7.1.3.2: Reductive elimination is faster from five-coordinate than six-coordinate complexes. (Michael Evans)

Square planar complexes may either take on an additional fifth ligand or lose a ligand to form an odd-coordinate complex before reductive elimination. Direct reductive elimination without dissociation or association is possible, too.

Reactivity trends in reductive elimination are opposite those of oxidative addition. More electron-rich ligands bearing electron-donating groups react more rapidly, since the ligands lose electron density as the reaction proceeds. More electron-poor metal centers—bearing π-acidic ligands and/or ligands with electron-withdrawing groups—react more rapidly, since the metal center gains electrons. Sterically bulky ancillary ligands promote reductive elimination since the release of X and Y can “ease” steric strain in the starting complex. Steric hindrance helps explain, for example, why coordination of a fifth ligand to a square planar complex promotes reductive elimination even though coordination increases electron density at the metal center. A second example: trends in rates of reductive eliminations of alkanes parallel the steric demands of the eliminating ligands: C–C > C–H > H–H.

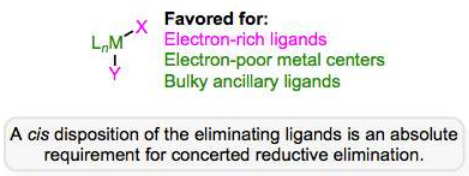


Figure 7.1.3.3: Reactivity trends for reductive eliminations. (Michael Evans)

Mechanistic trends for reductive elimination actually parallel trends in mechanisms of oxidative addition, since these two reactions are the microscopic reverse of one another. Non-polar and moderately polar ligands react by concerted or radical mechanisms; highly polarized ligands and/or very electrophilic metal complexes react by ionic (S_N2) mechanisms. The thermodynamics of reductive elimination must be favorable in order for it to occur! Most carbon–halogen reductive eliminations, for example, are thermodynamically unfavorable (this has turned out to be a good thing, especially for cross-coupling reactions).

Reductive elimination is an important step in many catalytic cycles—it usually comes near the "end" of catalytic mechanisms, just before product formation. For some catalytic cycles it's the turnover-limiting step, making it very important to consider! Hydrocyanation is a classic example; in the mechanism of this reaction, reductive elimination of C–CN is the slow step. Electron-poor alkyl ligands, derived from electron-poor olefins like unsaturated ketones, are bad enough at reductive elimination to prevent turnover altogether! Of course, the electronegative CN ligand is not helping things either…how would you design the ancillary ligands L to speed up this step?

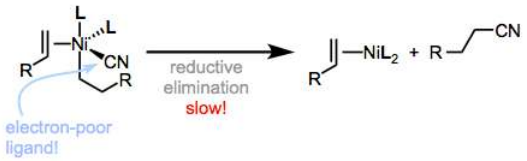


Figure 7.1.3.4: Reductive elimination is the turnover-limiting step of hydrocyanation. How would you design L to speed it up? (Michael Evans)

Dr. Michael Evans (Georgia Tech)

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 7.1.3: Reductive Elimination is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.1: Organometallic reactions** by Kai Landskron is licensed CC BY 4.0.
- **4.11: Reductive Elimination- General Ideas** by Michael Evans is licensed CC BY-NC-SA 4.0.

7.1.4: Sigma Bond Metathasis

Metal compounds with d^0 electron count are able to activate C-H bonds through σ bond metathesis reactions. **σ-bond metathesis** is a chemical reaction wherein a metal-ligand σ bond undergoes metathesis (exchange of parts) with the sigma bond in some other reagent. The reaction is illustrated by the exchange of lutetium(III) methyl complex with a hydrocarbon (R-H) (Figure 7.1.4.1). The oxidation state of the metal ion does not change during the reaction. This reactivity was first observed by Patricia L. Watson, a researcher at duPont.

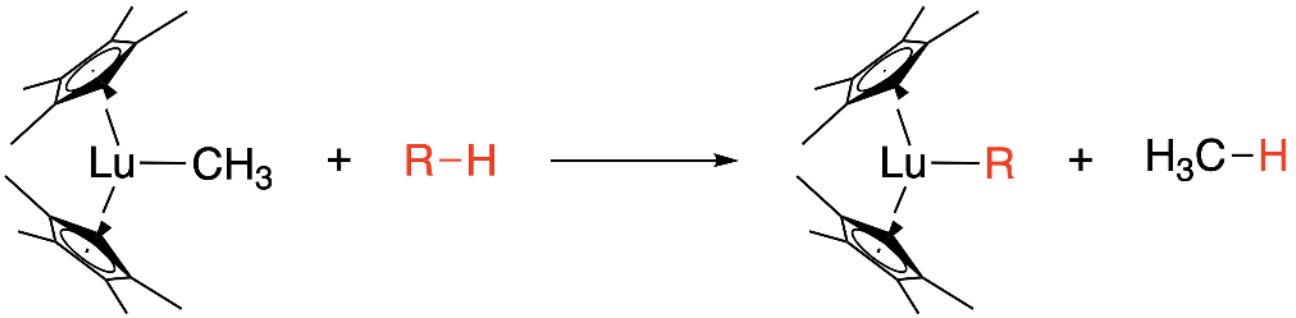


Figure 7.1.4.1: Example of σ bond metathesis; exchange of lutetium(III) methyl complex with a hydrocarbon. The R-H bond is activated and a new C-H bond is created. (CC-BY-SA; Kathryn Haas)

The reaction is mainly observed for complexes of metals with d^0 electron configuration, e.g. complexes of Sc(III), Zr(IV), Nb(IV), Ta(V), etc. Complexes of the f-block elements also participate, regardless of the number of f-electrons. For metals unsuited for redox, sigma bond metathesis provides a pathway for introducing substituents.

The details of the reaction mechanism are somewhat a matter of debate, however a currently accepted model is that it precedes through a cycloaddition and via a "kite-shaped" transition state (Figure 7.1.4.2). Indeed, the rate of the reaction is characterized by a highly negative entropy of activation, indicating an ordered transition state.

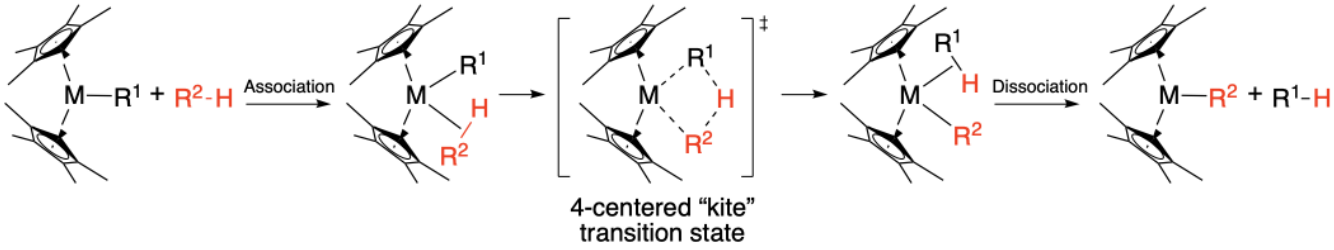


Figure 7.1.4.2: The currently accepted mode for the mechanism of σ bond metathesis involving a kite-like transition state. (CC-BY-SA; Kathryn Haas)

The reaction attracted much attention because hydrocarbons are normally unreactive substrates, whereas some sigma-bond metatheses are facile. Unfortunately the reaction does not readily allow the introduction of functional groups. It has been suggested that dehydrocoupling reactions proceed via sigma-bond metathesis.

Sources:

- https://en.Wikipedia.org/wiki/Sigma-bond_metathesis
- *Waterman, Rory (2013). "σ-Bond Metathesis: A 30-Year Retrospective". Organometallics. **32**: 7249–7263. doi:10.1021/om400760k.*

This page titled 7.1.4: Sigma Bond Metathasis is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.1.5: Application of Pincer Ligands

Pincer ligands are chelating agents that bind tightly to three adjacent coplanar sites of a metal complex. Stoichiometric and catalytic applications of pincer complexes have been studied at an accelerating pace since the mid-1970s.

Pincers often include one anionic, two-electron donor flanked by two neutral, two-electron donor groups. It consists of a rigid, planar backbone, usually consisting of aryl frameworks. The inflexibility of the pincer-metal interaction confers high thermal stability to the resulting complexes. This stability is in part ascribed to the constrained geometry of the pincer, which inhibits ligand exchange and cyclometallation of the pincer. In contrast, cyclometallation is often a significant deactivation process in the case of other types of chelates, in particular limiting their ability to effect C-H bond activation. The pincer ligand also creates a hydrophobic pocket around the reactive coordination site.

There are various types of pincer ligands that are used in transition metal catalysis. Often, they have the same two-electron donor flanking the metal centre, but this is not a requirement. Early examples of pincer ligands were anionic with a carbanion as the central donor site and flanking phosphine donors; these compounds are referred to as **PCP pincers**. Although the most common class of pincer ligands features PCP donor sets, variations have been developed where the phosphines are replaced by thioethers and tertiary amines. Many pincer ligands also feature nitrogenous donors at the central coordinating group position (see figure), such as pyridines. By altering the properties of the pincer ligands, it is possible to significantly alter the chemistry at the metal centre. Changing the hardness/softness of the donor, using electron-withdrawing groups (EWGs) in the backbone, and the altering the steric constraints of the ligands are all methods used to tune the reactivity at the metal centre.

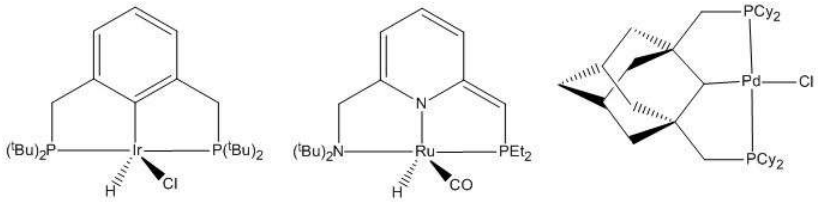
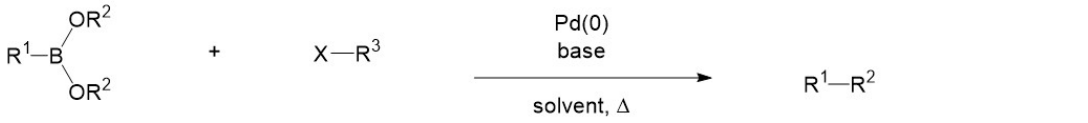


Figure 7.1.5.1: Examples of transition metal pincer complexes. (Scott0, Examples pincer complexes, CC BY-SA 3.0)

The Role of Pincer Complexes in Catalysis

Suzuki-Miyaura coupling

Pincer complexes have been shown to catalyse Suzuki-Miyaura coupling reactions, a versatile carbon-carbon bond forming reaction. Suzuki-Miyaura coupling (or Suzuki coupling) is a metal catalyzed reaction, typically with Pd, between an alkenyl (vinyl), aryl, or alkynyl organoborane (boronic acid or boronic ester, or special cases with aryl trifluoroborane) and halide or triflate under basic conditions. This reaction is used to create carbon-carbon bonds to produce conjugated systems of alkenes, styrenes, or biaryl compounds (Scheme 1).



R^1= aryl, alkene (vinyl), alkyne **R**^{2}= H (boronic acid), alkyl (boronic ester) **R**^{3}= aryl, alkene (vinyl), alkyne

X = halide (I, Br, Cl*) triflate (-OTf) *Cl requires special conditions for activation

Scheme 7.1.5.2: General reaction scheme of Suzuki cross coupling reaction. (Suzuki-Miyaura Coupling)

Modified conditions have demonstrated reactivity with less reactive substrates such as alkyl boranes (BR_3) or aryl or alkenyl chlorides by amending the base and ligands employed.

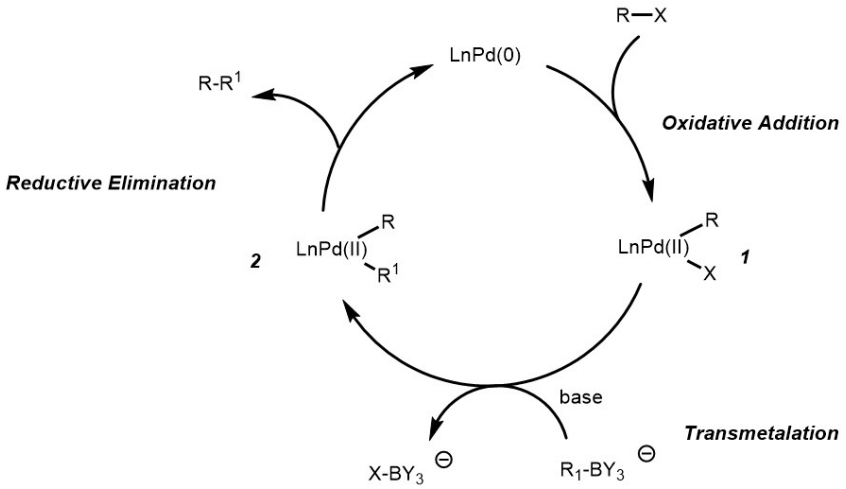
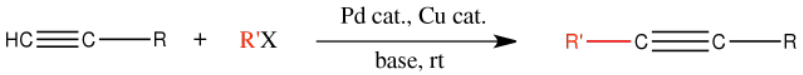


Figure 7.1.5.3: Suzuki coupling proceeds via three basic steps: oxidative addition, transmetallation, and reductive elimination. (Suzuki-Miyaura Coupling)

Sonogashira Coupling

The Sonogashira reaction (also called the Sonogashira-Hagihara reaction) is the cross coupling of aryl or vinyl halides with terminal alkynes to generate conjugated enynes and arylalkynes (Scheme 1). The reaction typically proceeds in the presence of a palladium(0) catalyst, a copper(I) cocatalyst, and an imine base. Alternative procedures describe Sonogashira coupling reactions performed without the Cu(I) cocatalyst.



R' = Aryl, Vinyl

X = I, Br, Cl, OTf

Scheme 7.1.5.4: *General reaction for Sonogashira Coupling*. (Jcap17, Sonogashira Cross-Coupling Reaction, CC BY-SA 3.0)

Dehydrogenation of alkanes

Alkanes undergo dehydrogenation at high temperatures. Typically this conversion is promoted heterogeneously because typically homogeneous catalysts do not survive the required temperatures (~200 °C) The corresponding conversion can be catalyzed homogeneously by pincer catalysts, which are sufficiently thermally robust. Proof of concept was established in 1996 by Jensen and co-workers. They reported that an iridium and rhodium pincer complex catalyze the dehydrogenation of cyclooctane with a turnover frequency of 12 min^{-1} at 200 °C. They found that the dehydrogenation was performed at a rate two orders of magnitude greater than those previously reported. The iridium pincer complex was also found to exhibit higher activity than the rhodium complex. This rate difference may be due to the availability of the Ir(V) oxidation state which allows stronger Ir-C and Ir-H bonds.

The homogeneously catalyzed process can be coupled to other reactions such as alkene metathesis. Such tandem reactions have not been demonstrated with heterogeneous catalysts.

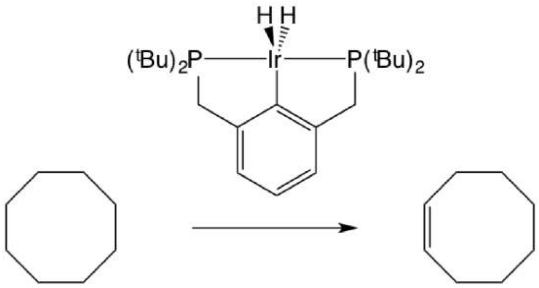


Figure 7.1.5.5: Iridium pincer complex catalyzing the dehydrogenation of cyclooctane to cyclooctene. (Paul Gray, Iridium Pincer Catalysis, CC BY-SA 3.0)

Sources:

- https://en.Wikipedia.org/wiki/Transi...pincer_complex
- Sonogashira Coupling
- Suzuki-Miyaura Coupling

This page titled 7.1.5: Application of Pincer Ligands is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

SECTION OVERVIEW

7.2: Reactions Invloving Modification of Unsaturated Ligands

This section will describe organometallic reactions that involve modification of unsaturated ligands.

7.2.1: Introduction to Insertion

7.2.2: CO Insertions (Alkyl Migration)

7.2.3: Migratory Insertion-1,2-Insertions

7.2.4: β-Elimination Reactions

7.2.5: Abstraction and Addition

This page titled 7.2: Reactions Invloving Modification of Unsaturated Ligands is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.2.1: Introduction to Insertion

We've seen that the metal-ligand bond is generally polarized toward the ligand, making the ligand nucleophilic. The ligand is especially nucleophilic in the case of X-type (anionic) ligands. When a nucleophilic, X-type ligand is positioned *cis* to a neutral, unsaturated ligand (L) in an organometallic complex, a migratory insertion reaction can occur. In a **migratory insertion reaction**, an anionic ligand (X^-) and a neutral unsaturated ligand (L) couple to form a new anionic ligand ($-LX) that is attached to the same metal (Figure \(7.2.1.1). The overall result is that an M-X bond is broken and M and X are added across a π bond of L. There is no change in oxidation state at the metal (unless the ligand is an alkylidene/alkylidyne), but the total electron count of the complex decreases by two during the actual insertion event.

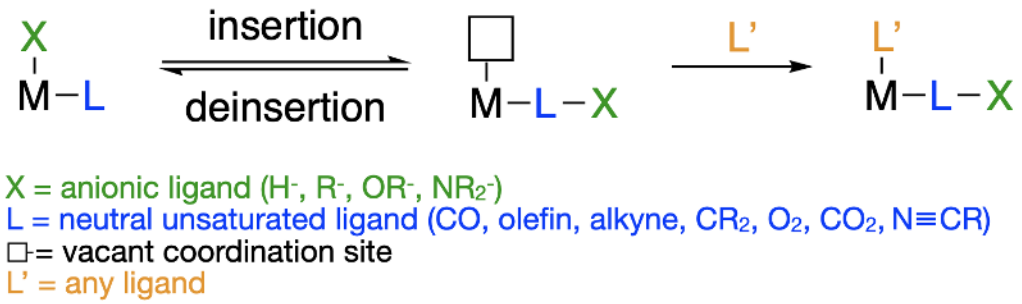


Figure 7.2.1.1: Migratory insertion (CC-BY-SA; Kathryn Haas)

The migratory insertion results in a decrease in coordination number and the creation of an open coordination site on the complex. The open coordination site can be filled by an added ligand (L') (Figure 7.2.1.1). The reverse of the insertion reaction is called a **deinsertion**. To drive the chemical equilibrium in the forward (insertion) direction, the reactant neutral ligand (or another neutral ligand) can be added in excess so that the neutral ligand fills the vacancy in the product complex and prevents the reverse (deinsertion) reaction. Typical neutral, unsaturated ligands are CO, olefins, alkynes, carbenes, dioxygen, carbon dioxide, and nitriles. Typical anionic ligands are hydrido, alkyl, aryl, alkoxy, and amido-ligands Figure 7.2.1.1.

The open site may appear where the unsaturated ligand was *or* where the X-type ligand was, depending on which group actually moved (see below). It is more common that the anionic X ligand moves (Figure 7.2.1.2).

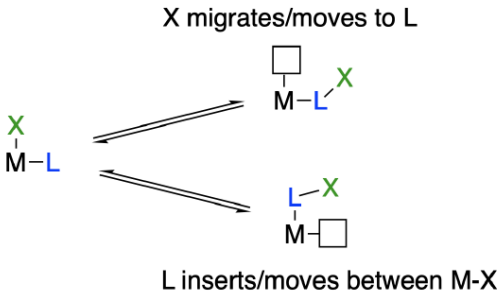


Figure 7.2.1.2: X can migrate onto unsaturated ligand L, or L can move to the original position of X. The former is more common for CO insertions. (CC-BY-SA; Kathryn Haas)

We can distinguish between two types of insertions, which differ in the number of atoms in the unsaturated ligand involved in the step. Insertions of CO, carbenes, and other η^1 unsaturated ligands are called **1,1-insertions** because the X-type ligand moves from its current location on the metal to one spot over, on the atom bound to the metal. η^2 ligands like alkenes and alkynes can also participate in migratory insertion; these reactions are called **1,2-insertions** because the X-type ligand slides two atoms over, from the metal to the distal atom of the unsaturated ligand (Figure 7.2.1.4).

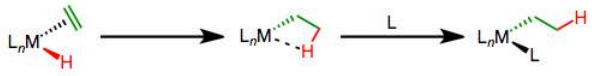


Figure 7.2.1.4: 1,2-insertion of an alkene and hydride. In some cases, an agostic interaction has been observed in the unsaturated intermediate. (Michael Evans)

This is really starting to look like the addition of M and X across a π bond! However, we should take care to distinguish this completely intramolecular process from the attack of a nucleophile or electrophile on a coordinated π system, which is a different beast altogether. Confusingly, chemists often jumble up all of these processes using words like “hydrometalation,” “carbometalation,” “aminometalation,” etc. Another case of big words being used to obscure ignorance! We’ll look at nucleophilic and electrophilic attack on coordinated ligands in separate posts.

This page titled 7.2.1: Introduction to Insertion is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.1: Organometallic reactions** by Kai Landskron is licensed CC BY 4.0.

7.2.2: CO Insertions (Alkyl Migration)

One of the most common types of migratory insertions is carbonyl insertion (Figure 7.2.2.3). The carbonyl insertion produces an acyl group. Notice in the example below that the complex goes from 18 to 16 total electrons after insertion. A dative ligand comes in to fill the empty coordination site. L can be a neutral or anionic ligand, and it can even be the carbonyl oxygen itself. To drive the reaction, the reaction can be carried out in the presence of a neutral ligand like free CO, which occupies the vacant site.

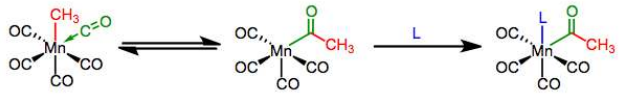


Figure 7.2.2.1: Migratory insertion into a metal-carbon bond. (Michael Evans)

Reactivity Trends in CO Insertions

Certain conditions *must* be met for migratory insertion to occur: the two ligands undergoing the process must be *cis*, and the complex must be stable with two fewer total electrons. Thermodynamically, the formed Y–X and covalent M–Y bonds must be more stable than the broken M–X and dative M–Y bonds for insertion to be favored. When the opposite is true, the microscopic reverse (**elimination** or **deinsertion**) will occur spontaneously.

Migratory aptitudes for insertion into CO have been studied extensively, and the general conclusion here is “it’s complicated.” A few ligands characterized by remarkably stable metal-ligand bonds don’t undergo insertion for thermodynamic reasons—the M–X bond is just too darn strong. Perfluoroalkyl complexes and metal hydrides are two notable examples. Electron-withdrawing groups on the X-type ligand, which strengthen the M–X bond, slow down insertion (likely for thermodynamic reasons though… Hammond’s postulate in action).

What factors affect the relative speed (kinetics) of favorable insertions? Sterics is one important variable. Both 1,1- and 1,2-insertions can relieve steric strain at the metal center by spreading out the ligands involved in the step. In 1,2-insertions, the X-type ligand removes itself completely from the metal! Unsurprisingly, then, bulky ligands undergo insertions more rapidly than smaller ligands. Complexes of the first-row metals tend to react more rapidly than analogous second-row metal complexes, and second-row metal complexes react faster than third-row metal complexes. This trend fits in nicely with the typical trend in M–C bond strengths: first row < second row < third row. Lewis acids help accelerate insertions into CO by coordinating to CO and making the carbonyl carbon more electrophilic. For a similar reason, CO ligands bound to electron-poor metal centers undergo insertion more rapidly than CO’s bound to electron-rich metals. Finally, for reasons that are still unclear, one-electron oxidation often increases the rate of CO insertion substantially.

Although the thermodynamics of alkene 1,2-insertion are more favorable for metal-carbon than metal-hydrogen bonds, M–H bonds react *much* more rapidly than M–C bonds in 1,2-insertions. This fact has been exploited for olefin hydrogenation, which would be much less useful if it had to complete with olefin polymerization (the result of repeated insertion of C=C into M–C) in the same reaction flask! More on that in the next post.

Stereochemistry in CO Insertions

Migratory insertion steps are full of stereochemistry! Configuration at the migrating alkyl group is retainedduring insertion—a nice piece of evidence supporting a concerted, intramolecular mechanism of migration.

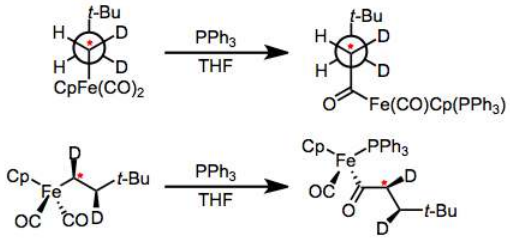


Figure 7.2.2.2: Migratory insertion occurs with retention of configuration at the migrating alkyl group. Two different views of the same reaction are shown here. (Michael Evans)

What about stereochemistry at the metal center? Migratory insertion may create a stereogenic center at the metal—see the iron example above. Whether the X-type ligand moves onto the unsaturated ligand or *vice versa* will impact the configuration of the

product complex. Calderazzo's study of this issue is one of my favorite experiments in all of organometallic chemistry! He took the simple labeled substrate in the figure below and treated it with dative ligand, encouraging insertion. Four products of insertion are possible, corresponding to reaction of the four CO ligands *cis* to the methyl ligand. Try drawing a few curved arrows to wrap your mind around the four possibilities, and consider both CO migration and Me migration as possible at this point.

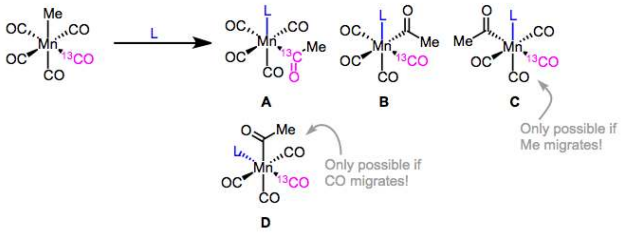


Figure 7.2.2.3: Insertion of the labeled complex shown could produce four products. Calderazzo did not observe product **D**, supporting a mechanism involving Me migration to CO. (Michael Evans)

Note that product **D** is impossible if we only allow the Me group to migrate—the spot *trans* to the labeled CO is another CO ligand, so that spot can only pick up L if CO migrates (not if Me migrates). On the other hand, product **C** must have come from the migration of Me, since the Me group has moved from a *cis* to a *trans*position relative to the labeled CO in product **C**. Calderazzo observed products **A**, **B**, and **C**, but not **D**, supporting a mechanism involving Me migration. Other experiments since support the idea that most of the time, the alkyl group migrates onto CO. Slick, huh?

I won't address insertions into alkylidenes, alkylidynes, and other one-atom unsaturated ligands in this post, as insertions into CO are by far the most popular 1,1 insertions in organometallic chemistry. In the next post, we'll dig more deeply into 1,2-insertions of alkenes and alkynes. Thanks for reading!

This page titled 7.2.2: CO Insertions (Alkyl Migration) is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.2.3: Migratory Insertion-1,2-Insertions

Insertions of π systems into M-X bonds are appealing in the sense that they establish two new σ bonds in one step, in a stereocontrolled manner. As we saw in the last post, however, we should take care to distinguish these fully intramolecular migratory insertions from intermolecular attack of a nucleophile or electrophile on a coordinated π-system ligand. The reverse reaction of migratory insertion, β-elimination, is not the same as the reverse of nucleophilic or electrophilic attack on a coordinated π system.

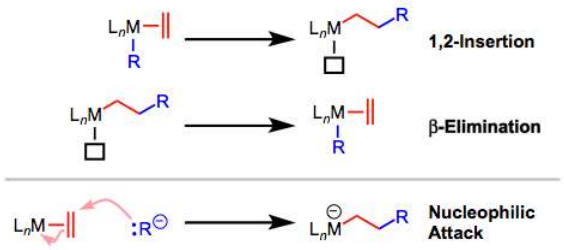


Figure 7.2.3.1: 1,2-Insertion is dinstinct from nucleophilic/electrophilic attack on coordinated ligands. (Michael Evans)

Like 1,1-insertions, 1,2-insertions generate a vacant site on the metal, which is usually filled by external ligand. For unsymmetrical alkenes, it's important to think about site selectivity: which atom of the alkene will end up bound to metal, and which to the other ligand? To make predictions about site selectivity we can appeal to the classic picture of the M–X bond as M + X^{-}. Asymmetric, polarized π ligands contain one atom with excess partial charge; this atom hooks up with the complementary atom in the M–R bond during insertion. Resonance is our best friend here!

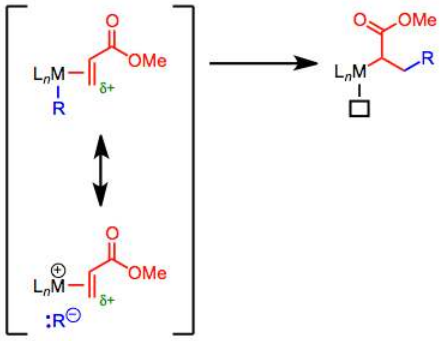


Figure 7.2.3.2: The site selectivity of 1,2-insertion can be predicted using resonance forms and partial charges. (Michael Evans)

A nice study by Yu and Spencer illustrates these effects in homogeneous palladium- and rhodium-catalyzed hydrogenation reactions. Unactivated alkenes generally exhibit lower site selectivity than activated ones, although steric differences between the two ends of the double bond can promote selectivity.

Reactivity Trends in 1,2-Insertions

The thermodynamics of 1,2-insertions of alkenes depend strongly on the alkene, but we can gain great insight by examining the structure of the product alkyl. Coordinated alkenes that give strong metal-alkyl bonds after migratory insertion tend to undergo the process. Hence, electron-withdrawing groups, such as carbonyls and fluorine atoms, tend to encourage migratory insertion—remember that alkyl complexes bearing these groups tend to have stable M–C bonds.

Insertions of alkenes into both M–H and M–R (R = alkyl) are favored thermodynamically, but the kinetics of M–R insertion are much slower. This observation reflects a pervasive trend in organometallic chemistry: M–H bonds react more rapidly than M–R bonds. The same is true of the reverse, β-elimination. Even in cases when both hydride and alkyl elimination are thermodynamically favored, β-hydride elimination is much faster. Although insertion into M–R is relatively slow, this elementary step is critical for olefin polymerizations that form polyalkenes (Ziegler-Natta polymerization). This reaction deserves a post all its own!

As the strength of the M–X bond increases, the likelihood that an L-type π ligand will insert into the bond goes down. Hence, while insertions into M–H and M–C are relatively common, insertions into M–N and M–O bonds are more rare. Lanthanides and

palladium are known to promote insertion into M–N in some cases, but products with identical connectivity can come from external attack of nitrogen on a coordinated π ligand. The diastereoselectivity of these reactions provides mechanistic insight—since migratory insertion is syn (see below), a syn relationship between Pd and N is to be expected in the products of migratory insertion. An anti relationship indicates external attack by nitrogen or oxygen.

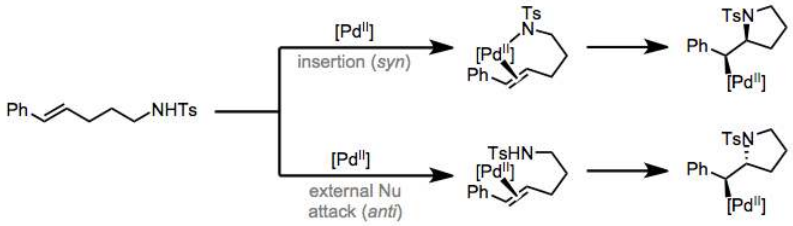


Figure 7.2.3.3: The diastereoselectivity of formal insertions provides insight about their mechanisms. (Michael Evans)

Stereochemistry of 1,2-Insertions

1,2-Insertion may establish two stereocenters at once, so the stereochemistry of the process is critical! Furthermore, 1,2-insertions and β-eliminations are bound by important stereoelectronic requirements. An analogy can be made to the E2 elimination of organic chemistry, which also has strict stereoelectronic demands. For migratory insertion to proceed, the alkene and X-type ligand must be syncoplanar during insertion; as a consequence of this alignment, X and MLn end up on the same face of the alkene after insertion. In other words, insertions into alkenes take place in a syn fashion. Complexes that have difficulty achieving a coplanar arrangement of C=C and M–X undergo insertion very slowly, if at all.

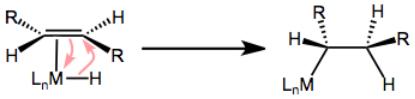


Figure 7.2.3.4: 1,2-Insertions take place in a syn fashion. The metal and X end up bound to the same face of the alkene. (Michael Evans)

This observation has important implications for β-elimination, too—the eliminating X and the metal must have the ability to align syn.

Insertions of Other π Systems

To close this post, let's examine insertions into π ligands other than alkenes briefly. Insertions of alkynes into metal-hydride bonds are known, and are sometimes involved in reactions that I refer to collectively as "hydrostuffylation": hydrosilylation, hydroesterification, hydrogenation, and other net H–X additions across the π bond. Strangely, some insertions of alkynes yield trans products, even though cis products are to be expected from syn addition of M–X. The mechanisms of these processes involve initial syn addition followed by isomerization to the trans complex via an interesting resonance form. The cis complex is the kinetic product, but it isomerizes over time to the more thermodynamically stable trans complex.

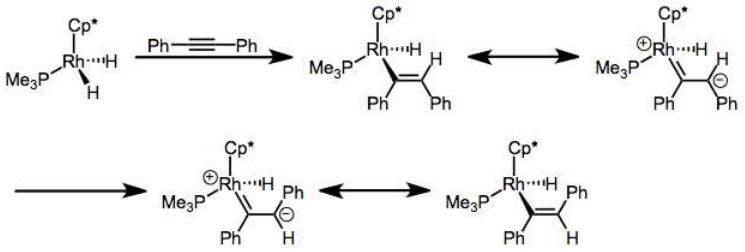


Figure 7.2.3.5: Migratory insertions of alkynes into M–H produce alkenyl complexes, which have been known to isomerize. (Michael Evans)

The strongly donating Cp* ligand supports the legitimacy of the zwitterionic resonance form—and suggests that the C=C bond may be weaker than it first appears!

Polyenes can participate in migratory insertion, and insertions of polyenes are usually quite favored because stabilized π-allyl complexes result. In one mind-bending case, a coordinated arene inserts into an M–Me bond in a syn fashion!

Have you ever stopped to consider that the addition of methyllithium to an aldehyde is a formal insertion of the carbonyl group into the Li–Me bond? It's true! We can think of these as (very) early-metal "insertion" reactions. Despite this precedent, migratory insertion reactions of carbonyls and imines into late-metal hydride and alkyl bonds are surprisingly hard to come by. Rhodium is the most famous metal that can make this happen—rhodium has been used in complexes for arylation and vinylation, for example. Insertion of X=C into the M–R bond is usually followed by β-hydride elimination, which has the nifty effect of replacing H in aldehydes and aldimines with an aryl or vinyl group.

Contributors and Attributions

Dr. Michael Evans (Georgia Tech)

This page titled 7.2.3: Migratory Insertion-1,2-Insertions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **4.5: Migratory Insertion- 1,2-Insertions** by Michael Evans is licensed CC BY-NC-SA 4.0.

7.2.4: β-Elimination Reactions

In organic chemistry class, one learns that elimination reactions involve the cleavage of a σ bond and formation of a π bond. A nucleophilic pair of electrons (either from another bond or a lone pair) heads into a new π bond as a leaving group departs. This process is called β-elimination because the bond β to the nucleophilic pair of electrons breaks. Transition metal complexes can participate in their own version of β-elimination, and metal alkyl complexes famously do so. Almost by definition, metal alkyls contain a nucleophilic bond—the M–C bond! This bond can be so polarized toward carbon, in fact, that it can promote the elimination of some of the world's worst leaving groups, like –H and –CH3. Unlike the organic case, however, the leaving group is not lost completely in organometallic β-eliminations. As the metal donates electrons, it receives electrons from the departing leaving group. When the reaction is complete, the metal has picked up a new π-bound ligand and exchanged one X-type ligand for another.

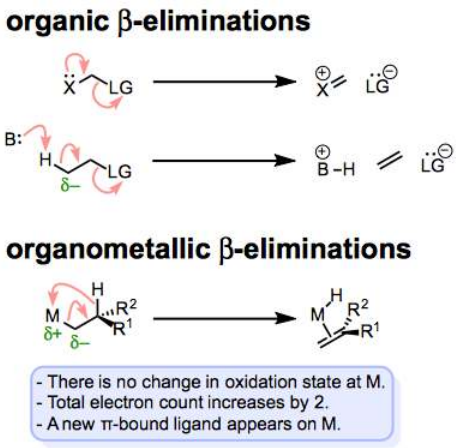


Figure 7.2.4.1: Comparing organic and organometallic β-eliminations. A nucleophilic bond or lone pair promotes loss or migration of a leaving group. (Michael Evans)

In this post, we'll flesh out the mechanism of β-elimination reactions by looking at the conditions required for their occurrence and their reactivity trends. Many of the trends associated with β-eliminations are the opposite of analogous trends in 1,2-insertion reactions. A future post will address other types of elimination reactions.

β-Hydride Elimination

The most famous and ubiquitous type of β-elimination is **β-hydride elimination**, which involves the formation of a π bond and an M–H bond. Metal alkyls that contain β-hydrogens experience rapid elimination of these hydrogens, provided a few other conditions are met.

The complex must have an open coordination site and an accessible, empty orbital on the metal center. The leaving group (–H) needs a place to land. Notice that after β-elimination, the metal has picked up one more ligand—it needs an empty spot for that ligand for elimination to occur. We can envision hydride "attacking" the empty orbital on the metal center as an important orbital interaction in this process.

The M–C_α and C_β–H bonds must have the ability to align in a syn coplanar arrangement. By "syn coplanar" we mean that all four atoms are in a plane and that the M–C_α and C_β–H bonds are on the same side of the C_α–C_β bond (a dihedral angle of 0°). You can see that conformation in the figure above. In the syn coplanar arrangement, the C–H bond departing from the ligand is optimally lined up with the empty orbital on the metal center. Hindered or cyclic complexes that cannot achieve this conformation do not undergo β-hydride elimination. The need for a syn coplanar conformation has important implications for eliminations that may establish diastereomeric olefins: β-elimination is stereospecific. One diastereomer leads to the (E)-olefin, and the other leads to the (Z)-olefin.

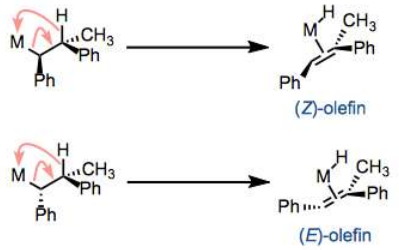


Figure 7.2.4.2: β-elimination is stereospecific. One diastereomer of reactant leads to the (Z)-olefin and the other to the (E)-olefin. (Michael Evans)

The complex must possess 16 or fewer total electrons. Examine the first figure one more time—notice that the total electron count of the complex increases by 2 during β-hydride elimination. Complexes with 18 total electrons don't undergo β-elimination because the product would end up with 20 total electrons. Of course, dissociation of a loose ligand can produce a 16-electron complex pretty easily, so watch out for ligand dissociation when considering the possibility of β-elimination in a complex. Ligand dissociation may be reversible, but β-Hydride elimination is almost always irreversible.

The metal must bear at least 2 d electrons. Now this seems a bit strange, as the metal has served as nothing but an empty bin for electrons in our discussion so far. Why would the metal center need electrons for β-hydride elimination to occur? The answer lies in an old friend: backbonding. The $\sigma_{C-H} \rightarrow M$ orbital interaction mentioned above is not enough to promote elimination on its own; an $M \rightarrow \sigma^*_{C-H}$ interaction is also required! I've said it before, and I'll say it again: backbonding is everywhere in organometallic chemistry. If you can understand and articulate it, you'll blow your instructor's mind.

Other β-Elimination Reactions

The leaving group does not need to be hydrogen, of course, and a number of more electronegative groups come to mind as better candidates for leaving groups. β-Alkoxy and β-amino eliminations are usually thermodynamically favored thanks to the formation of strong M–O and M–N bonds, respectively. These reactions are so favored in β-alkoxyalkyl "complexes" of alkali and alkaline earth metals (R–Li, R–MgBr, etc.) that using these as σ-nucleophiles at carbon is untenable. Such compounds eliminate immediately upon their formation. I had an organic synthesis professor in undergrad who was obsessed with this—using a β-alkoxyalkyl lithium or β-alkoxyalkyl Grignard reagent in a synthesis was a recipe for red ink. β-Haloalkyls were naturally off limits too.

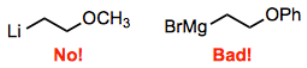


Figure 7.2.4.3: Watch out…these are not stable compounds! (Michael Evans)

The atom bound to the metal doesn't have to be carbon. β-Elimination of alkoxy ligands affords ketones or aldehydes bound at oxygen or through the C=O π bond (this step is important in many transfer hydrogenations, and an analogous process occurs in the Oppenauer oxidation). Amido ligands can undergo β-elimination to afford complexes of imines; however, this process tends to be slower than β-alkoxy elimination.

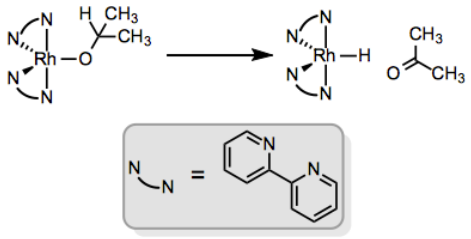


Figure 7.2.4.4: β-Elimination helps transfer the elements of dihydrogen from one organic compound to another.. (Michael Evans)

Incidentally, I haven't seen any examples in which the β atom is not carbon, but would be interested if anyone knows of an example!

Applications of β-Eliminations

As with many concepts in organometallic chemistry, there are two ways to think about applications of β-elimination. One can take either the “inorganic” perspective, which focuses on the metal center, or the “organic” perspective, which focuses on the ligands.

With the metal center in focus, we can recognize that β-hydride elimination has the wonderful side effect of establishing an M–H bond—a feat generally difficult to achieve in a selective manner via oxidative addition of X–H. If the ligand from which the hydrogen came displaced something more electronegative, the whole process represents reduction at the metal center. For example, imagine rhodium(III) chloride is mixed with sodium isopropoxide, $NaOCH(CH_3)_2$. The isopropoxide easily displaces chloride, and subsequent β-hydride elimination affords a rhodium hydride, formally reduced with respect to the chloride starting material. See p. 236 of this review for more.

With the ligand in focus, we see that the organic ligand is oxidized in the course of β-hydride elimination. Notice that the metal is reduced and the ligand oxidized! A π bond replaces a σ bond in the ligand, and if the conditions are right, this represents a bona fide oxidation (as opposed to a mere elimination). For example, oxidative addition into a C–H bond followed by β-hydride elimination at a C–H bond next door sets up an alkene where two adjacent C–H bonds existed before, an oxidation process. These dehydrogenation reactions are incredibly appealing in a theoretical sense, but still at an early stage when it comes to scope and practicality.

Summary

We already encountered β-hydride elimination in an earlier series of posts on metal alkyl complexes, where we noted that it’s a very common decomposition pathway for metal alkyls. β-Hydride elimination isn’t all bad, however, as it can be an important step in catalytic reactions that result in the oxidation of organic substrates (dehydrogenations and transfer hydrogenations) and in reactions that reduce metal halides to metal hydrides. The general idea of β-elimination involves the transfer of a leaving group from a ligand to the metal center with simultaneous formation of a π bond in the ligand. β-Elimination requires an open coordination site and at least two d electrons on the metal center, and eliminations of chiral complexes are stereospecific. The leaving group is commonly hydrogen, but need not be—the more electronegative the leaving group, the more favorable the elimination. Stronger π bonds in the product also encourage β-elimination, so eliminations that form carbonyl compounds or imines are common.

In the next post, we’ll explore other types of organometallic elimination reactions, which establish π bonds at different positions in metal alkyl or other complexes. α-Eliminations, for example, establish metal-carbon, -oxygen, or -nitrogen multiple bonds, which are generally difficult to forge through other means

Contributors and Attributions

- Dr. Michael Evans (Georgia Tech)

This page titled 7.2.4: β-Elimination Reactions is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **4.1: β-Elimination Reactions** by Michael Evans is licensed CC BY-NC-SA 4.0.

7.2.5: Abstraction and Addition

The nucleophilic and electrophilic addition and abstraction reactions can be viewed as ways of activating a ligand toward reaction with an external reagent. The external reagent reacts directly with the ligand, not with the metal center. The external reagent may be a nucleophile (Lewis Base) or an electrophile (Lewis acid).

Nucleophilic Addition and Abstraction

The reaction of an activated ligand with a nucleophilic reagent is favored if the activated ligand is electron poor. When the metal complex is either cationic and/or has spectator ligands that are are electron withdrawing, the reactive ligand becomes activated by being depleted of electron density. The attack of the nucleophile may result in the formation of a new bond between the nucleophile and the activated unsaturated substrate, in which case it is called nucleophilic addition. Alternatively, the reaction may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the nucleophilic abstraction. Some examples of nucleophilic addition and the abstraction reactions are discussed below.

Nucleophilic Addition

An example of a nucleophilic addition reaction is shown in Figure 7.2.5.1 The olefin is activated by its interaction with platinum. Pyridine is the nucleophile, and the result is a new C−N bond.

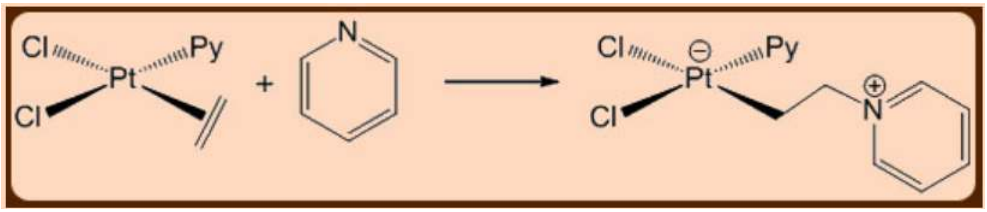


Figure 7.2.5.1: An example of addition of a nucleophile to an activated ligand.

Nucleophilic Abstraction

An example of a nucleophilic abstraction reaction is shown in Figure 7.2.5.2

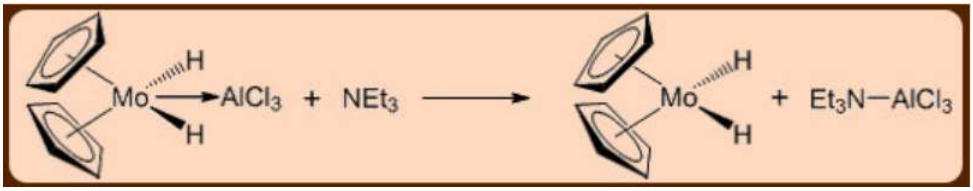


Figure 7.2.5.2: An example of abstraction by a nucleophile.

Electrophilic Addition and Abstraction

Similar to the nucleophilic addition and abstraction reactions, the electrophilic counterparts of these reactions also exist. An electrophilic attack is favored if the ligand-metal fragment is more electron rich. When the complex is anionic, the metal center is at low oxidation state, and/or when the spectator ligands are electron donating, the ligand becomes activated toward reaction with an electrophile. The reaction of activated ligands with electrophilic substrates may result in the formation of a new bond between the electrophile and the activated unsaturated substrate, in which case it is called electrophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the electrophilic abstraction.

Electrophilic Addition

An example of an electrophile being added to an activated ligand is shown in Figure 7.2.5.3 The allylic anion ligand uses its π electrons to react with hydrogen ion. This adds a hydrogen to the ligand, converting it from an anionic X-type ligand to a neutral L-type ligand .

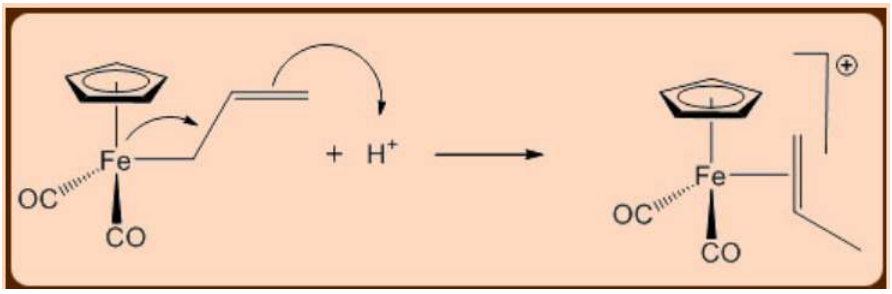


Figure 7.2.5.3: An example of electrophilic addition to an activated ligand.

Electrophilic Abstraction

Depending on whether the abstraction occurs at the α or β position with respect to the metal ion, the reaction is either classified as an α-abstraction or a β-abstraction.

An example of an α electrophilic abstraction reaction is shown in Figure 7.2.5.4

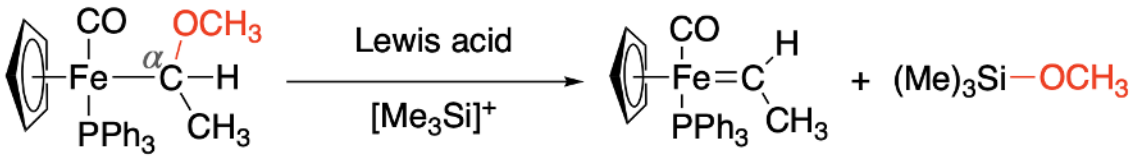


Figure 7.2.5.4: An example of an electrophilic α-abstraction. (CC-BY-SA; Kathryn Haas)

Two examples of a β electrophilic abstraction are shown in Figure 7.2.5.5

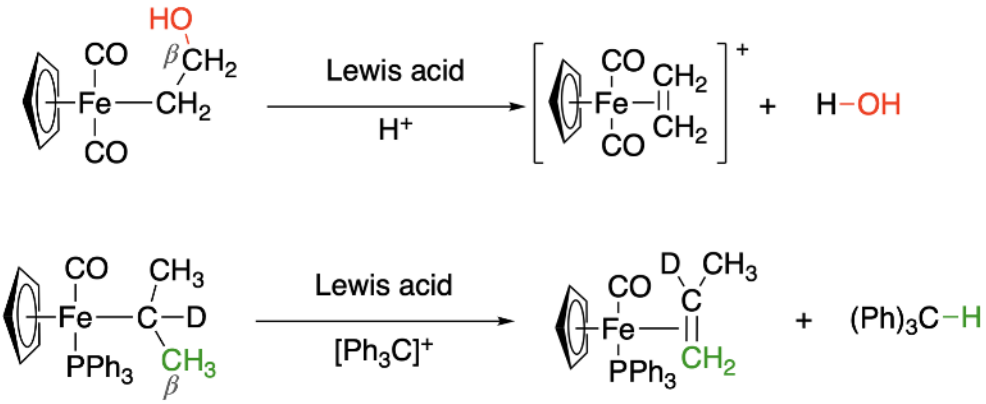


Figure 7.2.5.5: Two examples of electrophilic β-abstraction. (CC-BY-SA; Kathryn Haas)

This page titled 7.2.5: Abstraction and Addition is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **10.3: Nucleophilic and Electrophilic Addition and Abstraction** by M. S. Balakrishna & Prasenjit Ghosh is licensed CC BY-NC-SA 4.0. Original source: https://nptel.ac.in/courses/104101006.

SECTION OVERVIEW

7.3: Organometallic Catalysts

One of the most important uses of organometalic complexes is in the catalysis of chemical reactions. In this section, we will apply knowledge of reaction types and the skill of electron counting to understand organometalic catalytic cycles.

7.3.1: Catalytic Deuteration

7.3.2: Hydroformylation

7.3.3: Monsanto Acetic Acid Process

7.3.4: Wacker (Smidt) Process

7.3.5: Hydrogenation by Wilkinson's Catalyst

7.3.6: Olefin Metathesis

This page titled 7.3: Organometallic Catalysts is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

7.3.1: Catalytic Deuteration

Catalytic Deuteration of Benzene

Combinations of oxidative additions and reductive eliminations have many applications in the synthesis of organic molecules using an organometallic reactant.

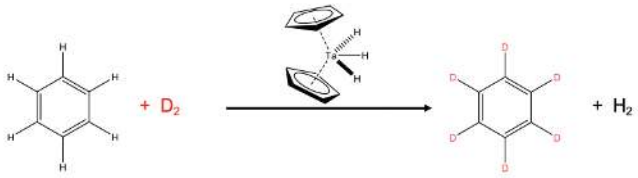


Figure 7.3.1.1 Deuteration of benzene

An example is the deuteration of benzene (Fig. 7.3.1.1). Deuterated benzene is an important solvent in NMR spectroscopy. Industrially, the deuteration is done using a dicyclopentadienyltrihydridotantalum(V) catalyst starting out from benzene and D_2. The D_2 is provided in excess to drive the chemical equilibrium to the right side.

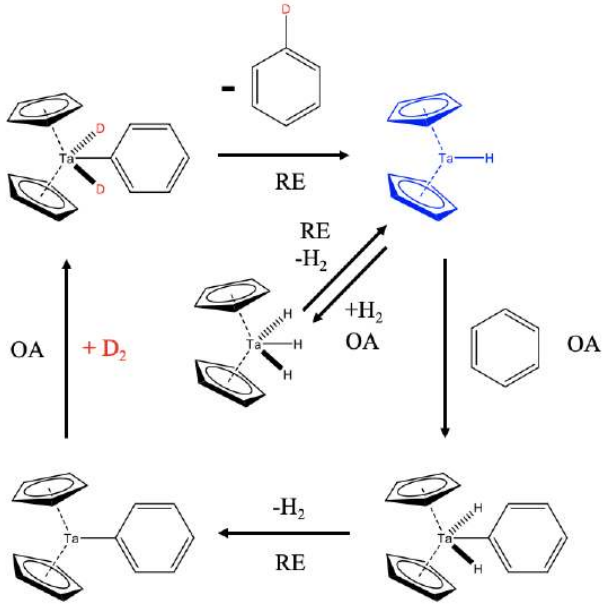


Figure 7.3.1.2 Mechanism of the catalytic deuteration of benzene

How does this reaction work mechanistically? This 18e Cp_2TaH_3 is actually a precatalyst that is in chemical equilibrium with H_2 and the 16e dicyclopentadienylhydrido tantalum(III) which is the actual catalyst (Fig. 7.3.1.2). Elimination of H_2 from the Ta(V) catalyst is a reductive elimination (RE) and the re-addition of H_2 to the Ta(III) species an oxidative addition (OA). In the presence of benzene, the Ta(III) species can oxidatively add benzene to form an 18e Ta(V) complex. This complex can reductively eliminate H_2 to form a 16e Cp_2Ta(III)-Ph complex. In the presence of deuterium this complex can add D_2 oxidatively to form an 18e Cp_2D_2Ta(V)-Ph complex. This species can then reductively eliminate a monodeuterated benzene molecule under formation of Cp_2Ta(III)-D. In the presence of enough D_2 this monodeuterated benzene can be further deuterated in subsequent catalytic cycles.

This page titled 7.3.1: Catalytic Deuteration is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.1: Organometallic reactions** by Kai Landskron is licensed CC BY 4.0.

7.3.2: Hydroformylation

Catalytic Olefin Hydroformylation

An important industrial reaction is the catalytic hydroformylation reaction, also known as oxo-process (Figure 7.3.2.1). It was discovered in 1938 by Otto Roelen at BASF. In the hydroformylation reaction an H atom and a formyl group are added to an alkene to form aldehydes. The reaction can produce both branched an linear aldehydes from terminal alkenes, CO, and H_2 using a carbonyl hydrides such as $HCo(CO)_4$ as a catalyst. The reaction is performed at about 100°C at a pressure of up to 100 atm.

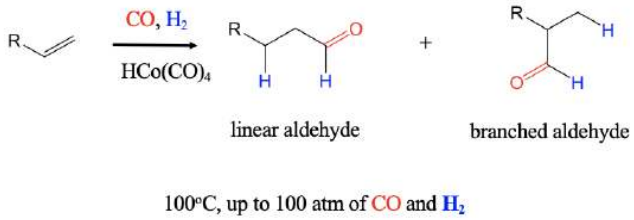


Figure 7.3.2.1: Catalytic olefin hydroformylation

Mechanism of the Catalytic Olefin Hydroformylation by $HCo(CO)_4$

How does the hydroformylation work mechanistically?

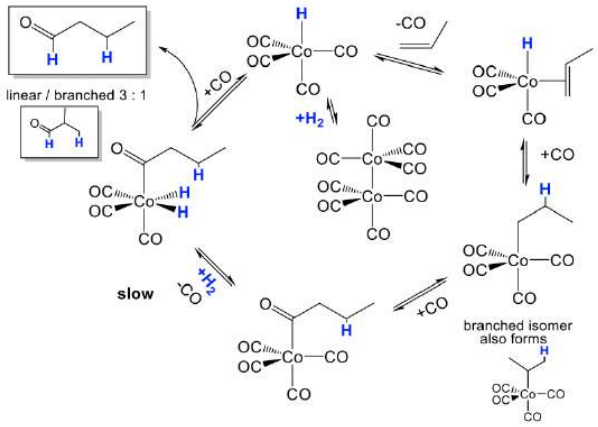


Figure 7.3.2.2: Mechanism of the catalytic olefin hydroformylation by $HCo(CO)_4$ (Attribution: A. Vedernikov, U Maryland (modified).)

The mechanism is illustrated for the hydroformylation of propene (Fig. 7.3.2.2). The actual catalyst $HCo(CO)_4$ is first formed from its precatalyst $Co_2(CO)_8$ in the presence of H_2 in a dinuclear oxidative addition reaction. The catalyst can undergo a substitution reaction in which a CO ligand is replaced by the olefin that binds side-on to the cobalt. This species can then undergo a migratory olefin insertion reaction. This leads to a mixture of linear and branched alkyl groups attached to the Co. A new CO ligand can add to the vacant site. The alkyl group can then insert into a carbonyl group in another migratory insert step, and the vacant site can be reoccupied by a new CO molecule. Then, H_2 is added in an oxidative addition. This is the slowest and rate-limiting step in the catalytic cycle. From the addition product the aldehyde can then be eliminated in a reductive elimination reaction. Addition of CO regenerates the catalyst, and the catalytic cycle can begin again.

Hydrocarbonylations

After the hydroformylation, a number of other hydrocarbonylations were developed, and industrially deployed.

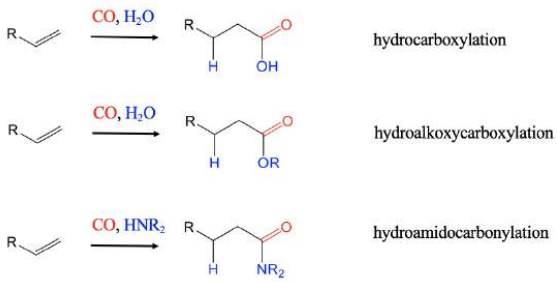


Figure 7.3.2.3: Hydrocarbonylation reactions

When hydrogen is replaced by H_2O hydrocarboxylations of alkenes lead to carboxylic acids (Fig. 7.3.2.3). With an alcohol instead of H_2 hydroalkoxycarbonylcations lead to esters. The employment of amines instead of H_2 leads to amides in hydroamidocarbonylation reactions.

This page titled 7.3.2: Hydroformylation is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.2: Organometallic Catalysts** by Kai Landskron is licensed CC BY 4.0.

7.3.3: Monsanto Acetic Acid Process

The Monsanto Acetic Acid Process

Another carbonylation reaction involving an organometallic catalyst is the Monsanto acetic acid process (Figure 7.3.3.1). It has been introduced by Monsanto in the 1970s for the industrial production of acetic acid from methanol. The reaction involves dual catalysis with HI and $[RhI_2(CO)_2]^-$ as a co-catalysts. How does this reaction work?

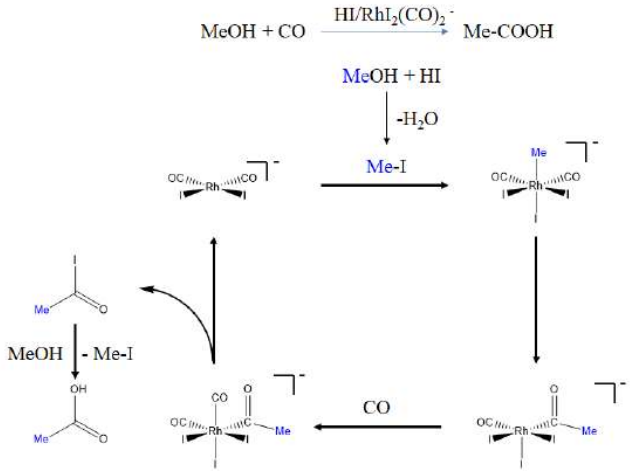


Figure 7.3.3.1: The catalytic cycle in the Monsanto acetic acid process

In the first step methanol reacts with HI to form methyl iodide. The methyl iodide then reacts with the Rh-catalyst in an oxidative addition reaction in which a methyl and an iodo group are added in trans-fashion to the square-planar Rh-complex to give an octahedral complex. The octahedral complex then undergoes a migratory insertion reaction with CO producing an acyl group and a vacant site. A CO molecule can then add to the vacant site. The acetyl iodide can then be eliminated in a reductive elimination to reform the Rh-catalyst thereby closing the catalytic cycle. The acetyl iodide can then react with methanol to form new methyl iodide and acetic acid. The methyl iodide can start a new catalytic cycle with the Rh-catalyst.

This page titled 7.3.3: Monsanto Acetic Acid Process is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.2: Organometallic Catalysts** by Kai Landskron is licensed CC BY 4.0.

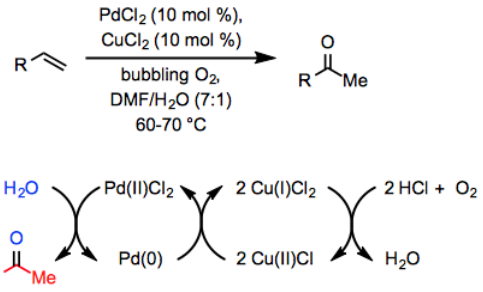
7.3.4: Wacker (Smidt) Process

See also Wacker Oxidation (Wikipedia)

The **Wacker oxidation** refers generally to the transformation of a terminal or 1,2-disubstituted alkene to a ketone through the action of catalytic palladium(II), water, and a co-oxidant. Variants of the reaction yield aldehydes, allylic/vinylic ethers, and allylic/vinylic amines. Because of the ease with which terminal alkenes may be prepared and the versatility of the methyl ketone group installed by the reaction, the Wacker oxidation has been employed extensively in organic synthesis.[1]

Introduction

The stoichiometric conversion of ethylene to acetaldehyde by an acidic, aqueous solution of $PdCl_2$ was discovered over a century ago,[2] but fifty years passed between the discovery of this reaction and the development of a catalytic method. In 1959, researchers at Wacker Chemie reported that a similar transformation takes place in an aqueous, acidic solution of catalytic $PdCl_2$ and a stoichiometric amount of $CuCl_2$ through which oxygen is bubbled (Equ. 7.3.4.1).[3]



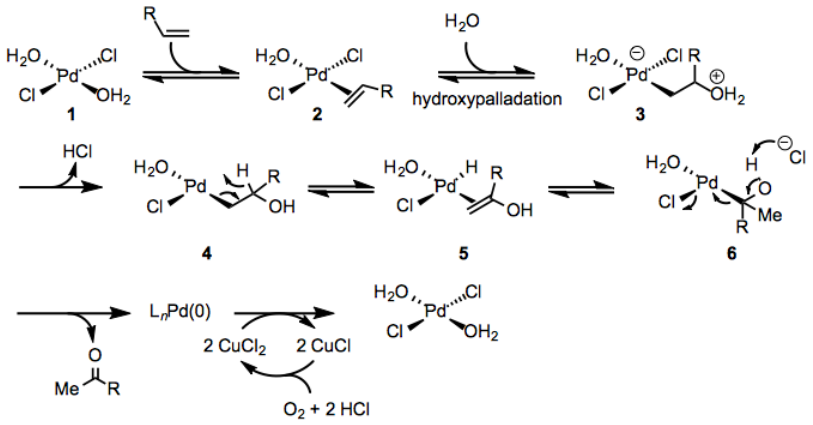
Equation 7.3.4.1

Since this initial report, the Wacker process has been widely applied in organic synthesis and has been extended to other classes of substrates and products. To encourage mixing of the organic reactants with the aqueous phase, a co-solvent is generally employed along with water. Dimethylformamide (DMF) is a common choice; when DMF is used as a co-solvent with a stoichiometric amount of CuCl under balloon pressure of oxygen, the reaction is called the "Tsuji-Wacker oxidation."[4] Applications of the Wacker oxidation to organic synthesis typically involve the installation of a methyl ketone moiety, which may subsequently undergo nucleophilic addition or deprotonation to form an enolate.

Mechanism and Stereochemistry

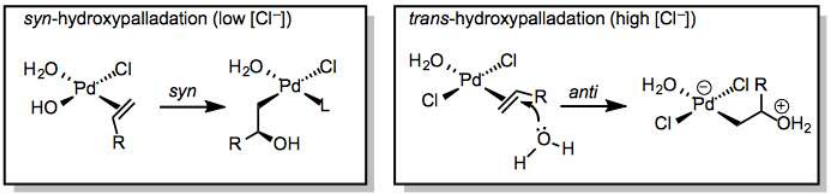
Prevailing Mechanism: Water Nucleophile

The mechanism of the Wacker oxidation has been studied both experimentally and theoretically (Eq. 2). The first step of the Wacker oxidation involves coordination of the the alkene to the palladium center to form π-complex **2**. Evidence for this step is provided by the relative sluggishness of electron-poor alkenes, which generally require higher catalyst loadings than unactivated alkenes. Hydroxypalladation then occurs to yield either zwitterionic complex **3** or neutral complex **4** depending on the mode of hydroxypalladation (see below). Studies employing deuterated substrates suggest that β-hydride elimination then occurs to afford enol complex **5**, which re-inserts into the Pd-H bond to afford complex **6**.[5] Computational studies support the involvement of chloride-assisted deprotonation in the subsequent step,[6] which affords the product and palladium(0). Oxidation of palladium(0) by copper(II) then occurs, regenerating palladium(II) species **1**. The role of copper(II) in the mechanism is poorly understood at present.



Equation 7.3.4.2

The mode of hydroxypalladation is an important issue for the Wacker oxidation. Hydroxypalladation may occur either in a *syn* fashion through an inner-sphere mechanism or in an *anti* fashion via nucleophilic attack on the coordinated alkene (Eq. 3). Although the stereocenter in **4** is ultimately destroyed upon elimination, the mode of hydroxypalladation can influence the site selectivity of the reaction. Markovnikov-type addition of water to the more substituted carbon of the alkene forms a methyl ketone, while attack of water at the less substituted position ultimately yields an aldehyde. The mode of hydroxypalladation has been shown to affect the distribution of ketone and aldehyde products, and is also important in stereoselective Wacker cyclization reactions. ***(2)***

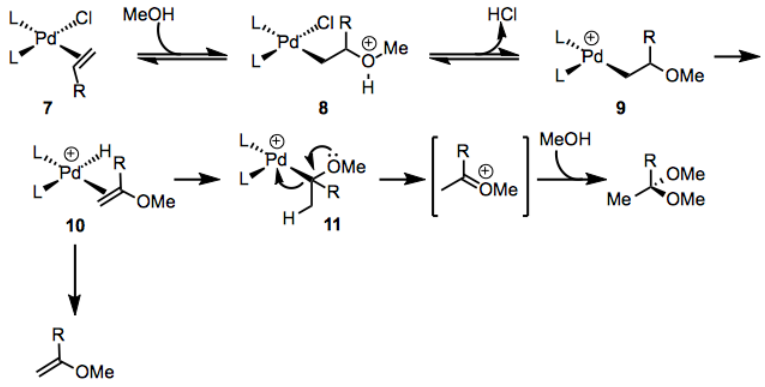


Equation 7.3.4.3

At low concentrations of chloride ion, *syn*-hydroxypalladation appears to be the norm.[7] Water coordinates to the metal and migratory insertion into the Pd-OH bond occurs to generate **4** directly. At high concentrations of chloride ion, chloride competes with hydroxide for binding at palladium, and thus *anti*-hydroxypalladation may occur.[8] ***(3)***

Prevailing Mechanism: Alcohol Nucleophiles

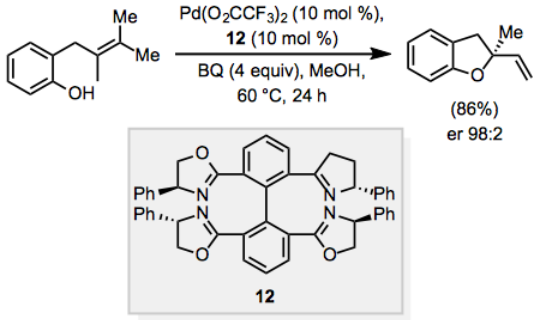
Alcohols may also be employed as nucleophiles in the Wacker process. The initial steps of the mechanism are similar to those for the Wacker oxidation with water, but the mechanisms diverge at alkoxy complex **11** (Eq. 4). Elimination of palladium occurs to generate an oxocarbenium ion, which may be captured by solvent to generate an acetal. Small amounts of vinyl ether products support the intermediacy of complex **10**.[9]



Equation 7.3.4.4

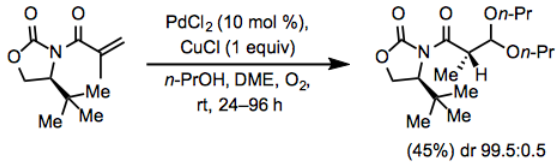
Enantioselective Variants

When the substrate contains a tethered nucleophile, such as a hydroxyl group or protected amine, the nucleophile may react to form a cyclic, allylic or vinylic ether or amine after β-hydride elimination. This process is known as the "Wacker cyclization," and when the product is allylic, a stereocenter may be established. Chiral ligands have been used to render the Wacker cyclization enantioselective. For example, use of tetra(dihydrooxazoline) ligand **12** and benzoquinone (BQ) as a co-oxidant resulted in formation of allylic ether product in an enantiomeric ratio of 98:2 (Eq. 5). [10]



Equation 7.3.4.5

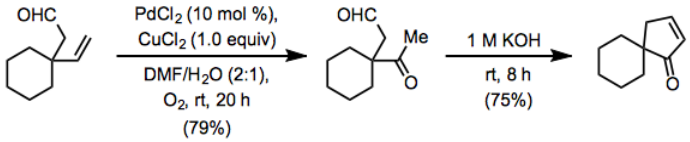
The Wacker process may also establish a stereocenter in 1,1-disubstituted alkenes via acetal formation. A chiral auxiliary in the alkene has been used successfully to generate chiral acetals with high diastereomeric ratio. The acetal forms at the more electron-deficient site of the alkene (Eq. 6).[11]



Equation 7.3.4.6

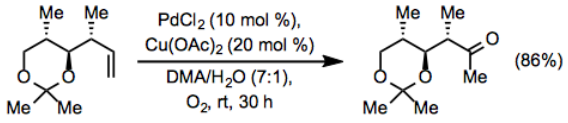
Scope and Limitations

Terminal alkenes are the most commonly employed substrates for the Wacker oxidation. Oxygen-containing functionality far from the reactive alkene is well tolerated by the reaction because palladium reacts selectively with the alkene in preference to lone pairs on oxygen. Wacker oxidation followed by intramolecular aldol condensation is a convenient method for the rapid synthesis of carbocycles (Eq. 7).[12]



Equation 7.3.4.7

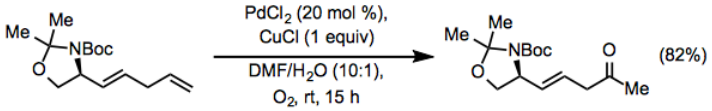
The original Wacker process and Tsuji-Wacker conditions can present problems for substrates containing acid-sensitive functionality, such as acetals and silyl ethers. Use of copper(II) chloride leads to the generation of strongly acidic hydrochloric acid. To mitigate this issue, a method employing copper(II) acetate has been developed. Some acid-sensitive groups are able to withstand the milder acetic acid generated by this method (Eq. 8).[13] Under similar conditions involving copper(I) chloride, a yield of only 56% was obtained.



Equation 7.3.4.8

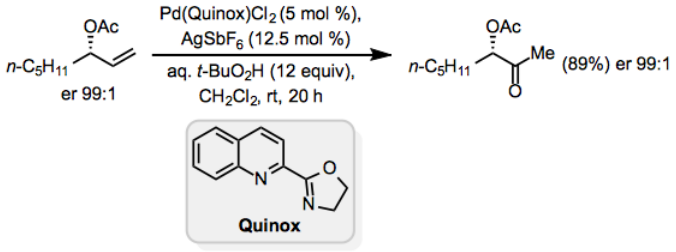
Unprotected amines coordinate strongly to palladium and thus cause problems for Wacker oxidations. Amines protected with electron-withdrawing substituents often do not interfere in Wacker oxidations,[14] although they may participate in aza-Wacker cyclizations if appropriately positioned in the substrate (see below).

Tri-substituted alkenes are completely inert to the conditions of the Wacker oxidation; only terminal and 1,1-disubstituted alkenes react. Terminal alkenes are usually oxidized selectively over internal alkenes, except under rather specialized circumstances.[15] Eq. 9 represents a typical case of selectivity for terminal alkenes.[14]



Equation 7.3.4.9

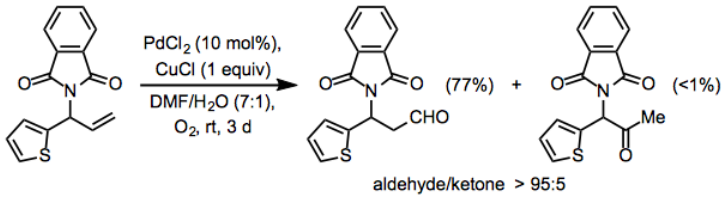
Lewis-basic functionality in the allylic or homoallylic position relative to the reactive alkene may cause unpredictable site selectivity in Wacker oxidations. Under standard Tsuji-Wacker conditions, unprotected allylic alcohols form mixtures of methyl ketone and aldehyde products.[16] The catalyst Pd(Quinox)Cl_2 was developed to address this problem; allylic alcohols react selectively in the presence of this catalyst to afford methyl ketones (Eq. 10).[17] *tert*-Butyl hydroperoxide (TBHP) is used as the oxygen source in this reaction.



Equation 7.3.4.10

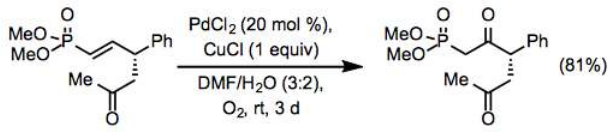
Protected, homoallylic alcohols generally form the methyl ketone selectively, but results are more unpredictable for unprotected homoallylic alcohols.[18]

Protected allylic amines generally give higher yields of aldehyde than comparable protected allylic alcohols; these results suggest that coordination of palladium to the Lewis base is responsible for the formation of aldehydes. Using a phthalimide group in the allylic position, the Wacker oxidation may be rendered completely selective for aldehydes (Eq. 11).[19]



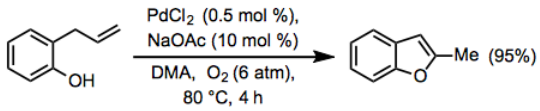
Equation 7.3.4.11

Site selectivity in reactions of internal alkenes is low unless an allylic or homoallylic Lewis base is present in the substrate. Electron-withdrawing groups can direct oxidation to the β position of the alkene (Eq. 12), but relatively high catalyst loadings are required.[20]



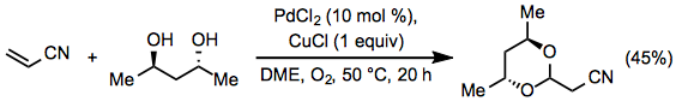
Equation 7.3.4.12

When an appropriately situated nucleophile is present in the substrate, Wacker cyclization may occur to yield an allylic or vinylic ether (Eq. 13).[21] The aza-Wacker cyclization involves protected amino nucleophiles such as sulfonamides.[22]



Equation 7.3.4.13

When an alcohol is used in stoichiometric or solvent quantities or a diol is present in the substrate, acetal formation may occur. Acetal formation, like ketone formation, generally occurs with Markovnikov selectivity. For example, a Michael acceptor forms an acetal at the β position in the presence of (*R*,*R*)-2,4-pentanediol (Eq. 14).[23]

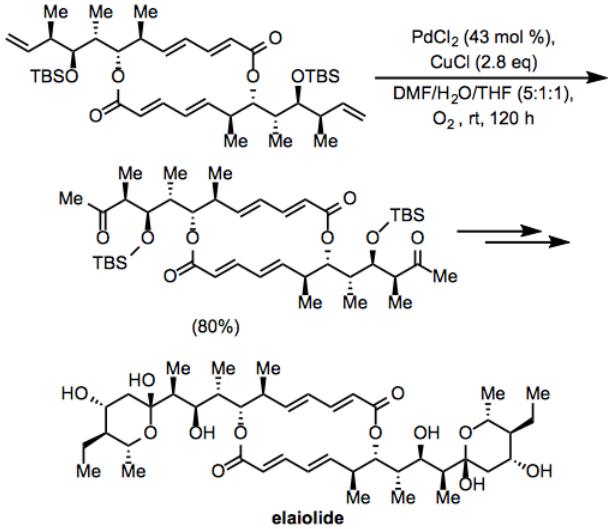


Equation 7.3.4.14

Synthetic Applications

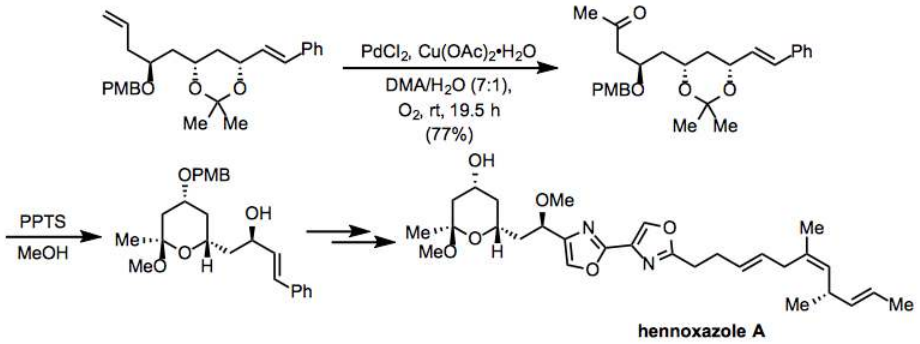
The Wacker oxidation has been used extensively in organic synthesis. A number of methods exist for the installation of terminal alkenes and the methyl ketone products of the reaction can be elaborated easily to more complex compounds. In addition, the reaction is aerobic and operationally simple.

The Wacker oxidation was employed in the course of synthesis of the macrolide elaiolide. Oxidation at two terminal alkenes in a C_2-symmetric intermediate afforded a diketone, which was subsequently elaborated to the symmetric natural product (Eq. 15).[24] Notably, the internal alkenes and esters in the intermediate appeared not to affect the oxidation.



Equation 7.3.4.15

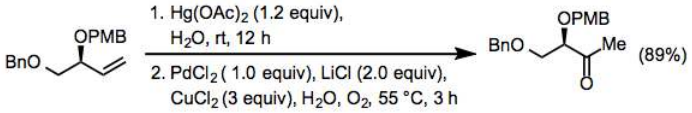
A modification of Tsuji-Wacker conditions employing copper(II) acetate was used in the course of a synthesis of hennoxazole A (Eq. 16).[25] After the oxidation, deprotection under acidic conditions led to the intramolecular formation of an acetal present in the target compound.



Equation 7.3.4.16

Comparison to Other Methods

Few true alternatives to the Wacker oxidation (that is, other hydration-oxidation reactions) are known. One rather harsh method involves oxymercuration followed by transmetalation to palladium (Eq. 17).[26]



Equation 7.3.4.17

Experimental Conditions and Procedure

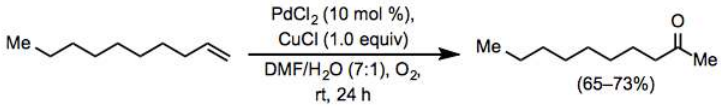
Typical Conditions

Tsuji-Wacker conditions represent a good starting point for experimental conditions for this reaction. Water is mixed with an organic co-solvent (often DMF) and 10 mol% $PdCl_2$, stoichiometric CuCl, and 1 atmosphere of oxygen gas. Copper(I) salts are generally superior to copper(II) salts because the former minimize the concentration of chloride in solution, encouraging *syn*-hydroxypalladation. Copper(I) is rapidly oxidized to copper(II) by dissolved oxygen; a period of 30 minutes prior to the introduction of the substrate is used to ensure that this oxidation is complete. For situations in which Tsuji-Wacker conditions fail, a wide variety of modifications of the reaction conditions may be employed.

Using high oxygen pressure and a judicious choice of solvent, Wacker oxidations can be carried out without the need for a co-oxidant. Certain ligands also promote direct O_2-coupled oxidations.[27]

Peroxides may also be used as the oxygen source in Wacker oxidations; these reactions do not require a co-oxidant. In the Pd(Quinox)/TBHP system, silver hexafluoroantimonate serves as a scavenger of chloride ions.

Experimental Procedure[4]



Equation 7.3.4.18

A 100-mL, 3-necked, round-bottomed flask was fitted with a magnetic stirring bar and a pressure-equalizing dropping funnel containing 1-decene (4.2 g, 30 mmol, 1.0 equiv). The flask was charged with a mixture of $PdCl_2$ (0.53 g, 3 mmol, 0.1 equiv), CuCl (2.97 g, 30 mmol, 1.0 equiv) and aqueous DMF (DMF/H_2O = 7:1, 24 mL). With the other outlets securely stoppered and wired down, an oxygen-filled balloon was placed over one neck, and the mixture was stirred at rt to allow oxygen uptake. After 1 h, the 1-decene (4.2 g, 30 mmol) was added over 10 min, and the solution was stirred vigorously at rt under an oxygen balloon. The color of the solution turned from green to black within 15 min and returned gradually to green. After 24 h, the mixture was poured into cold 3 N HCl (100 mL) and extracted with five, 50 mL portions of ether. The extracts were combined and washed successively with 50 mL of saturated aqueous $NaHCO_3$ solution, 50 mL of brine, and then dried over anhydrous magnesium sulfate. The solvent was removed by evaporation and the residue was distilled using a 15 cm Vigreux column to give 2-decanone as a colorless oil (3.0–3.4 g, 65–73%): bp 43.5 °C (1 mm Hg); IR (neat) 1722 cm^{-1}; ^1H NMR (CCl_4) δ 2.37 (t, J = 7 Hz, 2H), 2.02 (s, 3H), 0.7–1.8 (m, 15H).

References

1. Michel, B. W.; Steffens, L. D.; Sigman, M. S. *Org. React.* **2014**, *84*, 2. (doi: 10.1002/0471264180.or084.02)
2. Phillips, F. C. *Am. Chem. J.* **1894**, *16*, 255.
3. Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176.
4. [a] [b] Tsuji, J.; Nagashima, H.; Nemoto, H. *Org. Synth.* **1984**, *62*, 9.
5. Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabel, A. *Angew. Chem.* **1962**, *74*, 93.
6. Eshtiagh-Hosseini, H.; Beyramabadi, S. A.; Morsali, A.; Housaindokht, M. R. *J. Mol. Struct.: THEOCHEM* **2010**, *941*, 138.
7. Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246.
8. Bäckvall, J. E.; Akermark, B.; Ljunggren, S. O. *J. Chem. Soc., Chem. Commun.* **1977**, 264.
9. Balija, A. M.; Stowers, K. J.; Schultz, M. J.; Sigman, M. S. *Org. Lett.* **2006**, *8*, 1121.
10. Zhang, Y. J.; Wang, F.; Zhang, W. *J. Org. Chem.* **2007**, *72*, 9208.
11. Hosokawa, T.; Yamanaka, T.; Itotani, M.; Murahashi, S.-I. *J. Org. Chem.* **1995**, *60*, 6159.
12. Srikrishna, A.; Kumar, P. P. *J. Indian Chem. Soc.* **1999**, *76*, 521.
13. Smith, A. B., III; Cho, Y. S.; Friestad, G. K. *Tetrahedron Lett.* **1998**, *39*, 8765.
14. [a] [b] Reginato, G.; Mordini, A.; Verrucci, M.; Degl'Innocenti, A.; Capperucci, A. *Tetrahedron: Asymmetry* **2000**, *11*, 3759.
15. Ho, T.-L.; Chang, M. H.; Chen, C. *Tetrahedron Lett.* **2003**, *44*, 6955.
16. Muzart, J. *Tetrahedron* **2007**, *63*, 7505.
17. Michel, B. W.; Camelio, A. M.; Cornell, C. N.; Sigman, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 6076.
18. Kang, S.-K.; Jung, K.-Y.; Chung, J.-U.; Namkoong, E.-Y.; Kim, T.-H. *J. Org. Chem.* **1995**, *60*, 4678.
19. Weiner, B.; Baeza, A.; Jerphagnon, T.; Feringa, B. L. *J. Am. Chem. Soc.* **2009**, *131*, 9473.
20. Yan, B.; Spilling, C. D. *J. Org. Chem.* **2008**, *73*, 5385.
21. Mitsudome, T.; Umetani, T.; Nosaka, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 481.
22. Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444.
23. Hosokawa, T.; Ataka, Y.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 166.
24. Barth, R.; Mulzer, J. *Tetrahedron* **2008**, *64*, 4718.
25. Yokokawa, F.; Asano, T.; Shioiri, T. *Tetrahedron* **2001**, *57*, 6311.
26. Ellis, J. M.; Crimmins, M. T. *Chem. Rev.* **2008**, *108*, 5278.
27. Cornell, C. N.; Sigman, M. S. *Org. Lett.* **2006**, *8*, 4117.

Contributors

- This page is based on *Organic Reactions*. The primary collection of full *Organic Reactions* chapters is maintained by John Wiley & Sons.

This page titled 7.3.4: Wacker (Smidt) Process is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.3.5: Hydrogenation by Wilkinson's Catalyst

Organometallic Compounds as Hydrogenation Catalysts

Migratory insertions play an important role in catalysis.

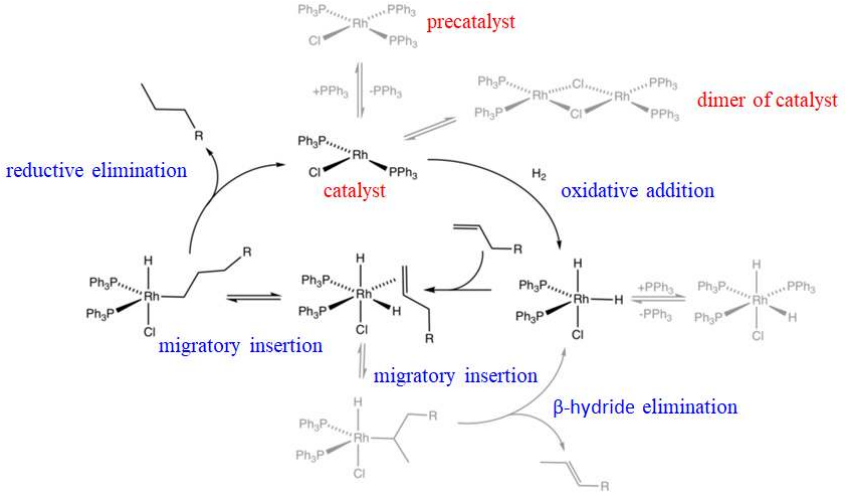


Figure 7.3.5.1: Mechanism of the Wilkinson hydrogenation catalyst (Attribution: Smokefoot / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0) https://commons.wikimedia.org/wiki/F...cleJMBrown.png)

For example a Rh-catalyst called the Wilkinson catalyst is an effective hydrogenation catalyst for olefins. The mechanism of the hydrogenation involves a combination of oxidative additions, olefin migratory insertions, and reductive eliminations (Fig. 7.3.5.1). Wilkinson's catalyst is the square planar chloro tris(triphenylphosphine) rhodium(I) complex. This molecule is actually a precatalyst that becomes the actual catalyst when it statistically loses a triphenylphosphine ligand producing chloro bis(triphenylphosphine) rhodium(I). The loss of this ligand is a reversible reaction, and thus the catalyst is in chemical equilibrium with the precatalyst. The actually catalyst is in a second chemical equilibrium with its dimer. The chloro bis(triphenylphosphine) rhodium(I) catalyst can undergo an oxidative addition in the presence of hydrogen to form a trigonal bipyramidal chlorodihydrido bis(triphenylphosphine) (III) rhodium complex. This species is in chemical equilibrium with an octahedral chlorodihydrido tris(triphenyl phosphine) rhodium(III) species that can form due to the presence of free triphenylphosphine ligands in the system. The trigonal bipyramidal species can then add an olefin that binds side-on to the Rh. Because the olefin is in cis-position to the hydride ligand it can undergo an olefin insertion. The Rh-C bond can either form with the first or the second carbon in the carbon chain of the olefin, giving a linear and a branched alkyl complex, respectively. The branched complex can undergo a β-hydride elimination thereby reforming the trigonal bipyramidal Rh-complex, and an olefin. This reaction is a side-reaction because the branched alkyl complex is sterically more crowded than the linear complex. The linear alkyl Rh complex can undergo a reductive elimination to form the linear alkane and the $RhCl(PPh_3)_2$ catalyst. This completes the catalytic cycle, and a new cycle can start.

This page titled 7.3.5: Hydrogenation by Wilkinson's Catalyst is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.2: Organometallic Catalysts** by Kai Landskron is licensed CC BY 4.0.

7.3.6: Olefin Metathesis

Olefin Metathesis

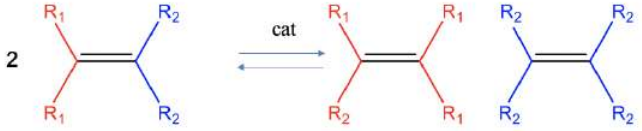


Figure 7.3.6.1: Olefin metathesis

Olefin metathesis is a reaction which allows to cut and rearrange C=C double bonds in olefins to make new olefins (Fig. 7.3.6.1). Formally, the carbon-carbon bond of the reactant is cleaved homoleptically and the two carbene fragments are combined in a different way. This reaction is typically an equilibrium reaction, and neither the reactants nor the products are clearly favored. This reaction is catalyzed by molybdenum arylamido carbene complexes or ruthenium carbene complexes.

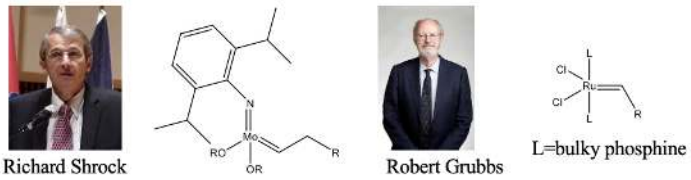


Figure 7.3.6.2: Shrock catalyst (Attribution: R._Schrock_-_IChO_2012_Opening_Ceremony.JPG: A.mela93derivative work: Materialscientist / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...hrock_2012.jpg) and (Attribution: The Royal Society / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...al_Society.jpg)

The former are called Shrock catalysts, and the latter Grubbs catalysts named after their discoverers Richard Shrock and Robert Grubbs who received the Nobel prize for Chemistry in 2005 (Fig. 7.3.6.2). The Schrock catalysts are more active, but also very sensitive to air and water. The Grubbs catalysts, while less active, are less sensitive to air and water.

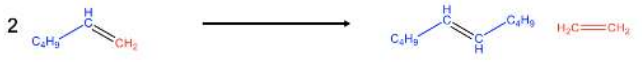


Figure 7.3.6.3: Regular metathesis

Olefin metathesis often allows for simpler preparation of olefins compared to other methods. Olefin metathesis is particularly powerful when one olefin product is gaseous because then it can be quite easily removed from the chemical equilibrium by purging. This drives the chemical equilibrium to the right side. An example is the preparation of 5-decene from 1-hexene. Cleavage of the C=C double bond in the hexene leads to C_5 and C_1 carbene fragments (Fig. 7.3.6.3). The two C_1 fragments can combine to form ethylene and the two C_5 fragments combine to 5-decene. The ethylene is volatile and can be purged from the reaction system thereby driving the chemical reaction to the right side.

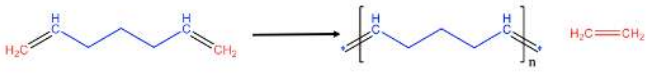


Figure 7.3.6.4: Acylic diene metathesis (ADMET)

The same principles can also be applied to produce polymers from dienes with two terminal C=C double bonds at the chain ends. This is called acylic diene metathesis (ADMET), Fig. 7.3.6.4 For instance the cleavage of the two terminal double bonds in a diene with seven C atoms leads to C_1 and C_5 fragments. The C_1 fragments can combine to form ethylene, and the C_5 fragments can combine to make an unsaturated polymer of the type $[CH(CH_2)_3CH]_n$. Again, the reaction can be driven to the right side by removing the gaseous ethylene from the reaction mixture through purging.

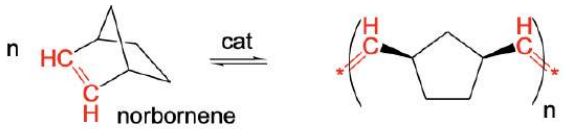


Figure 7.3.6.5: Ring-opening metathesis polymerization (ROMP)

Another variation of olefin metathesis is ring-opening metathesis polymerization (ROMP). It allows to make polymers from strained cycloolefins, for example norbornene. The reaction driving force is the relief of the strain. Because the strain is removed in the polymer, the chemical equilibrium lies far on the right side. The reaction product in norbornene is a polymer with 5-membered rings that are interconnected by ethylene -CH=CH- units (Fig. 7.3.6.5).

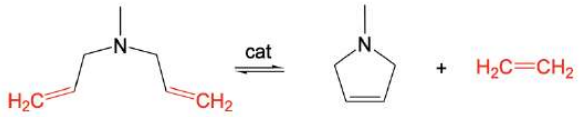


Figure 7.3.6.6: Ring-closing metathesis (RCM)

The opposite of ROMP is ring-closure metathesis (RCM). RCM allows for the preparation of unstrained rings with C=C double bonds from dienes with C=C double bonds that are five or six carbon atoms apart. This distance is suitable to produce unstrained rings. In the shown example a five-membered ring with a C=C double bond is formed from a diene with terminal C=C double bonds that are five atoms apart.

The Mechanism of Olefin Metathesis

What is the mechanism of olefin metathesis?

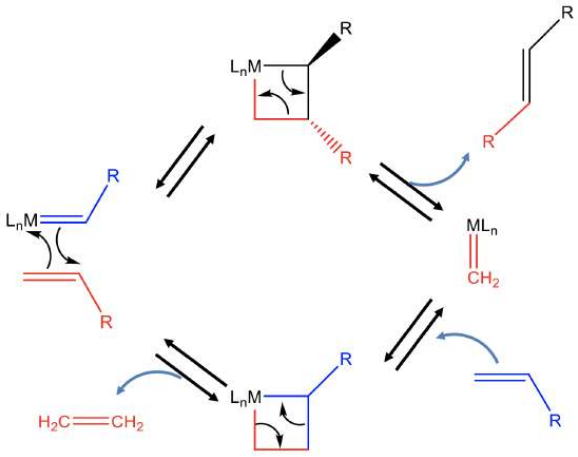


Figure 7.3.6.7: The mechanism of olefin metathesis

In the first step, the alkene adds to the the carbene fragment of the catalyst in a 2+2 cycloaddition reaction to produce an unstable intermediate with a highly strained four-membered ring (Fig. 7.3.6.7). This four membered ring can open to produce the first new alkene product R-CH=CH-R and a metal carbene species. This metal carbene can react with another reactant olefin to form another highly stained 4-ring intermediate via a 2+2 cycloaddition reaction. This ring can then reopen again to produce the second alkene metathesis product, in this case ethylene, and the original catalyst. The regenerated catalyst can then start a new catalytic cycle.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 7.3.6: Olefin Metathesis is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.2: Organometallic Catalysts** by Kai Landskron is licensed CC BY 4.0.

7.4: Heterogeneous Catalysts

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 7.4.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

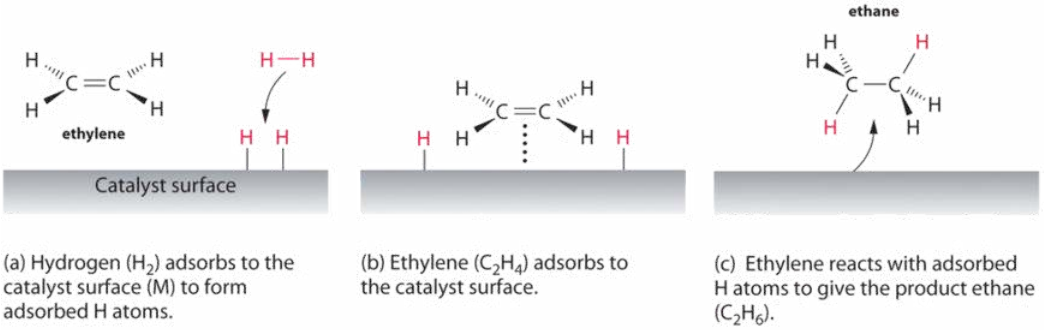


Figure 7.4.1: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 7.4.1 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 7.4.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 7.4.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$ (acrylonitrile)

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
catalytic hydrogenation	Ni, Pd, or Pt	$RCH{=}CHR' + H2 \rightarrow RCH_2{-}CH_2R'$	partially hydrogenated oils for margarine, and so forth

This page titled 7.4: Heterogeneous Catalysts is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

- **14.7: Catalysis** is licensed CC BY-NC-SA 3.0.

7.4.1: Ziegler-Natta Polymerizations

Another example of an organometallic catalytic reaction is the Ziegler-Natta olefin polymerization. This reaction is of high industrial importance for the production of olefins like polyethylene. There are both heterogeneous and homogeneous Ziegler-Natta catalysts. The mechanism for the homogeneous catalysts is generally well understood. Homogeneous catalysts are typically metallocene catalysts.

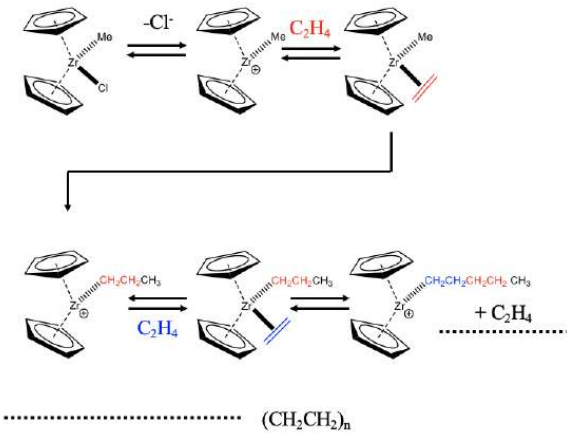


Figure 7.4.1.1: Zirconium-based Ziegler-Natta catalyst (Attribution: A. Vedernikov, U Maryland (modified).)

An example of a zirconium-based catalyst is shown (Fig. 7.4.1.1). The catalyst is a coordinatively unsaturated complex cation with two cyclopentadienyl rings and a methyl group. The catalyst is formed from its precatalyst, a neutral molecule with an additional chloro ligand. The catalyst oxidatively adds an olefin like an ethylene molecule to the coordinatively unsaturated site. This step is followed an olefin insertion step that produces a propyl group. The migratory insertion leads to the formation of a vacant site, that can be re-oocupied by another ethylene molecule. This molecule can insert into the propyl chain thereby prolonging the propyl chain to a pentyl chain. The olefin insertion step generates another vacant site that can be reoccupied by a new ethylene molecule. Repeating the catalytic cycle many times eventually leads to polyethylene.

The Ziegler-Natta (ZN) catalyst, named after two chemists: Karl Ziegler and Giulio Natta, is a powerful tool to polymerize α-olefins with high linearity and stereoselectivity (Figure 1). A typical ZN catalyst system usually contains two parts: a transition metal (Group IV metals, like Ti, Zr, Hf) compound and an organoaluminum compound (co-catalyst). The common examples of ZN catalyst systems include $TiCl_4$ + Et_3Al and $TiCl_3$ + $AlEt_2Cl$.

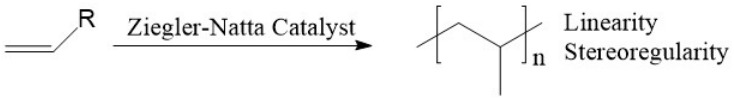


Figure 7.4.1.2: The generic reaction equation for polymerization of -olefins.

In 1953, German chemist Karl Ziegler discovered a catalytic system able to polymerize ethylene into linear, high molecular weight polyethylene which conventional polymerization techniques could not make.[1] The system contained a transition metal halide with a main group element alkyl compound (Figure 7.4.1.3).

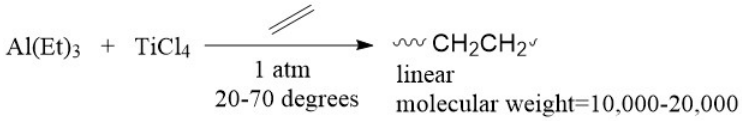


Figure 7.4.1.3: Linear polyethylene obtained by Ziegler's catalytic system (20-70).

Following the catalytic design, Italian chemist Giulio Natta found that polymerization of α-olefins resulted in stereoregular structures,[2] either syndiotactic or isotactic, depending on the catalyst used (Figure 7.4.1.4). Because of these important discoveries, Karl Ziegler and Giulio Natta shared the Nobel Prize in Chemistry in 1963.

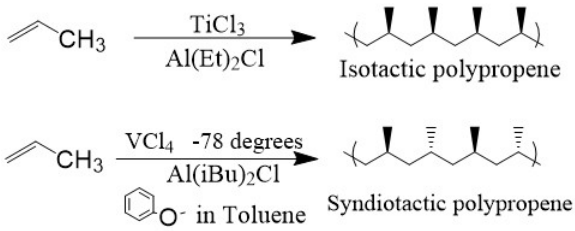


Figure 7.4.1.4: The ZN catalytic polymerization of linear polypropene with two different stereoregular structures.

Advantages over traditional polymerization method

Traditionally, polymerization of α-olefins was done by radical polymerization (Figure 7.4.1.5). Problem with this technique was that the formation of undesired allylic radicals leaded to branched polymers.[3] For example, radical polymerization of propene gived branched polymers with large molecular weight distribution. Also, radical polymerization had no control over stereochemistry. Linear unbranched polyethylene and stereoregulated polypropylene could not be fabricated by free radical polymerization. This technique largely limited the potential applications of these polymeric materials.

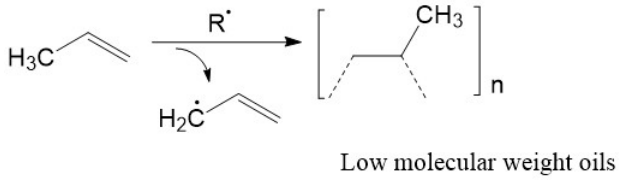


Figure 7.4.1.5: The radical polymerization of propylene using traditional method.

The invention of ZN catalyst successfully addressed these two problems. The catalyst can give linear α-olefin polymers with high and controllable molecular weights. Moreover, it makes the fabrication of polymers with specific tacticity possible. By controlling the stereochemistry of products, either syndiotactic or isotactic polymers can be achieved.

Mechanism of Ziegler-Natta catalytic polymerization

Activation of Ziegler-Natta catalyst

It is necessary to understand the catalyst's structure before understanding how this catalyst system works. Herein, $TiCl_4$+$AlEt_3$ catalyst system is taken as an example. The titanium chloride compound has a crystal structure in which each Ti atom is coordinated to 6 chlorine atoms. On the crystal surface, a Ti atom is surrounded by 5 chlorine atoms with one empty orbital to be filled. When Et_3Al comes in, it donates an ethyl group to Ti atom and the Al atom is coordinated to one of the chlorine atoms. Meanwhile, one chlorine atom from titanium is kicked out during this process. Thus, the catalyst system still has an empty orbital (Figure 7.4.1.6). The catalyst is activated by the coordination of $AlEt_3$ to Ti atom.

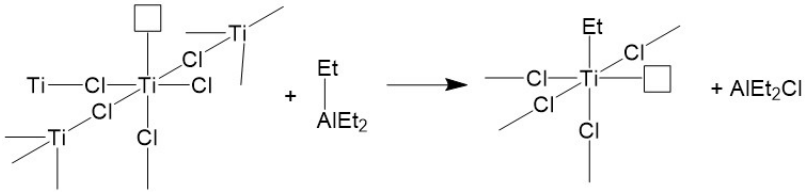


Figure 7.4.1.6: The activation of ZN catalyst system by coordination of $AlEt_3$ to Ti atom.

Initiation step

The polymerization reaction is initiated by forming alkene-metal complex. When a vinyl monomer like propylene comes to the active metal center, it can be coordinated to Ti atom by overlapping their orbitals. As shown in Figure 7.4.1.7, there is an empty dxy orbital and a filled dx^2-y^2 orbital in Ti's outermost shell (the other four orbitals are not shown here). The carbon-carbon double bond of alkene has a pi bond, which consists of a filled pi-bonding orbital and an empty pi-antibonding orbital. So, the alkene's pi-bonding orbital and the Ti's dxy orbital come together and share a pair of electrons. Once they're together, that Ti's dx^2-y^2 orbital comes mighty close to the pi-antibonding orbital, sharing another pair of electrons.

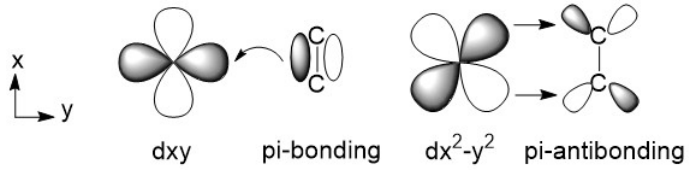


Figure 7.4.1.7: Molecular orbitals representation of monomer coordinating to metal center.

The formed alkene-metal complex (1) then goes through electron shuffling, with several pairs of electrons shifting their positions: The pair of electrons from the carbon-carbon pi-bond shifts to form Ti-carbon bond, while the pair of electrons from the bond between Ti and AlEt3' ethyl group shifts to form a bond between the ethyl group and the methyl-substituted carbon of propylene (Figure 7.4.1.8). After electron shuffling, Ti is back with an empty orbital again, needing electrons to fill it (2).

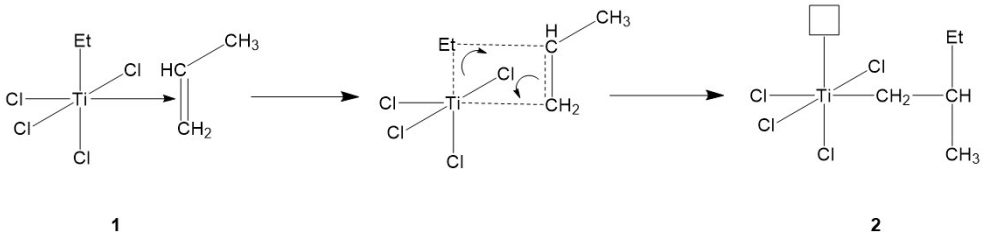


Figure 7.4.1.8: The formation process of alkene-metal complex.

Propagation step

When other propylene molecules come in, this process starts over and over, giving linear polypropylene (Figure 7.4.1.9).

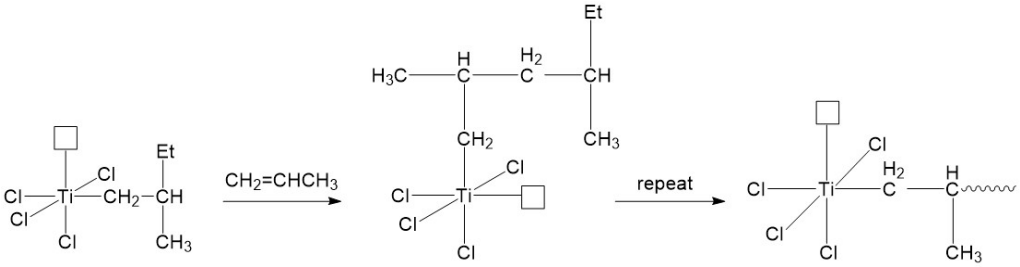


Figure 7.4.1.9: Propagation towards polymeric chains.

Termination step

Termination is the final step of a chain-growth polymerization, forming "dead" polymers (desired products). Figure 7.4.1.10 illustrates several termination approaches developed with the aid of co-catalyst $AlEt_3$.[4]

https://chem.libretexts.org/@go/page/429339

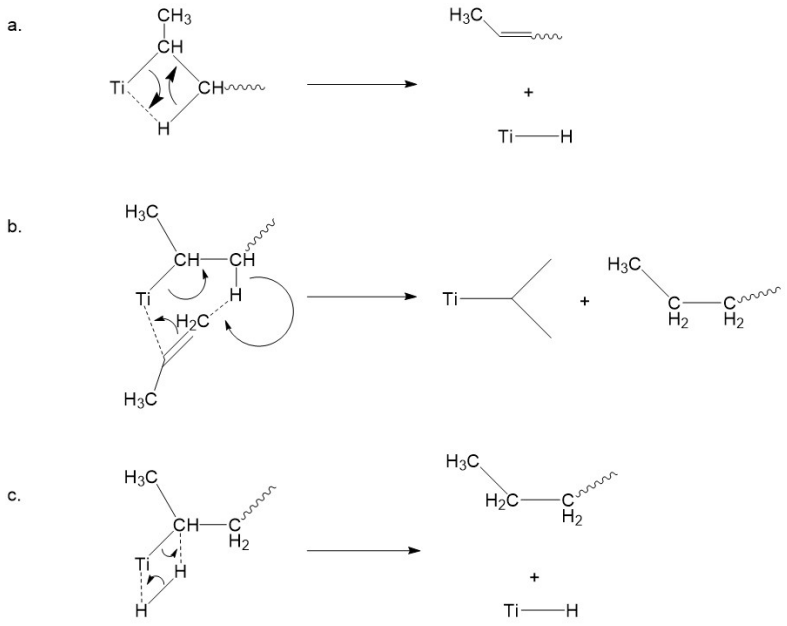


Figure 7.4.1.10: Three termination approaches: (a) β-elimination from the polymer chain, forming metal hydride; (b) β-elimination with hydrogen transfer to monomer; (c)hydrogenation.

Mechanistic study: kinetic isotope effect experiments

Unlike the mechanism discussed above, there is also a competing mechanism proposed by Ivin and coworkers.[5] They proposed that a 1,2-hydrogen shift occurs prior to monomer association, giving a carbene intermediate (Figure 7.4.1.11).

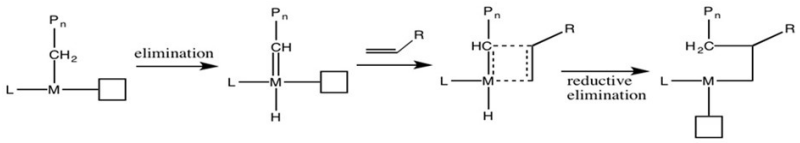


Figure 7.4.1.11: Alternative propagation mechanism: hydride shift prior to monomer association.

To determine the actual mechanism, Grubbs[6] conducted kinetic isotope effect (KIE) experiments. Due to their different weights, carbon-deuterium bond reacts slower than carbon-hydrogen bond (Figure 7.4.1.12). If such bonds are involved in the rate-determining step, the isotopic species should proceed in lower rate.

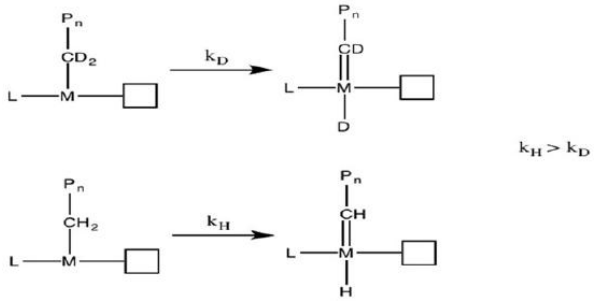


Figure 7.4.1.12: Carbon-deuterium bonds react slower than carbon-hydrogen bonds.

In Grubbs's experiment, deuterated ethylene and normal ethylene were catalyzed by Ziegler-Natta catalyst with 1:1 ratio (Figure 7.4.1.13). The result showed that H/D ratio in the resulting polymers was still 1:1.6 This indicated that no carbon-hydrogen bond cleavage or formation is involved in the rate determining step. Therefore, the mechanism proposed by Ivin was excluded.

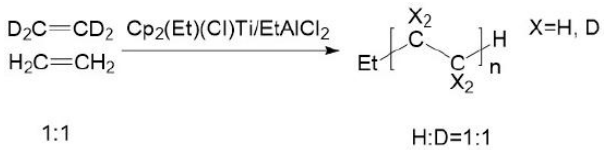


Figure 7.4.1.13: KIE experiment excludes Ivin's mechanism.

Regio- and stero-selectivity

Regio-selectivity

For propene polymerization, most ZN catalysts are highly regioselective, favoring 1,2-primary insertion [M-R + CH2=CH(Me)=M-CH2-CH(Me)(R)] (Figure 7.4.1.14), due to electronic and steric effects.[7]

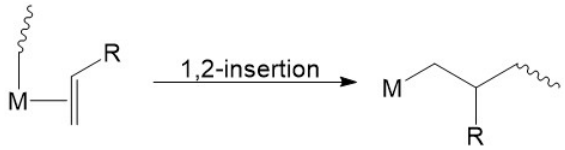


Figure 7.4.1.14: Primary insertion occurs in ZN-catalytic system to give regioselective products.

Stereo-selectivity

Stereochemistry of polymers made from ZN-catalyst can be well regulated by rational design of ligands. By using different ligand system, either syndiotactic or isotactic polymers can be obtained (Figure 7.4.1.15).

The relative stereochemistry of adjacent chiral centers within a macromolecule is defined as tacticity. Three kinds of stereochemistry are possible: isotactic, syndiotactic and atactic. In isotactic polymers, substituents are located on the same side of the polymer backbone, while substituents on syodiotactic polymers have alternative positions. In atactic polymers, substituents are placed randomly along the chain.

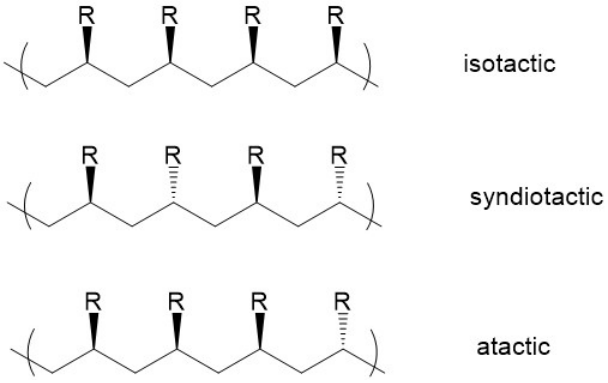


Figure 7.4.1.15: Tacticity of macromolecules

Choice of ZN catalyst regulates the stereochemistry. We use propylene polymerization as an example here. Recall the mechanism section, a monomer approaches the metal center and forms a four-membered ring intermediate. The binding of a monomer to the reactive metal-carbon bond should occur in from the least hindered site.[8] As shown in Figure 7.4.1.16, the trans-complex in which methyl on the growing chain is trans to the methyl group on the incoming monomer, should be energetically favored than the cis-complex, as the trans-complex experience less steric effect.

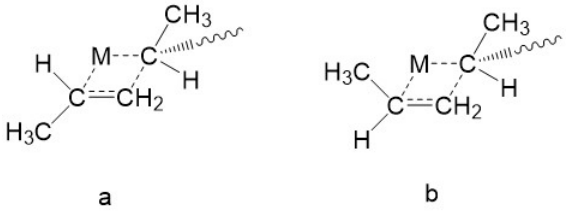


Figure 7.4.1.16: The active state a (trans) is more stable than b (cis) due to less steric effects of methyl groups.

Following the trans- complex, the methyl group on the newly added monomer is trans to that on the previous monomer. The step repeats so that a syndiotactic polypropylene is obtained (Figure 7.4.1.17a). However, if the metal center is coordinated with bulky ligands (e.g. –iBu, -Et2 groups), as denoted by Y in Figure 7.4.1.17b, the incoming monomer will adopt a cis-conformation to avoid serious steric effect with the bulky ligand. Thus, at the presence of bulky ligand, the propylene monomer is cis to the growing chain. This results in a isotactic product.

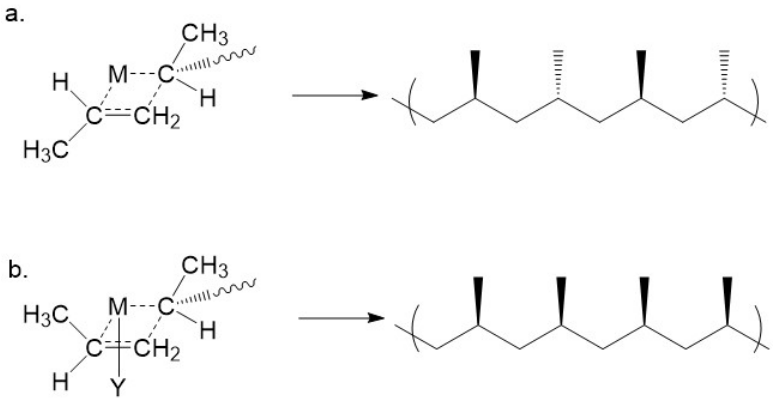


Figure 7.4.1.17: a. Trans-intermediate avoids 1,3-strain of methyl groups, producing syndiotactic polypropylene; b. at the presence of bulky ligand Y, a cis-intermediate is adopted, generating isotactic polypropylene.

Applications

ZN catalysts have provided a worldwide profitable industry with production of more than 160 billion pounds and creation of numerous positions.[9] These products have been extensively applied in different areas, largely improving the quality of people's life. They can catalyze α-olefins to produce various commercial polymers, like polyethylene, polypropylene and Polybutene-1. Polyethylene and polypropylene is reported to be the top two widely used synthetic plastic in the word.[10]

Among the polyethylene fabricated by ZN catalysts, there are three major classes: high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and ultra-high molecular weight polyethylene (UHMWPE). HDPE, a linear homopolymer, is widely applied in garbage containers, detergent bottles and water pipes because of its high tensile strength. Compared with HDPE whose branching degree is quite low, LLDPE has many short branches. Its better toughness, flexibility and stress-cracking resistance makes it suitable for materials like cable coverings, bubble wrap and so on. UHMWPE is polyethylene with a molecular weight between 3.5 and 7.5 million. This material is extremely tough and chemically resistant. Therefore, it is often used to make gears and artificial joints.

Compared to polyethylene, polypropylene has enhanced mechanical properties and thermal resistance because of the additional methyl group. Moreover, isotactic polypropylene is stiffer and more resistant to creep than atactic polypropylene. Polypropylene has a wide range of applications in clothing, medical plastics, food packing, and building construction.

Substrate scope and limitations

ZN catalysts are effective for polymerization of α-Olefins (ethylene, propylene) and some dienes (butadiene, isoprene). However, they don't work for some other monomers, such as 1.2 disubstituted double bonds. Vinyl chloride cannot be polymerized by ZN catalyst either, because free radical vinyl polymerization is initiated during the reaction. Another situation that ZN catalysts don't work is when the substrate is acrylate. The reason is that ZN catalysts often initiate anionic vinyl polymerization in those monomers.[11]

References

1. Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H., Polymerisation Von Athylen Und Anderen Olefinen. Angew Chem Int Edit 1955, 67 (16), 426-426.
2. Natta, G., Une Nouvelle Classe De Polymeres D Alpha-Olefines Ayant Une Regularite De Structure Exceptionnelle. J Polym Sci 1955, 16 (82), 143-154.
3. Mulhaupt, R., Catalytic polymerization and post polymerization catalysis fifty years after the discovery of Ziegler's catalysts. Macromol Chem Phys 2003, 204 (2), 289-327.
4. Sinn, H.; Kaminsky, W., Ziegler-Natta Catalysis. In Advances in Organometallic Chemistry, Stone, F. G. A.; Robert, W., Eds. Academic Press: 1980; Vol. Volume 18, pp 99-149.
5. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L.; Mahtab, R., Mechanism for the stereospecific polymerization of olefins by Ziegler–Natta catalysts. Journal of the Chemical Society, Chemical Communications 1978, (14), 604-606.
6. Soto, J.; Steigerwald, M. L.; Grubbs, R. H., Concerning the Mechanism of Ziegler-Natta Polymerization - Isotope Effects on Propagation Rates. J Am Chem Soc 1982, 104 (16), 4479-4480.

7. Busico, V.; Cipullo, R.; Pellecchia, R.; Ronca, S.; Roviello, G.; Talarico, G., Design of stereoselective Ziegler-Natta propene polymerization catalysts. P Natl Acad Sci USA 2006, 103 (42), 15321-15326.
8. Zambelli, A., Stereoregulation of Propylene Polymerization. Abstr Pap Am Chem S 1974, 34-34.
9. Ittel, S. D.; Johnson, L. K.; Brookhart, M., Late-metal catalysts for ethylene homo- and copolymerization. Chem Rev 2000, 100 (4), 1169-1203.
10. Macbride, R. R., High Molecular-Weight Polyethylene Drums Show Signs of Becoming Big Business. Mod Plast 1975, 52 (12), 10-&.
11. Ivan, B., Comparison of Living Polymerization Systems. Macromol Symp 1994, 88, 201-215.

Contributors and Attributions

- Fangyuan Dong and Ru Deng

This page titled 7.4.1: Ziegler-Natta Polymerizations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **12.2: Organometallic Catalysts** by Kai Landskron is licensed CC BY 4.0.

7.4.2: Water-Gas Shift Reaction

The **water-gas shift reaction** (WGSR) describes the reaction of carbon monoxide and water vapor (steam) at very high temperatures to form carbon dioxide and hydrogen:

$$\mathrm{CO + H_2O \rightleftharpoons CO_2 + H_2} \tag{7.4.2.1}$$

The WGSR is a highly valuable industrial reaction that is used in the manufacture of ammonia, hydrocarbons, methanol, and hydrogen. Its most important application is in the conversion of carbon monoxide or other hydrocarbons to produce hydrogen gas, an important source of fuel for a modern hydrogen economy. If hydrogen could be produced at low cost and using a renewable resource, it could significantly advance the movement to sustainable energy.

Most of the catalysts that are used for this process are heterogeneous catalysts. Unfortunately, the process using heterogeneous catalysts occurs only at extremely high temperatures and pressures. The high energy cost of performing the reaction limits its industrial utility, and there are efforts to produce homogeneous catalysts that catalyze the reaction at more mild conditions. Another limitation is that the reaction requires sufficient quantities of CO, which are primarily obtained from non-renewable coal or petroleum sources. However, there are processes that can convert methane gas, which is an abundant greenhouse gas, to .

The WGSR has been extensively studied for over a hundred years. The kinetically relevant mechanism depends on the catalyst composition and the temperature. Two mechanisms have been proposed: an associative Langmuir–Hinshelwood mechanism and a redox mechanism. The redox mechanism is generally regarded as kinetically relevant during the high-temperature WGSR (> 350 °C) over the industrial Fe-Cr catalyst. Historically, there has been much more controversy surrounding the mechanism at low temperatures. Recent experimental studies confirm that the associative carboxyl mechanism is the predominant low temperature pathway on metal-oxide-supported transition metal catalysts.

Associative mechanism

In 1920 Armstrong and Hilditch first proposed the associative mechanism. In this mechanism CO and H_2O are adsorbed onto the surface of the catalyst, followed by formation of an intermediate and the desorption of H_2 and CO_2. In general, H_2O dissociates onto the catalyst to yield adsorbed OH and H. The dissociated water reacts with CO to form a carboxyl or formate intermediate. The intermediate subsequently dehydrogenates to yield CO_2 and adsorbed H. Two adsorbed H atoms recombine to form H_2.

There has been significant controversy surrounding the kinetically relevant intermediate during the associative mechanism. Experimental studies indicate that both intermediates contribute to the reaction rate over metal oxide supported transition metal catalysts. However, the carboxyl pathway accounts for about 90% of the total rate owing to the thermodynamic stability of adsorbed formate on the oxide support. The active site for carboxyl formation consists of a metal atom adjacent to an adsorbed hydroxyl. This ensemble is readily formed at the metal-oxide interface and explains the much higher activity of oxide-supported transition metals relative to extended metal surfaces. The turn-over-frequency for the WGSR is proportional to the equilibrium constant of hydroxyl formation, which rationalizes why reducible oxide supports (e.g. CeO_2) are more active than irreducible supports (e.g. SiO_2) and extended metal surfaces (e.g. Pt). In contrast to the active site for carboxyl formation, formate formation occurs on extended metal surfaces. The formate intermediate can be eliminated during the WGSR by using oxide-supported atomically dispersed transition metal catalysts, further confirming the kinetic dominance of the carboxyl pathway.

Redox mechanism

The redox mechanism involves a change in the oxidation state of the catalytic material. In this mechanism, CO is oxidized by an O-atom intrinsically belonging to the catalytic material to form CO_2. A water molecule undergoes dissociative adsorption at the newly formed O-vacancy to yield two hydroxyls. The hydroxyls disproportionate to yield H_2 and return the catalytic surface back to its pre-reaction state.



Figure 7.4.2.1: Proposed associative and redox mechanisms of the water gas shift reaction. (Zwickipedia, WGS mechanism, CC BY-SA 3.0)

Source: https://en.Wikipedia.org/wiki/Water%...shift_reaction

This page titled 7.4.2: Water-Gas Shift Reaction is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.5: Problems

This page titled 7.5: Problems is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.5.1: Concept Review Questions Chapter 12

Concept Review Questions

Section 1

1) What is an oxidative addition?

2) What is a reductive elimination?

3) What is a cis and a trans addition, respectively?

4) Does the coordination number in oxidative additions always increase? Explain.

5) What is the reverse reaction of an oxidative addition?

6) What is a migratory insertion?

7) Are migratory insertions reversible reactions?

Section 2

1) Why are transition metal alkyl complexes that have alkyl groups longer than 1 carbon atom often unstable?

2) What is meant by beta-hydride elimination?

3) What is alpha-abstraction?

4) What is a nucleophilic displacement reaction?

5) What is meant by an oxidative addition of an intact ligand?

6) Write the catalytic cyclic for the deuteration of benzene with Cp_2TaH_3 as a catalyst. Name each reaction step.

7) What is Collman's reagent and how is it being used?

8) What is Wilkinson's catalyst, and what reactions can it be used for. Write the catalytic cycle.

9) Write done the reaction mechanism for the Ziegler-Natta olefin polymerization.

10) What is carbene migratory insertion?

11) Write down the catalytic cycle for the hydroformylation of olefins.

12) Name three hydrocarbonylation reactions. What are the reactants?

13) Write down the mechanism for the Monsanto acetic acid process.

14) What is olefin metathesis?

15) What is ring-opening olefin polymerization (ROMP)?

16) What is acyclic diene metathesis?

17) Why are olefins with terminal C=C double bonds particularly useful in olefin metathesis?

18) What is ring-closing metathesis?

19) What are the characteristics of Schrock and Grubbs catalysts, respectively?

20) Write down the catalytic cycle for olefin metathesis.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 7.5.1: Concept Review Questions Chapter 12 is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **Concept Review Questions Chapter 12** by Kai Landskron is licensed CC BY 4.0.

7.5.2: Homework Problems Chapter 12

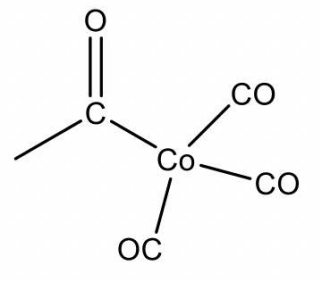
Homework Problems

Section 1

Exercise 1

The coordination compound $CH_3Co(CO)_4$ undegoes a migratory insertion. What is the reaction product?

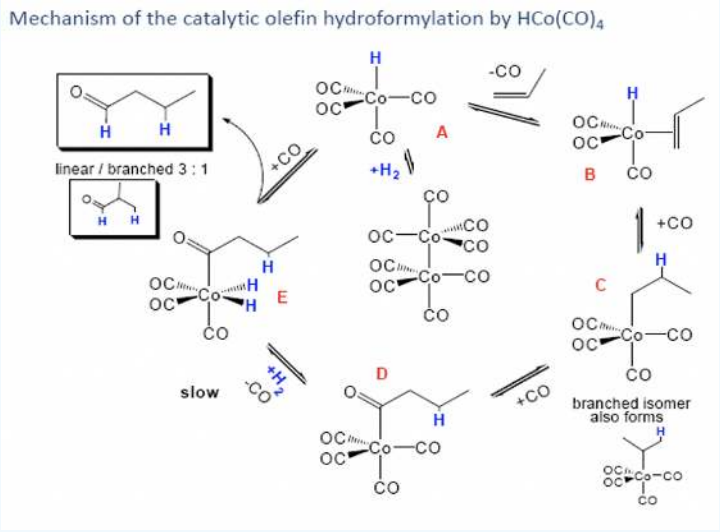
Answer



Section 2

Exercise 1

Identify all oxidative additions in the catalytic cycle of olefin hydroformylation:



Answer

Step D --> E is an oxidative addition

Formation of $HCo(CO)_4$ from $Co_2(CO)_8$ is also an oxidative addition.

Exercise 2

1. What are the reaction products of the following olefin metathesis reactions?

a) 2 CH_2=CH-Ph -->

b) n CH_2=CH-CH=CH_2 -->

Answer

a) $CH_2=CH_2$ and Ph-CH=CH-Ph

b) $CH_2=CH_2$ and $(CH=CH)_n$

Exercise 3

What reaction product would you expect would you expect from the following reaction:

$Fe(CO)_4^{2-} + CH_3CH_2I$ -->

Name the reaction.

Answer

$Fe(CO)_4CH_2CH_3^- + I^-$ Nucleophilic displacement

Exercise 4

Which of the following phosphines would you expect to be most suitable to stabilize metals in low oxidation states:

a) $P(CF_3)_3$

b) $P(CH_3)_3$

c) PH_3

Answer

a) $P(CF_3)_3$

Exercise 5

What reaction product would you expect from the following reaction?

$Pt(PPh_3)_4 + 4\ NPh_3$ -->

Answer

There would be no reaction.

Exercise 6

Which of the following complexes would likely be unstable:

a) $[PtCl_3(C_2H_5)]^{2-}$

b) $[PtCl_3(CH_3)]^{2-}$

c) $PtCl_4^{2-}$

Answer

a) $[PtCl_3(C_2H_5)]^{2-}$

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

This page titled 7.5.2: Homework Problems Chapter 12 is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

- **Homework Problems Chapter 12** by Kai Landskron is licensed CC BY 4.0.

SECTION OVERVIEW

8: Lanthanides and Actinides

8.1: The Lanthanides

8.1.1: Lanthanides- Properties and Reactions

8.1.1.1: Lanthanide Contraction

8.1.2: Chemistry of Cerium

8.1.3: Chemistry of Dysprosium

8.1.4: Chemistry of Europium

8.1.5: Chemistry of Gadolinium

8.1.5.1: Gadolinium(III) Chloride

8.1.6: Chemistry of Holmium

8.1.7: Chemistry of Lutetium

8.1.8: Chemistry of Neodymium

8.1.9: Chemistry of Praseodymium

8.1.10: Chemistry of Promethium

8.1.11: Chemistry of Samarium

8.1.12: Chemistry of Terbium

8.1.13: Chemistry of Thulium

8.1.14: Chemistry of Ytterbium

8.1.15: Chemistry of Yttrium

8.2: The Actinides

8.2.1: General Properties and Reactions of The Actinides

8.2.2: Chemistry of Americium

8.2.3: Chemistry of Berkelium

8.2.4: Chemistry of Californium

8.2.5: Chemistry of Curium

8.2.6: Chemistry of Einsteinium

8.2.7: Chemistry of Fermium

8.2.8: Chemistry of Lawrencium

8.2.9: Chemistry of Mendelevium

8.2.10: Chemistry of Neptunium

8.2.11: Chemistry of Nobelium

8.2.12: Chemistry of Plutonium

8.2.13: Chemistry of Protoactinium

8.2.14: Chemistry of Thorium

8.2.15: Chemistry of Uranium

Thumbnail: A billet of highly enriched uranium that was recovered from scrap processed at the Y-12 National Security Complex Plant. (Public Domain).

8: Lanthanides and Actinides is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

8.1: The Lanthanides

The Lanthanides consist of the elements in the f-block of period six in the periodic table. While these metals can be considered transition metals, they have properties that set them apart from the rest of the elements.

8.1.1: Lanthanides- Properties and Reactions

8.1.1.1: Lanthanide Contraction

8.1.2: Chemistry of Cerium

8.1.3: Chemistry of Dysprosium

8.1.4: Chemistry of Europium

8.1.5: Chemistry of Gadolinium

8.1.5.1: Gadolinium(III) Chloride

8.1.6: Chemistry of Holmium

8.1.7: Chemistry of Lutetium

8.1.8: Chemistry of Neodymium

8.1.9: Chemistry of Praseodymium

8.1.10: Chemistry of Promethium

8.1.11: Chemistry of Samarium

8.1.12: Chemistry of Terbium

8.1.13: Chemistry of Thulium

8.1.14: Chemistry of Ytterbium

8.1.15: Chemistry of Yttrium

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

8.1.1: Lanthanides- Properties and Reactions

The Lanthanides consist of the elements in the f-block of period six in the periodic table. While these metals can be considered transition metals, they have properties that set them apart from the rest of the elements.

Introduction

The Lanthanides were first discovered in 1787 when a unusual black mineral was found in Ytterby, Sweden. This mineral, now known as Gadolinite, was later separated into the various Lanthanide elements. In 1794, Professor Gadolin obtained yttria, an impure form of yttrium oxide, from the mineral. In 1803, Berzelius and Klaproth secluded the first Cerium compound. Later, Moseley used an x-ray spectra of the elements to prove that there were fourteen elements between Lanthanum and Hafnium. The rest of the elements were later separated from the same mineral. These elements were first classified as 'rare earth' due to the fact that obtained by reasonably rare minerals. However, this is can be misleading since the Lanthanide elements have a practically unlimited abundance. The term Lanthanides was adopted, originating from the first element of the series, Lanthanum.

Like any other series in the periodic table, such as the Alkali metals or the Halogens, the Lanthanides share many similar characteristics. These characteristics include the following:

- Similarity in physical properties throughout the series
- Adoption mainly of the +3 oxidation state. Usually found in crystalline compounds)
- They can also have an oxidation state of +2 or +4, though some lanthanides are most stable in the +3 oxidation state.
- Adoption of coordination numbers greater than 6 (usually 8-9) in compounds
- Tendency to decreasing coordination number across the series
- A preference for more electronegative elements (such as O or F) binding
- Very small crystal-field effects
- Little dependence on ligands
- Ionic complexes undergo rapid ligand-exchange

Electron Configuration

Similarly, the Lanthanides have similarities in their electron configuration, which explains most of the physical similarities. These elements are different from the main group elements in the fact that they have electrons in the f orbital. After Lanthanum, the energy of the 4f sub-shell falls below that of the 5d sub-shell. This means that the electron start to fill the 4f sub-shell before the 5d sub-shell.

The electron configurations of these elements were primarily established through experiments. The technique used is based on the fact that each line in an emission spectrum reveals the energy change involved in the transition of an electron from one energy level to another. However, the problem with this technique with respect to the Lanthanide elements is the fact that the 4f and 5d sub-shells have very similar energy levels, which can make it hard to tell the difference between the two.

Another important feature of the Lanthanides is the Lanthanide Contraction, in which the 5s and 5p orbitals penetrate the 4f sub-shell. This means that the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease that continues throughout the series.

Table 1: Electron Configurations of the Lanthanide Elements

Symbol	Idealized	Observed	Symbol	Idealized	Observed
La	$5d^16s^2$	$5d^16s^2$	Tb	$4f^85d^16s^2$	$4f^9\ 6s^2$ or $4f^85d^16s^2$
Ce	$4f^15d^16s^2$	$4f^15d^16s^2$	Dy	$4f^95d^16s^2$	$4f^{10}\ 6s^2$
Pr	$4f^25d^16s^2$	$4f^3\ 6s^2$	Ho	$4f^{10}5d^16s^2$	$4f^{11}\ 6s^2$
Nd	$4f^35d^16s^2$	$4f^4\ 6s^2$	Er	$4f^{11}5d^16s^2$	$4f^{12}\ 6s^2$
Pm	$4f^45d^16s^2$	$4f^5\ 6s^2$	Tm	$4f^{12}5d^16s^2$	$4f^{13}\ 6s^2$
Sm	$4f^55d^16s^2$	$4f^6\ 6s^2$	Yb	$4f^{13}5d^16s^2$	$4f^{14}\ 6s^2$
Eu	$4f^65d^16s^2$	$4f^7\ 6s^2$	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^16s^2$

Symbol	Idealized	Observed	Symbol	Idealized	Observed
Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1 6s^2$			

Properties and Chemical Reactions

One property of the Lanthanides that affect how they will react with other elements is called the basicity. Basicity is a measure of the ease at which an atom will lose electrons. In another words, it would be the lack of attraction that a cation has for electrons or anions. In simple terms, basicity refers to have much of a base a species is. For the Lanthanides, the basicity series is the following:

$$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$$

In other words, the basicity decreases as the atomic number increases. Basicity differences are shown in the solubility of the salts and the formation of the complex species. Another property of the Lanthanides is their magnetic characteristics. The major magnetic properties of any chemical species are a result of the fact that each moving electron is a micromagnet. The species are either diamagnetic, meaning they have no unpaired electrons, or paramagnetic, meaning that they do have some unpaired electrons. The diamagnetic ions are: La^{3+}, Lu^{3+}, Yb^{2+} and Ce^{4+}. The rest of the elements are paramagnetic.

Metals and their Alloys

The metals have a silvery shine when freshly cut. However, they can tarnish quickly in air, especially Ce, La and Eu. These elements react with water slowly in cold, though that reaction can happen quickly when heated. This is due to their electropositive nature. The Lanthanides have the following reactions:

- oxidize rapidly in moist air
- dissolve quickly in acids
- reaction with oxygen is slow at room temperature, but they can ignite around 150-200 °C
- react with halogens upon heating
- upon heating, react with S, H, C and N

Table 2: Properties of the Lathanides

Symbol	Ionization Energy (kJ/mol)	Melting Point (°C)	Boiling Point (°C)
La	538	920	3469
Ce	527	795	3468
Pr	523	935	3127
Nd	529	1024	3027
Pm	536		
Sm	543	1072	1900
Eu	546	826	1429
Gd	593	1312	3000
Tb	564	1356	2800
Dy	572	1407	2600
Ho	581	1461	2600
Er	589	1497	2900
Tm	597	1545	1727
Yb	603	824	1427
Lu	523	1652	3327

Periodic Trends: Size

The size of the atomic and ionic radii is determined by both the nuclear charge and by the number of electrons that are in the electronic shells. Within those shells, the degree of occupancy will also affect the size. In the Lanthanides, there is a decrease in atomic size from La to Lu. This decrease is known as the Lanthanide Contraction. The trend for the entire periodic table states that the atomic radius decreases as you travel from left to right. Therefore, the Lanthanides share this trend with the rest of the elements.

Table 3: Periodic Trends

Element	Atomic Radius (pm)	Ionic Radius (3+)	Element	Atomic Radius (pm)	Ionic Radius (3+)
La	187.7	106.1	Tb	178.2	92.3
Ce	182	103.4	Dy	177.3	90.8
Pr	182.8	101.3	Ho	176.6	89.4
Nd	182.1	99.5	Er	175.7	88.1
Pm	181	97.9	Tm	174.6	89.4
Sm	180.2	96.4	Yb	194.0	85.8
Eu	204.2	95.0	Lu	173.4	84.8
Gd	180.2	93.8			

Color and Light Absorbance

The color that a substance appears is the color that is reflected by the substance. This means that if a substance appears green, the green light is being reflected. The wavelength of the light determines if the light with be reflected or absorbed. Similarly, the splitting of the orbitals can affect the wavelength that can be absorbed. This is turn would be affected by the amount of unpaired electrons.

Table 4: Unpaired Electrons and Color

Ion	Unpaired Electrons	Color	Ion	Unpaired Electrons	Color
La^{3+}	0	Colorless	Tb^{3+}	6	Pale Pink
Ce^{3+}	1	Colorless	Dy^{3+}	5	Yellow
Pr^{3+}	2	Green	Ho^{3+}	4	Pink; yellow
Nd^{3+}	3	Reddish	Er^{3+}	3	Reddish
Pm^{3+}	4	Pink; yellow	Tm^{3+}	2	Green
Sm^{3+}	5	Yellow	Yb^{3+}	1	Colorless
Eu^{3+}	6	Pale Pink	Lu^{3+}	0	Colorless
Gd^{3+}	7	Colorless			

Occurrence in Nature

Each known Lanthanide mineral contains all the members of the series. However, each mineral contains different concentrations of the individual Lanthanides. The three main mineral sources are the following:

- Monazite: contains mostly the lighter Lanthanides. The commercial mining of monazite sands in the United States is centered in Florida and the Carolinas
- Xenotime: contains mostly the heavier Lanthanides
- Euxenite: contains a fairly even distribution of the Lanthanides

In all the ores, the atoms with a even atomic number are more abundant. This allows for more nuclear stability, as explained in the Oddo-Harkins rule. The Oddo-Harkins rule simply states that the abundance of elements with an even atomic number is greater than the abundance of elements with an odd atomic number. In order to obtain these elements, the minerals must go through a separating process, known as separation chemistry. This can be done with selective reduction or oxidation. Another possibility is an ion-exchange method.

The Oddo-Harkins Rule

The abundance of elements with an even atomic number is **greater** than the abundance of elements with an odd atomic number.

Applications

Metals and Alloys

The pure metals of the Lanthanides have little use. However, the alloys of the metals can be very useful. For example, the alloys of Cerium have been used for metallurgical applications due to their strong reducing abilities.

Non-nuclear

The Lanthanides can also be used for ceramic purposes. The almost glass-like covering of a ceramic dish can be created with the lanthanides. They are also used to improve the intensity and color balance of arc lights.

Nuclear

Like the Actinides, the Lanthanides can be used for nuclear purposes. The hydrides can be used as hydrogen-moderator carriers. The oxides can be used as diluents in nuclear fields. The metals are good for being used as structural components. The can also be used for structural-alloy-modifying components of reactors. It is also possible for some elements, such as Tm, to be used as portable x-ray sources. Other elements, such as Eu, can be used as radiation sources.

Practice Problems

1. Which elements are considered to be Lanthanides?
2. How do the Lanthanides react with oxygen?
3. What causes the Lanthanide Contraction?
4. Why do Lanthanides exhibit strong electromagnetic and light properties?
5. What do the Lanthanides have in common with the Noble Gases?

Answers

1. Elements Lanthanum (57) through Lutetium (71) on the periodic table are considered to be Lanthanides.
2. Lanthanides tend to react with oxygen to form oxides. The reaction at room temperature can be slow while heat can cause the reaction to happen rapidly.
3. The Lanthanide Contraction refers to the decrease in atomic size of the elements in which electrons fill the f-subshell. Since the f sub-shell is not shielded, the atomic size will decrease as the nuclear charge still increases.
4. Lanthanides exhibit strong electromagnetic and light properties because of the presence of unpaired electrons in the f-orbitals. The majority of the Lanthanides are paramagnetic, which means that they have strong magnetic fields.
5. Both the Lanthanides and Noble Gases tend to bind with more electronegative atoms, such as Oxygen or Fluorine.

References

1. Petrucci, Hardwood, Herring. "General Chemistry: Principles & Modern Applications". New Jersey: Macmillan Publishing Company, 2007.
2. Moeller, Therald. The Chemistry of the Lanthanides. New York: Reinhold Publishing Corporation, 1963.
3. Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

8.1.1: Lanthanides- Properties and Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

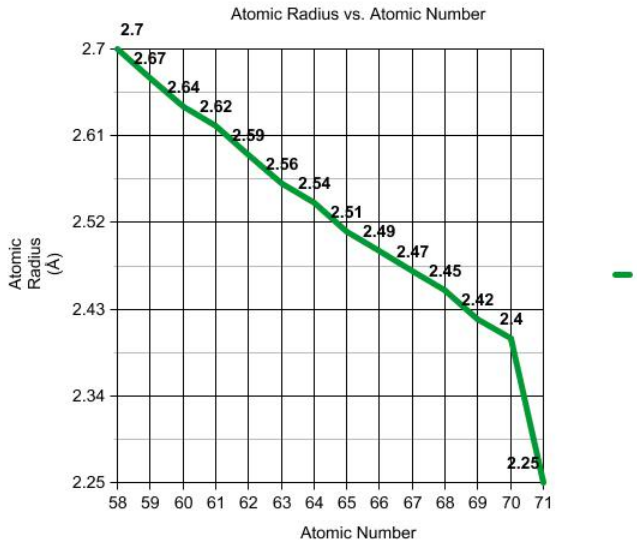
- **Lanthanides: Properties and Reactions** is licensed CC BY-NC-SA 4.0.

8.1.1.1: Lanthanide Contraction

The Lanthanide Contraction describes the atomic radius trend that the Lanthanide series exhibit. Another important feature of the The Lanthanide Contraction refers to the fact that the 5s and 5p orbitals penetrate the 4f sub-shell so the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease. This decrease in size continues throughout the series.

Introduction

The Lanthanide Contraction applies to all 14 elements included in the Lanthanide series. This series includes Cerium(Ce), Praseodymium(Pr), Neodymium(Nd), Promethium(Pm), Samarium(Sm), Europium(Eu), Gadolinium(Gd), Terbium(Tb), Dysprosium(Dy), Holmium(Ho), Erbium(Er), Thulium(Tm), Ytterbium(Yb), and Lutetium(Lu). The atomic radius, as according to the Lanthanide Contraction, of these elements decreases as the atomic number increases. We can compare the elements Ce and Nd by looking at a periodic table. Ce has an atomic number of 58 and Nd has an atomic number of 60. Which one will have a smaller atomic radius? Nd will because of its larger atomic number.

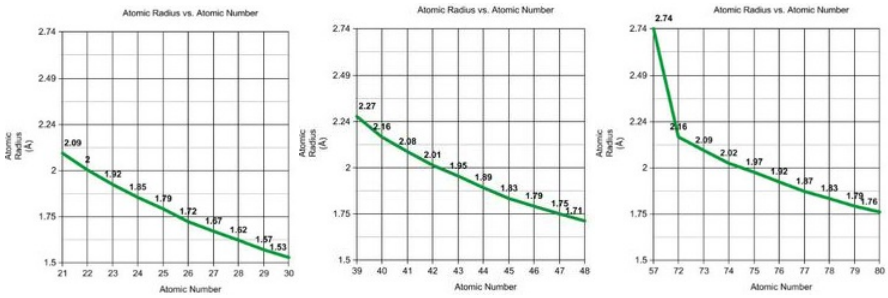


The graph shows the atomic radius decreasing as the atomic number is increasing, Lanthanide Contraction.

Shielding and its Effects on Atomic Radius

The Lanthanide Contraction is the result of a poor shielding effect of the 4f electrons. The shielding effect is described as the phenomenon by which the inner-shell electrons shield the outer-shell electrons so they are not effected by nuclear charge. So when the shielding is not as good, this would mean that the positively charged nucleus has a greater attraction to the electrons, thus decreasing the atomic radius as the atomic number increases. The s orbital has the greatest shielding while f has the least and p and d in between the two with p being greater than d.

The Lanthanide Contraction can be seen by comparing the elements with f electrons and those without f electrons in the d block orbital. Pd and Pt are such elements. Pd has 4d electrons while Pt has 5d and 4f electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the 4f electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller than expected radius.



Row 1 of Periodic Table D block Row 2 Row 3

The graphs depict the atomic radii of the first three rows of transition metals. We can apply the same principle as applied with the elements Pd and Pt to whole rows and columns. As we can see by comparing Row 1 with Row 2, the atomic radii differ greatly between the elements, but if we compare Row 2 with Row 3, the atomic radii do not have much difference. Elements with atomic number 23 and 41 lie in the same column of the periodic table and have a significantly large difference in atomic radii (atomic radii increases from Row 1 to Row 2), but elements 41 and 73, also in the same column, only differ slightly. This is the cause of introducing 4f electrons in Row 3. In Row 3, we would expect the elements to carry on the same trend as was witnessed between Rows 1 and 2 (large increase in atomic radii) but we do not. This is because the 4f orbitals are not doing a great job of shielding.

D Block Contraction (Scandide Contraction)

The d block contraction, also known as the Scandide Contraction, describes the atomic radius trend that the d block elements (Transition metals) experience. Normally the trend for atomic radius, moving across the periodic table is that the atomic radius decreases significantly. In the transition metals with D electrons as we move from left to right across the periodic table, the element's atomic radius only decreases slightly. This is because they have the same amount of s electrons, but are only differing in d electrons. These d electrons are in an inner shell (penultimate shell) and electrons are getting added to this shell, another shell is not created. The d electrons are not good at shielding the nuclear charge, so the atomic radius does not change much as electrons are added. Almost like disregarding the D electrons being added.

Effects on Ionization Energy and Properties

As the proton number increases and the atomic radius decreases, the ionization energy increases. This is due to a more positively charged nucleus and a greater pull on the electrons by the nucleus. A greater pull is the result of an increased effective nuclear charge. Effective nuclear charge is caused by the nucleus having a more positive charge than the negative charge on the electron (net positive charge). The density, melting point, and hardness increase from left to right throughout the Lanthanide Series. The Lanthanide Contraction makes chemical separation of the Lanthanides easier. The Lanthanide Contraction, while making the chemical separation of Lanthanides easier, it makes the separation of elements following the series a bit more difficult.

References

1. Petrucci, Harwood, Herring, and Madura. *General Chemistry Principles & Modern Applications*. 9th ed. Prentice Hall. Print.
2. Cotton, Simon. *Lanthanide and Actinide Chemistry*. Wiley. Print.

Problems

1. What is the cause of Lanthanide Contraction?
2. Which element has a greater atomic radius Gd or Tb and why?
3. Which element has a smaller atomic radius Dy or Yb and why?
4. Why do elements in Rows 2 and 3 that are in the same column have similar atomic radii?
5. Place the following elements in order of increasing atomic radius: Eu, Ce, Pr, Ho.
6. Which one of the following has the lowest density: Tb, Pm, Er, Tm, Ce

Answers:

1. The Lanthanide Contraction is caused by a poor shielding effect of the 4f electrons.
2. Gd because as atomic number increases, the atomic radius decreases.
3. Yb because it has a larger atomic number.

4. Because the elements in Row 3 have 4f electrons. These electrons are do not shield good, causing a greater nuclear charge. This greater nuclear charge has a greater pull on the electrons.
5. Ho, Eu, Pr, Ce
6. Ce

Contributors and Attributions

- Amrit Paul Bains (UCD)

8.1.1.1: Lanthanide Contraction is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Lanthanide Contraction** is licensed CC BY-NC-SA 4.0.

8.1.2: Chemistry of Cerium

Discovered by Berzelius and Hisinger in 1803, but not isolated as a metal until 1875, cerium (named for the asteroid Ceres) is the most abundant of the so-called rare-earth metals. It begins the series of lanthanides that runs from elements 58 to 71. In pure form the element is a malleable and ductile metal, similar in coloring to iron. It is much more reactive than iron, however, readily oxidizing in moist air and releasing hydrogen from boiling water. Friction from abrading a sample can cause it to ignite.

Although the metal itself is too reactive for most uses, compounds of cerium are used in glass making and photography. It has limited use in some special alloys as well. Most commercial grade cerium is derived from monazite sand which is a mixture of phosphates of many of the rare earth metals along with calcium and thorium.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Cerium** is licensed CC BY-NC-SA 4.0.

8.1.3: Chemistry of Dysprosium

The Greek word dysprositos (hard to get at) gives some indication of the scarcity of dysprosium, but only to a degree. It is about twice as abundant as uranium. The soft, silvery metal was discovered by de Boisbaudran in 1886 and it was finally isolated in 1906 by Urbain. A pure sample was not produced until the 1950s.

The pure metal oxidizes readily in air.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Dysprosium** is licensed CC BY-NC-SA 4.0.

8.1.4: Chemistry of Europium

Europium looks and feels a lot like lead, although it is not as dense. It was discovered in 1896 and isolated in 1901 by Demarcay, working with samples of supposedly "pure" samarium. Named for the continent of Europe, the element ranks thirteenth in abundance among the rare earth metals, but there is more of it than silver and gold combined.

It is the most reactive of the rare earth metals, behaving with water in a manner similar to calcium.

Generally refined from monazite sand, the pure metal has few applications, but you would find it less interesting to read this without some of its compounds which are used as activators and red phosphors in color CRT screens for television and computers.

Europium Anomaly

All lanthanoids tend to group together in nature because all the lanthanoids are most stable in their +3 oxidation state, and their bonding is nearly exclusively ionic/electrostatic. While the lanthanides have valent 4f electrons, the 4f orbitals are radially constricted and cannot achieve appropriate overlap with ligand orbitals to engage in sigma- or pi-bonding interactions. So they can all easily incorporate into similar minerals. Similarly, Europium is most stable in the +3 oxidation state, but can be easily reduced to the +2 oxidation state. This change in Lewis acidity and causes it to *phase separate* out into other minerals that the relatively hard +3 Lewis acids do not go into. It is well known as the *europium anomaly*.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Europium** is licensed CC BY-NC-SA 4.0.

8.1.5: Chemistry of Gadolinium

Gadolinium (from the mineral gadolinite, named for the Finnish chemist Gadolin) is a soft silvery-white metal that is used as an alloying agent in some steels and in the manufacture of some electronic components.

Credit for its discovery is shared by de Marignac who did extensive spectroscopic studies on the mixture then known as didymia, and by de Boisbaudran who finally isolated the metal in 1886.

The metal has a very large capacity for absorbing thermal neutrons, making it an excellent material for control rods in fission power plants.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Gadolinium** is licensed CC BY-NC-SA 4.0.

8.1.5.1: Gadolinium(III) Chloride

Gadolinium trichloride, $GdCl_3$, is a colorless, hygroscopic, water-soluble solid. It is commonly encountered as hexahydrate $GdCl_3 . 6H_2O$. Gadolinium trichloride can be synthesized by the reaction of solid gadolinium with HCl at 600 °C:

$$2\ Gd + 6\ HCl \longrightarrow 2\ GdCl_3 + 3\ H_2$$

Another way to prepare gadolinium trichloride is to synthesize $(NH_4)_2[GdCl_5]$ which can be decomposed at 300°C to $GdCl_3$.

$$10\ NH_4Cl + 2\ Gd \longrightarrow 2\ (NH_4)_2[GdCl_5] + 6\ NH_3 + 3\ H_2$$
$$2\ (NH_4)_2[GdCl_5] \longrightarrow \{NH_4[Gd_2Cl_7] + 3NH_4Cl\} \longrightarrow 2\ GdCl_3 + 4\ NH_4Cl$$

Gd^{3+} ions are of special interest for magnetic resonance imaging (MRI), since the Gd^{3+} species has an f^7 electronic configuration with seven unpaired electrons. This results in a highly paramagnetic behavior. As gadolinium salts are toxic, the Gd^{3+} ion has to complexed by a chelating agent (i.e. H5DTPA, diethylenetriaminepentaacetic acid) for usage in biomedical applications.

Contributors and Attributions

- Hans Lohninger (Epina eBook Team)

8.1.5.1: Gadolinium(III) Chloride is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Gadolinium(III) Chloride** is licensed CC BY-NC-SA 4.0.

8.1.6: Chemistry of Holmium

Holmium was discovered by Cleve in 1879 and named for the Latinized version of the name for Stockholm. Like most of the other rare-earth metals, it is silvery and soft, and can be pounded or rolled into very thin sheets. At normal temperatures it is fairly inert but will oxidize at high temperatures and humidities.

Like most of the rare-earth metals, holmium is generally obtained from monazite sand, where it is present to the extent of about 0.05%. Most holmium use is confined to research.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Holmium** is licensed CC BY-NC-SA 4.0.

8.1.7: Chemistry of Lutetium

Lutetium ranks among the rare-earths in abundance only above thulium and promethium (and there's none of that anyway!). It official name comes from an ancient name for Paris, Lutecia, but it has had many names, most recently lutecium (only a change in official spelling). It was discovered independently by von Welsbach and Urbain in 1907-08.

The refinement of ion exchange methods and their application to the separation of the rare-earths made the separation of lutetium from ytterbium possible. von Welsbach decided to rename ytterbium aldebaranium and picked cassiopium for element 71. Urbain preferred neoytterbium and lutecium. Urbain's choices eventually were accepted, altho

ugh the prefix was dropped from ytterbium and the spelling of lutecium was eventually changed.

The metal is the hardest and densest of the rare-earths and is the last of the lanthanides.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Lutetium** is licensed CC BY-NC-SA 4.0.

8.1.8: Chemistry of Neodymium

Discovered in 1885 along with praseodymium, neodymium is named from the Greek neos + didymos (new twin). The silvery-white metal oxidizes easily in air and reacts with water, displacing hydrogen gas. Although another of the "rare" earth metals, neodymium is actually more abundant than many better known metals such as gold, silver, tin and lead.

Misch metal, used in lighter flints, is about 18% neodymium. The element is also used in the manufacture of artificial rubies for laser applications.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Neodymium** is licensed CC BY-NC-SA 4.0.

8.1.9: Chemistry of Praseodymium

Praseodymium, which is named from the Greek prasios + didymos (green twin), was isolated and identified by von Welsbach in 1885 from what was known at the time as didymium. von Welsbach's work revealed that this "substance" actually contained two new elements, one of which was praseodymium (neodymium was the other).

Pure praseodymium is silvery-white and fairly soft. It oxidizes slowly in air and reacts vigorously with water to release hydrogen gas. It is used as an alloying agent along with magnesium for parts in aircraft engines. Misch metal is 5% praseodymium and is used for alloying steel and in flints used to create sparks in lighters. The glass in welder's goggles contains a mixture of praseodymium and neodymium.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Praseodymium** is licensed CC BY-NC-SA 4.0.

8.1.10: Chemistry of Promethium

The existence of promethium (for the Greek god, Promethius) was predicted in 1912 when Henry Moseley developed an x-ray method for determining integer atomic numbers of elements. An element was clearly missing between neodymium and samarium. It's existence was not confirmed until 1947 by Marinsky, Glendenin and Coryell.

Historical claims for the discovery of element 61 create an interesting trail from around 1925 in Florence (suggested name: florentium) to America in 1926 (suggested name: illinium). None of the claims, however, could be substantiated and today we know they were not simply a result of fleetingly small samples but rather poor work.

While spectral lines of promethium are evident in the light from some stars, it now seems apparent that no promethium is found in accessible areas of the earth--hence the difficulty in finding any! Initial attempts at synthesis of element 61 in a cyclotron at Ohio State University in 1941 led to the suggested name cyclonium. But the recognized synthesis and identification finally came at Oak Ridge in 1947.

The longest-lived isotope of promethium is Pm-145 with a half-life of 17.7 years. There are no significant commercial uses of the metal and so very little has been produced except for theoretical studies.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Promethium** is licensed CC BY-NC-SA 4.0.

8.1.11: Chemistry of Samarium

Named for the mineral samarskite from which it is extracted, samarium was isolated and identified by de Boisbaudran is 1879. The pure metal has a silver lustre and tarnishes slowly at room conditions. It is readily magnetized and holds its magnetism extremely well. Rare earth magnets (samarium-cobalt, for example) exploit this property.

Although it is present in samarskite, commercial production of samarium is from monazite sand which can contain as much as 2.8% Sm by weight.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Samarium** is licensed CC BY-NC-SA 4.0.

8.1.12: Chemistry of Terbium

Terbium is fourteenth in abundance among the 17 metals usually counted as "rare-earths", present in the earth's crust to the extent of only 0.9 ppm (about 1 teaspoon in every 63 tons of earth). Named for the Swedish village of Ytterby, the metal was discovered in 1843 by Mosander (along with erbium).

Small amounts of terbium are used in special lasers and some solid state devices. The monazite sand from which terbium is generally extracted contains only about 0.03% by weight of Tb.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Terbium** is licensed CC BY-NC-SA 4.0.

8.1.13: Chemistry of Thulium

The rarest of the naturally-occurring rare-earth metals, thulium was discovered in 1879 by Cleve, working from samples of erbia, an oxide of erbium. The metal is named for the ancient name for Scandinavia, Thule.

Like others in the lanthanide series, thulium is silver in color but it is also very soft---soft enough to cut with a knife.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Thulium** is licensed CC BY-NC-SA 4.0.

8.1.14: Chemistry of Ytterbium

The first of the so-called "rare-earths" to be discovered, ytterbium takes its name from the Swedish village Ytterby (also the source of the names for terbium, erbium and yttrium). Discovery is credited to de Marignac in 1878. Initial identification was tediously made from the same mixture that most chemists of the time worked from: oxides of the lanthanides which gave rise to the term "rare-earth" due to its powdery consistency and often brownish color. But with the chemical separation techniques available at the time, it was very difficult to distinguish these similar elements. Even ytterbium itself turned out to hide another element. Lutetium was separated from it in 1907.

Pure ytterbium is like most of the lanthanides: silvery and ductile, reacting slowly with air to form an oxide. Mostly obtained from monazite sand, ytterbium makes up about 0.03% of that mixture.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Ytterbium** is licensed CC BY-NC-SA 4.0.

8.1.15: Chemistry of Yttrium

Like the histories of the discoveries of many other rare-earths, the tale of erbium reads like a series of mistaken identities. These elements are generally found as oxides and most often together. Chemically, the oxides are very similar and at the time of their first examination were difficult to separate. Thus a sample of "lanthanum" might end up containing two additional elements that no one had bothered to look for. Many chemists thought that the oxides were elements themselves at one time.

The oxide of yttrium (which along with scandium and lanthanum is generally included with the "rare-earths") known as yttria was eventually found to contain erbia and terbia as well, the oxides of, respectively, erbium and terbium. But the two are so similar that they were often confused in early work and what we now call erbium was originally terbium! In both cases, the credit for discovery goes to Mosander (1843 for erbium) and both elements were named for the Swedish town of Ytterby (which, by the way, also lends its name to Ytterbium and Yttrium----certainly some kind of record where naming elements is concerned!).

Like most of the rare-earth metals, erbium is silvery and soft, tarnishing slightly in air.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Yttrium** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

8.2: The Actinides

The Actinide series contains elements with atomic numbers 89 to 103 and is the sixth period and third group of the periodic table. The series is the row below the Lanthanide series, which is located underneath the main body of the periodic table. Both the Lanthanide and Actinide series are referred to as Rare Earth Metals and have a high diversity in oxidation numbers. All of the Actinides are radioactive. The most famous actinide is Uranium.

8.2.1: General Properties and Reactions of The Actinides
8.2.2: Chemistry of Americium
8.2.3: Chemistry of Berkelium
8.2.4: Chemistry of Californium
8.2.5: Chemistry of Curium
8.2.6: Chemistry of Einsteinium
8.2.7: Chemistry of Fermium
8.2.8: Chemistry of Lawrencium
8.2.9: Chemistry of Mendelevium
8.2.10: Chemistry of Neptunium
8.2.11: Chemistry of Nobelium
8.2.12: Chemistry of Plutonium
8.2.13: Chemistry of Protoactinium
8.2.14: Chemistry of Thorium
8.2.15: Chemistry of Uranium

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

8.2.1: General Properties and Reactions of The Actinides

The Actinide series contains elements with atomic numbers 89 to 103 and is in the sixth period and the third group of the periodic table. The series is the row below the Lanthanide series, which is located underneath the main body of the periodic table. Lanthanide and Actinide Series are both referred to as Rare Earth Metals. These elements all have a high diversity in oxidation numbers and all are radioactive. The most common and known element is Uranium, which is used as nuclear fuel when its converted into plutonium, through a nuclear reaction.

History of the Actinides

The first actinides to be discovered were Uranium by Klaproth in 1789 and Thorium by Berezelius in 1829, but most of the Actinides were man-made products of the 20th century. Actinium and Protactinium are found in small portions in nature, as decay products of 253-Uranium and 238-Uranium. Microscopic amounts of Plutonium are made by neutron capture by Uranium, and yet occur naturally. Monazite is the principle Thorium ore. It is a phosphate ore that contains great amounts of Lanthanides in it. The main Uranium ore is U_3O_8 and is known as pitchblende, because it occurs in black, pitch-like masses. An example of pitchblende is located in the picture below. All elements past Uranium are man-made. Actinides require special handling, because many of them are radioactive and/or unstable. The radiation in actinides plays a large role in the chemistry and arrangement of particles in crystals.



*This is a picture of U_3O_8, a uranium, pitchblende ore, by Geomartin.

Common Properties

- All are radioactive due to instability.
- Majority synthetically made by particle accelerators creating nuclear reactions and short lasting.
- All are unstable and reactive due to atomic number above 83 (nuclear stability).
- All have a silvery or silvery-white luster in metallic form.
- All have the ability to form stable complexes with ligands, such as chloride, sulfate, carbonate and acetate.
- Many of the actinides occur in nature as sea water or minerals.
- They have the ability to undergo nuclear reactions.
- The emission of radioactivity, toxicity, pyrophoricity, and nuclear criticality are properties that make them hazardous to handle.
    - Emission of Radioactivity: The types of radiation the elements possess are alpha, beta, gamma, as well as when neutrons are produced by spontaneous fissions or boron, beryllium, and fluorine react with alpha-particles.
    - Toxicity: Because of their radioactive and heavy metal characteristics, they are considered toxic elements.
    - Pyrophoricity: Many actinide metals, hydrides, carbides, alloys and other compounds may ignite at room temperature in a finely divided state, which would result from spontaneous combustion fires and spreading of radioactive contaminates.
    - Nuclear Criticality: If fissionable materials are combined, a chain reaction could occur resulting in lethal doses of radioactivity, but it depends on chemical form, isotopic composition, geometry, size of surroundings, etc.
- The interaction of Actinides when radioactive with different types of phosphors will produce pulses of light.

Table 8.2.1.1: Actinide Properties

Atomic Number	Symbol	Name	Atomic Mass (g/mol)	Electron Configuration	Oxidation States	Year Discovered
89	Ac	Actinium	[227]	[Rn] $6d^1 7s^2$	+3	1899
90	Th	Thorium	232.04	[Rn] $6d^2 7s^2$	+2?,+3,+4	1829
91	Pa	Protactinium	231.04	[Rn] $5f^2 6d^1 7s^2$	+3,+4,+5	1913
92	U	Uranium	238.03	[Rn] $5f^3 6d^1 7s^2$	+3,+4,+5,+6	1789
93	Np	Neptunium	[237]	[Rn] $5f^4 6d^1 7s^2$	+3,+4,+5,+6,+7	1940
94	Pu	Plutonium	[244]	[Rn] $5f^6 7s^2$	+3,+4,+5,+6,+7	1940
95	Am	Americium	[243]	[Rn] $5f^7 7s^2$	+3,+4,+5,+6,+7?	1944
96	Cm	Curium	[247]	[Rn] $5f^7$ $6d^1 7s^2$	+3,+4,+5,+6?	1944
97	Bk	Berkelium	[247]	[Rn] $5f^9 7s^2$	+3,+4	1949
98	Cf	Californium	[251]	[Rn] $5f^{10} 7s^2$	+2,+3,+4	1950
99	Es	Einsteinium	[252]	[Rn] $5f^{11} 7s^2$	+2?,+3,+4?	1952
100	Fm	Fermium	[257]	[Rn] $5f^{12} 7s^2$	+2,+3	1952
101	Md	Mendelevium	[258]	[Rn] $5f^{13} 7s^2$	+2,+3	1955
102	No	Nobelium	[259]	[Rn] $5f^{14} 7s^2$	+2,+3	1957
103	Lr	Lawrencium	[262]	[Rn] $5f^{14} 6d^1 7s^2$	+3	1961

- [#]-mass number of the longest living isotope is given when the element has no stable nucleotides.
- (?)-oxidation state is unconfirmed

Actinides have been crucial in understanding nuclear chemistry and have provided valuable usage today, such as nuclear power. These examples illustrate their importance in understanding key concepts in nuclear chemistry and related topics.

Transition Metal

Actinides are in the f-block of the periodic table. The electron configuration of uranium is [Rn] $5f^3$ $6d^1$ $7s^2$. The reason for this arrangement unlike other conventional electron configurations such as Na with configuration of [Ne]$3s^2$. Results from difference in energy levels due to the fact that some orbitals fill in faster than others and explains why Actinides are transition metals. (see transition metals)

The electron configurations of the actinides are due to the following:

- The energy in the 6d orbitals is lower in energy than in the 5f orbitals.
- They fill 5f orbital, 6d orbital, then 7s orbital.
- The 5f orbitals are not shielded by the filled 6s and 6p subshells.
- There is a small energy gap between the $5f^n$ $7s^2$ and $5f^{n-1}$ 6d $7s^2$ configurations.
- The 5f orbitals do not shield each other from the nucleus effectively.
- The energies of the 5f orbital drop rapidly with increasing atomic number.

Chemistry

- **Actinium**
  - Its chemistry is dominated by (+3) O. S.
  - Its compounds are colorless.

- There are 29 known isotopes.
- It does not have absorption in the UV visible region between 400-1000nm.
- ^{227}Ac is strongly radioactive and so are its decay components.
- Actinium metal is silvery solid; obtained by reduction of oxide, fluoride or chloride w/ Group 1 metals; and oxidized rapidly in moist air.
- It forms insoluble fluoride and oxalate ($Ac_2(C_2O_4)_3*10H_2O$) compounds

- **Thorium**
  - It exhibits the +4 O.S. exclusively.
  - The chemistry in the +2 and +3 O.S. is restricted to iodides like ThI_2 and cyclopentadienyl $Th(C_5H_5)_3$.
  - It has wide coordination chemistry with oxygen donor ligands.
  - Thorium metal is bright and silvery-white and tarnishes to a dull black color when exposed to air. It is soft enough to be scratched with a knife and melts at 1750°. It slowly dissolves in dilute with hydrogen evolution and can be pyrophoric as a powder.
- **Protactinium**
  - It has been in existence longer than any other actinide.
  - ^{231}Pa has a half-life of $3.28*10^{14}$ which allows it to make chemical study easy for it.
  - It has α-emission, so it has appropriate radiochemical precautions.
  - The Pa metal is malleable, ductile, silvery, and has a melting point of about 1565°C. It is also a superconductor.
- **Uranium**
  - Many compounds exist between the O.S. of +3 to +6.
  - The main O.S. are +4 and +6.
  - Stability of O.S.
    - U^{3+} reduces to hydrogen
    - U^{4+} stable in aqueous solution in the absence of air
    - U^{5+} disproportionates rapidly into a mixture of U^{4+} and U^{6+} in aqueous solutions
    - U^{6+} stable in aqueous solutions
  - When pure it has a silvery appearance.
  - When attacked by air, yellow film then black coating develops, it is a mix of oxide and nitride.
  - Powder metal is pyrophoric in air.
  - Reacts readily with hot water to prevent substances from coming into contact in nuclear reactors
- **Neptunium**
  - It was the first transuranium element to be discovered in 1940.
  - There are 15 known isotopes, only ^{237}Np, w/ half-life of $2.14*10^6$ years, is useful for chemical experiments.
  - It exhibits O.S. of +3 to +7 in compounds.
  - It is a silvery metal, with a melting point of 637°C and a boiling point of 4174°C.
  - It has surface oxidation when exposed to air.
  - It is converted to NpO_2 at high temperatures.
- **Plutonium**
  - There are 15 known isotopes.
    - The masses range from 232 to 246.
    - The most important isotope is ^{239}Pu because it is fissionable and has a half-life of 24,100 years, which makes it easy for chemists to study.
  - It exhibits O.S. from +3 to +7.
    - The +3 and +4 O.S. are the most important, but compounds of the ions are well defined.
    - Pu^{+7} only exists under very alkaline conditions.
  - It has 6 allotropic metal forms, which makes it unusual.
    - They can form at normal pressure between room temperature and its melting point, 640°C.
    - It is dense, silvery and a reactive metal; more reactive than uranium or neptunium.

- When attacked by air, it forms a green-gray oxide coating.
- It reacts slowly with cold water, faster with dilute H_2SO_4, and dissolves quickly in dilute hydrochloric acid or hydrobromic acid.

- **Americium**
  - It has 12 known isotopes.
  - It was first made in 1944-1945 by Seaborg and his coworkers, where they decayed ^{239}Pu and ^{241}Pu to ^{241}Am, which has a half-life of 433 years.
    - ^{241}Am and ^{243}Am, which has a half-life of 7380 years are the most important isotopes, because their half-lives allow scientists to study their characteristics.
  - The metal is a slivery, ductile and very malleable.
    - It tarnishes in air slowly and dissolves in dilute hydrochloric acid quickly.
    - It reacts with heating with oxygen, halogens, and other nonmetals

- **Later Actinides (Cm, Bk, Cf, Es, Fm, Md, No, and Lr)**
  - Their chemistry is of mostly the M^{+3} state.
  - They all form binary compounds, such as trihalides.
  - Curium, berkelium, and californium have the following chemistry:
    - Oxidized by air to the oxide
    - Electropositive
    - Reacts with hydrogen on warming to form hydrides
    - Yields compounds on warming with group 5 and group 6 non-metals

Solubility and Precipitation

Knowing about the solubility and precipitations of actinides, help chemists understand their properties better. Not all Actinides have the same properties when it comes solubility and precipitation, but most of the Actinides have similar traits and characteristics.

The fluorides, hydroxides and oxalates of actinides have low solubilities. The lighter trivalent, having a valence of three electrons, are unstable in aqueous solutions, such as transplutonium elements. The actinides of light weight have a higher valence; for example, oxidation states of 4, 5 and 6 where they are more stable; and they form compounds with low solubility. Trivalent Actinides can be separated from slightly acidic solutions as phosphates, mildly acidic solutions as oxalates, strongly acidic solutions as fluorides, and from basic solutions as hydroxides or hydrous oxides.

Hydrogen peroxide precipitates Pu^{+4}, Th^{+4}, Ce^{+4}, U^{+4}, Np^{+4} and Pa^{+4}. Pu^{+4}, Th^{+4}, Np^{+4}, UO^{+2} and all trivalent actinides are precipitated by carbonate-free ammonium hydroxide. The solubility of Actinide hydroxides or hydrous oxides in strong ammonium carbonate solutions allow the separation or Uranium and Thorium from other members of the Ammonium hydroxide group, such as Fe, Ti, Al and other rare earth metals. Thorium can be precipitated from ammonia with aluminum or from aluminum as a fluoride or oxalate. Uranium is precipitated with hydrogen sulfide, unless a complexing agent is present, such as Tartaric acid ($C_4H_6O_6$), and can be precipitated with Ammonium sulfide, unless Ammonium carbonate is present.

Halides

A majority of actinides form halides with halogens at specific temperatures and trihalides are the most well known halides. The following are examples of Actinide compounds forming with halide compound creating actinide halide compounds:

$$\underbrace{Ac(OH)_3 + 3\,HF \xrightarrow{700^\circ C} AcF_3 + 3\,H_2O}_{Fluorides}$$

$$\underbrace{Ac_2O_3 + 6\,NH_4Cl \xrightarrow{250^\circ C} 2\,AcCl_3 + 6\,NH_3 + 3\,H_2O}_{Chlorides}$$

$$\underbrace{Ac_2O_3 + 2\,AlBr_3 \xrightarrow{750^\circ C} 2\,AcBr_3 + Al_2O_3}_{Bromides}$$

$$\underbrace{\mathrm{Th} + 2\,\mathrm{I_2} \xrightarrow{400^\circ C} \mathrm{ThI_4}}_{Iodides}$$

The halides are very important binary compounds, sometimes the most important. Although they may have radioactivity that causes problems, they are useful to study to understand the trends in the Actinide series. Below are some halide characteristics of the actinide series from Actinium to Einsteinium.

- **Actinium:**
  - forms halides in the oxidation state of +3 only.
- **Thorium:**
  - forms in the 2, 3, and 4 oxidation states.
  - exists in black and gold forms.
  - has high conductivity.
  - contains free electrons.
  - has all whites are solids.
  - forms many complexes with neutral donors.
  - has an eight coordination number (dodecahedron, sq antiprism).
- **Protactinium:**
  - forms many different types of halides and several oxyhalides.
  - chlorides ($PaCl_5$) are yellow-green, bromides ($PaBr_4$) are orange-red, fluorides (PaF_4) are brown, and iodides (PaI_3) are dark brown.
  - has six coordinate (dimeric), eight coordinate (dodecahedral and square antiprismatic), seven coordinate, and nine coodrdinate.
- **Uranium:**
  - forms halides in oxidation states from +3 to +6.
  - Uranium (VI): UF_6 (colorless, does not require use of elemental fluorine to be made, octahedral, volatile), UCl_6 (dark green, hydroscopic, octahedral, volatile).
  - Uranium (V): rare oxidation states, unstable, six and seven coordination.
  - Uranium (IV): most important uranium halides, U^{+4} does not have reducing tendencies, UI is stable but not to hydrolysis.
  - Uranium (III): ease of oxidation of U^{+3}, all made under reducing conditions, have typical structure of actinide trihalides, UF_3 (green, 11-coordinate structure), UCl_3 and UBr_3 (red, trigonal prism), UI_3 (8-coordinate, black).



Figure 1: Uraninite, also known as pitchblende, is the most common ore mined to extract uranium. (CC BY-SA 2.5; Joachimsthal).

- **Neptunium:**
  - has a range of halides in different O.S. but only fluorides are in above +4.
  - has purple and blue-white fluorides, has green chlorides, has green and red-orange and dark red bromides and has brown iodides.
  - NpF_6 forms a toxic and volatile vapor.
  - There also exists oxyhalides, such as $NpOF_3$ and NpOCl.
- **Plutonium:**
  - Has a low stability of high O.S.

- Only consists of trihalides and tetrahalides, but PuF_6 exists though; and it is very volatile, reactive, is best kept in its gas state, does not exist in solid state, and is decomposed by its own radiation.
- The trihalides have pastel colors: fluoride (violet-blue), chloride (blue-green), bromide (light-green), iodide (bright-green); +2 state is inaccessible.
- Its complexes are in the +4 state and are stable except for iodides.
- Its oxyhalides include $PuO_2Cl_2*H_2O$.

- **Americium:**
  - The dihalides become insoluble for the first time.
  - They are black solids.
  - Only the fluorides have higher than +3 O.S.
  - The trihalides are important and have pastel colors: fluoride and chloride are pink, bromide is white-pale yellow, and iodide is pale yellow.
- **Curium(III) Chloride:**
  - Is made by ^{244}Cm isotope which is converted to ^{248}Cm then heated to 1200°C and converted to oxide then chlorinated with HCl at 500°C to create $CmCl_3$.
- **Californium:**
  - The only oxidation state s are +3 and +2 and it only forms chloride and iodide halides.
  - The following are examples of Californium halides: $CfCl_3$, CfI_3, and CfI_2.
- **Einsteinium:**
  - Its only oxidation state is +3 and it only forms with chloride, fluorine, and even oxygen.
  - The following are examples of Einsteinium halides: $Es2O_3$, $EsCl_3$, EsF_3.

Oxides

All Actinides form oxides with different oxidation states. The most common oxides are of the form M_2O_3, where M would be one of the elements in the Actinide series. The earliest actinides have a closer relation to the transition metals, where the oxidation state is equal to the number of electrons on the outer shell. The +4 state is more stable in the Actinide series than in the Lanthanides. The following are the different oxides of the Actinide elements:

- M_2O_3:Ac, Pu-Es
- MO_2:Th, U-Cf
- M_2O_5:Pa, Np
- MO_3: U, Np(?)

(?)-Neptunium is unknown in this oxide state, but scientists assume it does exist.

Oxyhalides

The oxyhalides of Actinides are not binary but some are formed by earlier Actinides, for example, an aqueous Protactinium fluoride reacts with air to make PaO_2F, Thorium can form $ThOX_2$, Neptunium can make $NpOF_3$, Plutonium forms $PuOF_4$ and UO_2F_2 is made by Uranium (III) oxide and Hydrofluoric acid.

Uranium Hydride (UH_3)

The uranium in uranium hydride has an oxidation state of +3, which is strongly reducing, so it forms a stable hydride. Uranium hydride reacts with hydrogen gas at 250 degrees and swells up into a fine black powder, which is pyrophoric in air. It decomposes at higher temperatures to hydrogen and uranium powders. It can also react with many other compounds at certain temperatures to make halides, oxides, and other compounds, including the following:

- with HBr to make UBr_3
- with H_2O to make UO_2
- with Cl_2 to make UCl_4
- with HF to make UF_4
- with H_2S to make US_2

Nuclear Fission Reaction of Uranium

$$^{235}U + {}^{1}n \rightarrow {}^{236}U \rightarrow \text{fission fragments + neutrons + 3.20 x10}^{-11}\text{ J.}$$

235-Uranium is bombarded with neutrons and turns into 236-Uranium. The 236-Uranium then converts into smaller pieces, 2-3 neutrons are released along with energy. These extra neutrons help create a chain reaction as more neutrons come into contact with Uranium. This uncontrolled energy eventually leads to an explosion, which is the basis of the atomic bomb. To see a lab presentation of what this reaction looks like click on the video below.



Alpha Particles

The nucleus of Uranium emits radioactivity in the form of alpha particles. Alpha particles are Helium atoms with the atomic mass of 4 and an atomic number of 2. Alpha particles produce ions but have weak penetrating power that can easily be stopped by sheets of paper. Alpha particles produce large numbers of ions because of their collisions and near collisions with atoms, while traveling through matter. Their positive charge allows them to be deflected by electric and magnetic fields.

By using a nuclear equation and following two rules:

1. The sum of mass numbers must be the same on both sides.
2. The sum of atomic numbers must be the same on both sides

we can write equations, such as the following, where $^{4}_{2}\text{He}$ represents the alpha particle.

$$^{238}\text{U} \rightarrow {}^{234}\text{Th} + {}^{4}_{2}\text{He}$$

The rules for writing a nuclear equation can apply to other radioactive decay processes, such as beta particle or gamma ray decay.

Beta Particles

Beta particles are deflected by the electric and magnetic fields in the opposite direction from alpha particles. Because they are not as big or massive as alpha particles, they are deflected more strongly than alpha particles are. Beta particles are electrons that came from the nuclei of atoms in nuclear decay processes. Although beta particles do not have actual atomic numbers, its charge is extremely close to the atomic number of -1. Many times a beta particle is small enough that its charge could be ignored during calculations. When we think of beta decay processes, we can look at the following equations and imagine a neutron within the

nucleus of an atom converting to a proton or electron spontaneously. The proton remains in the nucleus and the electron is produced as a beta particle. The extra proton causes the atomic number to increase by one unit, but the mass number is unchanged.

- beta particle-ejected electron from nucleus of U

$$^{239}U \rightarrow ^{239}Np + \beta$$

- beta particle-ejected electron from nucleus of Np

$$^{239}Np \rightarrow ^{239}Pu + \beta^{-}$$

- beta particle-ejected electron from nucleus of U

$$^{237}U \rightarrow ^{237}Np + \beta^{-}$$

- beta particle-ejected electron from nucleus of Pa

$$^{234}Pa \rightarrow ^{234}U + \beta^{-}$$

- beta particle-ejected electron from nucleus of Th

$$^{234}Th \rightarrow ^{234}Pa + \beta^{-}$$

Gamma Rays

Gamma rays (γ) are radiation that is emitted when the nucleus is in an excited state due to excess energy. This energy is then released in the form of gamma rays. Gamma Rays are a form of electromagnetic energy such as visible light and hence are undeflected by electric and magnetic fields. The following are some examples of gamma ray reactions:

$$^{230}\mathrm{Th} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{231}\mathrm{Th} + \gamma$$

$$^{238}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}\mathrm{U} + \gamma$$

$$^{230}\mathrm{Th} \rightarrow {}^{230}\mathrm{Th} + \gamma$$

Applications

- Plutonium and Uranium are used as nuclear fuels and in weaponry.
- Thorium (ThO_2) is used as an incandescent gas mantle from the 1880s. They are now used for cooking, gas lanterns, and for decorative gas lights.
- The 238-Plutonium isotope…
  - Powered the Apollo-12 Lunar Mission's left behind generator. It generated under 1.5 kW of heat converted to electricity by thermoelectric elements.
  - Was a power source for orbiting satellites and missions to take pictures of Jupiter.
  - Powers pacemakers for the heart. The nuclear energy creates a longer lifetime use of the device.
- The 241-Americium isotope is used as ionizing sources for smoke detectors.
- Uranium is used in nuclear reactors in the form of fuel in rods suspended in water under a pressure of 70 to 150 atmospheres.

Problems

1. Which Actinides were the first to be discovered? Which Actinides were discovered in nature? What makes the Actinides you answered in the first questions different than the rest?
2. For the reaction of Actinium (III) hydroxide with hydrofluoric acid, a) write and balance the equation and b) explain what makes the O.S. of Actinium different than the other Actinides.
3. Explain why isotopes, such as ^{241}Am, ^{239}Pu and ^{237}Np extremely important and the main isotopes for their specific element.
4. What evidence shows that Actinides are very reactive, for the most part?
5. Describe what is happening during a beta particle equation.

Answers

1. The first Actinides to be discovered were Thorium and Uranium. The Actinides that were discovered in small portions in nature were Actinium and Protactinium. What makes these different from the rest is they were discovered naturally, and the Actinides all after Uranium were man-made.
2. a) $Ac(OH)_3$ +3HF+700°Cà AcF_3+3H_2O and b) The difference between Actinium and the other Actinides involving O.S. is Actinium only has one O.S. which is +3.
3. Those specific isotopes have various but extremely high half-lives, meaning they decay slowly, which makes it easy for scientists to study and experiment with each of them over long periods of time.
4. The evidence that shows Actinides are very reactive are they have low solubilities as halide compounds; and the lighter, trivalent Actinide compounds are unstable in aqueous solutions and can be easily precipitated out of acidic and basic environments.
5. During a beta particle equation,a neutron within the nucleus of an atom is converted to a proton or electron spontaneously. The proton remains in the nucleus and the electron is produced as a beta particle. The extra proton causes the atomic number to increase by one unit, but the mass number is unchanged.

References

1. Harwood, eta General Chemistry: Principles and Modern Applications ninth edition, Pearson. New Jersey 2007. Ch. 25 Nuclear Chemistry
2. Morss, Lester R., Edelstein Norman M., and Fuger Jean. The Chemistry of the Actinide and Transactinide Elements. Dordrecht: Springer, 2006.
3. Cotton, Simon. Lanthanide and Actinide Chemistry. Chichester, West Sussex, England; Hoboken, NJ: Wiley, 2006.
4. Moses, Alfred J.. Analytical Chemistry of the Elements. New York: The Macmillian Company, 1963.
5. Cotton, Simon. Lanthanides and actinides. Houndsmill, Basingstoke, Hampshire and London: Macmillan Education Company Ltd, 1991.

8.2.1: General Properties and Reactions of The Actinides is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **General Properties and Reactions of The Actinides** is licensed CC BY-NC-SA 4.0.

8.2.2: Chemistry of Americium

Element 95, americium, was discovered after element 96, but only just. Seaborg (see element 106), James, Morgan and Ghiorso share credit for the synthesis in 1944. Since the element is similar to europium (and below it in the periodic table) it seemed sensible to name element 105 for the American continent.

Americium-241 is the isotope first produced and is manufactured today in kilogram quantities for use in high-precision measuring devices and some home smoke detectors. All isotopes of the metal are radioactive, the longest half-life being about 7400 years.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Americium** is licensed CC BY-NC-SA 4.0.

8.2.3: Chemistry of Berkelium

Berkelium was synthesized by Thompson, Ghiorso and Seaborg (see element 106) in 1949 and named for the site of its discovery: Berkeley, California. The initial synthesis was achieved by bombarding Am-241 with alpha particles. Two neutrons are ejected and a nucleus of Bk-243 results.

$$ {}^{4}_{2}\mathrm{He} + {}^{241}_{95}\mathrm{Am} \rightarrow {}^{243}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}\mathrm{n} $$

The longest-lived isotope of berkelium is Bk-247 with a half-life of 1,400 years.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Berkelium** is licensed CC BY-NC-SA 4.0.

8.2.4: Chemistry of Californium

The fifth element in succession to emerge from the Berkeley, California cyclotron was element 98, californium (named after the State of origin). Credit for the synthesis is given to the team of Thompson, Street, Ghiorso and--of course--Seaborg (see element 106). Synthesis was achieved by bombarding Cm-242 with alpha particles. A neutron is ejected and a nucleus of Cf-245 results. The longest-lived isotope of californium, Cf-251, has a half-life of 890 years.

$$ {}^{4}_{2}\mathrm{He} + {}^{242}_{96}\mathrm{Cm} \rightarrow {}^{245}_{98}\mathrm{Cf} + {}^{1}_{0}\mathrm{n} $$

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Californium** is licensed CC BY-NC-SA 4.0.

8.2.5: Chemistry of Curium

"Simply" by bombarding the newly characterized Pu-239 with alpha particles, the Berkeley team of Seaborg (see element 106), James and Ghiorso managed to produce element 96 even before any element 95 had been made. Named in honor of Pierre and Marie Curie in 1944, curium is an actinide metal.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Curium** is licensed CC BY-NC-SA 4.0.

8.2.6: Chemistry of Einsteinium

Credit for the synthesis of element 99 was given to the Berkeley team of Ghiorso et. al. in 1952 and the radioactive metal was named for Albert Einstein. The photo above shows about 0.3 micrograms of an unidentified Es compound. Evidence for the feasibility of the synthesis came from the debris of the first hydrogen bomb explosion in which U-238 was apparently transformed into U-253 which becomes Es-253 by the loss of seven beta particles.

The laboratory synthesis of Es-253 begins with Pu-239 and goes through a five step process. The longest-lived isotope is Es-254 with a half-life of 276 days.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Einsteinium** is licensed CC BY-NC-SA 4.0.

8.2.7: Chemistry of Fermium

From evidence detected in the debris of the first hydrogen bomb test, the Berkeley team of Ghiorso et. al. succeeded in the synthesis of element 100 in 1952 and named it fermium after the Italian physicist Enrico Fermi. Fm-254 was produced by neutron bombardment of Es-253.

$$ {}^{1}_{0}\mathrm{n} + {}^{254}_{99}\mathrm{Es} \rightarrow {}^{254}_{99}\mathrm{Fm} $$

The longest-lived isotope of fermium is Fm-257 with a half-life of 80 days.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Fermium** is licensed CC BY-NC-SA 4.0.

8.2.8: Chemistry of Lawrencium

The last of the actinide metals and only the second of the transuranium elements that Glenn Seaborg was not involved with, element 103 was synthesized in 1961 by Ghiorso, Sikkeland, Larsh and Latimer at the Lawrence Radiation Laboratory (and named for Ernest Lawrence, the inventor of the cyclotron). Lr-256 is the most stable isotope with a half-life of 28 seconds.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Lawrencium** is licensed CC BY-NC-SA 4.0.

8.2.9: Chemistry of Mendelevium

Mendelevium (after Dmitri Mendeleev) was first synthesized in 1955 by Ghiorso, Harvey, Choppin, Thompson and Seaborg (see element 106). Es-253 was bombarded with alpha particles, ejecting a neutron and yielding a nucleus of Md-256. The most stable isotope is Md-258 with a half-life of 56 days.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Mendelevium** is licensed CC BY-NC-SA 4.0.

8.2.10: Chemistry of Neptunium

Neptunium (named for the planet Neptune) was the first of the transuranium elements to be synthesized (photo above is of the oxide). The synthesis took place at Berkeley, California, after initial examination of the decay products of U-235 suggested the possibility of a new element. Credit for the discovery goes to McMillan and Abelson in 1940. Although the neptunium on which the characterization work was done was synthesized in a cyclotron, we now know that minute amounts of the element exist in the environment (the longest-lived isotope has a half-life of about 2 million years). All isotopes of the metal are radioactive.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Neptunium** is licensed CC BY-NC-SA 4.0.

8.2.11: Chemistry of Nobelium

Discovered by Ghiorso, Sikkeland, Walton and Seaborg (see element 106) and named for Alfred Nobel, element 102 was originally named by a Swedish group working at the Nobel Institute of Physics in Stockholm. Details of their work, however, did not yield the expected results and the credit eventually shifted to the American team which decided to retain the original given name. The most stable isotope is No-259 with a half-life of just about 1 minute.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Nobelium** is licensed CC BY-NC-SA 4.0.

8.2.12: Chemistry of Plutonium

Discovered by Seaborg (see element 106) in 1941, plutonium was named for the 9th planet, completing the series of elements named for planets which begins with uranium. Evidence for the existence of plutonium was obtained from work with samples of neptunium and the eventual synthesis in fact results from the beta decay of neptunium-239.

The longest-lived isotope of plutonium is Pu-244 with a half-life of 82 million years. However the isotope of chief interest is Pu-239 which, like U-235, is fissionable. Most of the nuclear weapons built by the "great powers" today are based on Pu-239 which is derived from U-238 in special "breeder" reactors. Pu-239 is also a by-product of normal fission power reactors and accounts for a good deal of the concern over nuclear waste by-products since it is both highly radioactive and exceptionally toxic. Also, since the critical mass of plutonium is only about one third that of U-235, the possibility for terrorist diversion of the material is considered a serious matter.

A piece of plutonium about the size of a softball would feel hot to the touch because of the high level of alpha particle radiation given off. A somewhat larger piece of the metal would boil water within minutes. Plutonium is occasionally used in deep-space probes as a source of energy (too far from the sun for effective solar power), the heat being directly converted into electricity by a special device.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Plutonium** is licensed CC BY-NC-SA 4.0.

8.2.13: Chemistry of Protoactinium

Discovered in 1913 by Fajans and Göhring, and then isolated in 1934 by Grosse, protactinium is named from the Greek proto + actinium (parent of actinium). The silvery-white metal is extremely rare, very radioactive and highly poisonous. Originally called brevium by its discoverers because of the short life-time of the transition between Th-234 and U-234, a longer-lived isotope was eventually isolated and called protoactinium by Grosse. The name was shortened to its present form in 1949.

About 60 tons of pitchblende ore (which contains uranium, radium, and a host of other radioactive elements) yields about 125 grams of protactinium.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Protoactinium** is licensed CC BY-NC-SA 4.0.

8.2.14: Chemistry of Thorium

Thorium was discovered in 1828 by the Norwegian mineralogist Morten Thrane Esmark and was identified by the Swedish chemist Jons Jakob Berzelius. It was named after Thor, the Norse god of thunder. It is a gray, radioactive metal which is fairly abundant in the earth's crust (more than twice as much as tin) and is the first of the so-called "actinide" series which ends with lawrencium (element 103). The long half-life of the principal isotope, Th-232, (about 10^{10} years) insures that there will be plenty for quite some time to come!

Properties

The metal is fairly soft and malleable but darkens slowly in air due to oxidation. It reacts slowly with water at room temperature.

- melting point: 1842°C
- boiling point: 4788°C
- dimorphic: changes from a face-centered cubic to a body centered cubic at 1360 °C
- radioactive
- common oxidation state is +4 / also exist in +3, +2, +1
- weakly basic oxide
- paramagnetic

Applications of thorium include some special magnesium alloys and photosensors. The oxide is used in high-quality lenses. An isotope of thorium can be "bred" into uranium-234 by bombardment with slow neutrons. The U-234 is a fissile form of uranium and can be used in power plants.

Contributors and Attributions

Stephen R. Marsden

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

- **Chemistry of Thorium** is licensed CC BY-NC-SA 4.0.

8.2.15: Chemistry of Uranium

Uranium was named for the planet Uranus and discovered in 1789 by Klaproth. Isolation came in 1841 by Péligot and the radioactivity of the element was noted by Becquerel in 1896.

The pure metal is heavy, silver and lustrous. It tarnishes slowly in air

$$U(s) + O_2(g) \rightarrow UO_2(s)$$

which at ambient temperatures, UO_2 will gradually convert to U_3O_8. Uranium also reacts with boiling water.

Most of the naturally occurring uranium is the isotope U-238. This form of uranium is not fissionable, i.e., it cannot be used in atomic weapons or power plants. A much smaller percentage of naturally occurring uranium is the isotope U-235, which is fissionable. The process of "enriching" uranium to increase the proportion of U-235 in a sample is expensive and tedious but necessary to produce fuel that is usable in power plants and material for weapons.

The U-238 is not completely useless, however, as it can be "bred" into Pu-239 by bombardment with slow neutrons. This is how weapons-grade plutonium is produced. The use of Pu-239 in power plants is a controversial subject due to its toxicity and the fear of diversion by terrorist groups.

Contributors and Attributions

- Stephen R. Marsden

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

- **Chemistry of Uranium** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

9: Inorganic Materials and Nanotechnology

9.1: Electronic Properties of Materials - Superconductors and Semiconductors

9.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

9.1.2: Metal-Insulator Transitions

9.1.3: Superconductors

9.1.4: Periodic Trends- Metals, Semiconductors, and Insulators

9.1.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping

9.1.6: Semiconductor p-n Junctions

9.1.7: Diodes, LEDs and Solar Cells

9.1.8: Amorphous Semiconductors

9.1.9: Discussion Questions

9.1.10: Problems

9.1.11: References

9.2: Basic Science of Nanomaterials

9.2.1: Prelude to Basic Science of Nanomaterials

9.2.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets

9.2.3: Semiconductor Quantum Dots

9.2.4: Synthesis of Semiconductor Nanocrystals

9.2.5: Surface Energy

9.2.6: Nanoscale Metal Particles

9.2.7: Applications of Nanomaterials

9.2.8: Discussion Questions

9.2.9: Problems

9.2.10: References

9: Inorganic Materials and Nanotechnology is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

9.1: Electronic Properties of Materials - Superconductors and Semiconductors

Learning Objectives

- Explain the physical basis of the Hubbard and Mott models of metal-insulator transitions.
- Understand why good superconductors derive from bad metals.
- Know the structures and the periodic trends in band gaps and colors of semiconductors.
- Obtain the band gap of an intrinsic semiconductor from the temperature dependence of the conductivity.
- Predict the doping type when impurities or defects are introduced into a semiconductor.
- Correlate the band picture and Fermi level with n- or p-type doping.
- Understand the physical principles of operation of diodes, LEDs, solar cells, and FETs.
- Explain the differences in structures and electronic properties of crystalline and amorphous semiconductors.

The band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrödinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other and so their movement in molecules and in solids is ***correlated***.

9.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

9.1.2: Metal-Insulator Transitions

9.1.3: Superconductors

9.1.4: Periodic Trends- Metals, Semiconductors, and Insulators

9.1.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping

9.1.6: Semiconductor p-n Junctions

9.1.7: Diodes, LEDs and Solar Cells

9.1.8: Amorphous Semiconductors

9.1.9: Discussion Questions

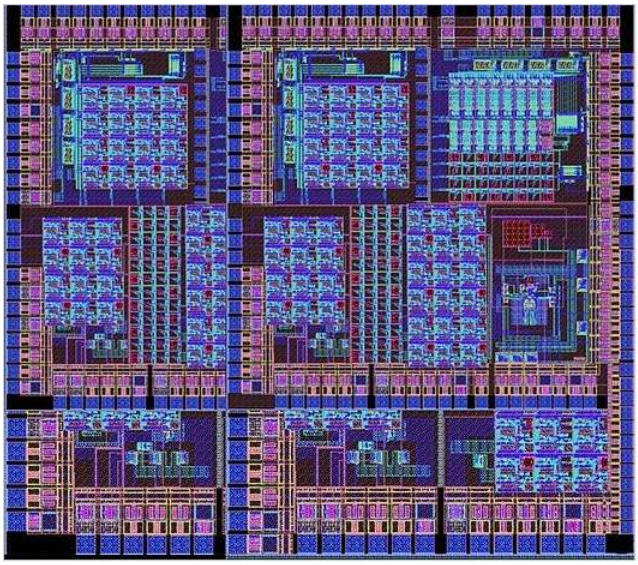
9.1.10: Problems

9.1.11: References

This page titled 9.1: Electronic Properties of Materials - Superconductors and Semiconductors is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

9.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

In Chapter 6 we developed an energy band picture for metals, starting from atomic orbitals and building up the molecular orbitals of the solid metallic crystal. This treatment gave us a useful picture of how electrons behave in metals, moving at very fast speed between scattering events, and migrating in an electric field at a slow drift velocity. It also taught us that a metal is something with a partially filled band, meaning that the Fermi level cuts through one of its bands of orbitals. An insulator or a semiconductor has a similar band picture, except that the bands are either completely full or completely empty. In this case the Fermi level lies in the gap between fully occupied and unoccupied bands. We will see in this chapter that the properties of semiconductors (along with their useful electronic applications) depend on the addition of small amounts of impurities ("dopants") that change the position of the Fermi level, resulting in conduction by electrons or "holes."



Modern integrated circuits contain billions of nanoscale transistors and diodes that are essential for logic and memory functions. Both kinds of devices rely on junctions between crystalline silicon regions that contain a few parts per million of boron or phosphorus impurities.

While the band picture works well for most crystalline materials, it does not tell us the whole story of conduction in solids. That is because the band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrödinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other and so their movement in molecules and in solids is ***correlated***. While this effect is weak in a "good" metal such as sodium - where the wavefunctions are highly delocalized - it can be quite important in other materials such as transition metal oxides. Correlated electron effects give rise to **metal-insulator transitions** that are driven by small changes in temperature, pressure, or composition, as well as to **superconductivity** - the passage of current with zero resistance at low temperatures. In this chapter we will develop some simple models to understand these interesting and important electronic properties of solids.

This page titled 9.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.2: Metal-Insulator Transitions

In Chapter 6 we learned that metals and insulators not only have different electrical properties but also have very different crystal structures. Metals tend to have high coordination numbers (typically 8 or 12) whereas insulators have low coordination numbers that can be rationalized as "octet" bonding arrangements. For example, in crystalline Si or Ge (diamond structure), each atom has four nearest neighbors. There are two electrons per bond, and thus each atom has eight electrons in its valence shell. Sn, the element below Ge, exists in two different forms, one (gray tin) with the diamond structure that is a brittle narrow-gap semiconductor, and the other (white tin) with a body-centered tetragonal structure that is a malleable metal. These two forms are very close in energy, and in fact metallic white tin transforms to the brittle semiconducting gray form at low temperature. Extremely cold weather in 18th century Europe caused many tin organ pipes to break and eventually turn to dust. This transformation has been called tin blight, tin disease, tin pest or tin leprosy. The dust is actually grey tin, which lacks the malleability of its metallic cousin white tin.

Under experimentally accessible temperatures and pressures, Si and Ge are always semiconducting (i.e., insulating), and Pb is always metallic. Why is Sn different? The reason has to do with orbital overlap. Theory tells us in fact that any (and all) insulators should become metallic at high enough pressure, or more to the point, at high enough density. For most insulators, however, the pressures required are far beyond those that we can achieve in the laboratory.

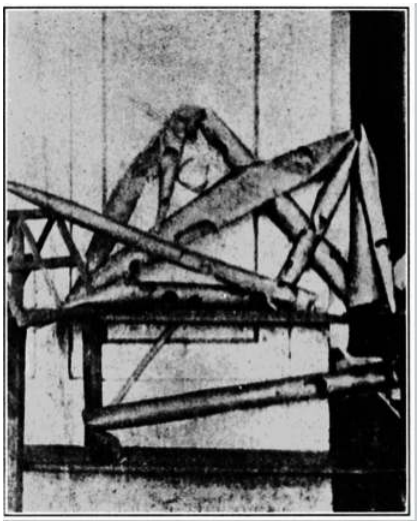
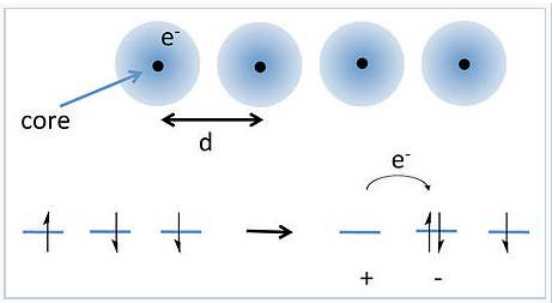


Figure 9.1.2.1: Organ pipes destroyed by "tin blight"

How can we rationalize the transition of insulators to the metallic state? Indeed, how can we understand the existence of insulators at all?

The Hubbard Model

Let's consider a chain of a large number (N) of atoms as we did in Chapter 6. For convenience, we can say that these are atoms such as H, Na, or Cs that have one valence electron. The simple band model we developed earlier suggests that the chain should be metallic, because N atoms combine to make N orbitals, and the N valence electrons only fill the band of orbitals halfway. But this conclusion doesn't depend on the density, which creates a paradox. If atoms in the chain are very far apart, we suspect that the electrons should localize on the atoms.

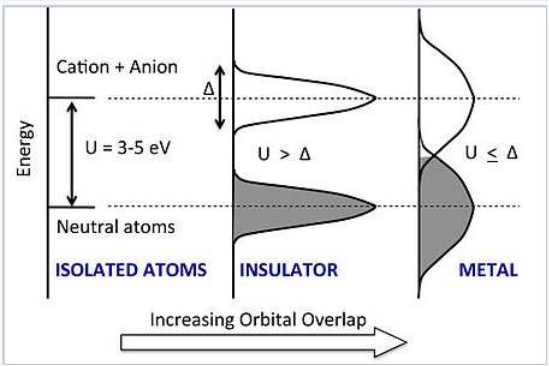


Electron hopping in a 1-D chain of atoms.

A solution to this problem was proposed by J. Hubbard in 1963.[1] Hubbard considered the energy required to transfer an electron from an atom to its nearest neighbor, as shown in the picture at the right. Because each atom already has one electron (with random spin), moving an electron over by one atom requires overcoming the energy of electron-electron repulsion to make a cation-anion pair. For well-separated atoms this energy (U) is given by:

$$U = IP - Ea - \frac{e^2}{4\pi\varepsilon_0 d} \tag{9.1.2.1}$$

where IP and EA are the ionization energy and electron affinity, ε_0 is the permittivity of free space, and the last term in the equation represents the coulombic attraction between the cation and the anion. For atoms such as alkali metals, U is on the order of 3–5 eV, which is much larger than the thermal energy kT. Thus we expect there to be very few anion-cation pairs at room temperature, and the chain of atoms should be insulating.

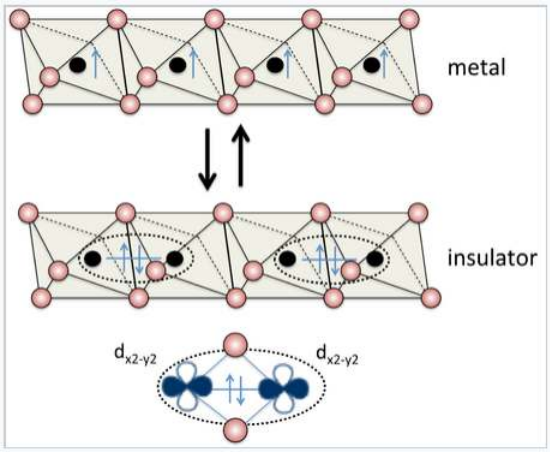


Energy vs. DOS for the chain of atoms as the density and degree of orbital overlap between atoms increases. Increasing overlap broadens the neutral atom and anion-cation states into bands, each of which has a bandwidth Δ. A transition to the metallic state occurs abruptly when Δ exceeds the Hubbard gap U.

What happens when we squeeze the atoms together? In the Hubbard model, as the distance between atoms decreases, the energies of both the neutral atom states and the anion-cation states broaden into bands, each of which has a band width Δ. The lower band can accommodate exactly *N* electrons (not *2N* as in the MO picture we developed earlier) because each orbital can only take one electron without spin-pairing. Thus for small Δ the lower band is full and the upper band is empty. However, as we continue to compress the chain, the orbital overlap becomes so strong that Δ ≈ U. At this point, the bands overlap and some of the electrons fill the anion-cation states. The chain then becomes conducting and the material is metallic.

Some materials, such as Sn and VO_2, happen to have just the right degree of orbital overlap to make the Hubbard transition occur by changing the temperature or pressure. Such materials can be very useful for electrical switching, as illustrated at the right for rutile structure VO_2. Most materials are far away from the transition, either on the metallic or insulating side. An interesting periodic trend that illustrates this concept can be seen among the transition metal monoxides, MO (M = Ti, V, Cr, Mn, Fe, Co, Ni), all of which have the NaCl structure. TiO and VO are metallic, because the 3d orbitals have significant overlap in the structure. However, CrO, MnO, FeO, CoO, and NiO are all insulators, because the 3d orbitals contract (and therefore Δ < U) going across the transition metal series. In contrast, the analogous sulfides (TiS, VS,....NiS) are all metallic. The sulfides have the NiAs structure, in

which all the metal atoms are eclipsed along the stacking axis (the hexagonal c-axis). The short metal-metal distances along that axis result in strong orbital overlap, making Δ > U.



Vanadium dioxide has the rutile structure, and in its undistorted form it is metallic, with one valence electron per V atom. Distortion of the lattice makes pairs of V atoms, resulting in an electronically insulating state. The metal-insulator transition can be driven reversibly by changing the temperature, pressure, or orbital occupancy. Electrical switching of this transition in VO_2 is being studied for applications in high performance thin film transistors[2]

The Mott Model

A simpler, less atomistic model of the metal-insulator transition was formulated by Neville Mott.[3] The Mott model considers the behavior of an electron in a material as a function of the density of all the other valence electrons. We know for a one-electron hydrogen-like atom (H, Na, Cs, etc.) the Schrödinger equation contains a potential energy term:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r}) \tag{9.1.2.2}$$

This potential energy function gives rise to familiar ladder of allowed energy levels in the hydrogen atom. However, in a metal, this Coulomb potential must be modified to include the screening of nuclear charge by the other electrons in the solid. In this case there is a **screened Coulomb potential**:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r})exp(-qr) \tag{9.1.2.3}$$

where q, which is the inverse of the **screening length**, is given by:

$$q^2 = 4m_e^2(\frac{3n}{\pi})^{\frac{1}{3}}(\frac{2\pi}{h}) \tag{9.1.2.4}$$

Here n is the density of atoms (or valence electrons), m_e is the electron mass, and h is Planck's constant. At distances much larger than the screening length q^{-1}, the electron no longer "feels" the charge on the nucleus. Mott showed that there is a critical density of electrons n_c above which the valence electrons are no longer bound by individual nuclei and are free to roam the crystal. This critical density marks the transition to the metallic state, and is given by the Mott criterion:

$$\mathbf{n_c^{\frac{1}{3}}\, a_H \approx 0.26} \tag{9.1.2.5}$$

In this equation, a_H is an effective Bohr radius for the valence electrons in the low-density limit, e.g. the average orbital radius of electrons in the 6s shell of a Cs atom when computing the value for Cs metal.



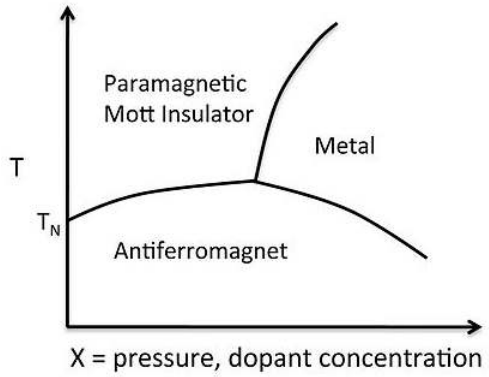
Solutions of lithium metal in liquid ammonia at low (top, ionic conductor) and higher (bottom, metal) Li concentration. From a video by Joshua Judkins

The important concept from the Mott model is that the metal-insulator transition depends very strongly on the **density of valence electrons.** This is consistent with the orbital overlap model of Hubbard, but also more general in the sense that it does not depend on a periodic structure of atoms. The Mott model is thus applicable to such diverse systems as metal atoms dissolved in liquid ammonia, metal atoms trapped in frozen gas matrices, and dopants in semiconductors.[4] In some systems, it is possible to continuously tune the density of valence electrons with rather striking results. For example, dissolving alkali metal (Li, Na, ...) in liquid ammonia (bp -33 ^{o}C) produces a blue liquid. The solvated alkali cations and negatively charged electrons impart ionic conductivity (as in a salt solution) but not electronic conductivity to the blue liquid ammonia solution. But as the concentration of electrons increases, a reflective, bronze-colored liquid phase forms that floats over the blue phase. This bronze phase is metallic and highly conducting. Eventually, with enough alkali metal added, the entire liquid is converted to the electronically conducting bronze phase.

The electrical switching of VO_2 between insulating and metallic phases (see above) can also be rationalized in terms of the Mott transition. Adding more electron density (by chemical or electric field doping) increases the concentration of valence electrons, driving the phase transition to the metallic state.

Thermodynamics and phase transitions

Thermodynamically, the metal-insulator transition is a **first-order phase transition**. In such a transition, the structure and properties change abruptly (think of the breakfast-to-lunch transition at McDonalds - there is just no way to get pancakes after, or hamburgers before 10:30 AM![5]). Thus in the case of Sn metal, the changes in structure (from four- to eight-coordination) and in electronic conductivity (insulator to metal) occur simultaneously. As in other first order phase transitions such as ice to water to steam, there is a latent heat associated with the transition and a discontinuity in derivative properties such as the heat capacity.



A typical phase diagram for a metal-insulator transition is shown at the right for V_2O_3. The octahedrally coordinated V^{3+} ion has a d^2 electron count, so there are two unpaired spins per atom, and at low temperature the spins in the lattice order

antiferromagnetically. As we learned in Chapter 8, above the Néel temperature an antiferromagnet becomes a paramagnet, which is also a Mott insulator. Increasing the pressure, or doping with electrons (e.g., by substituting some d^3 Cr^{3+} for V^{3+}) pushes the electron density over the Mott transition, the spins pair, and the solid becomes metallic.

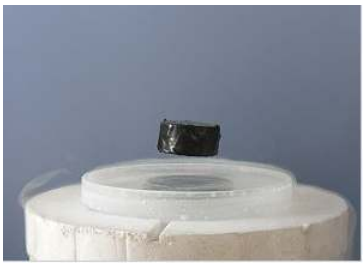
This page titled 9.1.2: Metal-Insulator Transitions is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.2: Metal-Insulator Transitions** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.3: Superconductors

Superconductivity refers to the flow of electrical current in a material with zero resistance. Such materials are very important for use in electromagnets, e.g., in magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR) machines, because once the current starts flowing in the coils of these magnets it doesn't stop. Magnetic levitation using superconductors - which, below a critical field strength, are perfect diamagnets that are not penetrated by magnetic flux lines - is also potentially relevant to future technologies such as magnetically levitated trains.

The phenomenon of superconductivity, first discovered in Hg metal in 1911 by Onnes, continues to be only partially understood. It is of great interest to physicists as a macroscopic quantum phenomenon, and to chemists and materials scientists who try to make better superconductors (especially those that superconduct at higher temperatures) and devices derived from them, such as superconducting quantum interference devices (SQUIDs), which are extremely sensitive magnetometers.

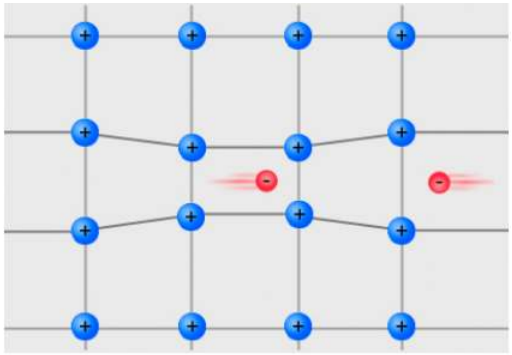


A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, excluding the magnetic field of the magnet. This current effectively forms an electromagnet that repels the magnet.

Spin pairing and zero resistance

The transition from the metallic to the superconducting state is related to the quantum phenomena of Bose-Einstein condensation and superfluidity. Individual electrons have spin = 1/2, and as such are fermions (particles with half-integer spin). Because of the Pauli exclusion principle, no more than two fermions can occupy the same quantum state (such as an orbital in a molecule or a solid). The familiar consequence of this rule is the aufbau filling of orbitals with spin-paired electrons in each energy level. In contrast, particles with integer spins - which are called bosons - do not have this restriction, and any number of bosons can occupy the same quantized energy level.

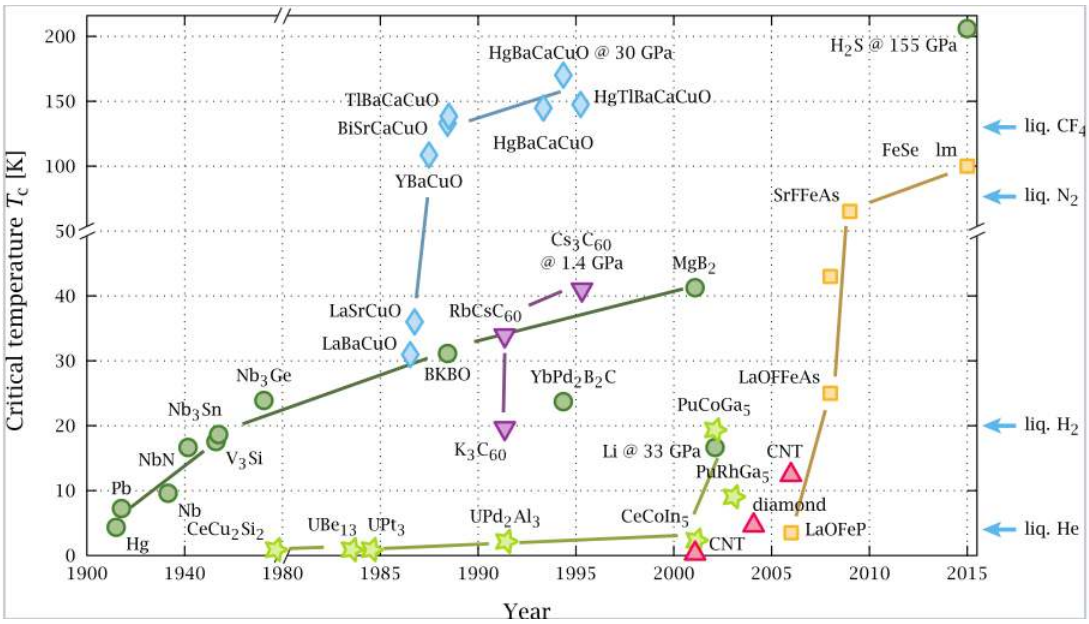
Superconductivity occurs when electrons spin pair into so-called Cooper pairs, which can travel through the lattice together. The electrons in a Cooper pair, although spin-paired, have a long-distance relationship: the spatial extent of a Cooper pair is a few nanometers in cuprate superconductors, and up to one micron in low T_c superconductors such as aluminum. Because its overall spin angular momentum is zero, a Cooper pair is a boson. When the temperature is low enough, the Cooper pairs "condense" into the lowest energy level. The second lowest energy level - which is typically a few meV above the ground state - is not accessible to them as long as the energy gap is larger than the thermal energy, kT. The scattering of electrons by the lattice then becomes forbidden by energy conservation because scattering dissipates energy, and the Cooper pairs cannot change their energy state. Thus the resistance (which arises from scattering, as we learned in Ch. 6) drops abruptly to zero below T_c. However, the Cooper pairs can be broken apart when they move fast, and thus superconductors turn back into normal metals (even below T_c) above some critical current density j_c. This phenomenon is also related to the critical magnetic field, H_c, that quenches superconductivity.



A trampoline for electrons

What causes electrons, which repel each other because of their negative charge, to pair up and travel together in superconductors? The mechanism - which must involve some kind of attractive interaction between electrons - is well understood for "conventional" superconductors which have relatively low transition temperatures, but is not yet known with certainty for high temperature oxide superconductors. In conventional, or BCS superconductors, the spin pairing is mediated by the lattice as shown in the figure at the left. A strong electron-lattice interaction causes a distortion in the lattice as an electron moves through. This elastic deformation is felt as an attractive force by a second electron moving in the opposite direction. This can be thought of as analogous to the interaction of two people jumping on a trampoline. The weight of the first person on the trampoline creates a "well" that attracts the second one, and they tend to move together (even if they don't like each other). Strange as this interaction seems, it is supported experimentally by isotope effects on T_c and by quantitative predictions of T_c values in conventional superconductors.

Bad metals make good superconductors. All superconductors are "normal" metals - with finite electrical resistance - above their critical transition temperature, T_c. If you ask where in the periodic table one might look for superconductors, the answer is surprising. The most conductive metals (Ag, Au, Cu, Cs, etc.) make the worst superconductors, i.e., they have the lowest superconducting transition temperatures, in many cases below 0.01 K. Conversely "bad" metals, such as niobium alloys, certain copper oxides, $K_xBa_{1-x}BiO_3$, MgB_2, FeSe, and alkali salts of C_{60}^{n-} anions, can have relatively high transition temperatures.

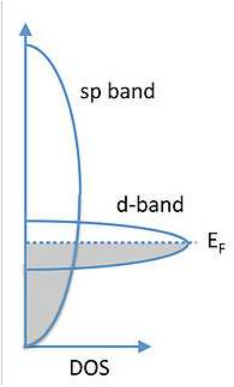


Timeline of superconducting materials, showing T_c vs. year of discovery.

We observe that most good superconductors appear in composition space very **near a metal-insulator transition**. In terms of our microscopic picture, orbital overlap in superconductors is poor, just barely enough to make them act as metals ($\Delta \approx U$) above T_c. In the normal state, superconductors with high T_c - which can be as high as 150 K - are typically "bad" metals. An important characteristic of such metals is that the **mean free path** of electrons (in the normal state, above T_c) is on the order of the lattice

spacing, i.e., **only a few Å**. In contrast, we learned in Ch. 6 that good metals such as Au, Ag, and Cu have electron mean free paths that are two orders of magnitude longer (ca. 40 nm). In a bad metal, the electron "feels" the lattice rather strongly, whereas in a good metal, the electrons are insensitive to small changes in the distance between metals atoms.

What does the band picture look like for a bad metal? The key point is that because orbital overlap is poor, the metal has a **high density of states** at the Fermi level. This is a universal property of high temperature superconductors and provides a clue of where to look for new and improved superconducting materials. Recall that transition elements in the middle of the 3d series (Cr, Fe, Co, Ni) were magnetic because of poor orbital overlap and weak d-d bonding. The elements below these - especially Nb, Ta, and W - have just barely enough d-d orbital overlap to be on the metallic side of the metal-insulator transition and to be "bad" metals. Carbides and nitrides of these elements are typically superconducting, with the carbon and nitrogen atoms serving to adjust the valence electron density, as illustrated in the table below.



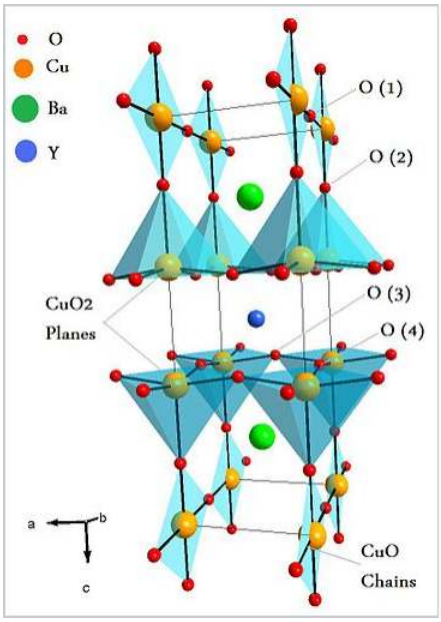
Generic E vs. DOS for a bad metal.

Compound	NbC	Mo_2N	TaC	VN	NbN	TaN	Nb_3Ge
T_c (K)	11.1	5.0	9.7	7.5	15.2	17.8	22.3

High T_c superconductors

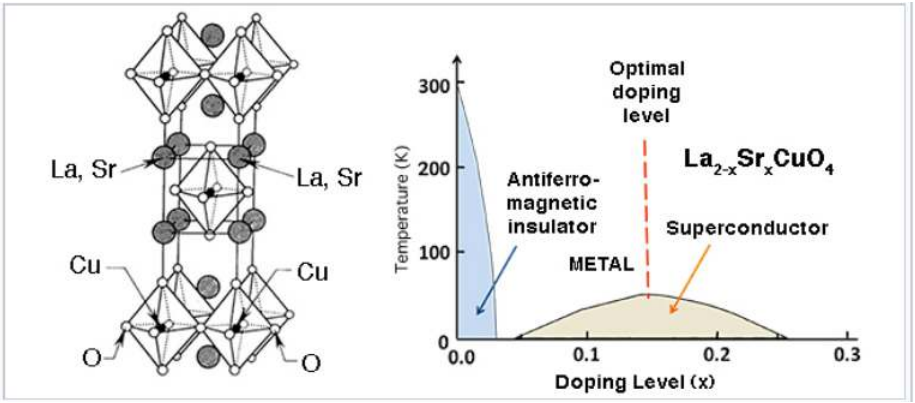
In addition to having weak orbital overlap in the metallic state - which results in a high DOS at E_F - high temperature superconductors also typically contain elements in mixed oxidation states (for example, $Cu^{2+/3+}$ or $Bi^{3+/5+}$) that are close in energy to the O^{2-}/O^- couple in the lattice. At ambient pressure, cuprate superconductors have the highest known T_c values, ranging between about 35 and 150 K. The crystal structures of these materials are almost all variants of the perovskite lattice, as shown at the right for the 1-2-3 superconductor $YBa_2Cu_3O_{7-\delta}$. An ideal perovskite lattice would have formula $ABO_3 = A_3B_3O_9$. In $YBa_2Cu_3O_{7-\delta}$, Y and Ba occupy the A cation sites, Cu occupies the B sites, and two of the nine O atoms are missing.

The $YBa_2Cu_3O_{7-\delta}$ lattice consists of mixed-valent copper(II/III) oxide sheets capped by oxygen atoms to form CuO_5 square pyramids. These sheets encapsulate the Y^{3+} cations. Copper(II) oxide ribbons that share the apical oxygen atoms of the square pyramids run in one direction through the structure. In $YBa_2Cu_3O_{7-\delta}$ and related materials, one component of the structure (here the Cu-O ribbons) acts as a **charge reservoir** to control the doping of the planar CuO_2 sheets, which are the elements of the structure that carry the supercurrent. Cuprate superconductors with Bi, Tl, or Hg-containing charge reservoir layers and multiple, eclipsed CuO_2 sheets in the unit cell tend to have the highest T_c values.



Crystal structure of $YBa_2Cu_3O_{7-\delta}$ (YBCO), the first superconductor with T_c above the boiling point of liquid nitrogen.

The connection between the metal-insulator transtion and superconductivity is nicely illustrated in the phase diagram of $La_{2-x}Sr_xCuO_4$, the first cuprate superconductor, which was discovered in 1986 by Georg Bednorz and K. Alex Müller. This compound has a rather simple structure in which rocksalt La(Sr)O layers are intergrown with perovskite $La(Sr)CuO_3$ layers. Undoped La_2CuO_4 contains only Cu^{2+} ions and is an antiferromagnetic insulator. As a small amount of Sr^{2+} is substituted for La^{3+}, some of the Cu^{2+} is oxidized to Cu^{3+}, and the lattice is doped with holes. As the doping level increases, the antiferromagnetic phase undergoes a first-order phase transition to a "bad" metal, and at slightly higher doping density the superconducting phase appears. The proximity of the superconducting phase to the metal-insulator transition is a hallmark of cuprate superconductors. A maximum T_c of 35K is observed at x = 0.15. Doping at higher levels moves the Fermi level beyond the point of highest DOS in the d-band of Cu and the superconducting phase then gradually disappears. It is interesting to compare this phase diagram with that of V_2O_3 (above), which also undergoes an antiferromagnetic insulator to "bad" metal transition as it is doped.



Crystal structure and phase diagram of the cuprate superconductor $La_{2-x}Sr_xCuO_4$. (LSCO)

This page titled 9.1.3: Superconductors is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

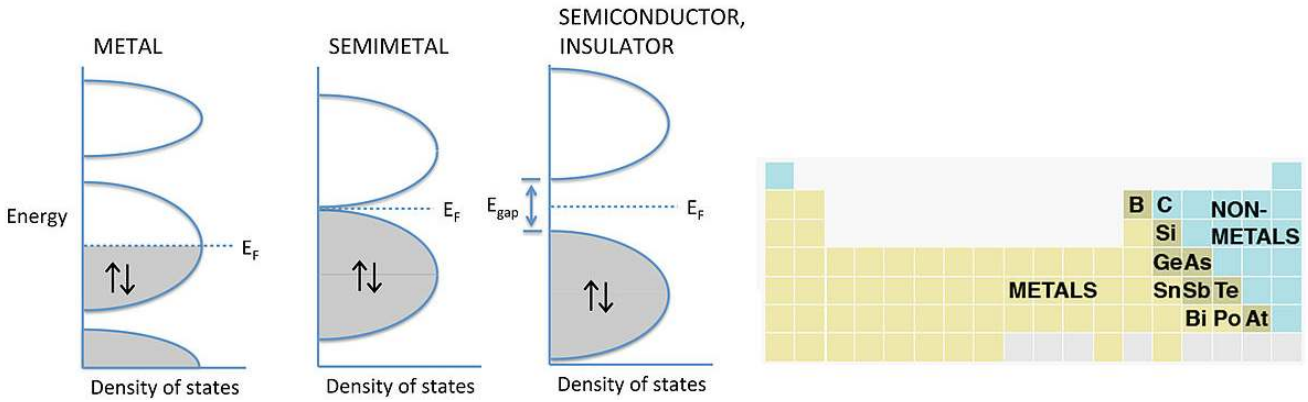
- **10.3: Superconductors** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.4: Periodic Trends- Metals, Semiconductors, and Insulators

As we consider periodic trends in the electronic properties of materials, it is important to review some of the key bonding trends we have learned in earlier chapters:

- Going down the periodic table, atoms in solids tend to adopt structures with higher coordination numbers.
- The second row of the periodic table is special, with strong s-p hybridization and π-bonding between atoms.
- Electrons in higher quantum shells are less strongly bound, so the energy difference between bonding and antibonding orbitals becomes smaller for heavier atoms.

We also know that most of the elements in the periodic table are metals, but the elements in the top right corner are insulating under ordinary conditions (1 atm. pressure) and tend to obey the octet rule in their compounds.



At the transition between metals and non-metals in the periodic table we encounter a crossover in electronic properties, as well as in other properties such as the acidity of the oxides (see Ch. 3). The group of elements at the border is loosely referred to as the metalloids. Several of these elements (such as C, Sn, and As) can exist as different allotropes that can be metals, insulators, or something in between.

A more rigorous delineation of the electronic properties of these elements (and of many compounds) can be made by considering their band structures and the **temperature dependence of the electronic conductivity**. As we have previously discussed, metals have partially filled energy bands, meaning that the Fermi level intersects a partially filled band. With increasing temperature, metals become poorer conductors because lattice vibrations (which are called phonons in the physics literature) scatter the mobile valence electrons. In contrast, semiconductors and insulators, which have filled and empty bands, become better conductors at higher temperature, since some electrons are thermally excited to the lowest empty band. The distinction between insulators and semiconductors is arbitrary, and from the point of view of metal-insulator transitions, all semiconductors are insulators. We typically call an insulator a semiconductor if its band gap (E_{gap}) is less than about 3 eV. A semimetal is a material that has a band gap near zero, examples being single sheets of sp^2-bonded carbon (graphene) and elemental Bi. Like a narrow gap semiconductor, a semimetal has higher conductivity at higher temperature.

This page titled 9.1.4: Periodic Trends- Metals, Semiconductors, and Insulators is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.4: Periodic Trends- Metals, Semiconductors, and Insulators** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy ≤ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

There are a number of places where we find semiconductors in the periodic table:

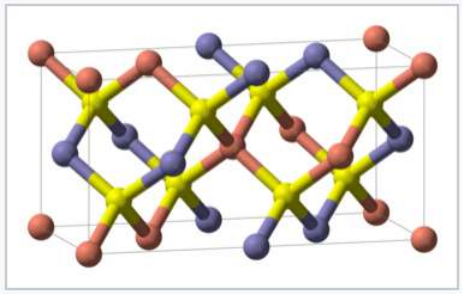
- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.



A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zincblende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,…), 3-5 (GaAs, AlSb, InP,…), 2-6 (CdSe, HgTe, ZnO,…), and 1-7 (AgCl, CuBr,…) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

C (diamond) > Si > Ge > α-Sn

E_{gap} (eV): 5.4 1.1 0.7 0.0

This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

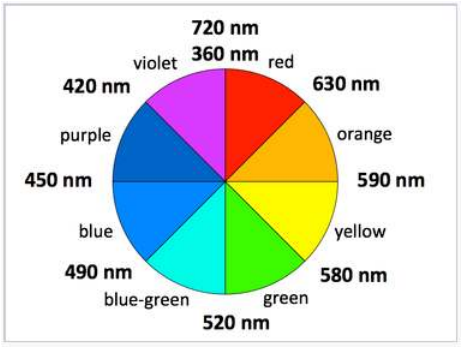
Ge < GaAs < ZnSe
0.7 1.4 2.8 eV

Sn < InSb < CdTe < AgI
0.0 0.2 1.6 2.8 eV

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference Δχ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.



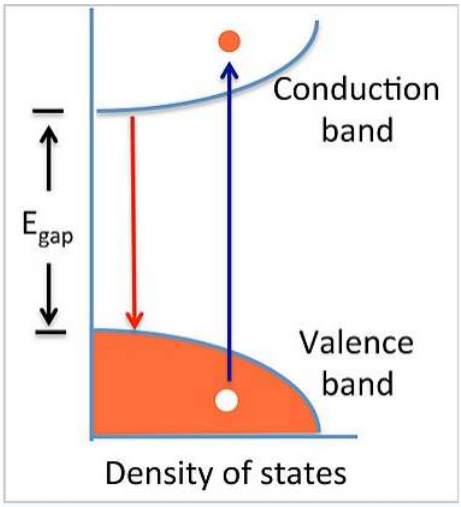
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS (E_{gap} = 2.6 eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy $E \geq E_{gap}$ to a semiconductor (blue arrow). The electron-hole pair recombines to release energy equal to E_{gap} (red arrow).

At equilibrium, the creation and annihilation of electron-hole pairs proceed at equal rates. This dynamic equilibrium is analogous to the dissociation-association equilibrium of H^+ and OH^- ions in water. We can write a mass action expression:

$$n \times p = K_{eq} = n_i^2$$

where n and p represent the number density of electrons and holes, respectively, in units of cm^{-3}. The intrinsic carrier concentration, n_i, is equal to the number density of electrons or holes in an undoped semiconductor, where $n = p = n_i$.

Note the similarity to the equation for water autodissociation:

$[H^+][OH^-] = K_w$

By analogy, we will see that when we increase n (e.g., by doping), p will decrease, and vice-versa, but their product will remain constant at a given temperature.

Temperature dependence of the carrier concentration. Using the equations $K_{eq} = e^{(\frac{-\Delta G^o}{RT})}$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, we can write:

$$n \times p = n_i^2 = e^{(\frac{\Delta S^o}{R})} e^{(\frac{-\Delta H^o}{RT})} \tag{9.1.5.1}$$

The entropy change for creating electron hole pairs is given by:

$$\Delta S^o = Rln(N_V) + Rln(N_V) = Rln(N_C N_V) \tag{9.1.5.2}$$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$$n_i^2 = N_C N_V e^{(-\Delta H^o RT)} \tag{9.1.5.3}$$

Since the volume change is negligible, $\Delta H^o \approx \Delta E^o$, and therefore $\frac{\Delta H^o}{R} \approx \frac{E_{gap}}{k}$, from which we obtain

$$n_i^2 = N_C N_V e^{(\frac{-E_{gap}}{kT})} \tag{9.1.5.4}$$

and finally

$$\mathbf{n = p = n_i = (N_C N_V)^{\frac{1}{2}} e^{(\frac{-E_{gap}}{2kT})}} \tag{9.1.5.5}$$

For pure Si (E_{gap} = 1.1 eV) with N ≈ $10^{22}/cm^3$, we can calculate from this equation a carrier density n_i of approximately $10^{10}/cm^3$ at 300 K. This is about 12 orders of magnitude lower than the valence electron density of Al, the element just to the left of Si in the periodic table. Thus we expect the conductivity of pure semiconductors to be many orders of magnitude lower than those of metals.

Conductivity of intrinsic semiconductors

The conductivity (σ) is the product of the number density of carriers (n or p), their charge (e), and their mobility (μ). Recall from Chapter 6 that μ is the ratio of the carrier drift velocity to the electric field and has units of cm^2/Volt-second. Typically electrons and holes have somewhat different mobilities (μ_e and μ_h, respectively) so the conductivity is given by:

$$\sigma = ne\mu_e + pe\mu_h \tag{9.1.5.6}$$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

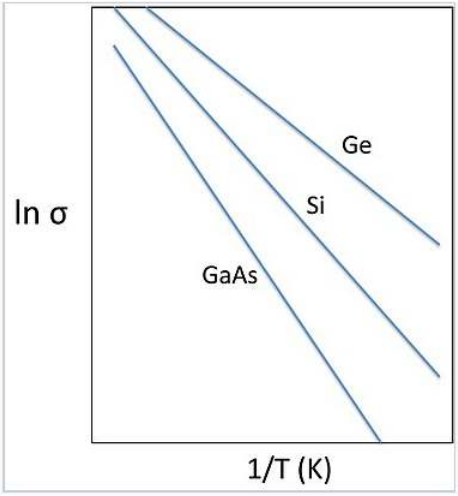
$$\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m} \tag{9.1.5.7}$$

where e is the fundamental unit of charge, τ is the scattering time, and m is the effective mass of the charge carrier.

Taking an average of the electron and hole mobilities, and using n = p, we obtain

$$\sigma = \sigma_o \mathbf{e}^{(\frac{-E_{gap}}{2kT})},\ where\ \sigma_o = 2(N_C N_V)^{\frac{1}{2}} e\mu \tag{9.1.5.8}$$

By measuring the conductivity as a function of temperature, it is possible to obtain the activation energy for conduction, which is $E_{gap}/2$. This kind of plot, which resembles an Arrhenius plot, is shown at the right for three different undoped semiconductors. The slope of the line in each case is $-E_{gap}/2k$.

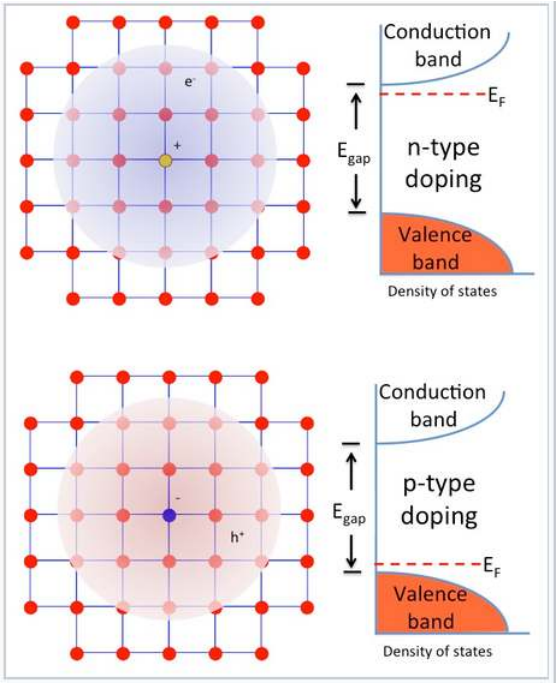


Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is $-E_{gap}/2k$.

Doping of semiconductors. Almost all applications of semiconductors involve controlled **doping**, which is the substitution of impurity atoms, into the lattice. Very small amounts of dopants (in the parts-per-million range) dramatically affect the conductivity of semiconductors. For this reason, very pure semiconductor materials that are carefully doped - both in terms of the concentration and spatial distribution of impurity atoms - are needed.

n- and p-type doping. In crystalline Si, each atom has four valence electrons and makes four bonds to its neighbors. This is exactly the right number of electrons to completely fill the valence band of the semiconductor. Introducing a phosphorus atom into the lattice (the positively charged atom in the figure at the right) adds an extra electron, because P has five valence electrons and only needs four to make bonds to its neighbors. The extra electron, at low temperature, is bound to the phosphorus atom in a hydrogen-like molecular orbital that is much larger than the 3s orbital of an isolated P atom because of the high dielectric constant of the semiconductor. In silicon, this "expanded" Bohr radius is about 42 Å, i.e., 80 times larger than in the hydrogen atom. The energy needed to ionize this electron – to allow it to move freely in the lattice - is only about 40–50 meV, which is not much larger the thermal energy (26 meV) at room temperature. Therefore the Fermi level lies just below the conduction band edge, and a large fraction of these extra electrons are promoted to the conduction band at room temperature, leaving behind fixed positive charges on the P atom sites. The crystal is **n-doped**, meaning that the majority carrier (electron) is negatively charged.

Alternatively, boron can be substituted for silicon in the lattice, resulting in **p-type** doping, in which the majority carrier (hole) is positively charged. Boron has only three valence electrons, and "borrows" one from the Si lattice, creating a positively charged hole that exists in a large hydrogen-like orbital around the B atom. This hole can become delocalized by promoting an electron from the valence band to fill the localized hole state. Again, this process requires only 40–50 meV, and so at room temperature a large fraction of the holes introduced by boron doping exist in delocalized valence band states. The Fermi level (the electron energy level that has a 50% probability of occupancy at zero temperature) lies just above the valence band edge in a p-type semiconductor.



n- and p-type doping of semiconductors involves substitution of electron donor atoms (light orange) or acceptor atoms (blue) into the lattice. These substitutions introduce extra electrons or holes, respectively, which are easily ionized by thermal energy to become free carriers. The Fermi level of a doped semiconductor is a few tens of mV below the conduction band (n-type) or above the valence band (p-type).

As noted above, the doping of semiconductors dramatically changes their conductivity. For example, the intrinsic carrier concentration in Si at 300 K is about 10^{10} cm^{-3}. The mass action equilibrium for electrons and holes also applies to doped semiconductors, so we can write:

$$n \times p = n_i^2 = 10^{20} cm^{-6} \; at \; 300K \tag{9.1.5.9}$$

If we substitute P for Si at the level of one part-per-million, the concentration of electrons is about 10^{16} cm^{-3}, since there are approximately 10^{22} Si atoms/cm^3 in the crystal. According to the mass action equation, if n = 10^{16}, then p = 10^4 cm^{-3}. There are three consequences of this calculation:

- The density of carriers in the doped semiconductor (10^{16} cm^{-3}) is much higher than in the undoped material (~10^{10} cm^{-3}), so the conductivity is also many orders of magnitude higher.
- The activation energy for conduction is only 40–50 meV, so the conductivity does not change much with temperature (unlike in the intrinsic semiconductor)
- The minority carriers (in this case holes) do not contribute to the conductivity, because their concentration is so much lower than that of the majority carrier (electrons).

Similarly, for p-type materials, the conductivity is dominated by holes, and is also much higher than that of the intrinsic semiconductor.

Chemistry of semiconductor doping. Sometimes it is not immediately obvious what kind of doping (n- or p-type) is induced by "messing up" a semiconductor crystal lattice. In addition to substitution of impurity atoms on normal lattice sites (the examples given above for Si), it is also possible to dope with vacancies - missing atoms - and with interstitials - extra atoms on sites that are not ordinarily occupied. Some simple rules are as follows:

- For substitutions, adding an **atom to the right** in the periodic table results in **n-type** doping, and an atom to the **left** in **p-type** doping.

  For example, when TiO_2 is doped with Nb on some of the Ti sites, or with F on O sites, the result is n-type doping. In both cases, the impurity atom has one more valence electron than the atom for which it was substituted. Similarly, substituting a small amount of Zn for Ga in GaAs, or a small amount of Li for Ni in NiO, results in p-type doping.

- **Anion vacancies** result in **n-type** doping, and **cation vacancies** in **p-type** doping.

  Examples are anion vacancies in CdS_{1-x} and WO_{3-x}, both of which give n-type semiconductors, and copper vacancies in $Cu_{1-x}O$, which gives a p-type semiconductor.

- **Interstitial cations** (e.g. Li) donate electrons to the lattice resulting in **n-type** doping. Interstitial anions are rather rare but would result in p-type doping.

Sometimes, there can be both p- and n-type dopants in the same crystal, for example B and P impurities in a Si lattice, or cation and anion vacancies in a metal oxide lattice. In this case, the two kinds of doping **compensate** each other, and the doping type is determined by the one that is in higher concentration. A dopant can also be present on more than one site. For example, Si can occupy both the Ga and As sites in GaAs, and the two substitutions compensate each other. Si has a slight preference for the Ga site, however, resulting in n-type doping.

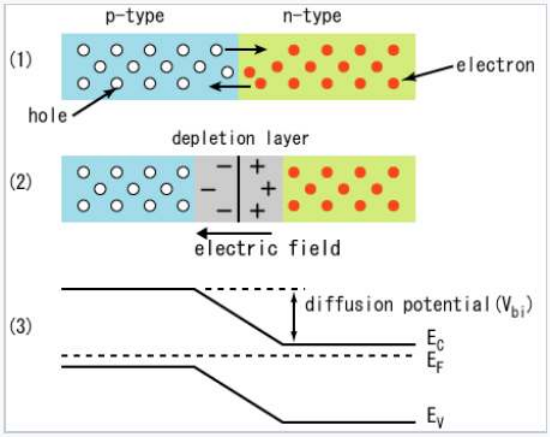
This page titled 9.1.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.6: Semiconductor p-n Junctions

Semiconductor p-n junctions are important in many kinds of electronic devices, including diodes, transistors, light-emitting diodes, and photovoltaic cells. To understand the operation of these devices, we first need to look at what happens to electrons and holes when we bring p-type and n-type semiconductors together. At the junction between the two materials, mobile electrons and holes annihilate each other, leaving behind the fixed + and - charges of the electron donor and electron acceptor dopants, respectively. For example, on the n-side of a silicon p-n junction, the positively charged dopants are P^+ ions and on the p-side the negatively charged dopants are B^-. The presence of these uncompensated electrical charges creates an electric field, the **built-in field** of the p-n junction. The region that contains these charges (and a very low density of mobile electrons or holes) is called the **depletion region**.

The electric field, which is created in the depletion region by electron-hole recombination, repels both the electrons (on the n-side) and holes (on the p-side) away from the junction. The concentration gradient of electrons and holes, however, tends to move them in the opposite direction by diffusion. At equilibrium, the flux of mobile carriers is zero because the field-driven migration flux is equal and opposite to the concentration-driven diffusion flux.



When p-type and n-type semiconductors are joined, electrons and holes are annihilated at the interface, leaving a depletion region that contains positively and negatively charged donor and acceptor atoms, respectively. At equilibrium, the Fermi level (E_F) is uniform throughout the junction. E_F lies just above the valence band on the p-type side of the junction and just below the conduction band on the n-type side.

The width of the depletion layer depends on the screening length in the semiconductor, which in turn depends on the dopant density. At high doping levels, the depletion layer is narrow (tens of nanometers across), whereas at low doping density it can be as thick as 1 µm. The depletion region is the only place where the electric field is nonzero, and the only place where the bands bend. Elsewhere in the semiconductor the field is zero and the bands are flat.

In the middle of p-n junction, the Fermi level energy, E_F, is halfway between the valence band, VB, and the conduction band, CB, and the semiconductor is intrinsic ($n = p = n_i$)

This page titled 9.1.6: Semiconductor p-n Junctions is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.6: Semiconductor p-n Junctions** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

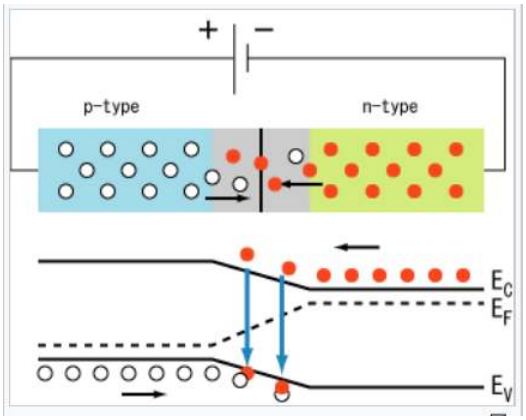
9.1.7: Diodes, LEDs and Solar Cells

Diodes are semiconductor devices that allow current to flow in only one direction. Diodes act as rectifiers in electronic circuits, and also as efficient light emitters (in LEDs) and solar cells (in photovoltaics). The basic structure of a diode is a junction between a p-type and an n-type semiconductor, called a p-n junction. Typically, diodes are made from a single semiconductor crystal into which p- and n- dopants are introduced.



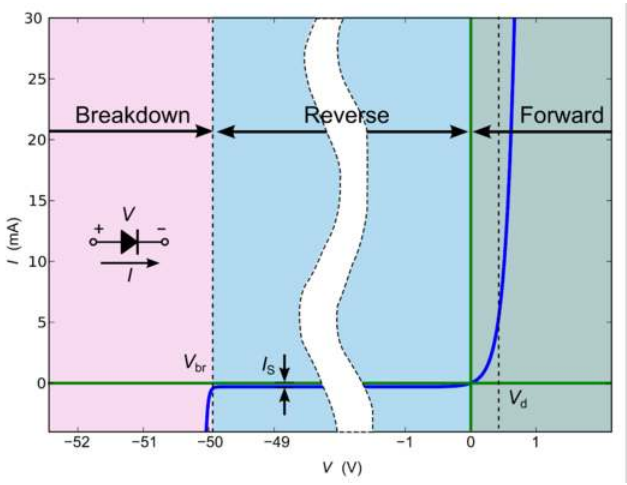
Closeup of a diode, showing the square-shaped semiconductor crystal *(black object on left)* (John Maushammer, Wikipedia, CC-BY-SA)

If the n-side of a diode is biased at positive potential and the p-side is biased negative, electrons are drawn to the n-side and holes to the p-side. This reinforces the built in potential of the p-n junction, the width of the depletion layer increases, and very little current flows. This polarization direction is referred to as "back bias." If the diode is biased the other way, carriers are driven into the junction where they recombine. The electric field is diminished, the bands are flattened, and current flows easily since the applied bias lowers the built-in potential. This is called "forward bias."



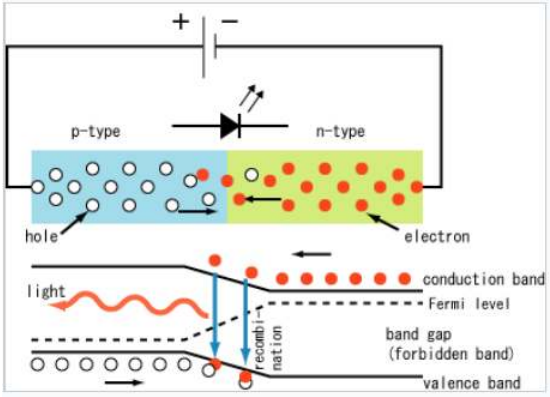
Electrons (red) and holes (white) in a forward-biased diode. (S-kei. Wikipedia, CC-BY-SA)

The figure on the left illustrates a forward-biased diode, through which current flows easily. As electrons and holes are driven into the junction (black arrows in lower left figure), they recombine (downward blue arrows), producing light and/or heat. The Fermi level in the diode is indicated as the dotted line. There is a drop in the Fermi level (equal to the applied bias) across the depletion layer. The corresponding diode i-V curve is shown on the right. The current rises exponentially with applied voltage in the forward bias direction, and there is very little leakage current under reverse bias. At very high reverse bias (typically tens of volts) diodes undergo avalanche breakdown and a large reverse current flows.



Diode i-V curve

A **light-emitting diode** or **LED** is a kind of diode that converts some of the energy of electron-hole recombination into light. This radiative recombination process always occurs in competition with non-radiative recombination, in which the energy is simply converted to heat. When light is emitted from an LED, the photon energy is equal to the bandgap energy. Because of this, LED lights have pure colors and narrow emission spectra relative to other light sources, such as incandescent and fluorescent lights. LED lights are energy-efficient and thus are typically cool to the touch.



Light-emitting diode (LED). (S-kei. Wikipedia, CC-BY-SA)

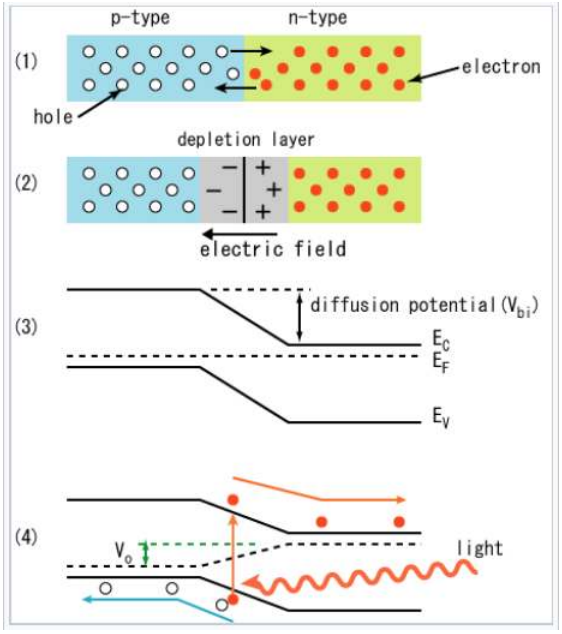
Direct-gap semiconductors such as GaAs and GaP have efficient luminescence and are also good light absorbers. In direct gap semiconductors, there is no momentum change involved in electron-hole creation or recombination. That is, the electrons and holes originate at the same value of the momentum wavevector **k**, which we encountered in Ch. 6. **k** is related to the momentum (also a vector quantity) by **p** = h**k**/2π. In a direct-gap semiconductor, the top of the valence band and the bottom of the conduction band most typically both occur at **k** = 0. Since the momentum of the photon is close to zero, photon absorption and emission are strongly allowed (and thus kinetically fast). Polar semiconductors such as GaAs, GaN, and CdSe are typically direct-gap materials. **Indirect-gap** semiconductors such as Si and Ge absorb and emit light very weakly because the valence band maximum and conduction band minimum do not occur at the same point in k-space. This means that a lattice vibration (a phonon) must also be created or annihilated in order to conserve momentum. Since this "three body" (electron, hole, phonon) process has low probability, the radiative recombination of electrons and holes is slow relative to non-radiative decay - the thermalization of electron-hole energy as lattice vibrations - in indirect-gap semiconductors. The momentum selection rule thus prevents light absorption/emission and there are no pure Si LEDs or Si-based lasers.



Prof. Shuji Nakamura holding a blue LED.

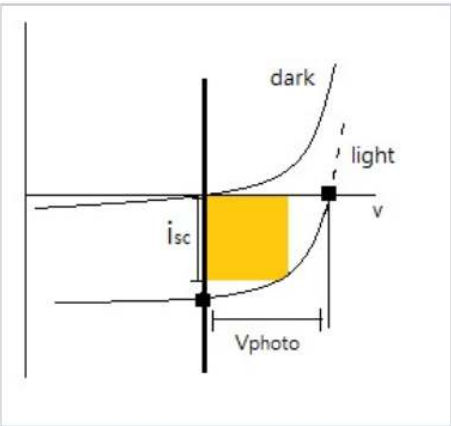
While red, orange, yellow, and green LEDs can be fabricated relatively easily from AlP-GaAs solid solutions, it was initially very difficult to fabricate blue LEDs because the best direct gap semiconductor with a bandgap in the right energy range is a nitride, GaN, which is difficult to make and to dope p-type. Working at Nichia Corporation in Japan, Shuji Nakamura succeeded in developing a manufacturable process for p-GaN, which is the basis of the blue LED. Because of the importance of this work in the development of information storage (Blu-Ray technology) and full-spectrum, energy-efficient LED lighting, Nakamura shared the 2014 Nobel Prize in Physics with Isamu Asaki and Hiroshi Amano, both of whom had made earlier contributions to the development of GaN diodes.

A **Solar cell**, or photovoltaic cell, converts light absorbed in a p-n junction directly to electricity by the photovoltaic effect. Photovoltaics is the field of technology and research related to the development of solar cells for conversion of solar energy to electricity. Sometimes the term solar cell is reserved for devices intended specifically to capture energy from sunlight, whereas the term photovoltaic cell is used when the light source is unspecified.



Photovoltaic effect in a semiconductor p-n junction. (S-kei. Wikipedia, CC-BY-SA)

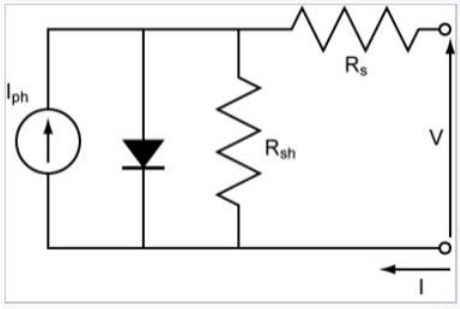
Photocurrent in p-n junction solar cells flows in the diode reverse bias direction. In the dark, the solar cell simply acts as a diode. In the light, the photocurrent can be thought of as a constant current source, which is added to the i-V characteristic of the diode. The relationship between the dark and light current in a photovoltaic cell is shown in the diagram at the left.



Current-voltage characteristic of a solar cell in the dark and under illumination with band gap light. The short-circuit photocurrent is indicated as i_{sc}, and the open-circuit photovoltage is V_{photo}. The maximum power generated by the solar cell is determined by the area of the orange box.

The built-in electric field of the p-n junction separates e^- h^+ pairs that are formed by absorption of bandgap light in the depletion region. The electrons flow downhill, towards the n-type side of the junction, the holes flow uphill towards the p-side. If $h\nu \geq E_{gap}$, light can be absorbed by promoting an electron from the valence band to the conduction band. Any excess energy is rapidly thermalized. Light with $h\nu > E_g$ thus can store only E_g worth of energy in an e^- h^+ pair. If light is absorbed outside of depletion region, i.e., on the n- or p-side of the junction where there is no electric field, minority carriers must diffuse into the junction in order to be collected. This process occurs in competition with electron-hole recombination. Because impurity atoms and lattice defects make efficient recombination centers, semiconductors used in solar cells (especially indirect-gap materials such as Si, which must be relatively thick in order to absorb most of the solar spectrum) must be very pure. Most of the cost of silicon solar cells is associated with the process of purifying elemental silicon and growing large single crystals from the melt.

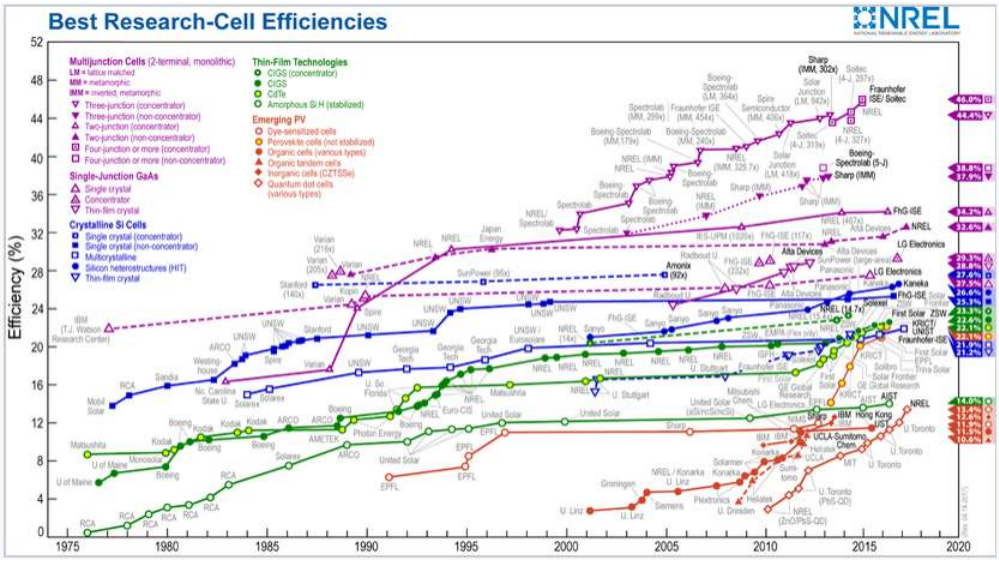
In the photodiode i-V curve above, V_{photo} is typically only about 70% of the bandgap energy E_{gap}. The photocurrent is limited by the photon flux, the recombination rate, and the re-emission of absorbed light.[6] The area of the orange rectangle indicates the power generated by the solar cell, which can be calculated as P = i x V. In good single crystal or polycrystalline solar cells made of Si, GaAs, CdTe, $CuIn_xGa_{1-x}Se_2$, or $(CH_3NH_3)PbI_3$ the quantum yield (the ratio of short circuit photocurrent to photon flux) is close to unity.



The equivalent circuit of a p-n junction solar cell, which results in the "light" i-V curve shown in the figure above. The solar cell is effectively a diode with a reverse-bias current source provided by light-generated electrons and holes. The shunt resistance (R_{sh}) in the equivalent circuit represents parasitic electron-hole recombination. A high shunt resistance (low recombination rate) and low series resistance (R_s) are needed for high solar cell efficiency.

Solar cells have many current applications. Individual cells are used for powering small devices such as electronic calculators. Photovoltaic arrays generate a form of renewable electricity, particularly useful in situations where electrical power from the grid is unavailable such as in remote area power systems, Earth-orbiting satellites and space probes, remote radio-telephones and water pumping applications. Photovoltaic electricity is also increasingly deployed in grid-tied electrical systems.

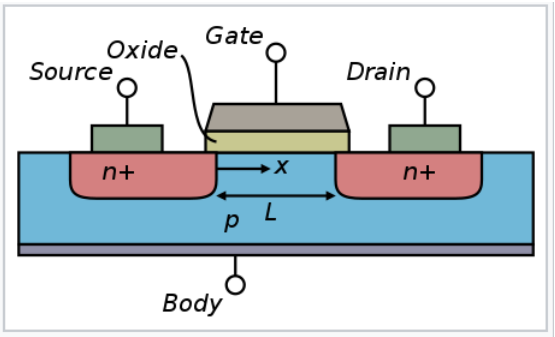
The cost of installed photovoltaics (calculated on a per-watt basis) has dropped over the past decade at a rate of about 13% per year, and has already reached grid parity in Germany and a number of other countries.[7] Photovoltaic grid parity is anticipated in U.S. power markets in the 2020 timeframe.[8] A major driver in the progressively lower cost of photovoltaic power is the steadily increasing efficiency of solar cells, which is shown in the graphic at the right. Higher efficiency solar cells require less area to deliver the same amount of power, and this lowers the "balance of system" costs such as wiring, roof mounting, etc., which scale as the area of the solar panels. Progress towards higher efficiency reflects improved processes for making photovoltaic materials such as silicon and gallium arsenide, as well as the discovery of new materials. Silicon solar cells are a mature technology, so they are now in the flat part of the learning curve and are approaching their maximum theoretical efficiencies. Newer technologies such as organic photovoltaics, quantum dot solar cells, and lead halide perovskite cells are still in the rising part of the learning curve.



Reported timeline of solar cell energy conversion efficiencies since 1976 (National Renewable Energy Laboratory)

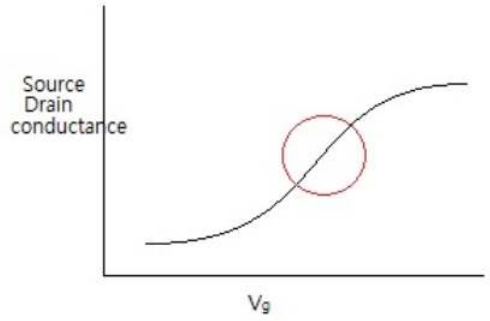
A **field effect transistor (FET)** is a transistor that uses an electric field to control the width of a conducting channel and thus the current in a semiconductor material. It is classified as unipolar transistor, in contrast to bipolar transistors.

Field effect transistors function as current amplifiers. The typical structure of Si-based FETs is one in which two n-type regions (the source and the drain) are separated by a p-type region. An oxide insulator over the p-type region separates a metal gate lead from the semiconductor. This structure is called a metal-oxide-semiconductor FET (or MOSFET). When voltage is applied between source and drain, current cannot flow because either the n-p or the p-n junction is back-biased. When a positive potential is applied to the gate, however, electrons are driven towards the gate, and locally the semiconductor is "inverted" to n-type. Then the current flows easily between the n-type source and drain through the n-channel. The current flow between the source and drain is many times larger than the current through the gate, and thus the FET can act as an amplifier. Current flow can also represent a logical "1," so FETs are also used in digital logic.



Cross section of an n-type MOSFET

In electronic devices such as microprocessors, field-effect transistors are kept in the off-state most of the time in order to minimize background current and power consumption. The FET shown above, which has n-type source and drain regions, is called an NMOS transistor. In a PMOS transistor, the source and drain regions are p-type and the gate is n-type. In **CMOS** (complementary metal-oxide semiconductor) integrated circuits, both NMOS and PMOS transistors are used. CMOS circuits are constructed in such a way that all PMOS transistors must have either an input from the voltage source or from another PMOS transistor. Similarly, all NMOS transistors must have either an input from ground or from another NMOS transistor. This arrangement results in low static power consumption.



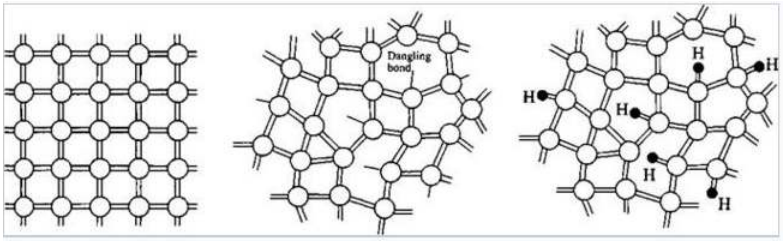
Transistors are most useful in the range of gate voltage (indicated by the red circle in the figure at the left) where the source-drain current changes rapidly. In this region it is possible to effect a large change in current between source and drain when a small signal is applied to the gate. An important figure of merit for FETs is the **subthreshold slope**, which is the slope a plot of log(current) vs. V_{gate}. An ideal subthreshold slope is one decade of current per 60 mV of gate bias. Typically, a decade change in source-drain current can be achieved with a change in gate voltage of ~70 mV. The performance of FETs as switches and amplifiers is limited by the subthreshold slope, which in turn is limited by the capacitance of the gate. It is desirable to have a very high gate capacitance, which requires a thin insulating oxide, but also to have a small leakage current, which requires a thick oxide. A current challenge in the semiconductor industry is to continue to scale FETs to even smaller nanoscale dimensions while maintaining acceptable values of these parameters. This is being done by developing new gate insulator materials that have higher dielectric constants than silicon oxide and do not undergo redox reactions with silicon or with metal gate leads. Only a few known materials (such as hafnium oxynitride and hafnium silicates) currently meet these stringent requirements.

This page titled 9.1.7: Diodes, LEDs and Solar Cells is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.7: Diodes, LEDs and Solar Cells** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

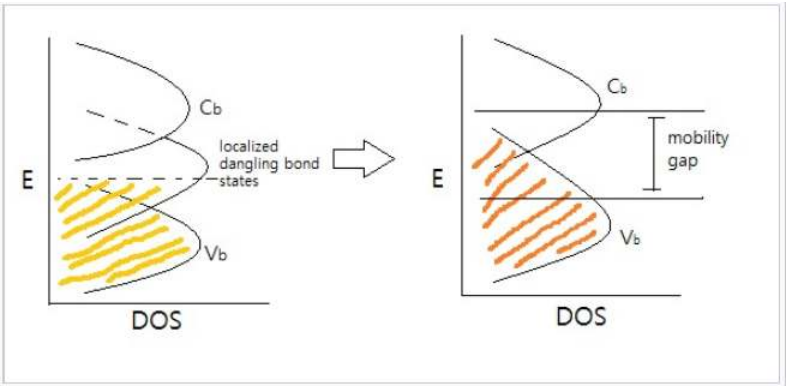
9.1.8: Amorphous Semiconductors

Amorphous semiconductors are disordered or glassy forms of crystalline semiconductor materials. Like non-conducting glasses, they are network structures with primarily covalent bonding. Crystalline silicon, which has the diamond structure, is an ordered arrangement of fused six-membered silicon rings, all in the "chair" conformation, as we saw in Ch. 8. The local bonding environment of the silicon atoms is tetrahedral. The silicon atoms in amorphous silicon (a-Si) are also predominantly tetrahedrally coordinated, but there is no long-range order in the structure. In addition to six-membered rings, there are five- and seven-membered rings, as well as some "dangling bond" sites in which Si atoms have only three nearest neighbors.



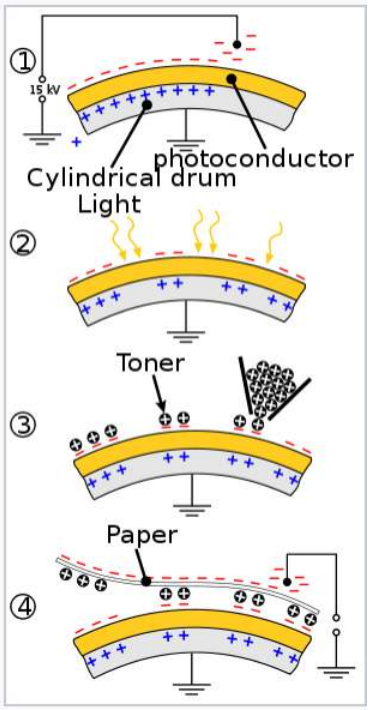
Schematic illustration of the structures of crystalline silicon (left), amorphous silicon (middle), and amorphous hydrogenated silicon (right)

Two of the most widely studied amorphous semiconductors are a-Si and amorphous selenium, a-Se. Si and Se can both be made in glassy form, usually by sputtering or evaporation at relatively low temperature. In a-Se, as in a-Si, locally, most of the atoms have their "normal" valence, but there are many defects and irregularities in the structure. Dangling bonds in amorphous semiconductors have orbital energies in the middle of gap, and electrons in these states are effectively non-bonding. Because these dangling bond sites are far apart from each other, there is little orbital overlap between them, and they also exist over a range of energies. Electrons in these mid-gap states are therefore **localized**, a phenomenon known as Anderson localizaton. Amorphous Si is insulating because electrons the Fermi level (in the middle of the gap) are not mobile in the lattice. These localized states create a mobility gap, and only electrons in states that are strongly bonding or antibonding are delocalized. Therefore, unmodified a-Si is not very useful as a semiconductor. However, by hydrogenating the material as it is formed (typically in a plasma of H atoms), the under-coordinated Si atoms are bonded to hydrogen atoms. This generates filled bonding and empty antibonding orbitals, the energies of which are outside the mobility gap. Hydrogenation thus lowers the density of states in the mobility gap. Hydrogenated amorphous silicon (a-Si:H) is insulating in the dark, but is a good photoconductor because light absorption creates electrons and holes in mobile states that are outside the mobility gap.



Energy vs. DOS for an amorphous semiconductor. Disorder and dangling bonds result in localized mid-gap states.

The photoconductivity of **amorphous Se** is exploited in xerography. A conductive drum coated with a-Se, which is insulating, is charged with static electricity by corona discharge from a wire. When the drum is exposed to a pattern of light and dark (the image to be duplicated), the illuminated a-Se areas become conductive and the static charge is dissipated from those parts of the drum. Carbon-containing toner particles then adhere via static charge to the areas that were not exposed to light, and are transferred and bonded to paper to make the copy. The speed of the process and the high resolution of pattern transfer depend on the very low conductivity of a-Se in the dark and its high conductivity under illumination.



Charging of amorphous Se and pattern transfer in the xerographic cycle.

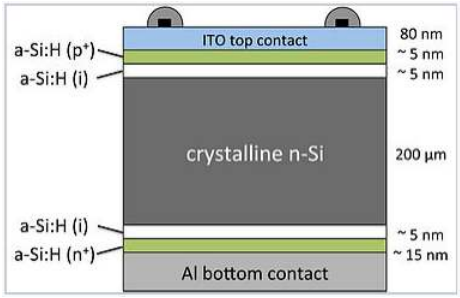
Amorphous hydrogenated Si is used in inexpensive thin film solar cells. The mobility gap is about 1.7 eV, which is larger than the bandgap crystalline of Si (1.1 eV). a-Si:H is a direct-gap material, and therefore thin films are good light absorbers. a-Si:H solar cells can be vapor-deposited in large-area sheets. p^+Si-a-Si:H-n^+Si cells have around 10% power conversion efficiency. However amorphous Si solar cells gradually lose efficiency as they are exposed to light. The mechanism of this efficiency loss, called the Staebler-Wronski effect,[9], involves photogenerated electron-hole pairs which have sufficient energy to cause chemical changes in the material. While the exact mechanism is still unclear, it has been proposed that the energy of electron-hole recombination breaks a weak Si-Si bond, and that one of the resulting dangling bonds abstracts a H atom, leaving a passivated Si-H center and a permanent dangling bond. The effect is minimized by hydrogenating a-Si and can be partially reversed by annealing.



A calculator that runs on solar and battery power

Thin layers of amorphous silicon are used in conjunction with crystalline silicon in heterojunction intrinsic thin-layer (HIT) solar cells.[10] Because the mobility gap of a-Si is wider than the bandgap of c-Si, there is a potential energy barrier at the amorphous-

crystalline interface that reflects electrons and holes away from that interface. At the p^+ contact, only holes can tunnel through the barrier, whereas only electrons can tunnel through the barrier to the n^+ contact. The passivation of surface defects that are sites of electron-hole recombination prevents a major loss mechanism in solar cells, increasing both the photovoltage and the photocurrent relative to conventional c-Si p-n junction cells. Panasonic and Sanyo have announced the production of HIT cells with power conversion efficiencies as high as 23%.



Layered structure of a HIT solar cell. The layers are not drawn to scale. A thick crystalline n-silicon layer is the light absorber, and photogenerated holes, which are the minority carriers, are reflected away from the aluminum back contact by the thin intrinsic a-Si layer there.

This page titled 9.1.8: Amorphous Semiconductors is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.8: Amorphous Semiconductors** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.9: Discussion Questions

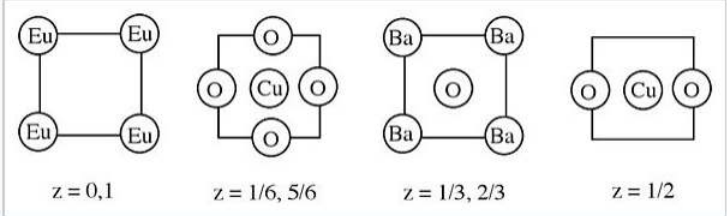
- How is magnetic ordering in the 3d transition metals (Fe, Co, Ni) and the absence of magnetism in the elements just below them (Ru, Ir, Pd) related to the metal-insulator transition?
- Why are good metals bad superconductors and vice-versa?
- Discuss why semiconducting oxides of early transition metals such as TiO_2 and Nb_2O_5 can be doped n-type but not p-type. Conversely, semiconducting late transition metal oxides such as NiO and Cu_2O can be doped p-type but not n-type.

This page titled 9.1.9: Discussion Questions is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.9: Discussion Questions** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.10: Problems

1. The structure of a high temperature superconductor containing barium, europium, copper, and oxygen is shown below. What are the coordination environments of Cu in this compound? This structure is actually closely related to perovskite, ABO_3. Explain the relationship between this structure and the ideal perovskite structure.



2. VO_2 can exist in insulating or metallic form, depending on temperature and pressure. Which form would be stabilized by increasing the temperature? Explain your answer.

3. Explain briefly how and why the bandgaps for octet p-block semiconductors vary (1) with the average principal quantum number, and (2) with the electronegativity difference between anion and cation.

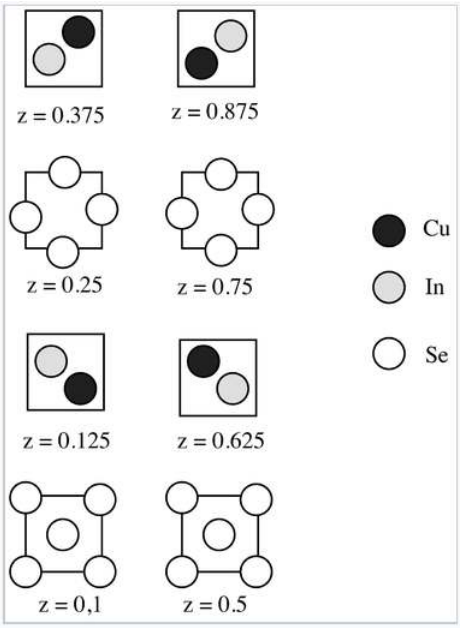
4. Indicate the type of conduction (n or p) in the following: (a) Se-doped GaAs, (b) $InAs_{1-x}$, where $x << 1$, (c) $Li_{0.05}Ni_{0.95}O$, (d) Li_xWO_3, where $x << 1$.

5. The structure of copper indium selenide, a semiconductor used in thin film solar cells, is shown below in sections.

(a) What is the stoichiometry of the compound?

(b) What kind of doping (n or p) will occur if a small amount of iodine is substituted for selenium?

(c) What kind of doping (n or p) will occur if a small fraction of the indium sites are occupied by copper atoms?

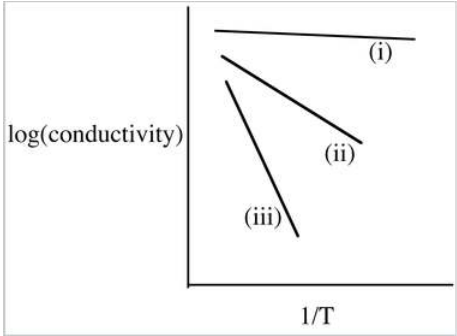


6. Using 1 eV = 1240 nm, predict the colors of anatase TiO_2 (Eg = 3.1 eV), SiC (2.0 eV), $ZnSnP_2$ (1.7 eV), $ZnGeP_2$ (1.9 eV), and InP (1.27 eV).

7. The conductivity of a certain intrinsic (undoped) semiconductor increases by a factor of two when the temperature is raised from 300 to 330 K. What is the bandgap (in eV)? R = 8.314 J/mol-K, 1 eV/atom = 96.52 kJ/mole.

8. Pure Ge is much more conductive than pure Si. Given their bandgaps (0.74 and 1.15 eV, respectively), estimate the ratio of their conductivities at room temperature.

9. The figure below illustrates the trends in conductivity vs. inverse temperature for Si, Ge, and As-doped Ge. Identify lines (i), (ii), and (iii) with the appropriate materials. Explain why the slope of line (i) is close to zero.



10. Sketch a silicon p-n junction, showing the depletion region, band bending, and the Fermi level in the absence of light or applied potential. In the dark, the p-n junction acts as a rectifier. (a) Which way do electrons and holes flow most easily in the dark? (b) Does the built in electric field increase or decrease under forward bias? (c) In the light, the junction acts as a photodiode. In this case, under short circuit conditions, do electrons flow in the same direction or in the opposite direction as in (a)? Explain.

This page titled 9.1.10: Problems is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.10: Problems** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.1.11: References

1. Hubbard, J. (1963). "Electron Correlations in Narrow Energy Bands". *Proceedings of the Royal Society of London* **276** (1365): 238–257. doi:10.1098/rspa.1963.0204. Bibcode: 1963RSPSA.276..238H.
2. T. Mizokawa, Metal-insulator transitions: orbital control, Nature Physics 9, 612–613 (2013), doi: doi:10.1038/nphys2769
3. N. F. Mott, (1961) "The Transition to the Metallic State," Phil. Mag. 6, 287. DOI: 10.1080/14786436108243318.
4. P. P. Edwards and M. J. Sienko (1982) "The Transition to the Metallic State," Acc. Chem. Res. 15, 87-93. DOI: 10.1021/ar00075a004
5. Recent data have disproven this assertion; MacDonalds has finally responded to public opinion and is offering breakfast after 10:30 AM. But the laws of thermodynamics remain immutable and eternal
6. E. Yablonovitch, O. Miller, and S. Kurtz, "Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit," IEEE Journal of Photovoltaics, vol. 2, no. 3, pp. 303-311, July 2012.
7. "Recent facts about photovoltaics in Germany". Fraunhofer ISE. 7 January 2015. Retrieved 17 February 2015.
8. Energy Information Administration, (November 2010). Levelized Cost of New Generation Resources in the Annual Energy Outlook 2011.
9. Staebler, D. L. and Wronski, C. R. Optically induced conductivity changes in discharge-produced hydrogenated amorphous silicon. J. Appl. Physics. 51(6), June 1980.
10. Mishima, T., Taguchi, M., Sakata, H., Maruyama, E., 2011. Development status of high efficiency HIT solar cells. Sol. Energy Mater. Sol. Cell. 95, 18–21. doi:10.1016/j.solmat.2010.04.030

This page titled 9.1.11: References is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **10.11: References** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

SECTION OVERVIEW

9.2: Basic Science of Nanomaterials

Learning Objectives

- Understand the physical basis of mesoscopic behavior in nanoscale semiconducting and magnetic particles.
- Describe how the particle-in-a-box equation applies to electrons in quantum wells.
- Use the Brus formula to calculate the band gap energy of nanoscale semiconductor particles.
- Use the surface energy concept to calculate changes in the melting point and vapor pressure of nanoparticles.
- Describe the methods used to make semiconducting and metal nanocrystals of uniform size.
- Explain the origin of the localized surface plasmon resonance effect in metal nanoparticles.
- Describe the emerging analytical and biomedical applications of metal nanoparticles.

Nanomaterials describe materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers, but is usually 1—100 nm. Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.

9.2.1: Prelude to Basic Science of Nanomaterials

9.2.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets

9.2.3: Semiconductor Quantum Dots

9.2.4: Synthesis of Semiconductor Nanocrystals

9.2.5: Surface Energy

9.2.6: Nanoscale Metal Particles

9.2.7: Applications of Nanomaterials

9.2.8: Discussion Questions

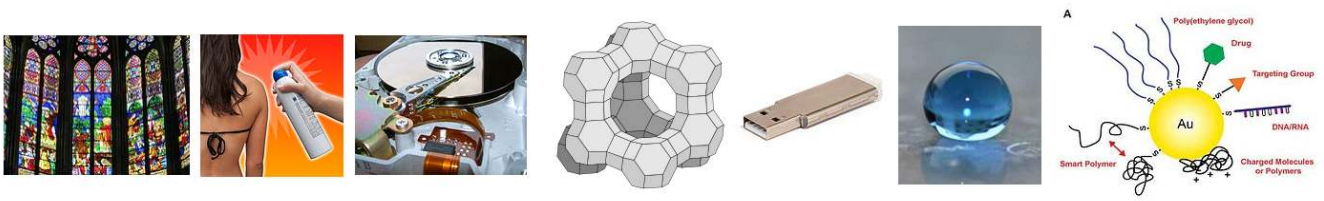
9.2.9: Problems

9.2.10: References

This page titled 9.2: Basic Science of Nanomaterials is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

9.2.1: Prelude to Basic Science of Nanomaterials

What do stained glass, sunscreen, magnetic hard drives, heterogeneous catalysts, consumer electronics, stain-resistant clothing, self-cleaning glass, and medical diagnostics all have in common? All of them derive some special property and utility from **nanoscale materials**: ordinary elements and inorganic compounds such as gold, silver, TiO_2, chromium, SiO_2, and silicon that acquire different properties when their characteristic dimensions are somewhere between **1 and 100 nm**. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.



This page titled 9.2.1: Prelude to Basic Science of Nanomaterials is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

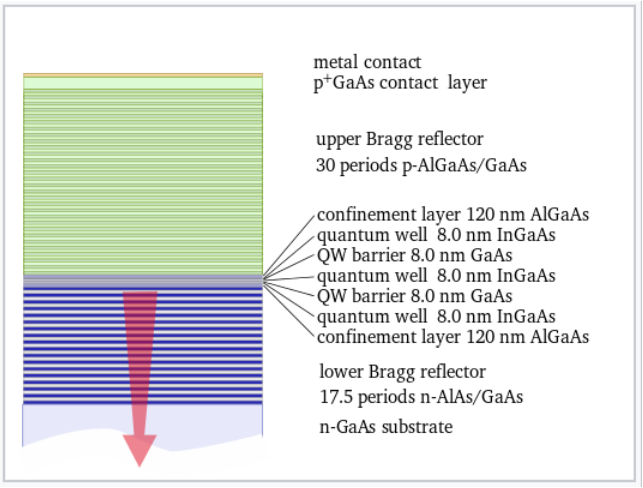
- **11.1: Prelude to Basic Science of Nanomaterials** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets

The special properties of nanomaterials do not derive from different laws of physics, which are the same for objects large and small. For example, Newton's second law ($F = ma$), Coulomb's law ($E = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$), and the laws of energy and momentum conservation are the same for buckyballs (C_{60}) and full-size soccer balls. Nevertheless, the physics of electrons, atoms, and photons naturally produce **characteristic length scales**, some of which we have already seen. For example, in Chapter 6 we discovered that the mean free path of an electron in a good metal is about 40 nm. In Chapter 10, we learned that the Bohr radius of an electron or hole in doped Si is about 4 nm, and that the coherence length of Cooper pairs in semiconductors is somewhere between a few nm and 1 μm. When objects become small relative to these characteristic lengths, their physical properties change in interesting ways. Materials that exist at the relevant length scale are called ***mesoscopic*** (meso = "between," scopic = "size") meaning that they cross over from one kind of behavior - the bulk behavior of large objects - to another. This length scale is different for different kinds of properties, but for many it happens between 1 and 100 nm. We illustrate this point with a few examples.

The cavity laser

A vertical cavity surface-emitting laser (or VCSEL) is a semiconductor-based device that emits light in the vertical direction relative to the plane of the chip. These devices are being developed and used for high power applications such as laser surgery, infrared illumination for military surveillance, and laser cutting tools. The basic design of a VCSEL is shown at the right. The VCSEL is basically a light-emitting diode, incorporating p-type and n-type regions of the III-V semiconductor (Al,Ga)As. However, it has two special features. First, the refractive index of the semiconductor is modulated above and below the junction to make Bragg mirrors. These mirrors reflect light emitted in the junction, so that the photon density becomes very high there, a necessary condition for stimulated emission and lasing. The Bragg mirror stack is asymmetric (thinner on the bottom), so that light can escape from the junction in one direction only. Second, the junction itself consists of a thin "quantum well" layer of (In,Ga)As, a III-V semiconductor with a smaller band gap than the surrounding (Al,Ga)As layers.

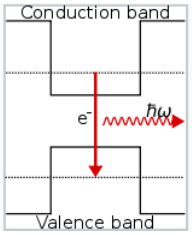


A VCSEL device structure. This is a *bottom-emitting multiple-quantum-well* VCSEL.

The **quantum well** structure, the band diagram of which is illustrated at the left, is the nanoscale part of the laser. The energies of the conduction and valence bands of (Al,Ga)As flank those of the thin (In,Ga)As layer. Therefore, electrons and holes injected into that layer cannot escape: electrons in (In,Ga)As do not have enough energy to climb "up" to the conduction band of (Al,Ga)As and holes cannot climb "down." Electrons confined to such a small well behave as a particle-in-a-box (as we learned in the context of electrides in Chapter 9).

The electron has a kinetic energy defined by the equation:

$$KE = \frac{h^2 n^2}{8mL^2} \tag{9.2.2.1}$$



We can calculate the energy difference between the lowest (n=1) and next lowest (n=2) levels, which is inversely proportional to the square of the thickness (L) of the (In,Ga)As layer. In this calculation we need to use the effective mass of the electron in (In,Ga)As, which is about 7% of the electron rest mass[1]. With an 8 nm thick layer, this energy is:

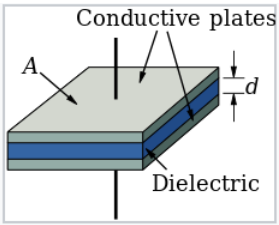
$$E = \frac{(2^2 - 1^2)(6.626 \cdot 10^{-34} Js)^2}{8 \cdot 0.07 \cdot (9.1 \cdot 10^{-31} kg)(8 \cdot 10^{-9} m)^2} = 4.0 \cdot 10^{-20} J = 0.25 eV \qquad (9.2.2.2)$$

The VCSEL cavity will thus have a resonant energy of 0.25 eV and emit photons at this energy in the infrared (λ ≈ 5000 nm). Note that because of the inverse square dependence of the cavity energy on layer thickness, lasers based on this design can only function at nanoscale dimensions. When the cavity is three times thicker, its resonant energy becomes comparable to the thermal energy at room temperature (kT = 0.026 eV), and the lasing effect is thermally "washed out."

Coulomb blockade

A capacitor is a (macroscopic) device that stores electrical charge. The basic structure of a capacitor is shown at the right. When a voltage is applied to such a device, it develops a charge (± Q) on the two plates that is proportional to the voltage:

$$C = \frac{Q}{V} \qquad (9.2.2.3)$$



Basic design of a parallel plate capacitor of area *A* and with a dielectric thickness of *d*

The magnitude of the capacitance C is determined by the permittivity ε and the dimensions of the dielectric layer, A and d.

$$C = \frac{\varepsilon A}{d} \qquad (9.2.2.4)$$

We can also calculate the work done in charging the capacitor up (i.e., the energy stored by charging the capacitor) by integrating the voltage times the charge:

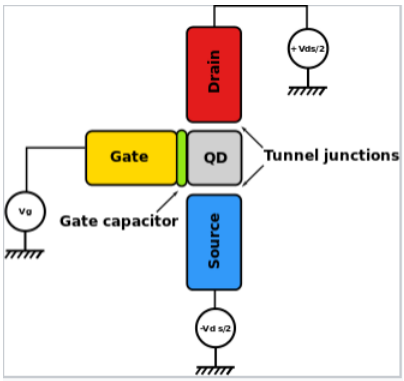
$$E = int_0^Q V(q)dq = \int_0^Q \frac{q}{C} dq = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2 = \frac{1}{2}VQ \qquad (9.2.2.5)$$

Now it is interesting to ask, what happens to a capacitor when we make it very small? This is of particular interest in a device called a **single electron transistor**, a schematic diagram of which is shown at the right. The metallic gate lead is separated from a "quantum dot," which can be a metal or semiconductor particle, by a thin dielectric layer. This metal-dielectric-metal sandwich acts as a capacitor, and from the equation above, the energy needed to charge it by a single electron (Q = e) is:

$$E = \frac{e^2}{2C} \qquad (9.2.2.6)$$

where e is the charge of the electron, 1.602 x 10^{-19} Coulomb. If the gate width and lateral dimensions are very small - say 2 nm as is readily achievable in self-assembled Coulomb blockade devices[2][3] - then for a typical insulating dielectric, a voltage of about

200 mV is needed to charge the quantum dot by a single electron. Again, this effect is unique to the nanoscale, because a 10 times larger device area would make the single-electron charging voltage about 20 mV, which is smaller than the thermal energy kT (26 meV). Thus for devices larger than about 5-6 nm, individual electron charging events are washed out at room temperature by thermal fluctuations.

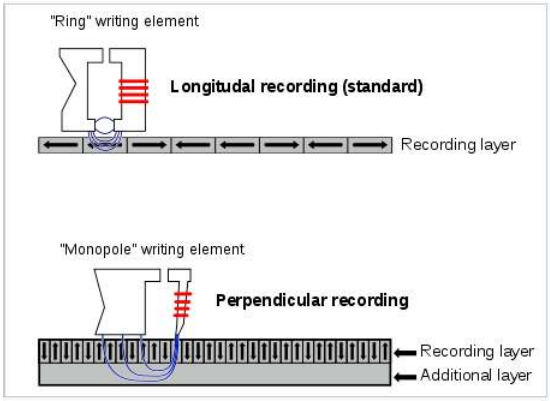


Schematic of a single-electron transistor.

How can a **nanoscale capacitor** like this act as a **transistor**, which functions as a switch in an electrical circuit? The effect comes from the mutual repulsion of electrons. An electron on the quantum dot repels any other electron that would be forced onto it by applying a small voltage between the source and the drain. Hence the conductance of the quantum dot is very low at a gate bias of zero volts, or at any gate bias (200, 400, 600 mV...) that places an integer number (1, 2, 3,...) of electrons on the dot. But halfway in between these voltages (e.g., at 100, 300, 500 mV) the energy is the same whether there are n or n+1 electrons on the dot. This means that electrons can hop on and off without changing their energy, i.e., they can tunnel through the dot from source to drain. This effect gives peaks in the conductance of the dot at regular steps in the gate voltage. In effect, the gate can act as a switch, as in a conventional field-effect transistor. Single-electron transistors are being researched as ultra-sensitive electrometers and single-molecule chemical sensors, since a tiny change in the electrostatic environment of the dot can switch the device on or off.

Nanoscale magnets

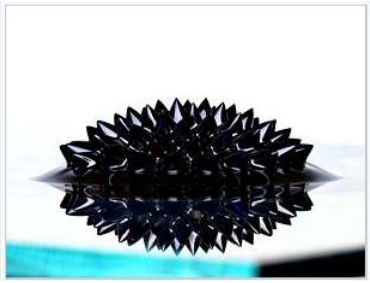
Ferro- and ferrimagnetic materials such as iron and chromium oxide are used for digitial storage of information in hard disks. The individual memory bits, which can be oriented perpendicular or parallel to the plane of the disk as shown at the right, store a logical "0" or "1" depending on the orientation of their magnetic dipole. To be useful, this information must be non-volatile, i.e., the magnetic bit must retain its polarization in the absence of an applied field from the read/write head.



Longitudinal and perpendicular recording, two types of writing heads on a hard disk.

The storage density of such magnetic memories is impressive. A 2.5" hard drive can now store 1 TB of information, using rod-shaped magnetic grains that are approximately 0.5 µm long. We now have good synthetic methods for making these same materials as crystals with dimensions of only a few nanometers. Why aren't those nanocrystals used to make even more dense memory disks?

The reason is that the energy needed to flip the magnetization (i.e., to turn a "0" into a "1" and vice-versa) is strongly size-dependent. For a ferro- or ferrimagnet this energy is equal to Mr^3, where M is the magnetic energy per unit volume and r is the characteristic dimension (e.g., the length of the edge of a cube, or the diameter of a sphere) of the magnetic grain. For typical materials such as iron, this energy becomes comparable to kT when r is about 3-5 nm. Such small particles are superparamagnetic, meaning that they still have a large magnetic moment because of the ordering of their spins, but they do not retain a permanent polarization in the absence of an applied magnetic field. Superparamagnetic particles are thus not useful for magnetic memories, but they are interesting and practical in other ways, for example in ferrofluids, magnetic resonance imaging (MRI), and some emerging medical diagnostic and therapeutic applications.



A ferrofluid containing superparamagnetic Fe_3O_4 nanoparticles, which are coated with oleic acid and suspended in oil, in the field of a strong permanent magnet.

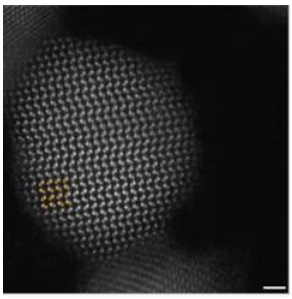
In these three illustrative examples (involving light emission, electronic conduction, and magnetic behavior), the transition to new properties involves a crossover in which the characteristic energy of the system is comparable to the thermal energy kT. It just so happens that for many physical phenomena, this crossover occurs on the length scale of nanometers.

This page titled 9.2.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

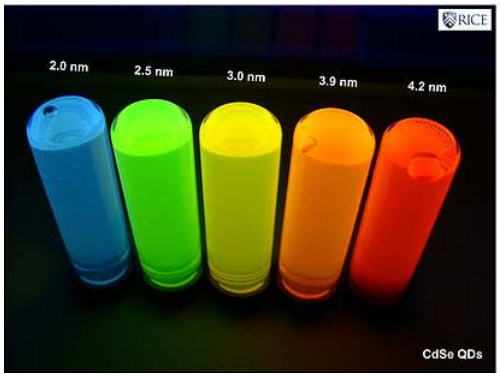
9.2.3: Semiconductor Quantum Dots

One of the most fascinating and well-studied mesoscopic effects occurs with semiconductor particles of various shapes when one or more of their dimensions is in the range of a few nanometers. These so-called "quantum dots" (0D), "quantum rods" (1D) and "nanosheets" (2D) acquire striking new electronic and optical properties.



Atomic resolution image of a CdSe nanoparticle.

The synthesis of semiconductor quantum dots, which is discussed in more detail below, is sufficiently well controlled to give essentially perfect crystals of a few thousand atoms, something that is statistically impossible in a macroscopic crystal. An image of such a crystal is shown at the right. In the synthesis, these crystals can be capped with an epitaxial layer of ligands or by a shell of a wider bandgap semiconductor (such as ZnS in the case of CdSe), so that the inner core is effectively a quantum well. Electron-hole pairs formed by excitation of the core semiconductor are confined there and cannot reach the external surface of the particle, where they might otherwise be trapped and recombine thermally. Consequently, the quantum yield for bandgap emission of semiconductor quantum dots is typically high, giving rise to the bright emission colors shown at the right for CdSe particles of different sizes. Because of their strong and narrow emission bands, quantum dots are of interest as luminescent tags for biological imaging applications, and also as light absorbers and emitters in solar cells and LEDs.



Emission colors of CdSe nanoparticles of different sizes. Smaller particles emit blue light because the exciton energy increases as the size decreases.

The size-dependence of the emission color comes primarily from a particle-in-a-box effect. The electron and hole that are created when the quantum dot absorbs light are bound together as an **exciton** by the confines of the "box". Louis Brus used first-order perturbation theory to determine that the bandgap of a semiconductor quantum dot is given approximately by:[4]

$$E_{gap} = E_{gap,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \qquad (9.2.3.1)$$

where R is the particle radius, μ is the electron-hole reduced mass ($1/\mu = 1/m_e^* + 1/m_h^*$), m_e^* and m_h^* are the electron and hole effective masses, and ε is the dielectric constant of the semiconductor. In this equation, the first term after the bulk bandgap is the kinetic energy due to confinement of the exciton, and the second term represents the electrostatic attractive energy between the confined electron and hole. Because the energy is a function of R^2, it can be widely tuned across the visible spectrum by changing the size of the quantum dot.

This page titled 9.2.3: Semiconductor Quantum Dots is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

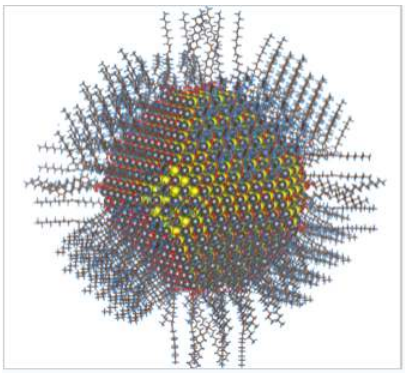
- **11.3: Semiconductor Quantum Dots** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.4: Synthesis of Semiconductor Nanocrystals

Early work on the quantum size effect in semiconductor nanoparticles used simple metathesis reactions in the synthesis. For example, CdSe and PbS can be precipitated at ambient temperature by the reactions:

$$CdCl_{2(aq)} + H_2Se_{(g)} = CdSe_{(s)} + 2\,HCl_{(aq)}$$

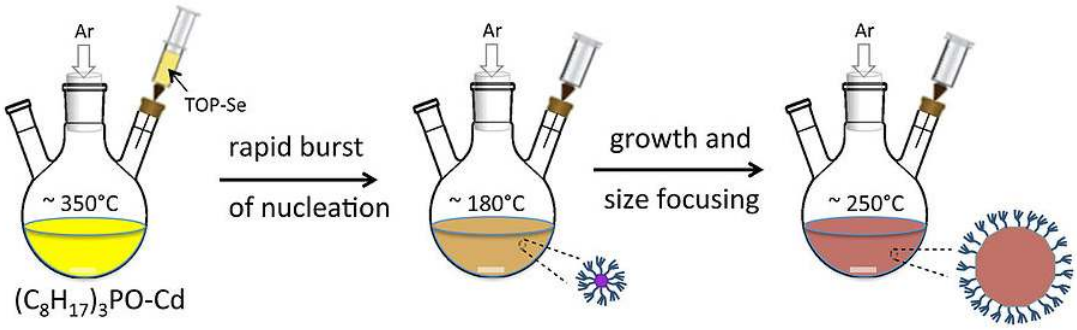
$$Pb(NO_3)_2 + H_2S_{(g)} = PbS_{(s)} + 2\,HNO_{3(aq)}$$



Complete atomistic model of a 5 nm diameter colloidal lead sulfide nanoparticle with surface passivation by oleic acid, oleyl and hydroxyl groups.

The growth of the particles was restricted by carrying out these reactions in different matrices, such as in polymer films or the silicate cages of zeolites, and capping ligands were also sometimes used to limit particle growth. While these reactions did produce nanoparticles, in general a broad distribution of particle sizes was obtained. The particles were also unstable to **Ostwald ripening** - in which large particles grow at the expense of smaller ones in order to minimize the total surface energy - because of the reversibility of the acid-forming synthetic reactions in aqueous media. The lack of good samples prevented detailed studies and the development of applications for semiconductor quantum dots.

A very important development in nanoparticle synthesis came in the early 1990's, when Murray, Norris, and Bawendi introduced the first non-aqueous, controlled growth process for II-VI semiconductor quantum dots.[5] The keys to this synthesis were (1) to use non-aqueous solvents and capping ligands to stabilize the products against ripening, (2) to carry out the reaction at high temperature to ensure good crystallinity, and (3) to separate the steps of particle **nucleation** and **growth**, and thereby obtain particles of uniform size. This procedure is illustrated below:

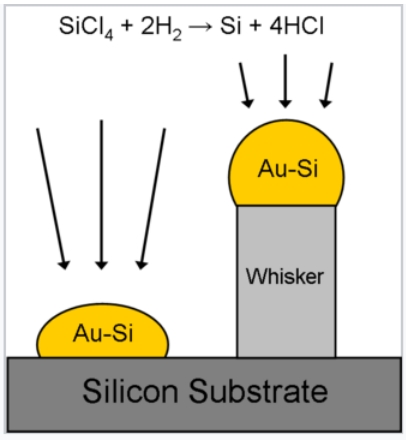


The synthesis is carried out in a coordinating, high boiling solvent that is a mixture of trioctylphosphine (**TOP**) and trioctylphosphine oxide (**TOPO**). In early experiments, organometallic cadmium compounds such as diethylcadmium were used as the metal source, but it was later found that these highly toxic and pyrophoric compounds could be replaced by CdO. At the start of the reaction, a selenium source, typically bis(trimethylsilyl)selenium, $[(CH_3)_3Si]_2Se$, dissolved in TOP is rapidly injected into the hot (350 °C) reaction mixture. The reaction causes a rapid burst of nanoparticle nucleation, but the temperature also drops as the cold solvent is injected and so the nucleation event ends quickly. The cooled solution now contains nanocrystal seeds. It is supersaturated in TOPO-Cd and TOP-Se, but particle growth proceeds slowly until the solution is heated again to the growth temperature, ca. 250°C. Particle growth and **size-focusing** occurs because small particles require less added material to grow by an

amount ΔR than larger particles. This is because the volume of an added shell around a spherical seed is $4\pi R^2\Delta R$, so for larger R, ΔR is smaller. Very narrow particle size distributions can be obtained under conditions of high supersaturation, where the rate of nanoparticle growth is fast relative to particle dissolution and Ostwald ripening.[6] The size distribution can then be narrowed further by adding a non-solvent such as hexane to the cooled reaction mixture. The largest particles precipitate first, followed by smaller particles. Because the nanoparticles are capped with a ligand shell of TOP, they can be re-suspended in organic solvents once they are size-separated.

The high temperature synthesis of semiconductor quantum dots has been applied to a broad variety of materials including II-VI, III-V, and IV-VI semiconductors. Monodisperse nanoparticles of **controlled shapes** can be made by variants of this method. For example, it is possible to adjust the conditions so that CdSe nucleates in the zincblende polymorph as tetrahedrally shaped seeds, and then grow polar wurtzite "arms" onto each triangular face, resulting in nanocrystal tetrapods. Numerous other nanocrystal shapes such as rods, arrowheads, rice (tapered rods), and polar structures such as Janus rods can be made by variants of this technique. These shape-control strategies often involve the use of ligands that adsorb specifically to certain crystal faces and inhibit their growth. For example, hexylphosphonic acid ligands adsorb selectively to Cd-rich crystal faces and thus lead to the growth of prismatic wurtzite-phase CdSe nanocrytals.

A second widely used method of semiconductor nanocrystal synthesis involves growth from molecular precursors and molten metal droplets, as shown in the figure at the right. The **vapor-liquid-solid (VLS)** and related **solution-liquid-solid (SLS)** growth processes rely on the fact that semiconductors such as Si, Ge, GaAs, InP, and others are soluble at high temperatures in liquid metals such as Au and Cu. The catalytic reduction of a molecule such as silicon tetrachloride ($SiCl_4$) at the surface of a gold nanocrystal liberates HCl gas and creates a solid solution of Si in Au. The presence of Si lowers the melting point of Au, and as more $SiCl_4$ reacts, a liquid **eutectic** droplet of the Si-Au alloy is formed. When this droplet becomes supersaturated in Si, a silicon nanocrystal nucleates and grows. This reaction can be performed on the surface of a macroscopic Si crystal, in which case nanocrystal "whiskers" grow from the surface, typically as single crystals and with an epitaxial orientation that is determined by the Si crystal face of the substrate. The diameter of the whiskers is controlled by the radius of the Au drops, which can be as small as a few nanometers and as large as several microns. Using this technique, "forests" of nanowires or microwires can be grown. Because the composition of the nanowire depends on the precursor being fed to the Au droplets, it is possible to make "totem pole" structures with varied compositions along the nanowire axis. Semiconductor shells can also be grown around the wires by **chemical vapor deposition (CVD)**. The VLS process can also be adapted to complex compositions for which no molecular precursor is available by using a laser to ablate the semiconductor from a solid target.



Epitaxial growth of silicon nanowires catalyzed by gold nanoparticles in the vapor-liquid-solid (VLS) process.

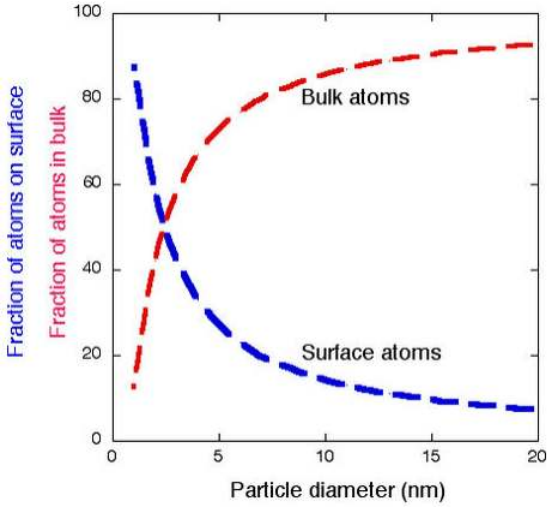
Semiconductor nanowires made by this method are the basis of extremely sensitive **biosensors**, in which a molecular binding event anywhere along the wire strongly affects its electrical conductivity.[7] Nanowire and microwire arrays are also being studied as **solar cell** and **lithium battery** materials, as well as nanoscale electronic and optoelectronic devices.

This page titled 9.2.4: Synthesis of Semiconductor Nanocrystals is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.4: Synthesis of Semiconductor Nanocrystals** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.5: Surface Energy

Nanoparticles have a substantial fraction of their atoms on the surface, as shown in the plot at the right.[8] This high surface area to volume ratio is an important factor in many of the physical properties of nanoparticles, such as their **melting point** and **vapor pressure**, and also in their **reactivity**. Heterogeneous catalysts, for example, are often based on nanoparticles because the catalytically reactive atoms are those that are on the surface of the particle.



The surface energy is always positive. A key quantity that is connected with the chemistry of all surfaces is the **surface energy**. This is the (thermodynamically unfavorable) energy of making "dangling bonds" at the surface. Atoms at the surface are under-coordinated, and because breaking bonds costs energy, surface atoms always have higher energy than atoms in the bulk. This happens regardless of whether the bonding is covalent (as in a metal), ionic (in a salt), or non-covalent (in a liquid such as water). We see this effect, for example, in water droplets that bead up on a waxy surface. The droplet contracts into a sphere (against the force of gravity that works to flatten it) in order to minimize the number of dangling hydrogen bonds at the surface.

In the case of metal or semiconductor particles, strong covalent bonds are broken at the surface. For example, a gold atom in bulk face-centered cubic Au has 12 nearest neighbors, but a gold atom on the (111) surface of the crystal (the most dense crystal plane of gold) has six nearest neighbors in-plane and three underneath, for a total of 9. We might expect the surface energy of this crystal face to be a little less (because the remaining bonds will become slightly stronger) than 3/12 = **1/4 of the bonding energy** of bulk Au, and this is in fact a fairly good rule of thumb for many materials. When translated into energy per unit area, the surface energy of metals and inorganic salts is usually in the range of 1-2 J/m^2.

Example: The sublimation energy of bulk gold is 334 kJ/mol, and the surface energy is 1.5 J/m^2. What percentage of the bulk bonding energy is lost by atoms at the (111) surface of a gold crystal?

To solve this problem, we need to know the surface area per Au atom. Gold has the face-centered cubic structure, and the unit cell edge length is 4.08 Å. From this we can determine that the Au-Au distance is 4.08/1.414 = 2.88 Å. In a hexagonal array of gold atoms with this interatomic spacing, the surface area per atom is (2.88 Å)^2 x 0.866 = 7.2 Å^2. Multiplying by Avogadro's number, we find that the area per mole of Au surface atoms on the (111) crystal face is **4.3 x 10^4 m^2.**

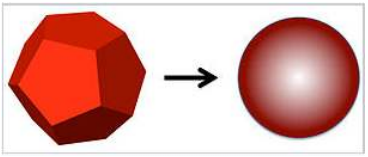
Now we multiply this area by the surface energy:

$(4.3 \times 10^4 \frac{m^2}{mol}) \times (1.5 \frac{J}{mol}) \times (\frac{1kJ}{1000J}) = \mathbf{+65kJ}$ per mole of Au surface atoms.

$\frac{65kJ}{334kJ} \times 100\% = \mathbf{19\%}$ of the bulk bonding energy is lost by atoms at the surface.

It is clear from this example that the surface energy of nanoparticles can have a major effect on their physical properties, since a large fraction of the atoms in a nanoparticle are on the surface. A good example of this is the dramatic depression of the **melting point**.

Solid nanocrystals are in general faceted, whereas liquid droplets made by melting nanocrystals adopt a spherical shape to minimize the surface area.



A faceted solid nanocrystal melts into a spherical droplet in order to minimize its surface energy.

Let's consider melting a silver nanocrystal that is 2 nm in diameter, meaning that about 1/2 of the atoms are on the surface. The spherical liquid droplet has lower surface area than the faceted crystal. For example, a cube has 1.24 times the surface area of a sphere of the same volume. If the decrease in surface area is about 20% upon melting, and the surface energy is about 1/4 of the bulk bonding energy of the atoms, then for a 2 nm diameter nanocrystal we would estimate that:

$$\Delta H^o_{fusion} \approx \Delta H^o_{fusion,\ bulk} - (\frac{1}{2})(0.25)(\frac{1}{4})\Delta H^o_{vap} = \Delta H^o_{fusion,\ bulk} - 0.025\Delta H^o_{vap,\ bulk} \quad (9.2.5.1)$$

where $\Delta H°_{vap,\ bulk}$, the heat of vaporization, is the total bonding energy of atoms in a bulk crystal. For silver, $\Delta H°_{fusion,\ bulk}$ = 11.3 kJ/mol and $\Delta H°_{vap,\ bulk}$ = 250 kJ/mol. From this we can calculate the heat of fusion of a 2 nm Ag nanocrystal:

$$\Delta H^o_{fusion} \approx 11.3 - (0.025)(25) = 5.1 \frac{kJ}{mol} \quad (9.2.5.2)$$

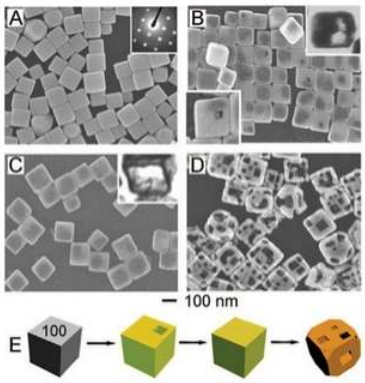
The melting point of bulk silver is 962 °C = 1235 K. Assuming that the entropy of fusion is the same in the bulk and in the nanocrystal, the melting point of the nanocrystal should be $1234K \times (\frac{5.1}{11.3}) = 557K = 284^{\circ}C$, a drop of almost 700 degrees from the bulk value. Experimentally, the melting point of a 2 nm diameter silver nanocrystal drops about **800 degrees below that of the bulk,** to 127 °C.[9] This is a whopping big change in the melting point, which is in reasonable agreement with our rough estimate.

The same effect - energetic destabilization of the surface atoms relative to bulk atoms - results in the **lower boiling point**, **higher vapor pressure**, **higher solubility**, and **higher reactivity** of nanocrystals relative to microcrystals (or larger crystals) of the same material.

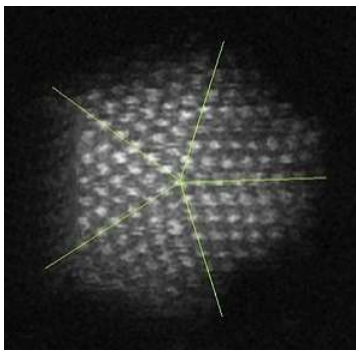
This page titled 9.2.5: Surface Energy is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.5: Surface Energy** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.6: Nanoscale Metal Particles



Nanoscale metal particles have been the subject of intense research over the past 20 years, especially because of their unusual **optical**, **magnetic**, and **catalytic** properties. The synthesis of metal nanocrystals in various shapes has become increasingly sophisticated and rational, like the synthesis of semiconductor nanocrystals described above. By controlling the separate phases of nucleation and growth, and by using ligands that cap specific crystal faces during growth, it is possible to make metal nanocrystals of uniform size in a variety of interesting and useful shapes including cubes, truncated cubes, octahedra, triangular prisms, and high aspect ratio rods. By exploiting displacement reactions that replace one metal with another, complex hollow shapes such as nanocages (as shown at the left) can be made starting with other shapes. In this case, solid silver nanocubes are transformed to gold nanocages.



Five-fold twinning in a gold nanoparticle

The interesting optical properties of nanocrystalline Au, Ag, Cu, and a number of other metals, derive from the collective oscillation of their valence electrons, a phenomenon known as **plasmon resonance**. Remember that in these metals, the electron mean free path is long (about 100 times larger than the size of the atoms), so the valence electrons feel only the average positive charge of the atomic cores as they zoom around the crystal. Light impinging on the metal acts as an oscillating electric field, pushing and pulling on the valence electrons at the characteristic frequency of the light wave. The situation is very much like a pendulum or a weight on a spring. The electrons, pushed away from their equilibrium positions, feel a restoring force that is proportional to their displacement. Their motion can be described by **Hooke's Law**:

$$F = kx \tag{9.2.6.1}$$

where the spring constant k determines the "stiffness" of the spring. In the case of the plasmon resonance, k is proportional to the number density of valence electrons n, and the square of the electronic charge e:

$$k = \frac{ne^2}{\varepsilon_0} \tag{9.2.6.2}$$

The **resonant frequency** of the plasma oscillation is given by:

$$\omega_p = (\frac{k}{m})^{\frac{1}{2}} = (\frac{ne^2}{m_e \varepsilon_0}^{\frac{1}{2}} \quad (9.2.6.3)$$

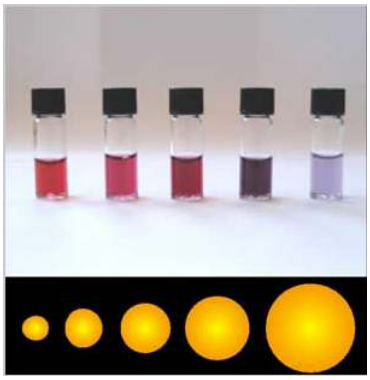
where m_e is the electron mass. For most metals, the plasmon resonance is in the ultraviolet part of the spectrum, but for a few metals like Au, Ag, and Cu it is in the visible.



The Lycurgus cup (4th century Roman glass) derives its unique coloration from noble metal nanoparticles. The cup is red in transmitted light and green in scattered (reflected) light.

For metal particles that are much smaller than the wavelength of light, this effect is called the **localized surface plasmon resonance**, or LSPR. There are three important consequences of the LSPR effect:

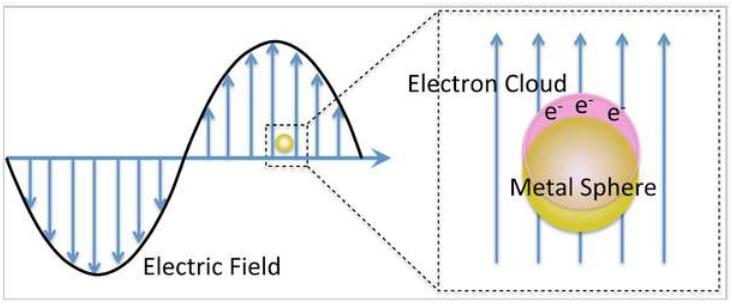
- The **local electric field** of the incoming light wave is greatly **enhanced** at the particle surface. This gives rise to huge enhancement factors in optical processes such as **Raman scattering** and **fluorescence**. Thus, certain analytical spectroscopic techniques are greatly enhanced by LSPR.
- Near the plasmon resonance frequency, metal nanocrystals **absorb** and **scatter light** very strongly. This makes them brightly reflective, and the strong light absorption can be exploited for light-induced local heating. These properties are being applied in medical diagnostics and therapy, e.g., for detection and photothermal destruction of cancer cells. By adjusting the size and shape of the gold nanoparticles, which are more stable than Ag and Cu in biological media, the plasmon frequency can be tuned to the tissue-transparent near-IR region of the spectrum between 700 and 900 nm. Small quantities of plasmonic Ag and Au particles also make brightly colored and strongly scattering pigments, e.g. in stained glass as shown above at the right.
- The plasmon frequency is sensitive to the refractive index of the particle's surroundings, i.e., its chemical environment. This makes metal nanoparticles of special interest for **sensing and biosensing** applications.



The colors of plasmonic gold nanoparticles depend on their size and shape.

Theory of light scattering and absorption by metal nanoparticles

The valence electrons in metal nanoparticles oscillate in the electric field of a light wave. While the nature of these oscillations is somewhat complex in metal particles that are non-spherical, the theory for spherical particles is relatively simple and in fact was worked out over 100 years ago by German physicist Gustav Mie.



Mie considered the interaction of a spherical particle with a **uniform electric field, E,** oscillating at angular frequency ω (= 2π f). This is a good approximation when the particle diameter is much smaller than the wavelength of light, as shown on the left. The particle is embedded in a uniform, insulating material (e.g. a solvent) that has a dielectric constant ε_{diel}. For insulators, ε_{diel} is a positive real number.

The dielectric constant ε of a metal is actually a complex number:

$$\varepsilon = \varepsilon^{'} + i\varepsilon'' \tag{9.2.6.4}$$

Here the real part, ε', is related to the refraction of light, and the imaginary part, ε", is related to light absorption. Both ε' and ε" are dependent on the frequency of the light. For metals near the plasmon resonance frequency, ε' is typically a *negative number.*

The **cross-section for absorption** of the light wave by the particle is:

$$\sigma_{absorption} = \frac{9\omega}{c}\epsilon_{diel}^{\frac{3}{2}} V \frac{\epsilon''_{metal}}{(\epsilon^{'}_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{9.2.6.5}$$

and the **cross-section for scattering** is:

$$\sigma_{scattering} = \frac{3}{2\pi}(\frac{\omega^4}{c})\epsilon_{diel}^2 V^2 \frac{(\epsilon^{'}_{metal} - \epsilon_{diel})^2 + (\epsilon''_{metal})^2}{(\epsilon^{'}_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{9.2.6.6}$$

The sum of these two is the **cross-section for extinction**:

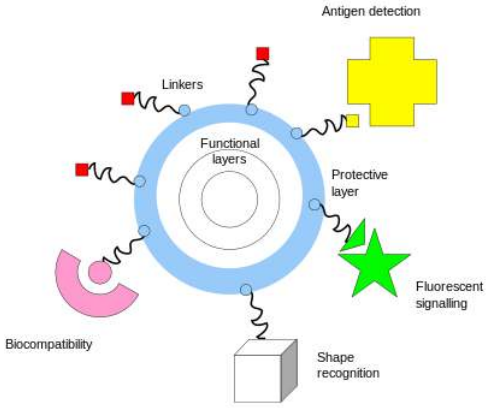
$$\sigma_{extinction} = \sigma_{absorption} + \sigma_{scattering} \tag{9.2.6.7}$$

These cross-sections become large when the (ε'_{metal} + $2\varepsilon_{diel}$) term in the denominator becomes small. This occurs when

$$\epsilon^{'}_{metal} \simeq -2\epsilon_{diel} \tag{9.2.6.8}$$

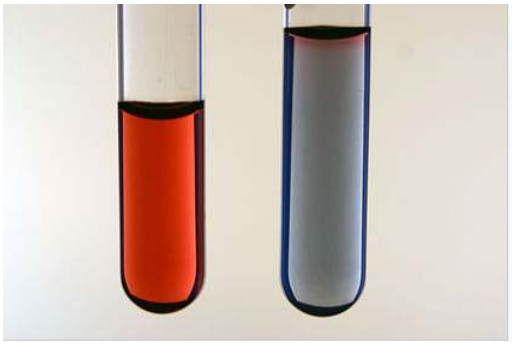
For 15 nm diameter gold nanoparticles in water, this happens at about 580 nm, resulting in the characteristic wine-red color of colloidal gold solutions. Changing the solution environment (e.g., by adsorbing a molecule onto the gold surface) changes ε_{diel} and thus alters the color slightly.

It is important to note that the cross-section for **scattering** is proportional to the **square of the volume** of the particle, V^2, whereas the absorption is proportional to V. This means that very small gold particles (< 5 nm) are strongly absorbing but not strongly scattering. Larger particles (>30 nm) scatter light very strongly. Depending on the application, therefore, we choose larger or smaller particles.



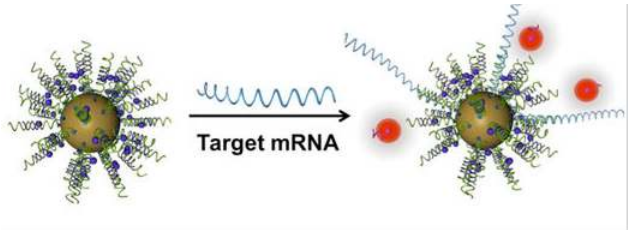
One of the key complementary properties of noble metal nanoparticles that is important to their use in biomedicine is the ease with which they can be **covalently conjugated** with polymers or small molecules, typically via thiol or amine bonds at their surface. This imparts biological recognition properties to the particles that enables them to bind to specific biomolecular targets. The figure at the left illustrates some of the functionality that can be imparted to nanoparticles through surface functionalization.

Functionalization of gold nanoparticles with thiol-terminated single-stranded DNA was the basis of one of the first nanoparticle sensors, developed by the Mirkin group at Northwestern University. **DNA-coated nanoparticles** have the characterstic wine-red plasmonic color of spherical nano-gold. However, when these particles are linked together by a complementary DNA strand, the resonance frequency shifs, resulting in a blue color. This color change, illustrated in the figure at the right, provides a "litmus test" for the presence of the target DNA sequence.[10] "Melting" of the DNA - heating it to the temperature at which double stranded DNA dissociates to make single strands - reverses the color change. The DNA hybridization/melting transition is highly **cooperative** because of the aggregation of many gold particles, so the transition temperature is very sharp. With proper temperature control, the color change can be sensitive to a **single base mismatch** in the target DNA that is detected by this method.



Aggregation of Au nanoparticles (in this case by adding salt to a colloidal solution) causes a color change from wine red (left) to blue (right). Photo credit: George Lisensky, Beloit College

Subsequent research has developed sophisticated diagnostic and therapeutic ("theranostic") applications for these **spherical nucleic acid**[11] particles. These particles easily penetrate cell membranes and can report on the chemistry happening inside living cells.



General schematic of nanoflare-based detection.

An important property of gold nanoparticles in these applications is their ability to **quench** the **fluorescence** of reporter molecules that are near their surface. Nucleic acid strands that contain a hairpin loop can position fluorescent molecules near the gold surface, where their fluorescence is turned off by nanoparticle quenching. Hybridization of these sequences to target RNA or DNA causes the fluorescence to turn on by moving the fluorescent molecule away from the nanoparticle surface. These so called "nanoflares" can thus signal the up- or down-regulation of specific genes inside cells. Nanoflares are the basis of the Verigene System, developed and commercialized by Nanosphere, Inc. to detect markers for infectious diseases and cancers.

This page titled 9.2.6: Nanoscale Metal Particles is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.6: Nanoscale Metal Particles** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.7: Applications of Nanomaterials

PowerPoint slides for this section

This page titled 9.2.7: Applications of Nanomaterials is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.7: Applications of Nanomaterials** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.8: Discussion Questions

- Explain how separating the nucleation and growth steps leads to nanoparticles of uniform size.
- A recent paper by Delia Milliron and coworkers (*Nature*, 2013, *500*, 323–326, doi:10.1038/nature12398) describes plasmonic indium-tin-oxide (ITO) nanoparticles that can control the infrared transparency of windows. Explain how the plasmon resonance wavelength of the nanoparticles can be tuned by electrochemical doping, and how the invention could save some of the energy used to heat and cool buildings.

This page titled 9.2.8: Discussion Questions is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.8: Discussion Questions** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.9: Problems

1. Consider a spherical gold nanoparticle that contains 500 atoms. If the diameter of an atom is approximately 3 Å, what fraction of the gold atoms in the particle are on the surface?

2. Now consider small droplets of mercury that contains 500 atoms. Mercury atoms are also about 3 Å in diameter. The heat of vaporization of bulk mercury is 64.0 kJ/mol, and the vapor pressure of mercury is 0.00185 torr = 2.43 x 10^{-6} atm. The surface tension of mercury (γ_{Hg}) is 0.518 N/m, and the surface excess energy can be calculated as $\gamma_{Hg}A$, where A is the surface area. Using this information and the Clausius-Clapyron equation ($P = const \cdot \exp(-\Delta H_{vap}/RT)$), calculate the vapor pressure of these small droplets of mercury.

3. James Heath and coworkers (Phys. Rev. Lett. 1995, 75, 3466) have observed Ostwald ripening in thin films of gold nanoparticles at room temperature. Starting with an uneven distribution of particle sizes, they find that the large particles grow at the expense of smaller ones. Can you explain this observation, based on your answers to problems (1) and (2)?

4. The bandgap of bulk germanium is 0.67 eV. What bandgap would you expect for a 4 nm diameter Ge nanocrystal? Use the Brus formula,

$$\Delta E_{gap} \approx \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \tag{9.2.9.1}$$

where R is the particle radius, ε_{Ge} = 16.2, h = 6.6 10^{-34} J s, 1 eV = 1.6 10^{-19} J, 1 J = 1 kg m^2/s^2. and $e^2/4\pi\varepsilon_0$ = 1.44 10^{-9} eV m. Assume that the electron-hole reduced mass μ is approximately 40% of the free electron mass, m_e = 9.1 10^{-31} kg.

5. Grecian Formula (a hair coloring product) until recently contained lead acetate, which reacts with the cysteine in hair to make PbS. In bulk form, PbS is a semiconductor with a band gap of 0.3 eV (1 eV = 1240 nm). The particles are initially very small but grow as more Grecian Formula is applied and reacts with cysteine. As the particles grow, they change progressively from colorless to yellow to black. Explain why the particles are initially colorless and why their color changes. (Grecian formula now uses Bi, which is less toxic than Pb, and works by the same mechanism)

This page titled 9.2.9: Problems is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.9: Problems** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

9.2.10: References

1. C.T. Liu, S. Y. Lin, D. C. Tsui, H. Lee, and D. Ackley, Appl. Phys. Lett. 1988, 53, 2510. DOI: 10.1063/1.100409.
2. D. L. Feldheim, K. C. Grabar, M. J. Natan, and T. E. Mallouk, "Electron Transfer in Self-Assembled Inorganic Polyelectrolyte/Metal Nanoparticle Heterostructures," J. Am. Chem. Soc., 118, 7640-1 (1996)
3. S. Chen, R. W. Murray, and S. W. Feldberg, "Quantized Capacitance Charging of Monolayer-Protected Au Clusters," J. Phys. Chem. B 1998, 102, 9898-9907.
4. Brus, Louis E. (1984). "Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state". J. Chem. Phys. 80, 4403. DOI: 10.1063/1.447218.
5. C. B. Murray, D. J. Norris, and M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites," J. Am. Chem. Soc. 1993, 115, 8706–8715. DOI: 10.1021/ja00072a025.
6. Y. Yin and A. P. Alivisatos, "Colloidal nanocrystal synthesis and the organic–inorganic interface," Nature 2005, 437, 664-670. DOI: 10.1038/nature04165
7. G. Zheng, F. Patolsky, Y. Cui, W. U. Wang and C. M. Lieber, "Multiplexed electrical detection of cancer markers with nanowire sensor arrays," Nature Biotechnol. 2005, 23, 1294 - 1301. DOi:10.1038/nbt1138.
8. K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic, and D. Zhang, "Nanocrystals as Stoichiometric Reagents with Unique Surface Chemistry," J. Phys. Chem. 1996, 100, 12142–12153. DOI: 10.1021/jp960224x.
9. S. A. Little, T. Begou, R. W. Collins, and S. Marsillac, Appl. Phys. Lett. 2012, 100, 051107. DOI: 10.1063/1.3681367
10. Mirkin, C. A., et al., A DNA-based method for rationally assembling nanoparticles into macroscopic materials. *Nature* 1996, 382 (6592), 607-609.
11. Cutler, J. I., et al., Spherical Nucleic Acids. *J Am Chem Soc* 2012, 134 (3), 1376-1391.

This page titled 9.2.10: References is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Chemistry 310 (Wikibook) via source content that was edited to the style and standards of the LibreTexts platform.

- **11.10: References** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

Index

A

actinide
8.2.1: General Properties and Reactions of The Actinides
Actinide series
8.2.1: General Properties and Reactions of The Actinides
actinium
4.2.1: Chemistry of Actinium
8.2.13: Chemistry of Protoactinium
aerospace industry
4.3.4: Chemistry of Titanium
AgCl
4.10.4.1: Silver Chloride
aktinos
4.2.1: Chemistry of Actinium
Albert Einstein
8.2.6: Chemistry of Einsteinium
Alfred Nobel
8.2.11: Chemistry of Nobelium
alkene
6.5.1: Linear π Systems
Alkyl Complexes
6.6.1: Metal Alkyls
alpha particles
8.2.1: General Properties and Reactions of The Actinides
aluminum
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
aluminum oxide
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
amalgams
4.11.3: Chemistry of Mercury
americium
8.2.2: Chemistry of Americium
ammonia
4.1.5: Introduction to Transition Metals II
Anders Ekenberg
4.4.3: Chemistry of Tantalum
Andrés Manuel del Rio
4.4.4: Chemistry of Vanadium
anode
4.1.6.2: The Extraction of Copper
anomalous nickel
4.9.2: Chemistry of Nickel
Antonio de Ulloa
4.9.4: Chemistry of Platinum
arene
6.5.1: Linear π Systems
argentite
4.1.6.4: The Extraction of Silver
argentium
4.10.4: Chemistry of Silver
argento cyanide
4.1.6.4: The Extraction of Silver
aromatic
6.5.1: Linear π Systems
aromatic ligands
6.5.1: Linear π Systems
arthropods
4.1.8: Transition Metals in Biology
atomic number
4.1.3: General Trends among the Transition Metals
atomic orbitals
4.1.7: Oxidation States of Transition Metals
atomic radius
4.1.4: Introduction to Transition Metals I
8.1.1.1: Lanthanide Contraction
Aufbau principle
1.2.2.3: Aufbau Principle
4.1.5: Introduction to Transition Metals II
aurum
4.10.2: Chemistry of Gold

B

barycenter
3.2.1: Crystal Field Theory
Becquerel
8.2.15: Chemistry of Uranium
bent
1.3.2: Valence Shell Electron-Pair Repulsion
Berezelius
8.2.1: General Properties and Reactions of The Actinides
Berg
4.6.3: Chemistry of Rhenium
Berkeley
4.5.3: Chemistry of Seaborgium
4.7.1: Chemistry of Hassium
4.9.1: Chemistry of Darmstadtium
8.2.4: Chemistry of Californium
8.2.5: Chemistry of Curium
8.2.6: Chemistry of Einsteinium
8.2.7: Chemistry of Fermium
8.2.10: Chemistry of Neptunium
Berkelium
8.2.3: Chemistry of Berkelium
beryllium
1.3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium
Berzelius
4.3.5: Chemistry of Zirconium
8.1.2: Chemistry of Cerium
8.2.14: Chemistry of Thorium
beta elimination
6.6.1: Metal Alkyls
beta elmination
6.6.1: Metal Alkyls
7.2.4: β-Elimination Reactions
beta particles
8.2.1: General Properties and Reactions of The Actinides
Big Bertha
4.5.2: Chemistry of Molybdenum
biological systems
4.1.8: Transition Metals in Biology
biology
4.1.8: Transition Metals in Biology
blast furnace
4.1.6.3: The Extraction of Iron
4.1.6.3.1: Iron Production
block diagonal
1.4.3.2: Representations of Point Groups
Blue Copper Proteins
4.1.8: Transition Metals in Biology
Bohrium
4.6.1: Chemistry of Bohrium
boiling points
4.1.4: Introduction to Transition Metals I
bond angle
1.3.2: Valence Shell Electron-Pair Repulsion
bridging ligands
2.6: Coordination Frameworks

C

Cadmium
4.11.1: Chemistry of Cadmium
4.11.1.1: Cadmium Sulfide
Cadmium sulfide
4.11.1.1: Cadmium Sulfide
cadmium yellow
4.11.1: Chemistry of Cadmium
calcium oxide
4.1.6.3: The Extraction of Iron
calcium silicate
4.1.6.3: The Extraction of Iron
californium
8.2.4: Chemistry of Californium
Calomel
4.11.3: Chemistry of Mercury
carbene
6.6.2: Carbenes
carbenes
6.6.2: Carbenes
Cast iron
4.1.6.3: The Extraction of Iron
catalyst
4.4.4: Chemistry of Vanadium
4.7.2: Chemistry of Iron
catalytic activity
4.1.5: Introduction to Transition Metals II
Ceres
8.1.2: Chemistry of Cerium
Cerium
8.1.2: Chemistry of Cerium
character (matrix)
1.4.3.2: Representations of Point Groups
character table
1.4.3.3: Character Tables
Charles Wood
4.9.4: Chemistry of Platinum
chelate ring
2.4: Isomerism
chemical properties
4.1.4: Introduction to Transition Metals I
4.10.4: Chemistry of Silver
Chemical Reduction
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
Chemistry Properties
4.11.4: Chemistry of Zinc
chirality
1.4.4.1: Chirality
chlorargyrite
4.10.4.1: Silver Chloride
chloride ions
4.1.5: Introduction to Transition Metals II
Choppin
8.2.9: Chemistry of Mendelevium
chroma
4.1.8: Transition Metals in Biology
chrome yellow paint
4.5.1.1: Chemistry of Chromium

chromium
4.1.2: Electron Configuration of Transition Metals
4.5.1: Chemistry of Chromium
4.5.1.1: Chemistry of Chromium
Cleve
8.1.6: Chemistry of Holmium
CO
4.1.2: Electron Configuration of Transition Metals
4.8.1: Chemistry of Cobalt
CO Insertions
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
cobalt
4.1.2: Electron Configuration of Transition Metals
4.8.1: Chemistry of Cobalt
coke
4.1.6.3.1: Iron Production
cold fusion
4.9.3: Chemistry of Palladium
colored compounds
4.1.5: Introduction to Transition Metals II
columbite
4.4.2: Chemistry of Niobium
4.6.3: Chemistry of Rhenium
complex ion
4.1.5: Introduction to Transition Metals II
4.5.1.1: Chemistry of Chromium
configuration
4.1.7: Oxidation States of Transition Metals
cooperativity
4.1.8: Transition Metals in Biology
coordinate covalent bond
2.1: Prelude to Coordination Chemistry I - Structure and Isomers
coordination compounds
2.1: Prelude to Coordination Chemistry I - Structure and Isomers
coordination framework
2.6: Coordination Frameworks
Copenhagen
4.3.2: Chemistry of Hafnium
Copernicium
4.11.2: Chemistry of Copernicium
copper
4.1.2: Electron Configuration of Transition Metals
4.1.6.2: The Extraction of Copper
4.10.1: Chemistry of Copper
copper pyrites
4.10.1: Chemistry of Copper
copper refining
4.1.6.2: The Extraction of Copper
corrosion resistance
4.3.1: Group 4 Elemental Properties
Corrosive Sublimate
4.11.3: Chemistry of Mercury
Cr
4.1.2: Electron Configuration of Transition Metals
Crabtree
6.5.3: Odd-numbered π Systems
crystal field orbitals
6.5.1: Linear π Systems
crystal field stabilization energy
3.2.1: Crystal Field Theory
crystal field theory
3.2.1: Crystal Field Theory
Cu
4.1.2: Electron Configuration of Transition Metals
Curium
8.2.5: Chemistry of Curium
cyanide process
4.1.6.4: The Extraction of Silver
cyclopentadienyl ligands
6.5.3: Odd-numbered π Systems
cyclopropanations
6.6.2: Carbenes
cyclotron
4.6.4: Chemistry of Technetium
Cytochromes
4.1.8: Transition Metals in Biology
cytos
4.1.8: Transition Metals in Biology

D

D Block Contraction
8.1.1.1: Lanthanide Contraction
d block element
4.1.5: Introduction to Transition Metals II
Darmstadt
4.8.3: Chemistry of Meitnerium
4.9.1: Chemistry of Darmstadtium
4.10.3: Chemistry of Roentgenium
4.11.2: Chemistry of Copernicium
Darmstadtium
4.9.1: Chemistry of Darmstadtium
dative
6.5.1: Linear π Systems
dative actor ligands
6.5.1: Linear π Systems
dearomatization
6.5.1: Linear π Systems
Decomposition
6.6.1: Metal Alkyls
deinsertion
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
delocalization
4.1.4: Introduction to Transition Metals I
delocalized
4.1.7: Oxidation States of Transition Metals
Densities
4.1.4: Introduction to Transition Metals I
deoxymyoglobin
4.1.8: Transition Metals in Biology
deuterons
4.6.4: Chemistry of Technetium
diamagnetic
4.1.3: General Trends among the Transition Metals
4.1.7: Oxidation States of Transition Metals
diastereomeric
6.5.1: Linear π Systems
dichalcogenides
4.3.1: Group 4 Elemental Properties
Diode
9.1.7: Diodes, LEDs and Solar Cells
9.1.8: Amorphous Semiconductors
9.1.9: Discussion Questions
9.1.10: Problems
9.1.11: References
dipole moment
1.3.2: Valence Shell Electron-Pair Repulsion
1.3.3: Molecular Polarity
Dmitri Mendeleev
8.2.9: Chemistry of Mendelevium
double bond
4.6.2.1: Chemistry of Manganese
Dubna
4.4.1: Chemistry of Dubnium
Dubnium
4.4.1: Chemistry of Dubnium
Ductile
4.8.1: Chemistry of Cobalt
dysprositos
8.1.3: Chemistry of Dysprosium
Dysprosium
8.1.3: Chemistry of Dysprosium

E

effective nuclear charge
1.2.2.4: Shielding
4.1.3: General Trends among the Transition Metals
Einsteinium
8.2.6: Chemistry of Einsteinium
electrochemical series
4.1.6.2: The Extraction of Copper
electrolysis
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
Electrolytic Refining
4.1.6.2: The Extraction of Copper
electron affinity
1.2.3.2: Electron Affinity
electron configuration
4.1.2: Electron Configuration of Transition Metals
4.1.7: Oxidation States of Transition Metals
8.1.1: Lanthanides- Properties and Reactions
electron configurations
4.1.3: General Trends among the Transition Metals
electron–electron repulsions
4.1.3: General Trends among the Transition Metals
electronegativities
4.1.3: General Trends among the Transition Metals
electronegativity
1.3.2.3: Electronegativity and Atomic Size Effects
4.1.4: Introduction to Transition Metals I
electronic configuration
4.1.7: Oxidation States of Transition Metals
electronic structure
4.1.3: General Trends among the Transition Metals
electrophilic attack
6.5.1: Linear π Systems
6.6.1: Metal Alkyls
electropositive
4.2.5: Group 3 Elemental Properties
4.3.1: Group 4 Elemental Properties
electropositive character
4.2.5: Group 3 Elemental Properties
electropositive metals
4.2.5: Group 3 Elemental Properties
Element 112
4.11.2: Chemistry of Copernicium
Element 44
4.7.4: Chemistry of Ruthenium
Elemental Properties
4.2.5: Group 3 Elemental Properties
4.3.1: Group 4 Elemental Properties
elimination
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
enantiomers
1.4.4.1: Chirality
endothermic reaction
4.1.6.3: The Extraction of Iron
energy diagrams
4.1.7: Oxidation States of Transition Metals

Enrico Fermi
8.2.7: Chemistry of Fermium
enterobactin
4.1.8: Transition Metals in Biology
enthalpies
4.1.3: General Trends among the Transition Metals
enthalpies of hydration
4.1.3: General Trends among the Transition Metals
Ernest Lawrence
8.2.8: Chemistry of Lawrencium
europium
8.1.4: Chemistry of Europium
Europium Anomaly
8.1.4: Chemistry of Europium
Extracting
4.1.6.2: The Extraction of Copper
Extracting iron
4.1.6.3: The Extraction of Iron
extraction
4.1.6.4: The Extraction of Silver
4.3.4: Chemistry of Titanium
4.10.1: Chemistry of Copper
4.11.3: Chemistry of Mercury
extraction of Copper
4.10.1: Chemistry of Copper
Extraction of Iron
4.1.6.3: The Extraction of Iron
Extraction of Silver
4.1.6.4: The Extraction of Silver

F

Fajans
8.2.13: Chemistry of Protoactinium
Fausto Elhuyar
4.5.4: Chemistry of Tungsten
Fe
4.1.2: Electron Configuration of Transition Metals
Fermium
8.2.7: Chemistry of Fermium
ferrichrome
4.1.8: Transition Metals in Biology
ferritin
4.7.2.1: Iron in Humans
ferrum
4.7.2: Chemistry of Iron
first row transition metals
4.1.2: Electron Configuration of Transition Metals
Fischer carbenes
6.6.2: Carbenes
formal charge
1.3.1.3: Formal Charge
Fractionation
4.3.4: Chemistry of Titanium
Froth flotation
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
Fungi
4.1.8: Transition Metals in Biology

G

Göhring
8.2.13: Chemistry of Protoactinium
Gadolin
8.1.5: Chemistry of Gadolinium
gadolinite
4.6.3: Chemistry of Rhenium
8.1.1: Lanthanides- Properties and Reactions
8.1.5: Chemistry of Gadolinium
Gadolinium
8.1.5: Chemistry of Gadolinium
Gadolinium trichloride
8.1.5.1: Gadolinium(III) Chloride
galvanizing
4.11.4: Chemistry of Zinc
gamma rays
8.2.1: General Properties and Reactions of The Actinides
Ghiorso
8.2.3: Chemistry of Berkelium
8.2.4: Chemistry of Californium
8.2.5: Chemistry of Curium
8.2.6: Chemistry of Einsteinium
8.2.7: Chemistry of Fermium
8.2.8: Chemistry of Lawrencium
8.2.9: Chemistry of Mendelevium
8.2.11: Chemistry of Nobelium
Glenn Seaborg
8.2.8: Chemistry of Lawrencium
Glenn T. Seaborg
4.5.3: Chemistry of Seaborgium
globulin
4.7.2.1: Iron in Humans
gold
4.10.2: Chemistry of Gold
Gold metal
4.10.2: Chemistry of Gold
greenockite
4.11.1.1: Cadmium Sulfide
Grosse
8.2.13: Chemistry of Protoactinium
group 3
4.2.5: Group 3 Elemental Properties
group 4
4.3: Transition Metals
4.3.1: Group 4 Elemental Properties
group 5
4.4.5: Group 5 Elemental Properties

H

Haber process
4.1.5: Introduction to Transition Metals II
4.7.2: Chemistry of Iron
Hafnia
4.3.2: Chemistry of Hafnium
Hafnium
4.3.2: Chemistry of Hafnium
Hahnium
4.4.1: Chemistry of Dubnium
halides
8.2.1: General Properties and Reactions of The Actinides
hardening agent
4.7.4: Chemistry of Ruthenium
Harvey
8.2.9: Chemistry of Mendelevium
Hassium
4.7.1: Chemistry of Hassium
hawleyite
4.11.1.1: Cadmium Sulfide
heavy stone
4.5.4: Chemistry of Tungsten
Heck reaction
6.5.1: Linear π Systems
hematite
4.1.6.3.1: Iron Production
Hemerythrin
4.1.8: Transition Metals in Biology
Hemocyanin
4.1.8: Transition Metals in Biology
hemoglobin
4.1.8: Transition Metals in Biology
Henry Roscoe
4.4.4: Chemistry of Vanadium
Hexaaqua Ions
4.5.1.1: Chemistry of Chromium
hexaaquachromium
4.5.1.1: Chemistry of Chromium
hexaaquacobalt
4.8.1: Chemistry of Cobalt
High carbon steel
4.1.6.3: The Extraction of Iron
high temperatures
4.3.1: Group 4 Elemental Properties
Hisinger
8.1.2: Chemistry of Cerium
Hofmann
4.11.2: Chemistry of Copernicium
Holmium
8.1.6: Chemistry of Holmium
Hubbard model
9.1.2: Metal-Insulator Transitions
Human
4.7.2.1: Iron in Humans
Humans
4.7.2.1: Iron in Humans
hydration
4.1.3: General Trends among the Transition Metals
Hydricity
6.4.3: Hydrides and Dihydrogen Complexes
hydride complexes
6.4.3: Hydrides and Dihydrogen Complexes
Hydrocyanation
7.1.3: Reductive Elimination
hydrogen bonding
1.3.4: Hydrogen Bonding
hydrogenation
4.1.5: Introduction to Transition Metals II
hypervalency
1.3.1: Lewis Electron-Dot Diagrams
hypervalent molecule
1.3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)
hypovalency
1.3.1: Lewis Electron-Dot Diagrams

I

impurities
4.1.6.3.1: Iron Production
inorganic
4.11: Transition Metals
Insertions
7.2.3: Migratory Insertion-1,2-Insertions
ionic
4.2.5: Group 3 Elemental Properties
ionization energies
4.1.3: General Trends among the Transition Metals
4.1.4: Introduction to Transition Metals I
4.1.5: Introduction to Transition Metals II

ionization energy
1.2.3.1: Ionization energy
4.1.4: Introduction to Transition Metals I
8.1.1.1: Lanthanide Contraction
ionization potential
1.2.3.1: Ionization energy
ions
4.1.6.2: The Extraction of Copper
4.1.7: Oxidation States of Transition Metals
Iridium
4.8.2: Chemistry of Iridium
iron
4.1.2: Electron Configuration of Transition Metals
4.1.6.3.1: Iron Production
4.7.2: Chemistry of Iron
4.7.2.1: Iron in Humans
iron ions
4.7.2: Chemistry of Iron
iron oxide
4.1.6.3: The Extraction of Iron
Iron Production
4.1.6.3.1: Iron Production
Iron–Sulfur Proteins
4.1.8: Transition Metals in Biology
isomerism
2.4: Isomerism
isotopes
4.5.1: Chemistry of Chromium

J

Johan Gahn
4.6.2: Chemistry of Manganese
Johann Gottlob Lehmann
4.5.1: Chemistry of Chromium
Jons Jakob Berzelius
8.2.14: Chemistry of Thorium
Juan Elhuyar
4.5.4: Chemistry of Tungsten

K

Kepert Model
2.5: Coordination Numbers and Structures
kerosene
4.2.2: Chemistry of Lanthanum
Klaproth
4.3.5: Chemistry of Zirconium
8.2.1: General Properties and Reactions of The Actinides
8.2.15: Chemistry of Uranium
Kulinkovich cyclopropanation
6.5.1: Linear π Systems
Kupfernickel
4.9.2: Chemistry of Nickel

L

lanthanein
4.2.2: Chemistry of Lanthanum
Lanthanide Contraction
4.1.3: General Trends among the Transition Metals
4.4.5: Group 5 Elemental Properties
8.1.1.1: Lanthanide Contraction
lanthanides
8.1.1: Lanthanides- Properties and Reactions
8.1.2: Chemistry of Cerium
lanthanoids
8.1.4: Chemistry of Europium
lanthanum
4.2.2: Chemistry of Lanthanum
Latimer
8.2.8: Chemistry of Lawrencium
Lawrence Radiation Laboratory
8.2.8: Chemistry of Lawrencium
Lawrencium
8.2.8: Chemistry of Lawrencium
ligand
4.1.5: Introduction to Transition Metals II
4.5.1.1: Chemistry of Chromium
6.6.2: Carbenes
Ligand Close Packing (LCP)
1.3.2.4: Ligand Close Packing
ligand exchange
4.5.1.1: Chemistry of Chromium
4.8.1: Chemistry of Cobalt
4.10.1: Chemistry of Copper
Ligand Field Stabilization Energy
3.3.3: Ligand Field Stabilization Energy
ligand substitution
6.5.1: Linear π Systems
7.1.1: Ligand Dissociation and Substitution
Ligands
4.1.5: Introduction to Transition Metals II
4.1.8: Transition Metals in Biology
7.1.3: Reductive Elimination
limestone
4.1.6.3: The Extraction of Iron
4.1.6.3.1: Iron Production
linear
1.3.2: Valence Shell Electron-Pair Repulsion
Lise Meitner
4.8.3: Chemistry of Meitnerium
Louis Nicolas Vauquelin
4.5.1: Chemistry of Chromium
Lutetium
8.1.7: Chemistry of Lutetium

M

magnes
4.6.2: Chemistry of Manganese
magnetic properties
4.5.1: Chemistry of Chromium
Magnetic Susceptibility
3.1.2: Magnetic Susceptibility
magnetite
4.1.6.3.1: Iron Production
magnetochemical series
3.4.6: The Magnetochemical Series
manganese
4.1.2: Electron Configuration of Transition Metals
4.6.2: Chemistry of Manganese
4.6.2.1: Chemistry of Manganese
Marcus Theory
5.8.1: Outer Sphere Electron Transfer
margarine
4.1.5: Introduction to Transition Metals II
Marie Curie
8.2.5: Chemistry of Curium
Martin Klaproth
4.3.4: Chemistry of Titanium
Meitnerium
4.8.3: Chemistry of Meitnerium
melting
4.3.4: Chemistry of Titanium
melting point
4.7.4: Chemistry of Ruthenium
melting points
4.1.4: Introduction to Transition Metals I
Mendeleev
4.2.3: Chemistry of Scandium
4.6.3: Chemistry of Rhenium
4.6.4: Chemistry of Technetium
Mendelevium
8.2.9: Chemistry of Mendelevium
mercury
4.11.3: Chemistry of Mercury
metal
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
metal alkyl complexes
7.2.4: β-Elimination Reactions
Metal carbenes
6.6.2: Carbenes
metal cations
4.1.3: General Trends among the Transition Metals
metal element
4.2.3: Chemistry of Scandium
Metal Extraction
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
metal hydrides
6.4.3: Hydrides and Dihydrogen Complexes
metal ion
4.1.8: Transition Metals in Biology
metal ions
4.1.3: General Trends among the Transition Metals
4.1.5: Introduction to Transition Metals II
4.1.8: Transition Metals in Biology
metallacyclopropane
6.5.1: Linear π Systems
metallic bonding
4.1.4: Introduction to Transition Metals I
Metallic Characteristics
4.11.1: Chemistry of Cadmium
Metallic Properties
4.2.3: Chemistry of Scandium
4.5.1: Chemistry of Chromium
metallic radii
4.1.4: Introduction to Transition Metals I
Metalloenzyme
4.1.8: Transition Metals in Biology
Metalloenzymes
4.1.8: Transition Metals in Biology
Metalloprotein
4.1.8: Transition Metals in Biology
Metalloproteins
4.1.8: Transition Metals in Biology
methylene
6.6.2: Carbenes
microscopic reversibility
7.1.3: Reductive Elimination
Migratory insertion
6.4.3: Hydrides and Dihydrogen Complexes
6.6.1: Metal Alkyls
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
7.2.3: Migratory Insertion-1,2-Insertions
Mild steel
4.1.6.3: The Extraction of Iron
mining
4.1.6.3: The Extraction of Iron
Mn
4.1.2: Electron Configuration of Transition Metals
molar enthalpies
4.1.4: Introduction to Transition Metals I
mollusks
4.1.8: Transition Metals in Biology

molybdenite
4.6.3: Chemistry of Rhenium
molybdenum
4.5.2: Chemistry of Molybdenum
4.5.2.1: Molybdenum Disulfide
Molybdenum disulfide
4.5.2.1: Molybdenum Disulfide
molybdos
4.5.2: Chemistry of Molybdenum
monazite sand
8.1.4: Chemistry of Europium
Morten Thrane Esmark
8.2.14: Chemistry of Thorium
multicellular organisms
4.1.8: Transition Metals in Biology
Myoglobin
4.1.8: Transition Metals in Biology

N
neodymium
8.1.8: Chemistry of Neodymium
Neptune
8.2.10: Chemistry of Neptunium
Neptunium
8.2.10: Chemistry of Neptunium
Ni
4.1.2: Electron Configuration of Transition Metals
Nickel
4.1.2: Electron Configuration of Transition Metals
4.9.2: Chemistry of Nickel
Nickel Compounds
4.9.2: Chemistry of Nickel
Niels Bohr
4.6.1: Chemistry of Bohrium
Nielsbohrium
4.4.1: Chemistry of Dubnium
Niobe
4.4.2: Chemistry of Niobium
Niobium
4.4.2: Chemistry of Niobium
Nobelium
8.2.11: Chemistry of Nobelium
noble gas configuration
4.1.7: Oxidation States of Transition Metals
Noddack
4.6.3: Chemistry of Rhenium
nonmetallic character
4.1.4: Introduction to Transition Metals I
nuclear charge
4.1.3: General Trends among the Transition Metals
nuclear chemistry
4.6.2: Chemistry of Manganese
nuclear fission
8.2.1: General Properties and Reactions of The Actinides
Nuclear Research
4.7.1: Chemistry of Hassium
nucleophilic aromatic substitution
6.5.1: Linear π Systems
nucleophilic attack
6.6.1: Metal Alkyls

O
octahedral
1.3.2: Valence Shell Electron-Pair Repulsion
octamer
4.1.8: Transition Metals in Biology
odor
4.7.3: Chemistry of Osmium
olefin metathesis
6.6.2: Carbenes
olefin polymerization
6.5.1: Linear π Systems
orbital
4.1.2: Electron Configuration of Transition Metals
ore
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
4.1.6.4: The Extraction of Silver
ores
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
4.1.6.2: The Extraction of Copper
organic chemistry
6.4.3: Hydrides and Dihydrogen Complexes
7.2.4: β-Elimination Reactions
Organic Radicals
4.1.8: Transition Metals in Biology
organometallic chemistry
6.4.3: Hydrides and Dihydrogen Complexes
osme
4.7.3: Chemistry of Osmium
Osmium
4.7.3: Chemistry of Osmium
Outer Sphere Electron Transfer
5.8.1: Outer Sphere Electron Transfer
Oxidation
4.4.4: Chemistry of Vanadium
oxidation numbers
4.1.7: Oxidation States of Transition Metals
Oxidation State
4.1.5: Introduction to Transition Metals II
4.1.7: Oxidation States of Transition Metals
4.4.5: Group 5 Elemental Properties
oxidation states
4.1.2: Electron Configuration of Transition Metals
4.1.7: Oxidation States of Transition Metals
4.4.4: Chemistry of Vanadium
Oxidative addition
6.4.3: Hydrides and Dihydrogen Complexes
6.6.1: Metal Alkyls
7.1.2: Oxidative Addition
7.1.3: Reductive Elimination
oxidative ligation
7.1.2: Oxidative Addition
oxidative ligations
6.4.3: Hydrides and Dihydrogen Complexes
oxidizing agent
4.6.2.1: Chemistry of Manganese
oxygen transport
4.1.8: Transition Metals in Biology

P
Péligot
8.2.15: Chemistry of Uranium
Palladium
4.9.3: Chemistry of Palladium
Pallas
4.9.3: Chemistry of Palladium
paramagnetic
4.1.3: General Trends among the Transition Metals
4.1.7: Oxidation States of Transition Metals
particle in a box
1.2.2.1: Particle in a Box
penetration
1.2.2.4: Shielding
periodic table
4.1.5: Introduction to Transition Metals II
periodic trends
4.3.1: Group 4 Elemental Properties
8.1.1: Lanthanides- Properties and Reactions
Peter Simon Pallas
4.5.1: Chemistry of Chromium
philosopher's stone
1.1.3: History of Inorganic Chemistry
physical properties
4.1.4: Introduction to Transition Metals I
4.1.7: Oxidation States of Transition Metals
4.11.4: Chemistry of Zinc
pi system
6.5.1: Linear π Systems
6.5.3: Odd-numbered π Systems
pi systems
6.5.1: Linear π Systems
6.5.3: Odd-numbered π Systems
plasmons
9.2.6: Nanoscale Metal Particles
platinum
4.9.3: Chemistry of Palladium
4.9.4: Chemistry of Platinum
Platinum Group Metals
4.8.4: Chemistry of Rhodium
4.9.4: Chemistry of Platinum
plutonium
8.2.12: Chemistry of Plutonium
point groups
1.4.2: Point Groups
Potassium chromium sulfate
4.5.1.2: Potassium Chromium Sulfate
powerful reductants
4.2.5: Group 3 Elemental Properties
Praseodymium
8.1.9: Chemistry of Praseodymium
precipitation
8.2.1: General Properties and Reactions of The Actinides
promethium
8.1.7: Chemistry of Lutetium
8.1.10: Chemistry of Promethium
protein
4.1.8: Transition Metals in Biology
4.7.2.1: Iron in Humans
protein environment
4.1.8: Transition Metals in Biology
proteins
4.1.8: Transition Metals in Biology
4.7.2.1: Iron in Humans
Protoactinium
8.2.13: Chemistry of Protoactinium
purification
4.1.6.2: The Extraction of Copper
pyrometallurgy
4.1.6.3.1: Iron Production

Q
Quintuple Bond
4.5.1: Chemistry of Chromium

R
radioactive
4.2.1: Chemistry of Actinium
radioactive metal
4.2.1: Chemistry of Actinium

radioactivity
8.2.15: Chemistry of Uranium
Rare Earth Metals
8.2.1: General Properties and Reactions of The Actinides
reactive metal
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
reactive metals
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
reactivity
4.1.3: General Trends among the Transition Metals
reactivity series
4.1.6.2: The Extraction of Copper
Reactivity Trends
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
7.2.3: Migratory Insertion-1,2-Insertions
recycling
4.1.6.3: The Extraction of Iron
redox
4.1.6.2: The Extraction of Copper
4.7.2: Chemistry of Iron
redox potential
4.1.8: Transition Metals in Biology
redox titration
4.7.2: Chemistry of Iron
reducing agent
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
4.1.6.2: The Extraction of Copper
4.1.6.3: The Extraction of Iron
4.3.4: Chemistry of Titanium
4.4.4: Chemistry of Vanadium
Reduction
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
4.1.6.3: The Extraction of Iron
4.3.4: Chemistry of Titanium
4.5.1.1: Chemistry of Chromium
reduction of the ore
4.1.6.3: The Extraction of Iron
Reductive elimination
6.6.1: Metal Alkyls
7.1.2: Oxidative Addition
7.1.3: Reductive Elimination
Removal of carbon
4.1.6.3: The Extraction of Iron
Removal of other elements
4.1.6.3: The Extraction of Iron
Removal of sulfur
4.1.6.3: The Extraction of Iron
resonance
1.3.1.1: Resonance
resonance structures
1.3.1.1: Resonance
Rhenium
4.6.3: Chemistry of Rhenium
Rhenus
4.6.3: Chemistry of Rhenium
Rhine river
4.6.3: Chemistry of Rhenium
Rhodium
4.8.4: Chemistry of Rhodium
rhodon
4.8.4: Chemistry of Rhodium
ring slippage
6.5.1: Linear π Systems
Roentgenium
4.10.3: Chemistry of Roentgenium
rotation axis
1.4.3.2: Representations of Point Groups
Ruthenium
4.7.4: Chemistry of Ruthenium
Rutherfordium
4.3.3: Chemistry of Rutherfordium

S

Samarium
8.1.11: Chemistry of Samarium
samarskite
8.1.11: Chemistry of Samarium
Sc
4.1.2: Electron Configuration of Transition Metals
Scandide Contraction
8.1.1.1: Lanthanide Contraction
Scandium
4.1.2: Electron Configuration of Transition Metals
4.1.5: Introduction to Transition Metals II
4.2.3: Chemistry of Scandium
Scheele
4.5.2: Chemistry of Molybdenum
4.6.2: Chemistry of Manganese
Seaborg
8.2.3: Chemistry of Berkelium
8.2.4: Chemistry of Californium
8.2.5: Chemistry of Curium
8.2.8: Chemistry of Lawrencium
8.2.9: Chemistry of Mendelevium
8.2.11: Chemistry of Nobelium
8.2.12: Chemistry of Plutonium
Seaborgium
4.5.3: Chemistry of Seaborgium
Second Row Transition Metal
4.1.2: Electron Configuration of Transition Metals
seesaw
1.3.2: Valence Shell Electron-Pair Repulsion
Sg
4.5.3: Chemistry of Seaborgium
shielding
1.2.2.4: Shielding
shielding effect
8.1.1.1: Lanthanide Contraction
shielding effects
4.1.4: Introduction to Transition Metals I
Shrock carbenes
6.6.2: Carbenes
siderophores
4.1.8: Transition Metals in Biology
Sikkeland
8.2.8: Chemistry of Lawrencium
8.2.11: Chemistry of Nobelium
silver
4.10.4: Chemistry of Silver
Silver chloride
4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate
4.10.4: Chemistry of Silver
4.10.4.1: Silver Chloride
Silver nitrate
4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate
4.10.4: Chemistry of Silver
4.10.4.2: Silver Nitrate
Simple ligands
4.1.5: Introduction to Transition Metals II
sioful
4.10.4: Chemistry of Silver
site selectivity
6.5.1: Linear π Systems
Smithson Tennant
4.7.3: Chemistry of Osmium
4.8.2: Chemistry of Iridium
sodium hydroxide
4.1.6.1: An Introduction to the Chemistry of Metal Extraction
solubility
8.2.1: General Properties and Reactions of The Actinides
Soviet
4.5.3: Chemistry of Seaborgium
4.6.1: Chemistry of Bohrium
Soviet Union
4.3.3: Chemistry of Rutherfordium
Special steels
4.1.6.3: The Extraction of Iron
spectator
6.5.1: Linear π Systems
spectrochemical series
3.4.4: The Spectrochemical Series
sphalerite
4.11.1.1: Cadmium Sulfide
square pyramidal
1.3.2: Valence Shell Electron-Pair Repulsion
steel
4.1.6.3: The Extraction of Iron
steel industry
4.6.2: Chemistry of Manganese
stereochemistry
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
7.2.3: Migratory Insertion-1,2-Insertions
stereoselectivity
6.5.1: Linear π Systems
stereospecific
7.2.4: β-Elimination Reactions
Stockholm
8.1.6: Chemistry of Holmium
Street
8.2.4: Chemistry of Californium
subshell
4.6.2: Chemistry of Manganese
Subshells
4.1.2: Electron Configuration of Transition Metals
substitution reactions
6.5.3: Odd-numbered π Systems
substitutions
7.1.1: Ligand Dissociation and Substitution
superconductor
9.1.3: Superconductors
symmetry elements
1.4.1: Symmetry Elements and Operations
symmetry operation
1.4.3.2: Representations of Point Groups
symmetry operations
1.4.1: Symmetry Elements and Operations

T

Tacke
4.6.3: Chemistry of Rhenium
Tantalum
4.4.2: Chemistry of Niobium
4.4.3: Chemistry of Tantalum
Tantalus
4.4.2: Chemistry of Niobium
4.4.3: Chemistry of Tantalum

Technetium
4.6.4: Chemistry of Technetium
temperature
4.1.6.3: The Extraction of Iron
Terbium
8.1.12: Chemistry of Terbium
tetrahalides
4.3.1: Group 4 Elemental Properties
Tetrahedral
1.3.2: Valence Shell Electron-Pair Repulsion
tetramer
4.1.8: Transition Metals in Biology
The Kroll process
4.3.4: Chemistry of Titanium
thermal conductivities
4.1.3: General Trends among the Transition Metals
Thompson
8.2.3: Chemistry of Berkelium
8.2.4: Chemistry of Californium
8.2.9: Chemistry of Mendelevium
Thor
8.2.14: Chemistry of Thorium
thorium
8.2.14: Chemistry of Thorium
thulium
8.1.7: Chemistry of Lutetium
8.1.13: Chemistry of Thulium
Ti
4.1.2: Electron Configuration of Transition Metals
titanium
4.1.2: Electron Configuration of Transition Metals
4.3.4: Chemistry of Titanium
Titanium Extraction
4.3.4: Chemistry of Titanium
Titanium tetrachloride
4.3.4: Chemistry of Titanium
titration
4.7.2: Chemistry of Iron
titrations
4.6.2.1: Chemistry of Manganese
trans effect
5.7: The Trans Effect
transition metal
4.1.3: General Trends among the Transition Metals
4.1.4: Introduction to Transition Metals I
4.1.5: Introduction to Transition Metals II
4.1.7: Oxidation States of Transition Metals
4.2.3: Chemistry of Scandium
8.2.1: General Properties and Reactions of The Actinides
Transition Metal Ion
4.1.7: Oxidation States of Transition Metals
Transition Metal Ions
4.1.7: Oxidation States of Transition Metals
transition metals
4.1.2: Electron Configuration of Transition Metals
4.1.3: General Trends among the Transition Metals
4.1.4: Introduction to Transition Metals I
4.1.8: Transition Metals in Biology
8.1.1: Lanthanides- Properties and Reactions
transmetalation
6.6.1: Metal Alkyls
transuranium
8.2.10: Chemistry of Neptunium
transuranium elements
8.2.10: Chemistry of Neptunium
Trends
4.1.3: General Trends among the Transition Metals
trigonal bipyramidal
1.3.2: Valence Shell Electron-Pair Repulsion
Trigonal Planar
1.3.2: Valence Shell Electron-Pair Repulsion
trigonal prismatic coordination
2.5: Coordination Numbers and Structures
trigonal pyramidal
1.3.2: Valence Shell Electron-Pair Repulsion
tungsten
4.5.4: Chemistry of Tungsten
tungsten carbide
4.5.4: Chemistry of Tungsten

U

University of California at Berkeley
4.3.3: Chemistry of Rutherfordium
unnilseptium
4.6.1: Chemistry of Bohrium
unsaturated ligands
7.2.1: Introduction to Insertion
7.2.2: CO Insertions (Alkyl Migration)
uranium
8.2.1: General Properties and Reactions of The Actinides
8.2.15: Chemistry of Uranium
Uranus
8.2.15: Chemistry of Uranium

V

v
4.1.2: Electron Configuration of Transition Metals
valence electron
4.1.3: General Trends among the Transition Metals
valence shell electron pair repulsion theory
1.3.2: Valence Shell Electron-Pair Repulsion
Vanadis
4.4.4: Chemistry of Vanadium
vanadium
4.1.2: Electron Configuration of Transition Metals
4.4.4: Chemistry of Vanadium
4.4.5: Group 5 Elemental Properties
variable oxidation states
4.1.5: Introduction to Transition Metals II
vinylidenes
6.6.2: Carbenes
violett octaeders
4.5.1.2: Potassium Chromium Sulfate
VSEPR
1.3.2: Valence Shell Electron-Pair Repulsion

W

Wacker oxidation
6.5.1: Linear π Systems
Walton
8.2.11: Chemistry of Nobelium
water
4.1.5: Introduction to Transition Metals II
William Gregor
4.3.4: Chemistry of Titanium
William Wollaston
4.9.3: Chemistry of Palladium
Wittig reaction
6.6.2: Carbenes
Wrought iron
4.1.6.3: The Extraction of Iron
wurtzite
4.11.1.1: Cadmium Sulfide

Y

Ytterbium
8.1.14: Chemistry of Ytterbium
Ytterby
4.2.4: Chemistry of Yttrium
8.1.1: Lanthanides- Properties and Reactions
8.1.14: Chemistry of Ytterbium
8.1.15: Chemistry of Yttrium
Yttrium
4.2.4: Chemistry of Yttrium
8.1.15: Chemistry of Yttrium

Z

zeroth ionization energy
1.2.3.2: Electron Affinity
zinc
4.1.2: Electron Configuration of Transition Metals
4.1.5: Introduction to Transition Metals II
4.11.4: Chemistry of Zinc
zink
4.11.4: Chemistry of Zinc
zircon
4.3.5: Chemistry of Zirconium
Zirconium
4.3.5: Chemistry of Zirconium
Zn
4.1.2: Electron Configuration of Transition Metals

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: CHEM 4210: Inorganic Chem II (Siddiquee)

Webpages: 309

Applicable Restrictions: Noncommercial

All licenses found:

- Undeclared: 66.3% (205 pages)
- CC BY-NC 4.0: 11.7% (36 pages)
- CC BY-SA 4.0: 8.7% (27 pages)
- CC BY-NC 3.0: 5.5% (17 pages)
- CC BY-NC-SA 4.0: 3.6% (11 pages)
- CC BY 4.0: 3.6% (11 pages)
- CC BY-NC-SA 3.0: 0.6% (2 pages)

By Page

- CHEM 4210: Inorganic Chem II (Siddiquee) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Basic Inorganic Concepts - *Undeclared*
    - 1.1: Introduction to Inorganic Chemistry - *Undeclared*
      - 1.1.1: What is Inorganic Chemistry? - *Undeclared*
      - 1.1.2: Inorganic vs Organic Chemistry - *Undeclared*
      - 1.1.3: History of Inorganic Chemistry - *CC BY-NC-SA 4.0*
      - 1.1.4: Perspectives - *Undeclared*
      - 1.1.5: Practice problems - *Undeclared*
    - 1.2: Atomic Structure - *Undeclared*
      - 1.2.1: Historical Development of Atomic Theory - *Undeclared*
        - 1.2.1.1: The Periodic Table - *Undeclared*
        - 1.2.1.2: Discovery of Subatomic Particles and the Bohr Atom - *CC BY-NC-SA 3.0*
      - 1.2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions - *CC BY-NC-SA 4.0*
        - 1.2.2.1: Particle in a Box - *CC BY-NC-SA 4.0*
        - 1.2.2.2: Quantum Numbers and Atomic Wave Functions - *CC BY-NC-SA 4.0*
        - 1.2.2.3: Aufbau Principle - *CC BY-NC-SA 4.0*
        - 1.2.2.4: Shielding - *CC BY-NC-SA 4.0*
      - 1.2.3: Periodic Properties of Atoms - *Undeclared*
        - 1.2.3.1: Ionization energy - *CC BY-NC-SA 3.0*
        - 1.2.3.2: Electron Affinity - *CC BY-NC 4.0*
        - 1.2.3.3: Covalent and Ionic Radii - *CC BY-NC 4.0*
      - 1.2.4: Problems - *Undeclared*
    - 1.3: Simple Bonding Theory - *Undeclared*
      - 1.3.1: Lewis Electron-Dot Diagrams - *CC BY-NC 4.0*
        - 1.3.1.1: Resonance - *CC BY-NC 3.0*
        - 1.3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms) - *CC BY-NC 4.0*
        - 1.3.1.3: Formal Charge - *CC BY-NC 4.0*
        - 1.3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium - *CC BY-NC 4.0*
      - 1.3.2: Valence Shell Electron-Pair Repulsion - *CC BY-NC-SA 4.0*
        - 1.3.2.1: Lone Pair Repulsion - *Undeclared*
        - 1.3.2.2: Multiple Bonds - *Undeclared*
        - 1.3.2.3: Electronegativity and Atomic Size Effects - *Undeclared*
        - 1.3.2.4: Ligand Close Packing - *Undeclared*
      - 1.3.3: Molecular Polarity - *Undeclared*
      - 1.3.4: Hydrogen Bonding - *Undeclared*
      - 1.3.5: Problems - *Undeclared*
    - 1.4: Symmetry and Group Theory - *Undeclared*
      - 1.4.1: Symmetry Elements and Operations - *Undeclared*
      - 1.4.2: Point Groups - *Undeclared*
        - 1.4.2.1: Groups of Low and High Symmetry - *Undeclared*
        - 1.4.2.2: Other Groups - *Undeclared*

- 1.4.3: Properties and Representations of Groups - *Undeclared*
  - 1.4.3.1: Matrices - *Undeclared*
  - 1.4.3.2: Representations of Point Groups - *Undeclared*
  - 1.4.3.3: Character Tables - *Undeclared*
- 1.4.4: Examples and Applications of Symmetry - *Undeclared*
  - 1.4.4.1: Chirality - *CC BY-NC 4.0*
  - 1.4.4.2: Molecular Vibrations - *CC BY-NC 4.0*
- 1.4.P: Problems (under construction) - *Undeclared*

2: d-Block Metal Chemistry- General Considerations - *CC BY 4.0*
- 2.1: Prelude to Coordination Chemistry I - Structure and Isomers - *CC BY 4.0*
- 2.2: History - *CC BY-NC-SA 4.0*
- 2.3: Nomenclature and Ligands - *Undeclared*
- 2.4: Isomerism - *CC BY 4.0*
- 2.5: Coordination Numbers and Structures - *CC BY 4.0*
- 2.6: Coordination Frameworks - *CC BY 4.0*
- 2.P: Problems - *CC BY 4.0*

3: d-Block Metal Chemistry- Coordination Complexes - *CC BY-NC 3.0*
- 3.1: Evidence for Electronic Structures - *CC BY-NC 3.0*
  - 3.1.1: Thermodynamic Data - *CC BY-NC 4.0*
  - 3.1.2: Magnetic Susceptibility - *CC BY-NC 4.0*
  - 3.1.3: Electronic Spectra - *CC BY-NC 4.0*
  - 3.1.4: Coordination Number and Molecular Shapes - *CC BY-NC 4.0*
- 3.2: Bonding Theories - *CC BY-NC 3.0*
  - 3.2.1: Crystal Field Theory - *CC BY-NC 4.0*
- 3.3: Ligand Field Theory - *CC BY-NC 3.0*
  - 3.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex - *CC BY-NC 4.0*
  - 3.3.2: Orbital Splitting and Electron Spin - *CC BY-NC 4.0*
  - 3.3.3: Ligand Field Stabilization Energy - *CC BY-NC 4.0*
  - 3.3.4: Tetrahedral Complexes - *CC BY-NC 4.0*
  - 3.3.5: Square-Planar Complexes - *CC BY-NC 4.0*
- 3.4: Angular Overlap - *CC BY-NC 3.0*
  - 3.4.1: Sigma Bonding in the Angular Overlap Model - *CC BY-NC 4.0*
  - 3.4.2: Pi Acceptors in the Angular Overlap Model - *CC BY-NC 4.0*
  - 3.4.3: Pi Donors in the Angular Overlap Model - *CC BY-NC 4.0*
  - 3.4.4: The Spectrochemical Series - *CC BY-NC 4.0*
  - 3.4.5: The Magnitude of Parameters $e\sigma$, $e\pi$ and Δ - *CC BY-NC 4.0*
  - 3.4.6: The Magnetochemical Series - *CC BY-NC 4.0*
- 3.5: The Jahn-Teller Effect - *CC BY-NC 3.0*
- 3.6: Four- and Six-Coordinate Preferences - *CC BY-NC 3.0*
- 3.7: Other Shapes - *CC BY-NC 3.0*
- 3.P: Problems - *CC BY-NC 3.0*

4: d-Block Metal Chemistry - *Undeclared*
- 4.1: Properties of Transition Metals - *Undeclared*
  - 4.1.1: A Brief Survey of Transition-Metal Chemistry - *Undeclared*
  - 4.1.2: Electron Configuration of Transition Metals - *Undeclared*
  - 4.1.3: General Trends among the Transition Metals - *Undeclared*
  - 4.1.4: Introduction to Transition Metals I - *Undeclared*
  - 4.1.5: Introduction to Transition Metals II - *CC BY-NC 4.0*
  - 4.1.6: Metallurgy - *Undeclared*
    - 4.1.6.1: An Introduction to the Chemistry of Metal Extraction - *CC BY-NC 4.0*
    - 4.1.6.2: The Extraction of Copper - *CC BY-NC 4.0*
    - 4.1.6.3: The Extraction of Iron - *CC BY-NC 4.0*
      - 4.1.6.3.1: Iron Production - *Undeclared*
    - 4.1.6.4: The Extraction of Silver - *Undeclared*
      - 4.1.6.4.1: Preparation and uses of Silver chloride and Silver nitrate - *Undeclared*
  - 4.1.7: Oxidation States of Transition Metals - *Undeclared*
  - 4.1.8: Transition Metals in Biology - *CC BY-NC-SA 4.0*
- 4.2: Transition Metals - *Undeclared*
  - 4.2.1: Chemistry of Actinium - *Undeclared*
  - 4.2.2: Chemistry of Lanthanum - *Undeclared*
  - 4.2.3: Chemistry of Scandium - *Undeclared*
  - 4.2.4: Chemistry of Yttrium - *Undeclared*
  - 4.2.5: Group 3 Elemental Properties - *Undeclared*
- 4.3: Transition Metals - *Undeclared*
  - 4.3.1: Group 4 Elemental Properties - *Undeclared*
  - 4.3.2: Chemistry of Hafnium - *Undeclared*
  - 4.3.3: Chemistry of Rutherfordium - *Undeclared*
  - 4.3.4: Chemistry of Titanium - *Undeclared*
  - 4.3.5: Chemistry of Zirconium - *Undeclared*

- 4.4: Transition Metals - *Undeclared*
  - 4.4.1: Chemistry of Dubnium - *Undeclared*
  - 4.4.2: Chemistry of Niobium - *Undeclared*
  - 4.4.3: Chemistry of Tantalum - *Undeclared*
  - 4.4.4: Chemistry of Vanadium - *CC BY-NC 4.0*
  - 4.4.5: Group 5 Elemental Properties - *Undeclared*
- 4.5: Transition Metals - *Undeclared*
  - 4.5.1: Chemistry of Chromium - *Undeclared*
    - 4.5.1.1: Chemistry of Chromium - *CC BY-NC 4.0*
    - 4.5.1.2: Potassium Chromium Sulfate - *Undeclared*
  - 4.5.2: Chemistry of Molybdenum - *Undeclared*
    - 4.5.2.1: Molybdenum Disulfide - *Undeclared*
  - 4.5.3: Chemistry of Seaborgium - *Undeclared*
  - 4.5.4: Chemistry of Tungsten - *Undeclared*
- 4.6: Transition Metals - *Undeclared*
  - 4.6.1: Chemistry of Bohrium - *Undeclared*
  - 4.6.2: Chemistry of Manganese - *Undeclared*
    - 4.6.2.1: Chemistry of Manganese - *CC BY-NC 4.0*
  - 4.6.3: Chemistry of Rhenium - *Undeclared*
  - 4.6.4: Chemistry of Technetium - *Undeclared*
- 4.7: Transition Metals - *Undeclared*
  - 4.7.1: Chemistry of Hassium - *Undeclared*
  - 4.7.2: Chemistry of Iron - *CC BY-NC 4.0*
    - 4.7.2.1: Iron in Humans - *Undeclared*
  - 4.7.3: Chemistry of Osmium - *Undeclared*
  - 4.7.4: Chemistry of Ruthenium - *Undeclared*
- 4.8: Transition Metals - *Undeclared*
  - 4.8.1: Chemistry of Cobalt - *CC BY-NC 4.0*
  - 4.8.2: Chemistry of Iridium - *Undeclared*
  - 4.8.3: Chemistry of Meitnerium - *Undeclared*
  - 4.8.4: Chemistry of Rhodium - *Undeclared*
- 4.9: Transition Metals - *Undeclared*
  - 4.9.1: Chemistry of Darmstadtium - *Undeclared*
  - 4.9.2: Chemistry of Nickel - *Undeclared*
  - 4.9.3: Chemistry of Palladium - *Undeclared*
  - 4.9.4: Chemistry of Platinum - *Undeclared*
- 4.10: Transition Metals - *Undeclared*
  - 4.10.1: Chemistry of Copper - *CC BY-NC 4.0*
  - 4.10.2: Chemistry of Gold - *Undeclared*
  - 4.10.3: Chemistry of Roentgenium - *Undeclared*
  - 4.10.4: Chemistry of Silver - *Undeclared*
    - 4.10.4.1: Silver Chloride - *Undeclared*
    - 4.10.4.2: Silver Nitrate - *Undeclared*
- 4.11: Transition Metals - *Undeclared*
  - 4.11.1: Chemistry of Cadmium - *Undeclared*
    - 4.11.1.1: Cadmium Sulfide - *Undeclared*
  - 4.11.2: Chemistry of Copernicium - *Undeclared*
  - 4.11.3: Chemistry of Mercury - *Undeclared*
  - 4.11.4: Chemistry of Zinc - *Undeclared*

- 5: Reactions of Complexes - *Undeclared*
  - 5.1: Introduction to Reactions of Metal Complexes - *CC BY-NC 3.0*
  - 5.2: Substitutions Reactions - *Undeclared*
    - 5.2.1: Introduction to Substitution Reactions - *Undeclared*
    - 5.2.2: Inert and Labile Complexes - *Undeclared*
    - 5.2.3: Mechanistic Possibilities - *CC BY-NC 3.0*
  - 5.3: Kinetics Hint at the Reaction Mechanism - *CC BY-SA 4.0*
    - 5.3.1: Rate Law for Dissociative Mechanisms - *CC BY-SA 4.0*
    - 5.3.2: Rate Laws for Interchange Mechanisms - *CC BY-SA 4.0*
    - 5.3.3: Rate Law for Associative Mechanisms - *CC BY-NC 3.0*
    - 5.3.4: Preassociation Complexes - *CC BY-NC 3.0*
    - 5.3.5: Activation Parameters - *CC BY-NC 3.0*
    - 5.3.6: Some Reasons for Differing Mechanisms - *CC BY-NC 3.0*
  - 5.4: Experimental Evidence in Octahedral Substitutions - *Undeclared*
    - 5.4.1: Dissociation - *Undeclared*
    - 5.4.2: Linear Free Energy Relationships - *Undeclared*
    - 5.4.3: Associative Mechanisms - *Undeclared*
    - 5.4.4: The conjugate base mechanism - *Undeclared*
    - 5.4.5: The Kinetic Chelate Effect - *Undeclared*
  - 5.5: Stereochemistry of Octahedral Reactions - *Undeclared*
    - 5.5.1: Substitution in trans-en octahedral complexes - *Undeclared*
    - 5.5.2: Substitution in cis-en octahedral complexes - *Undeclared*
    - 5.5.3: Isomerization of Chelate Rings - *Undeclared*
  - 5.6: Substitutions in Square Planar Complexes - *Undeclared*
    - 5.6.1: Kinetics and Stereochemistry of Square Planar Reactions - *Undeclared*
    - 5.6.2: Evidence for Associative Reactions - *Undeclared*
  - 5.7: The Trans Effect - *CC BY-NC 3.0*
  - 5.8: Redox Mechanisms - *Undeclared*

- 5.8.1: Outer Sphere Electron Transfer - *CC BY-NC 4.0*
- 5.8.2: Inner Sphere Electron Transfer - *CC BY-NC 4.0*
- 5.9: Reactions of Coordinated Ligands - *Undeclared*
  - 5.9.1: Metal-catalyzed Hydrolysis - *Undeclared*
  - 5.9.2: Template Reactions - *Undeclared*
  - 5.9.3: Electrophilic Substitutions - *Undeclared*

6: Catalysis - *Undeclared*
- 6.1: Introduction to Organometallic Chemistry - *Undeclared*
- 6.2: Nomenclature, Ligands, and Classification - *Undeclared*
- 6.3: Electron Counting in Organometallic Complexes - *Undeclared*
  - 6.3.1: The 18 Electron Rule - *CC BY 4.0*
  - 6.3.2: Simplifying the Organometallic Complex by Deconstruction - *Undeclared*
- 6.4: Survey of Organometallic Ligands - *Undeclared*
  - 6.4.1: Carbon Monoxide (Carbonyl Complexes) - *Undeclared*
  - 6.4.2: Ligands similar to CO - *CC BY 4.0*
  - 6.4.3: Hydrides and Dihydrogen Complexes - *Undeclared*
- 6.5: Bonding between Metal Atoms and Organic Pi Systems - *Undeclared*
  - 6.5.1: Linear π Systems - *Undeclared*
  - 6.5.2: Cyclic π systems - *Undeclared*
  - 6.5.3: Odd-numbered π Systems - *Undeclared*
  - 6.5.4: Fullerene Complexes - *Undeclared*
- 6.6: Metal-Carbon Bonds - *Undeclared*
  - 6.6.1: Metal Alkyls - *Undeclared*
  - 6.6.2: Carbenes - *Undeclared*
  - 6.6.3: Carbyne (Alkylidyne) Complexes - *Undeclared*
  - 6.6.4: Carbido and Cumulene Complexes - *CC BY-SA 4.0*
  - 6.6.5: Carbon Wires- Polyyne and Polyene Bridges - *Undeclared*
- 6.7: Characterization of Organometallic Complexes - *CC BY-NC-SA 4.0*

7: Organometallic Reactions and Catalysis - *Undeclared*
- 7.1: Reactions Involving Gain or Loss of Ligands - *Undeclared*
  - 7.1.1: Ligand Dissociation and Substitution - *Undeclared*
  - 7.1.2: Oxidative Addition - *Undeclared*
  - 7.1.3: Reductive Elimination - *Undeclared*
  - 7.1.4: Sigma Bond Metathasis - *Undeclared*
  - 7.1.5: Application of Pincer Ligands - *Undeclared*
- 7.2: Reactions Invloving Modification of Unsaturated Ligands - *Undeclared*
  - 7.2.1: Introduction to Insertion - *Undeclared*
  - 7.2.2: CO Insertions (Alkyl Migration) - *Undeclared*
  - 7.2.3: Migratory Insertion-1,2-Insertions - *Undeclared*
  - 7.2.4: β-Elimination Reactions - *Undeclared*
  - 7.2.5: Abstraction and Addition - *Undeclared*
- 7.3: Organometallic Catalysts - *CC BY 4.0*
  - 7.3.1: Catalytic Deuteration - *Undeclared*
  - 7.3.2: Hydroformylation - *Undeclared*
  - 7.3.3: Monsanto Acetic Acid Process - *Undeclared*
  - 7.3.4: Wacker (Smidt) Process - *Undeclared*
  - 7.3.5: Hydrogenation by Wilkinson's Catalyst - *Undeclared*
  - 7.3.6: Olefin Metathesis - *Undeclared*
- 7.4: Heterogeneous Catalysts - *Undeclared*
  - 7.4.1: Ziegler-Natta Polymerizations - *CC BY-NC-SA 4.0*
  - 7.4.2: Water-Gas Shift Reaction - *Undeclared*
- 7.5: Problems - *Undeclared*
  - 7.5.1: Concept Review Questions Chapter 12 - *CC BY 4.0*
  - 7.5.2: Homework Problems Chapter 12 - *CC BY 4.0*

8: Lanthanides and Actinides - *Undeclared*
- 8.1: The Lanthanides - *Undeclared*
  - 8.1.1: Lanthanides- Properties and Reactions - *Undeclared*
    - 8.1.1.1: Lanthanide Contraction - *Undeclared*
  - 8.1.2: Chemistry of Cerium - *Undeclared*
  - 8.1.3: Chemistry of Dysprosium - *Undeclared*
  - 8.1.4: Chemistry of Europium - *Undeclared*
  - 8.1.5: Chemistry of Gadolinium - *Undeclared*
    - 8.1.5.1: Gadolinium(III) Chloride - *Undeclared*
  - 8.1.6: Chemistry of Holmium - *Undeclared*
  - 8.1.7: Chemistry of Lutetium - *Undeclared*
  - 8.1.8: Chemistry of Neodymium - *Undeclared*
  - 8.1.9: Chemistry of Praseodymium - *Undeclared*
  - 8.1.10: Chemistry of Promethium - *Undeclared*
  - 8.1.11: Chemistry of Samarium - *Undeclared*
  - 8.1.12: Chemistry of Terbium - *Undeclared*
  - 8.1.13: Chemistry of Thulium - *Undeclared*
  - 8.1.14: Chemistry of Ytterbium - *Undeclared*
  - 8.1.15: Chemistry of Yttrium - *Undeclared*
- 8.2: The Actinides - *Undeclared*

- 8.2.1: General Properties and Reactions of The Actinides - *Undeclared*
- 8.2.2: Chemistry of Americium - *Undeclared*
- 8.2.3: Chemistry of Berkelium - *Undeclared*
- 8.2.4: Chemistry of Californium - *Undeclared*
- 8.2.5: Chemistry of Curium - *Undeclared*
- 8.2.6: Chemistry of Einsteinium - *Undeclared*
- 8.2.7: Chemistry of Fermium - *Undeclared*
- 8.2.8: Chemistry of Lawrencium - *Undeclared*
- 8.2.9: Chemistry of Mendelevium - *Undeclared*
- 8.2.10: Chemistry of Neptunium - *Undeclared*
- 8.2.11: Chemistry of Nobelium - *Undeclared*
- 8.2.12: Chemistry of Plutonium - *Undeclared*
- 8.2.13: Chemistry of Protoactinium - *Undeclared*
- 8.2.14: Chemistry of Thorium - *Undeclared*
- 8.2.15: Chemistry of Uranium - *Undeclared*

- 9: Inorganic Materials and Nanotechnology - *Undeclared*
  - 9.1: Electronic Properties of Materials - Superconductors and Semiconductors - *CC BY-SA 4.0*
    - 9.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors - *CC BY-SA 4.0*
    - 9.1.2: Metal-Insulator Transitions - *CC BY-SA 4.0*
    - 9.1.3: Superconductors - *CC BY-SA 4.0*
    - 9.1.4: Periodic Trends- Metals, Semiconductors, and Insulators - *CC BY-SA 4.0*
    - 9.1.5: Semiconductors- Band Gaps, Colors, Conductivity and Doping - *CC BY-SA 4.0*
    - 9.1.6: Semiconductor p-n Junctions - *CC BY-SA 4.0*
    - 9.1.7: Diodes, LEDs and Solar Cells - *CC BY-SA 4.0*
    - 9.1.8: Amorphous Semiconductors - *CC BY-SA 4.0*
    - 9.1.9: Discussion Questions - *CC BY-SA 4.0*
    - 9.1.10: Problems - *CC BY-SA 4.0*
    - 9.1.11: References - *CC BY-SA 4.0*
  - 9.2: Basic Science of Nanomaterials - *CC BY-SA 4.0*
    - 9.2.1: Prelude to Basic Science of Nanomaterials - *CC BY-SA 4.0*
    - 9.2.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets - *CC BY-SA 4.0*
    - 9.2.3: Semiconductor Quantum Dots - *CC BY-SA 4.0*
    - 9.2.4: Synthesis of Semiconductor Nanocrystals - *CC BY-SA 4.0*
    - 9.2.5: Surface Energy - *CC BY-SA 4.0*
    - 9.2.6: Nanoscale Metal Particles - *CC BY-SA 4.0*
    - 9.2.7: Applications of Nanomaterials - *CC BY-SA 4.0*
    - 9.2.8: Discussion Questions - *CC BY-SA 4.0*
    - 9.2.9: Problems - *CC BY-SA 4.0*
    - 9.2.10: References - *CC BY-SA 4.0*

- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*