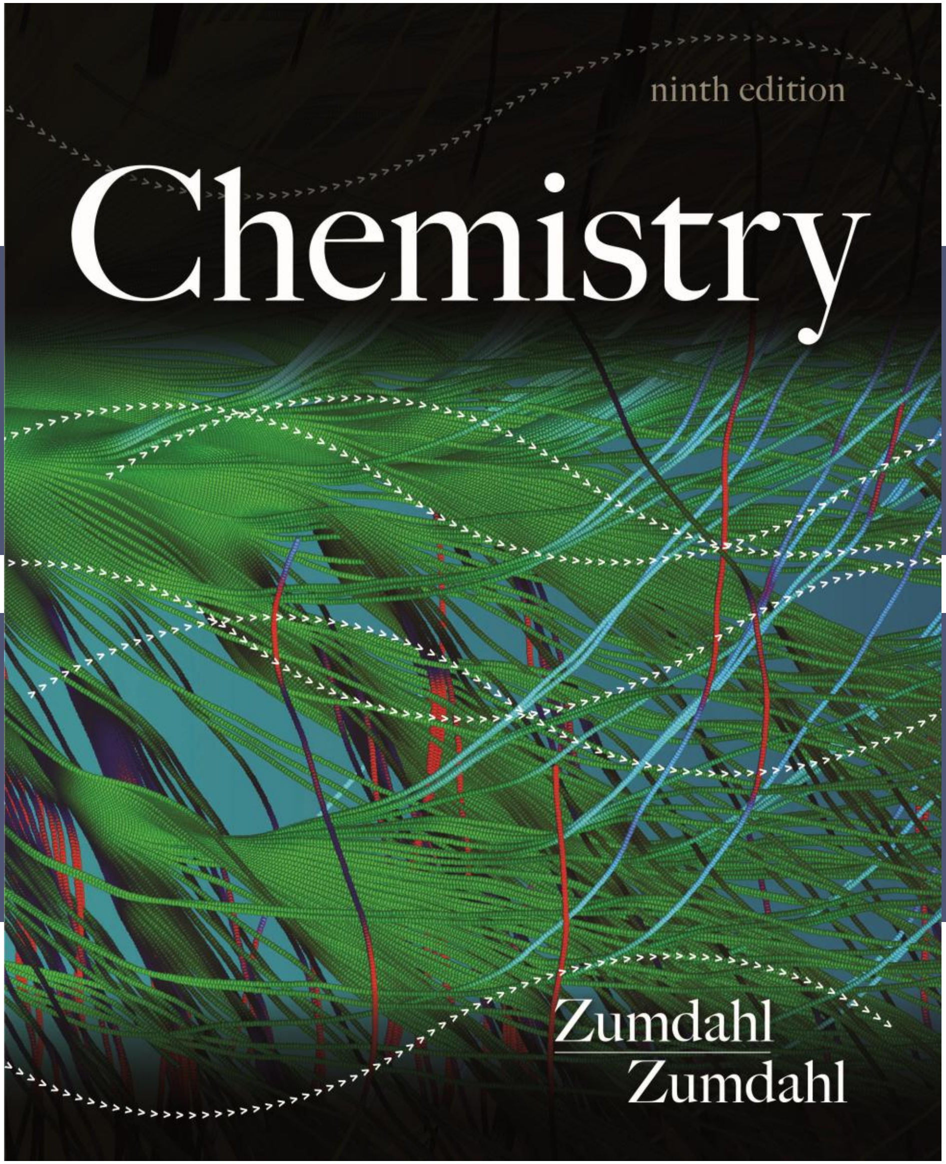

Chapter 21

Transition Metals and Coordination Chemistry

Chapter 21

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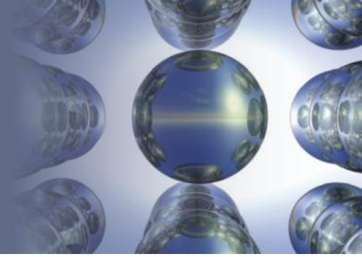
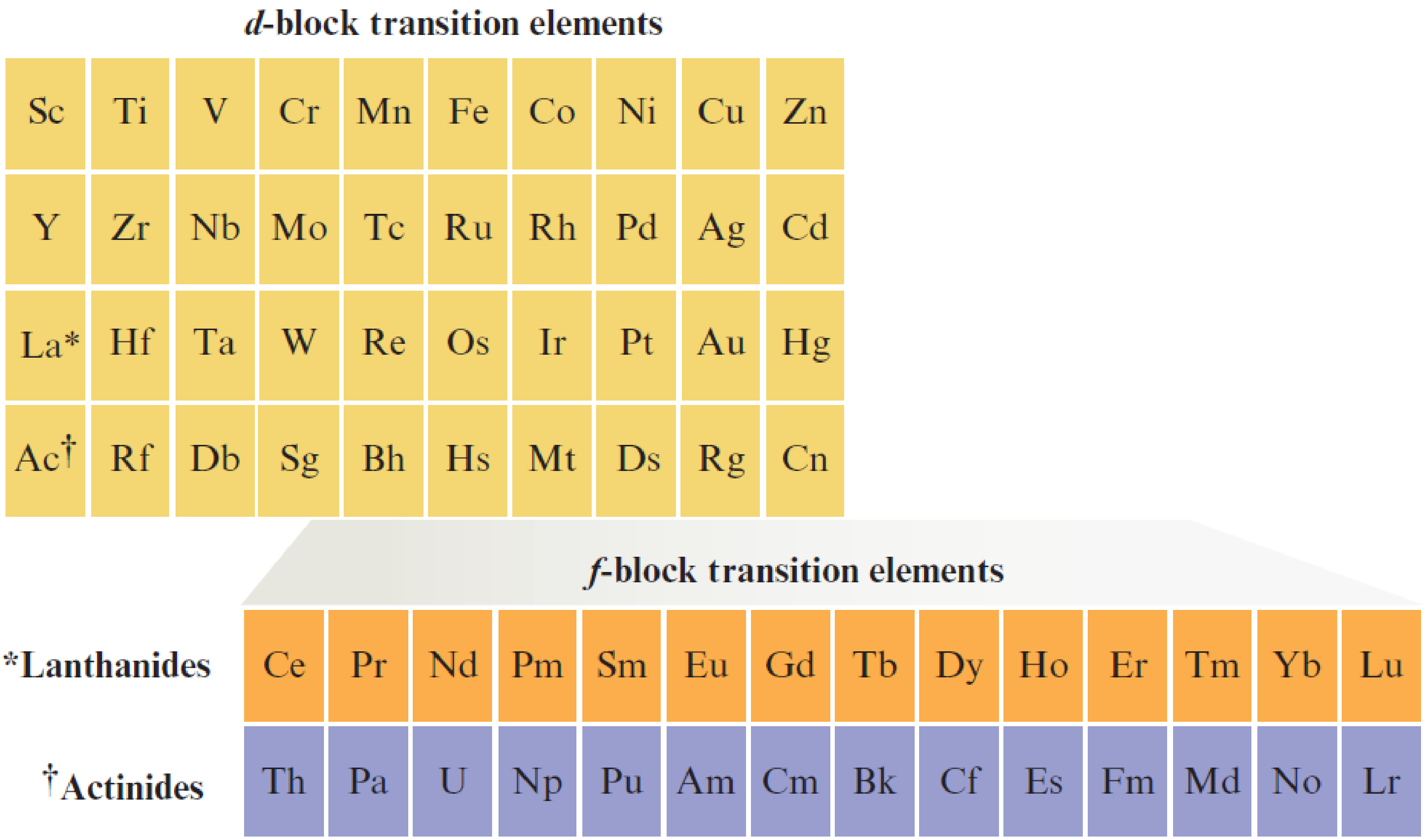


Transition Metals - Properties

- Show great similarities within a given period and a given vertical group
  - Attributed to the fact that inner electrons are the last electrons added
    - *d*-block transition metals receive *d* electrons
    - Lanthanides and actinides receive *f* electrons
    - Inner electrons cannot participate easily in bonding

Figure 21.1 - Transition Elements on the Periodic Table

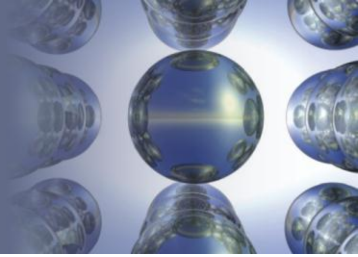


d-block transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac†	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn

f-block transition elements

***Lanthanides**	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Transition Metals - Properties (Continued 1)

- Behave like typical metals
  - Possess metallic luster and high electrical and thermal conductivities
- Display variations in physical properties
  - Melting points
    - Tungsten - 3400° C
    - Mercury - 25° C
  - Iron and titanium are hard and strong, whereas copper and gold are relatively soft

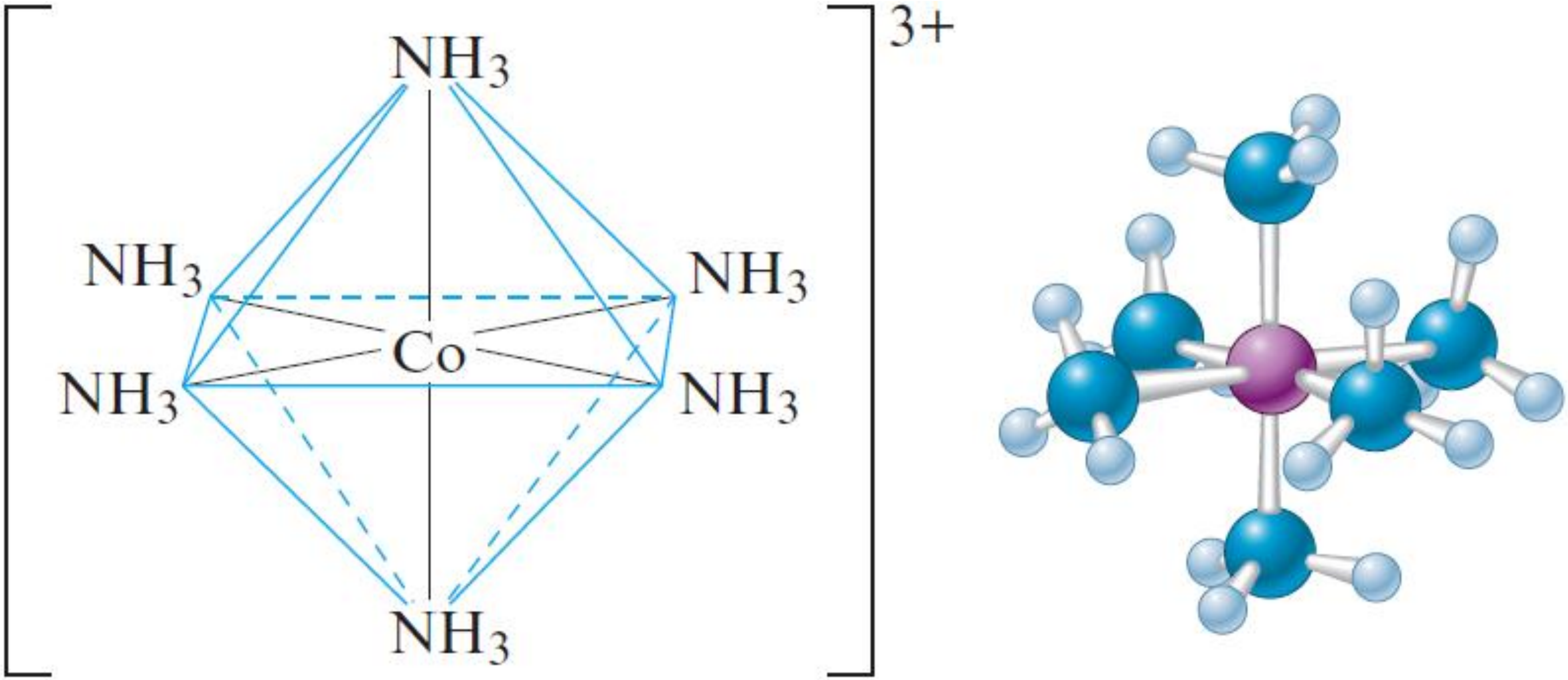
Transition Metals - Properties (Continued 2)

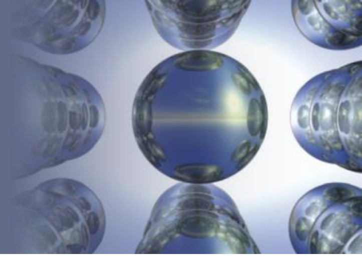
- Display variations in chemical reactivity
  - Example - Some transition metals react readily to form oxides
    - The oxides of chromium, nickel, and cobalt adhere to the metallic surface and protect the metal from further oxidation
    - The oxide of iron scales off, exposing new metal to corrosion

Forming Ionic Compounds - Trends

- More than one oxidation state is often found
- Cations are often complex ions
  - **Complex ions**: Species where the transition metal ion is surrounded by a certain number of ligands
    - Ligands - Molecules or ions that behave as Lewis bases
  - Example
    - $[Co(NH_3)_6]Cl_3$ contains $Co(NH_3)_6^{3+}$ cations and Cl^- anions

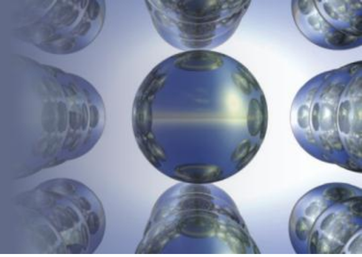
A Complex Ion - $Co(NH_3)_6^{3+}$





Forming Ionic Compounds - Trends (Continued)

- Compounds are colored
  - Transition metal ion in the complex ion can absorb visible light of specific wavelengths
- Compounds are paramagnetic
  - Contain unpaired electrons



First-Row Transition Metals - Electron Configurations

- 3*d* orbitals begin to fill after the 4*s* orbital is complete
- Exceptions
    - Chromium (Cr) - $[\mathrm{Ar}]4s^1 3d^5$
    - Copper - $[\mathrm{Ar}]4s^1 3d^{10}$
- A set of orbitals with the same energy is said to be degenerate

First-Row Transition Metals - Electron Configurations

(Continued)

- First-row transition metal ions do not have 4*s* electrons
  - Energy of the 3*d* orbitals is significantly less than that of the 4*s* orbital
  - Example
    - Configuration of neutral titanium - $[Ar]4s^2 3d^2$
    - Configuration of Ti^{3+} - $[Ar]3d^1$

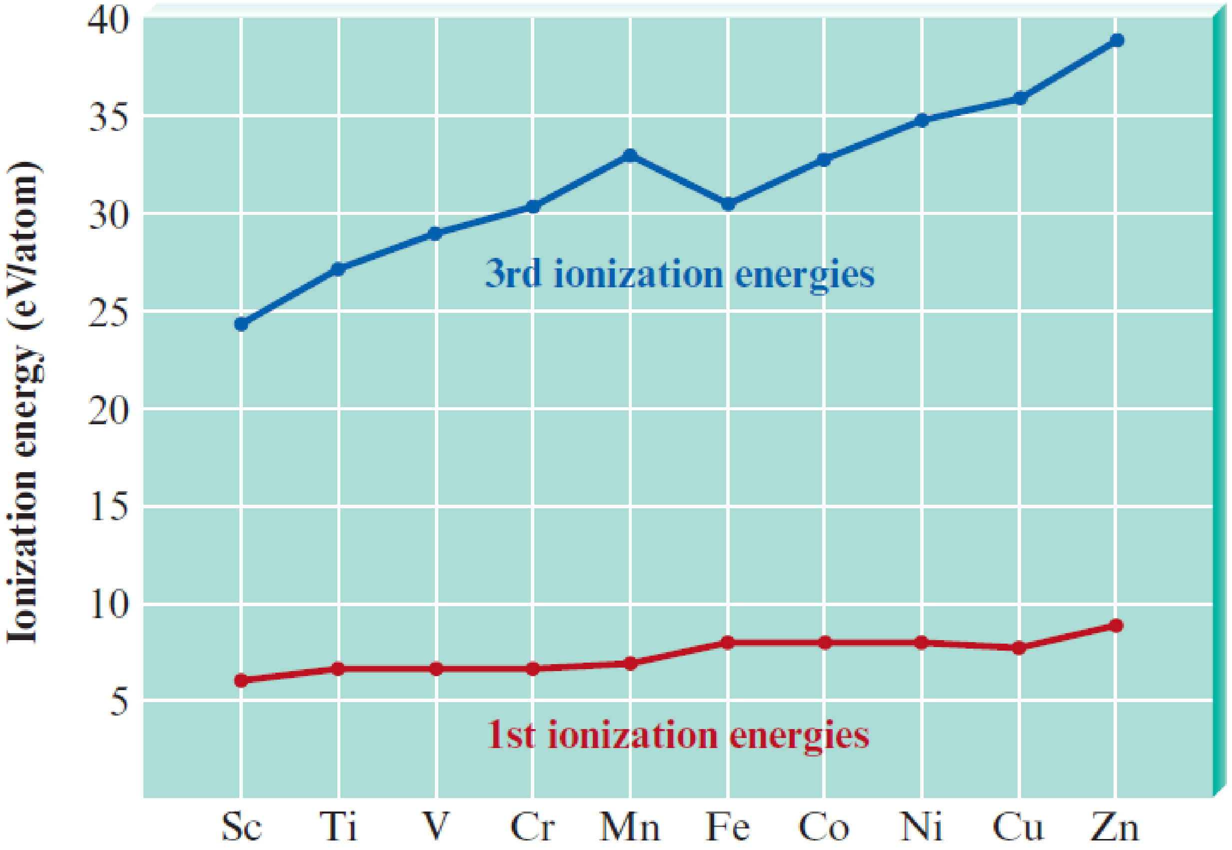
Oxidation States

- Transition metals can form a variety of ions by losing one or more electrons
- Note
    - For the first five elements, the maximum possible oxidation state is related to the loss of all the 4*s* and 3*d* electrons

Ionization Energy

- Increases gradually from left to right across the period
  - Third ionization energy increases faster than the first ionization energy
    - Proves that there is significant decline in the energy of the 3*d* orbitals while going across the period

Figure 21.2 - Plots of the First and Third Ionization Energies for the First-Row Transition Metals



Standard Reduction Potentials

- Half-reaction of a metal that acts as a reducing agent

$$\mathrm{M} \rightarrow \mathrm{M}^{n+} + ne^{-}$$

  - This is the reverse of the conventional half-reactions
- The metal with most positive potential is the best reducing agent

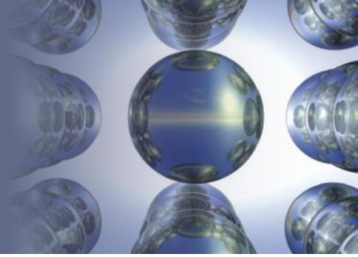
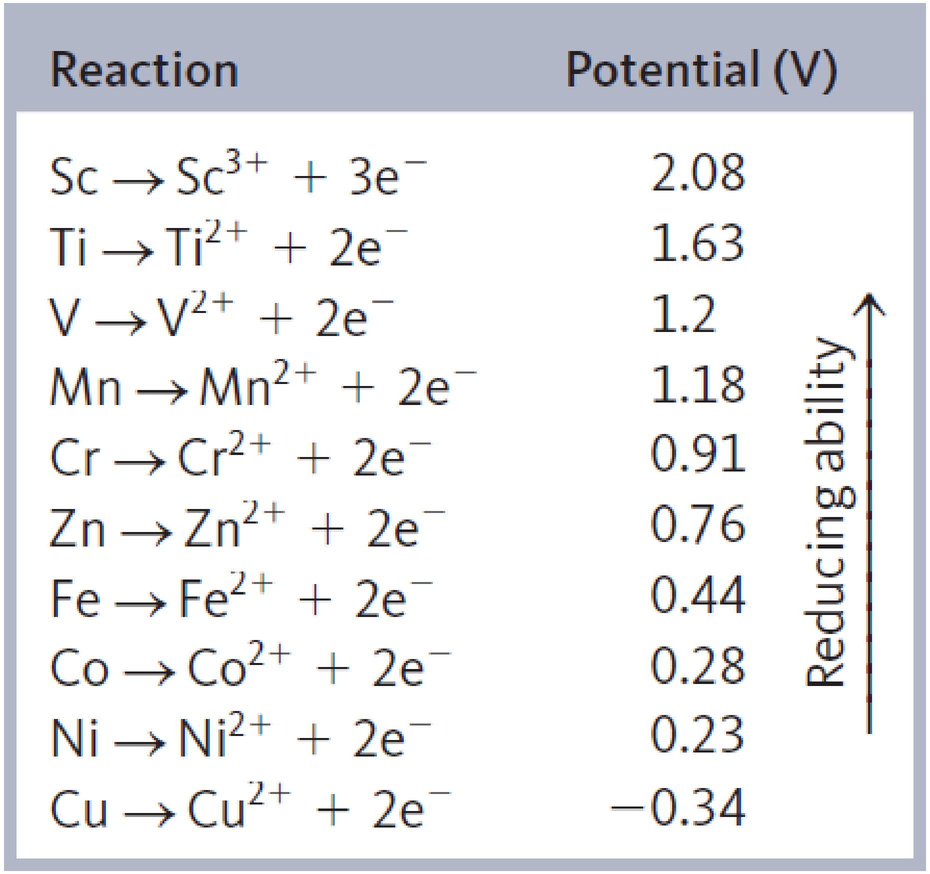


Table 21.3 - Relative Reducing Abilities of the First-Row Transition Metals in Aqueous Solution



Reaction	Potential (V)
$Sc \rightarrow Sc^{3+} + 3e^-$	2.08
$Ti \rightarrow Ti^{2+} + 2e^-$	1.63
$V \rightarrow V^{2+} + 2e^-$	1.2
$Mn \rightarrow Mn^{2+} + 2e^-$	1.18
$Cr \rightarrow Cr^{2+} + 2e^-$	0.91
$Zn \rightarrow Zn^{2+} + 2e^-$	0.76
$Fe \rightarrow Fe^{2+} + 2e^-$	0.44
$Co \rightarrow Co^{2+} + 2e^-$	0.28
$Ni \rightarrow Ni^{2+} + 2e^-$	0.23
$Cu \rightarrow Cu^{2+} + 2e^-$	−0.34

Standard Reduction Potentials (Continued)

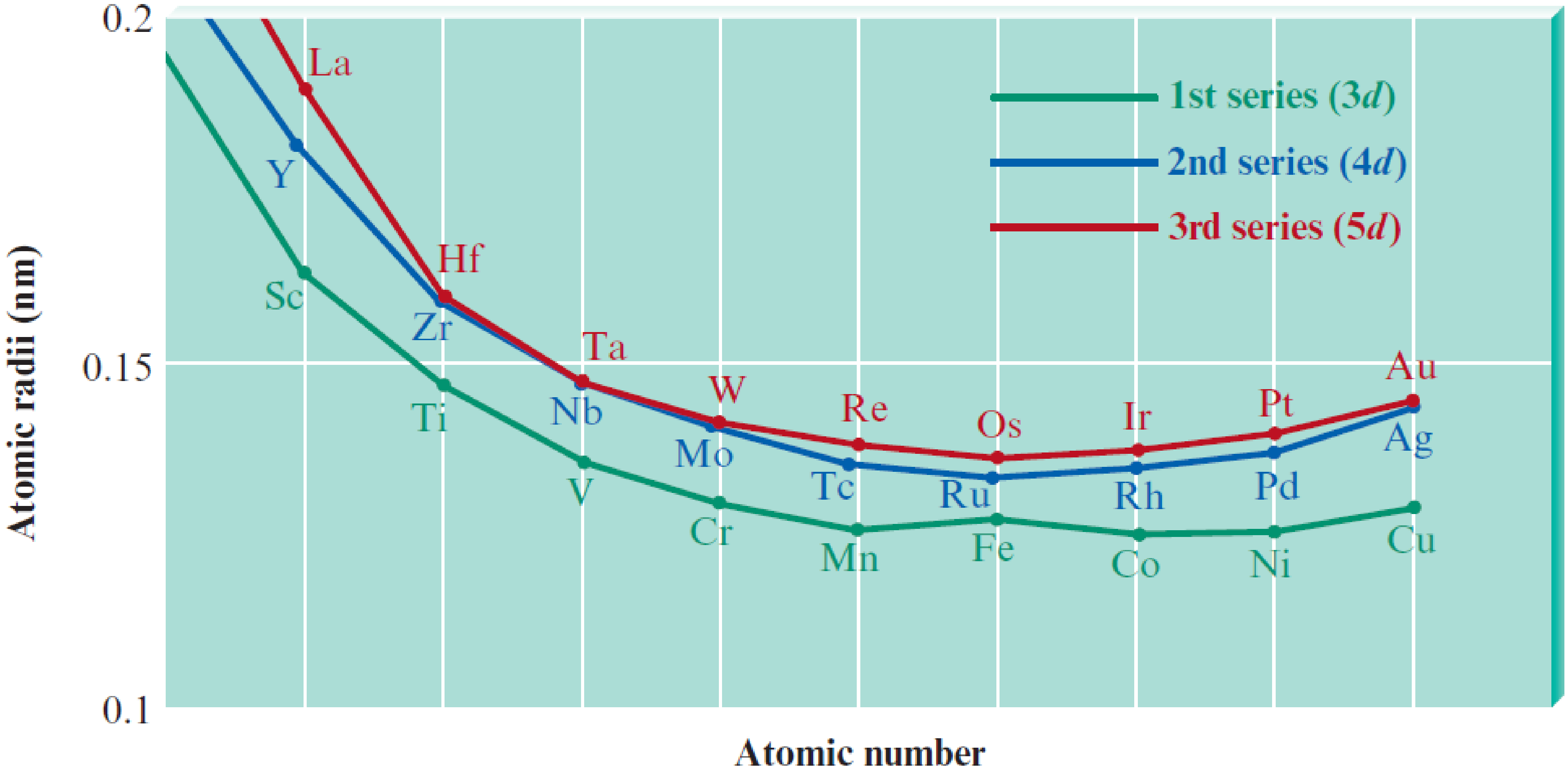
$$2H^{+} + 2e^{-} \rightarrow H_2$$

- For this reaction, E° = 0
    - All metals except Cu can reduce H^{+} ions to $H_2(g)$ in 1 *M* aqueous solution of strong acid

$$M(s) + 2H^{+}(aq) \rightarrow H_2(g) + M^{2+}(aq)$$

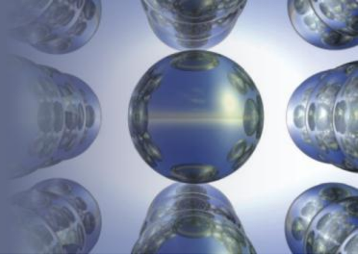
- The reducing abilities of the first-row transition metals decrease going from left to right across the period
    - Exceptions - Chromium and zinc

Figure 21.3 - Atomic Radii of the 3*d*, 4*d*, and 5*d* Transition Series



4*d* and 5*d* Transition Series - Trends

- 4*d* and 5*d* metals are similar in size
- **Lanthanide contraction**: The decrease in the atomic radii of the **lanthanide series** elements, going from left to right in the periodic table
  - Caused by increase in nuclear charge
  - Offsets the normal increase in size due to going from one principal quantum level to another



4*d* and 5*d* Transition Series - Trends (Continued 1)

- Differences in size between 4*d* and 5*d* transition elements in a group increase gradually from left to right
- Useful properties of 4*d* and 5*d* metals
  - Zirconium and zirconium oxide are highly resistant to high temperatures
    - Used along with niobium and molybdenum alloys in space vehicle parts

4*d* and 5*d* Transition Series - Trends (Continued 2)

- Tantalum displays high resistance to the attack of body fluids
    - Used for replacement of bones
- Platinum group metals
    - Used as catalysts for industrial processes

Scandium

- Rare element
- Exists in compounds in the +3 oxidation state
- Chemistry strongly resembles that of the lanthanides
    - Most of its compounds are colorless and diamagnetic
- Scandium metal is prepared by electrolysis of molten $ScCl_3$

Titanium

- Low density and high strength
  - Used in jet engines and to make pipes, pumps, and reaction vessels in the chemical industry
- Titanium(IV) oxide, TiO_2
  - Highly opaque substance
    - Used as white pigment in paper, paint, and plastics
  - Main ores - Rutile and ilmenite
- Exists in compounds in the +4 oxidation state

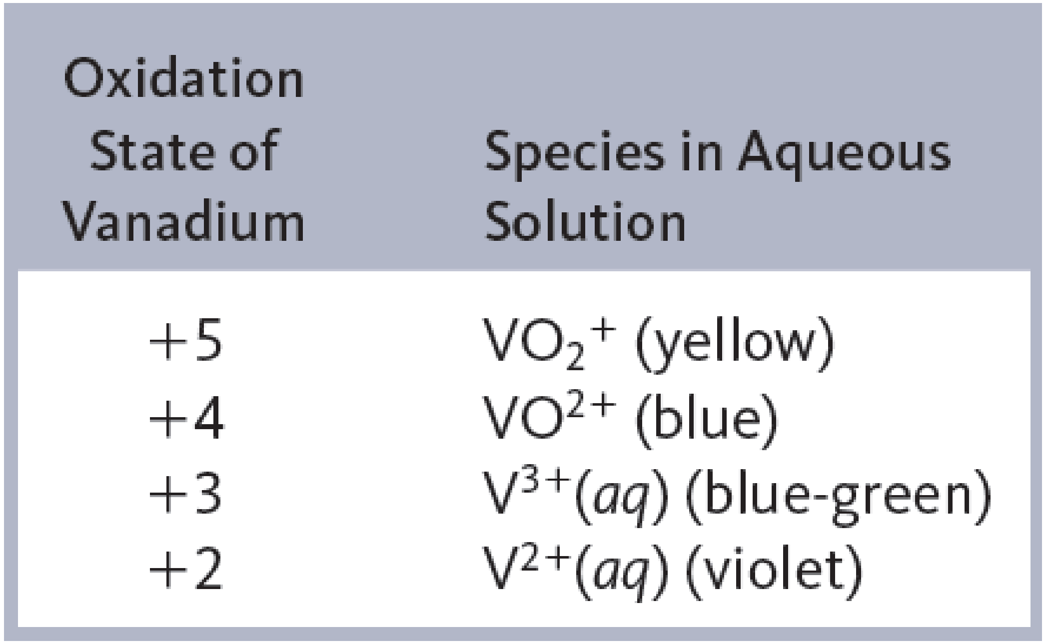
Titanium (Continued)

- Titanium(III) compounds
  - Produced by reduction of the +4 state
  - Exists as the purple $Ti(H_2O)_6^{3+}$ ion in aqueous solution
    - Slowly oxidized to titanium(IV) by air
- Titanium(II)
  - Not stable in aqueous solution
  - Exists in solid state in compounds such as TiO and the dihalides of general formula TiX_2

Vanadium

- Used in alloys with titanium and iron
- Hard and corrosion resistant
- Vanadium(V) oxide (V_2O_5)
  - Useful industrial catalyst for the production of sulfuric acid
- Pure form can be extracted from the electrolytic reduction of fused salts
- Principal oxidation state: +5

Table 21.4 - Oxidation States and Species for Vanadium in Aqueous Solution



Oxidation State of Vanadium	Species in Aqueous Solution
+5	VO_2^+ (yellow)
+4	VO^{2+} (blue)
+3	$V^{3+}(aq)$ (blue-green)
+2	$V^{2+}(aq)$ (violet)

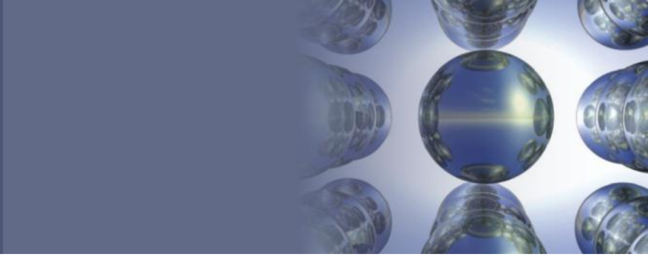
Chromium

- Rare element and an important industrial material
- Chief ore - Chromite ($FeCr_2O_4$)
  - Reduced by carbon to produce ferrochrome, which can be added to iron for making steel

$$\mathrm{FeCr_2O_4}(s) + 4\mathrm{C}(s) \rightarrow \underbrace{\mathrm{Fe}(s) + 2\mathrm{Cr}(s)}_{\text{Ferrochrome}} + 4\mathrm{CO}(g)$$

Chromium (Continued 1)

- Chromium metal
  - Hard and brittle
  - Maintains a bright surface by creating a tough invisible oxide coating
- Forms compounds in which Cr has the oxidation state +2, +3, or +6
- Chromous ion (Cr^{2+}) is a powerful reducing agent in aqueous solution



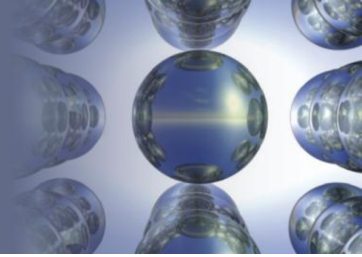
Chromium (Continued 2)

- Chromium (VI) species are excellent oxidizing agents in acidic solution
  - Reduction of dichromate ion ($Cr_2O_7^{2-}$) to the Cr^{3+} ion
    - Oxidizing ability of dichromate ion is pH-dependent

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E° = 1.33\ V$$

  - Exists as the chromate ion in a basic solution
    - Less powerful as an oxidizing agent

$$Cr_2O_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightarrow Cr(OH)_3(s) + 5OH^-(aq) \qquad E° = -0.13\ V$$



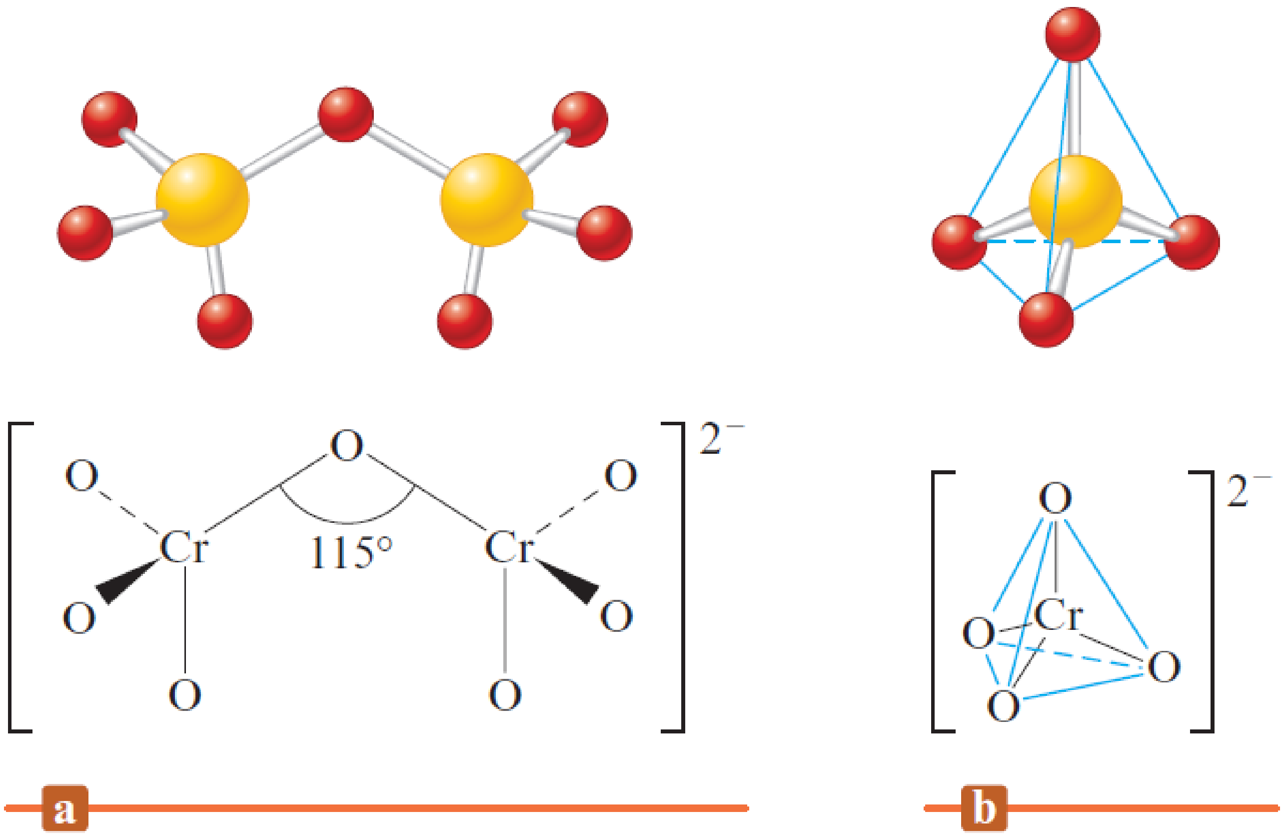
Chromium (Continued 3)

- Red chromium(VI) oxide dissolves in H_2O
    - Product is a strongly acidic, red-orange solution

$$2CrO_3(s) + H_2O(l) \rightarrow 2H^+(aq) + Cr_2O_7^{2-}(aq)$$

- When made basic, the solution turns yellow
    - Chromate salts can be obtained
- Cleaning solution - Mixture of chromium(VI) oxide and concentrated H_2SO_4
    - Powerful oxidizing medium that can remove organic materials from analytical glassware

Figure 21.4 - Structures of the Chromium(VI) Anions



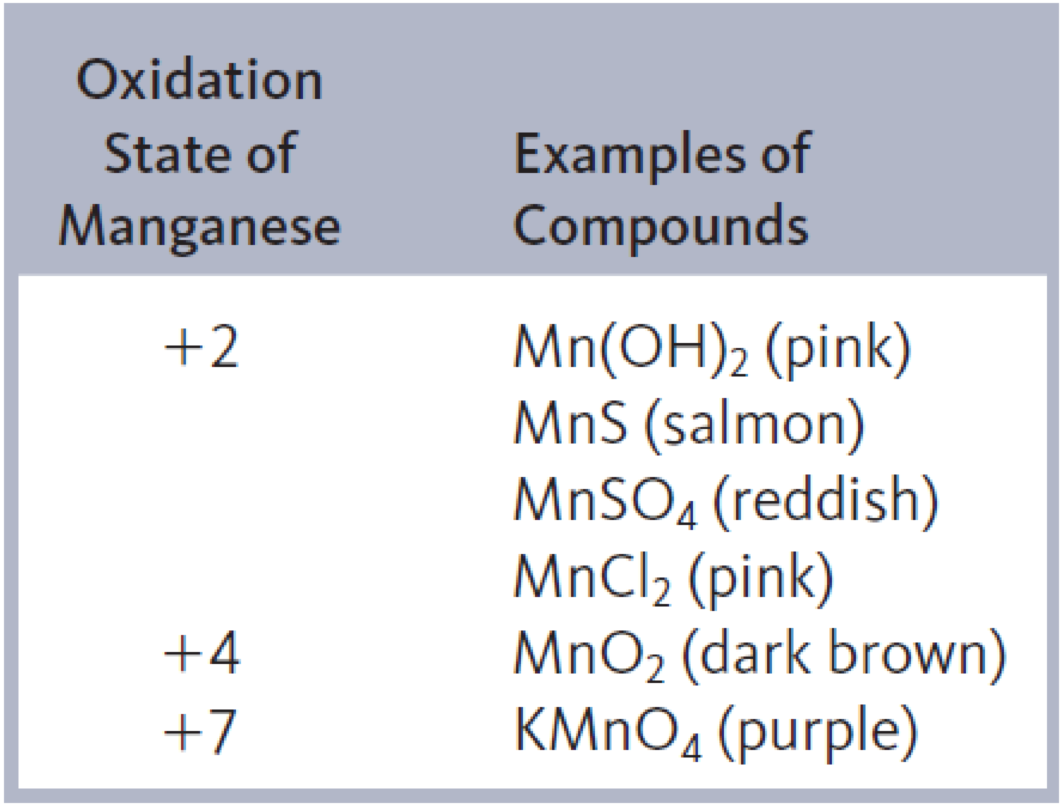
$Cr_2O_7^{2-}$ exists in acidic solution

CrO_4^{2-} exists in basic solution

Manganese

- Used for producing hard steel, which is used for rock crushers, bank vaults, and armor plates
- Source - Manganese nodules
    - Found on the ocean floor in the form of spherical rocks
        - Rocks contain mixtures of manganese, iron oxides, and small traces of cobalt, nickel, and copper
- Exists in all oxidation states from +2 to +7

Table 21.6 - Some Compounds of Manganese in its most Common Oxidation States

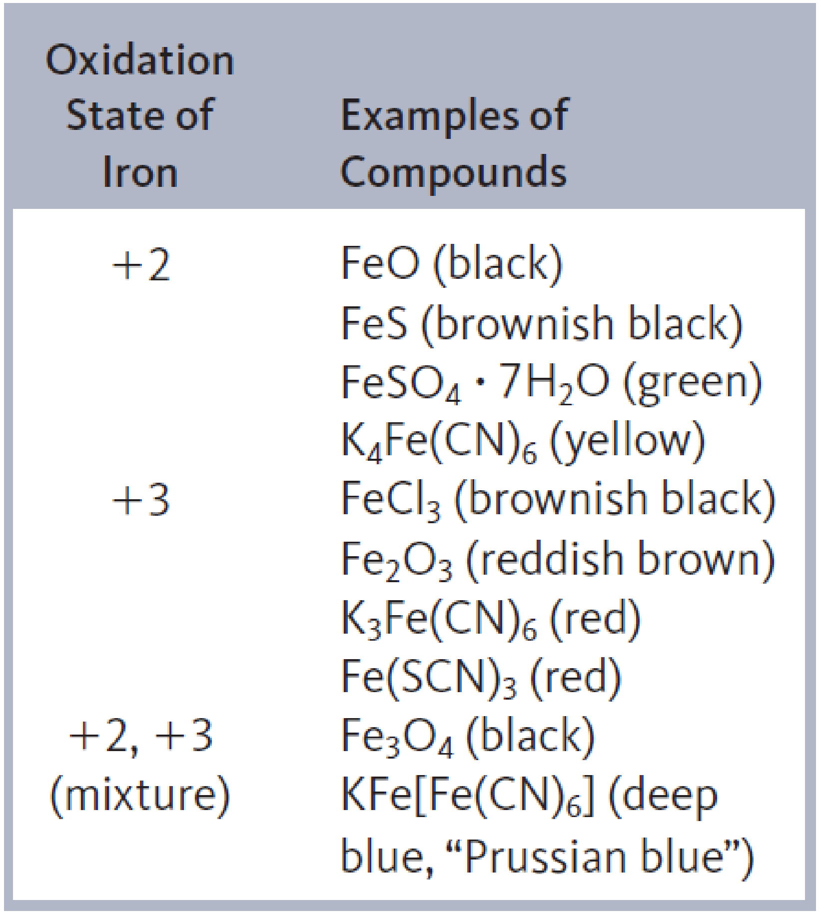


Oxidation State of Manganese	Examples of Compounds
+2	$Mn(OH)_2$ (pink) MnS (salmon) $MnSO_4$ (reddish) $MnCl_2$ (pink)
+4	MnO_2 (dark brown)
+7	$KMnO_4$ (purple)

Iron

- Most abundant heavy metal
- Appears white and lustrous
- Highly reactive toward oxidizing agents
    - Example - Iron rapidly oxidizes in moist air to form rust
- Chemistry of iron involves its +2 and +3 oxidation states

Table 21.7 - Typical Compounds of Iron



Oxidation State of Iron	Examples of Compounds
+2	FeO (black)
	FeS (brownish black)
	$FeSO_4 \cdot 7H_2O$ (green)
	$K_4Fe(CN)_6$ (yellow)
+3	$FeCl_3$ (brownish black)
	Fe_2O_3 (reddish brown)
	$K_3Fe(CN)_6$ (red)
	$Fe(SCN)_3$ (red)
+2, +3 (mixture)	Fe_3O_4 (black)
	$KFe[Fe(CN)_6]$ (deep blue, “Prussian blue”)

Cobalt

- Rare element
    - Ores - Smaltite ($CoAs_2$) and cobaltite ($CoAsS$)
- Appears bluish white
- Used in alloys such as stainless steel and stellite
- Chemistry of cobalt involves its +2 and +3 oxidation states
- Forms a wide variety of coordination compounds

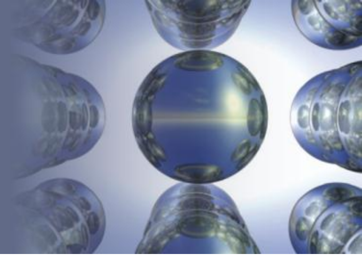
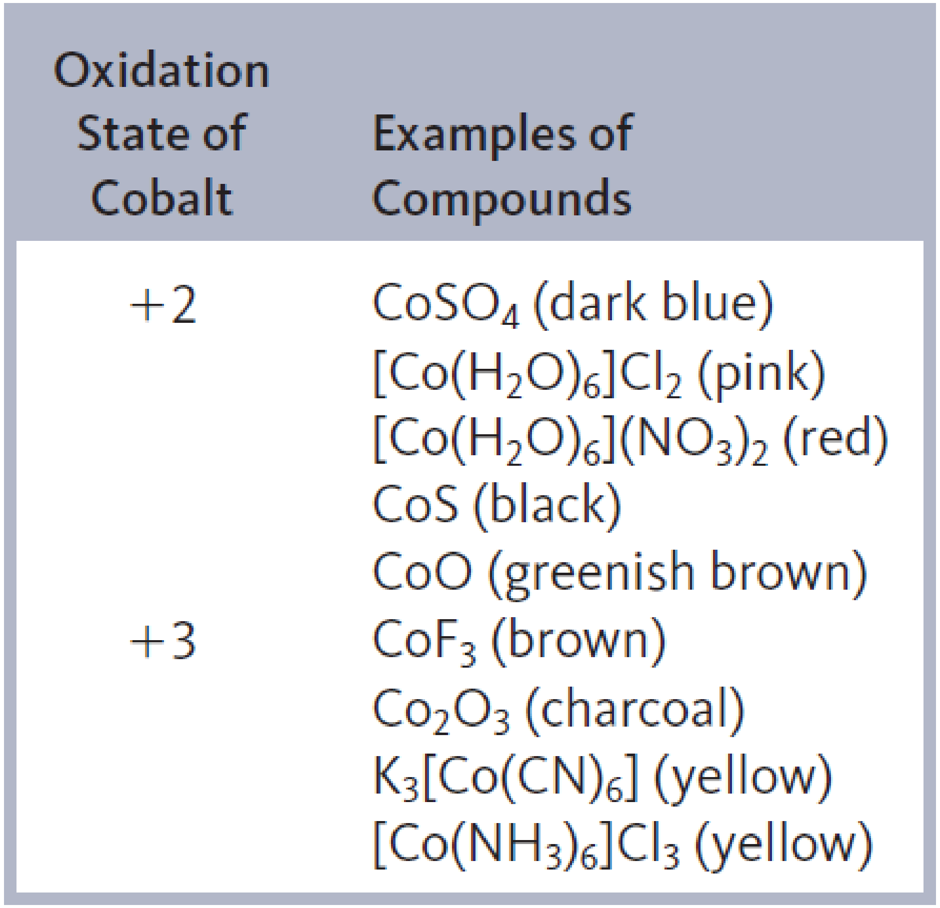
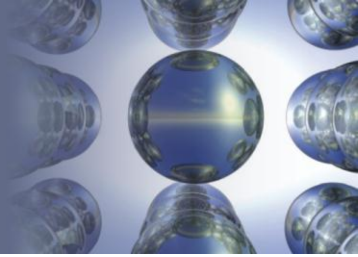


Table 21.8 - Typical Compounds of Cobalt



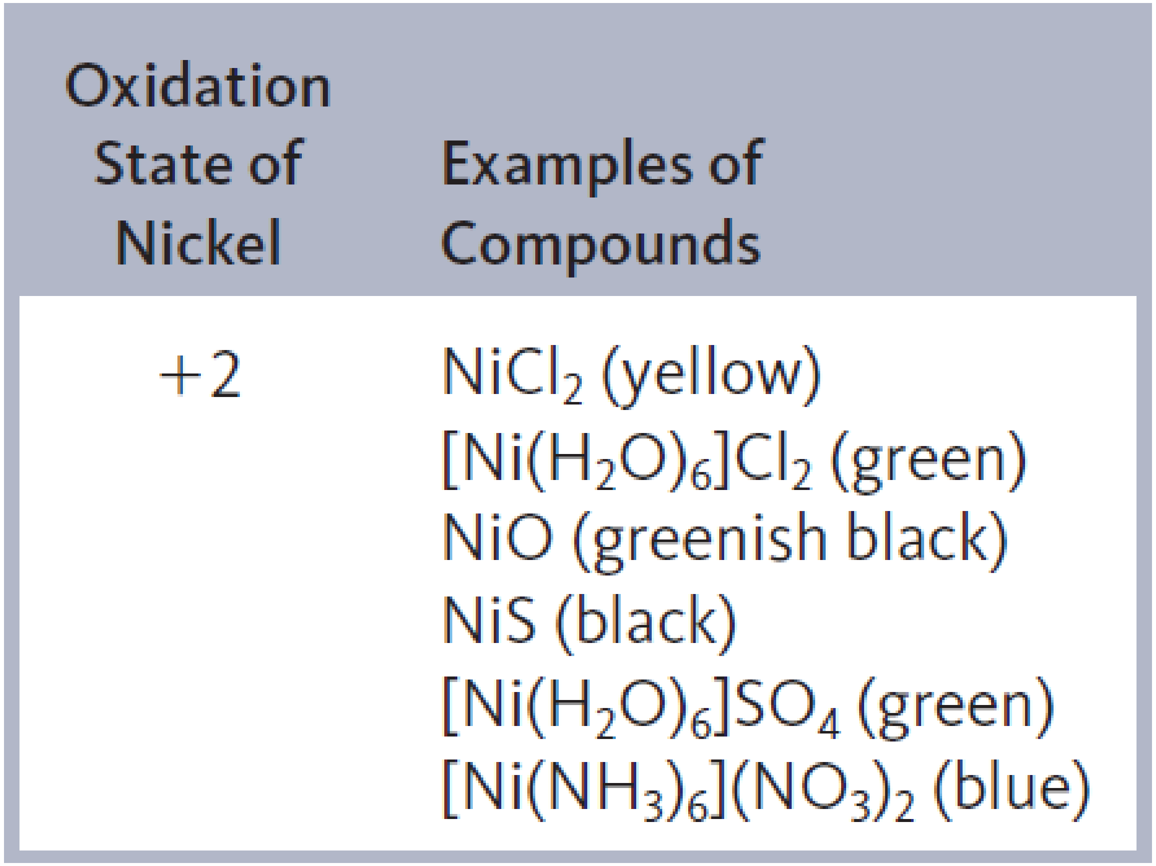
Oxidation State of Cobalt	Examples of Compounds
+2	$CoSO_4$ (dark blue) $[Co(H_2O)_6]Cl_2$ (pink) $[Co(H_2O)_6](NO_3)_2$ (red) CoS (black) CoO (greenish brown)
+3	CoF_3 (brown) Co_2O_3 (charcoal) $K_3[Co(CN)_6]$ (yellow) $[Co(NH_3)_6]Cl_3$ (yellow)



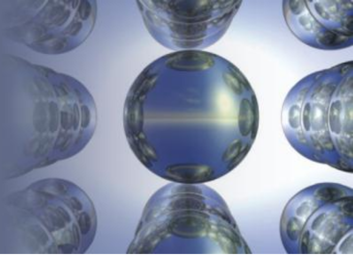
Nickel

- Found in ores in combination with arsenic, antimony, and sulfur
- Silvery white metal
- Has high electric and thermal conductivity
- Resistant to corrosion
  - Used for plating active metals and in the production of alloys such as steel
- Exists in compounds in the +2 oxidation state

Table 21.9 - Typical Compounds of Nickel



Oxidation State of Nickel	Examples of Compounds
+2	$NiCl_2$ (yellow) $[Ni(H_2O)_6]Cl_2$ (green) NiO (greenish black) NiS (black) $[Ni(H_2O)_6]SO_4$ (green) $[Ni(NH_3)_6](NO_3)_2$ (blue)



Copper

- Widely abundant in natural ores that contain sulfides, arsenides, chlorides, and carbonates
- Valued for its high electrical conductivity and its resistance to corrosion
  - Used for plumbing and electrical applications
- Constituent in alloys such as brass, sterling silver, and gold (18-karat)

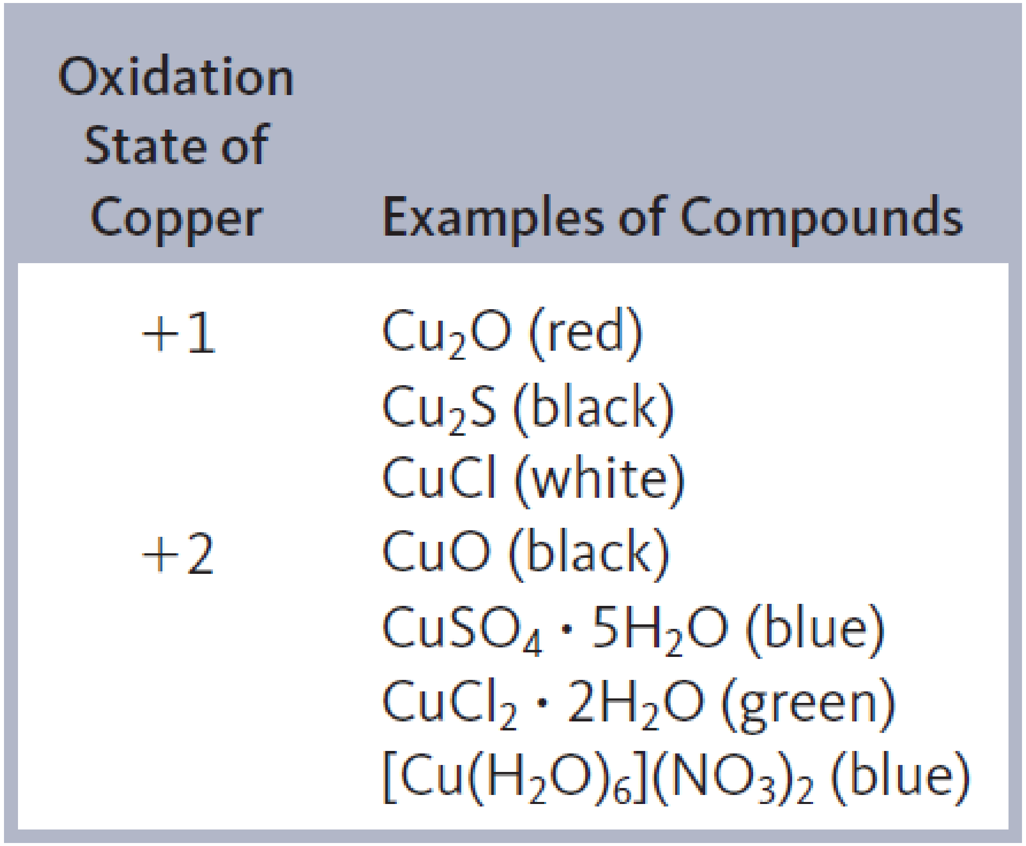
Copper (Continued)

- Corrodes when exposed to air
  - Produces a green patina that consists of basic copper sulfate

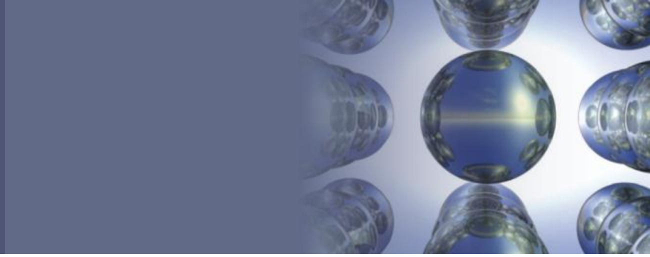
$$3\mathrm{Cu}(s) + 2\mathrm{H_2O}(l) + \mathrm{SO_2}(g) + 2\mathrm{O_2}(g) \rightarrow \underbrace{\mathrm{Cu_3(OH)_4SO_4}(s)}_{\text{Basic copper sulfate}}$$

- Chemistry of copper principally involves the +2 oxidation state
- Can be toxic if consumed in large amounts

Table 21.11 - Typical Compounds of Copper



Oxidation State of Copper	Examples of Compounds
+1	Cu_2O (red) Cu_2S (black) CuCl (white)
+2	CuO (black) $CuSO_4 \cdot 5H_2O$ (blue) $CuCl_2 \cdot 2H_2O$ (green) $[Cu(H_2O)_6](NO_3)_2$ (blue)

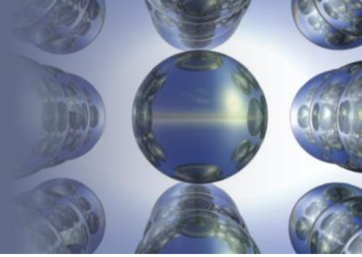


Zinc

- Refined from sphalerite (ZnS), which occurs with galena (PbS)
- White and lustrous
- Highly active metal
    - Excellent reducing agent and has the tendency to tarnish rapidly
- Used for galvanizing steel
- Forms colorless salts in the +2 oxidation state

Coordination Compound

- Consists of a complex ion and counterions
    - Complex ion - Transition metal ion with its attached ligands
    - **Counterions**: Anions or cations that are required to produce a compound with no net charge
- Example - $[Co(NH_3)_5Cl]Cl_2$
    - Brackets indicate the complex ion composition



Alfred Werner

- Proposed that transition metal ions have two types of valence
  - Primary valence - Ability to form ionic bonds with oppositely charged ions
    - Currently termed as the **oxidation state**
  - Secondary valence - Ability to bind to ligands (Lewis bases) and form complex ions
    - Currently termed as the **coordination number**

Coordination Number

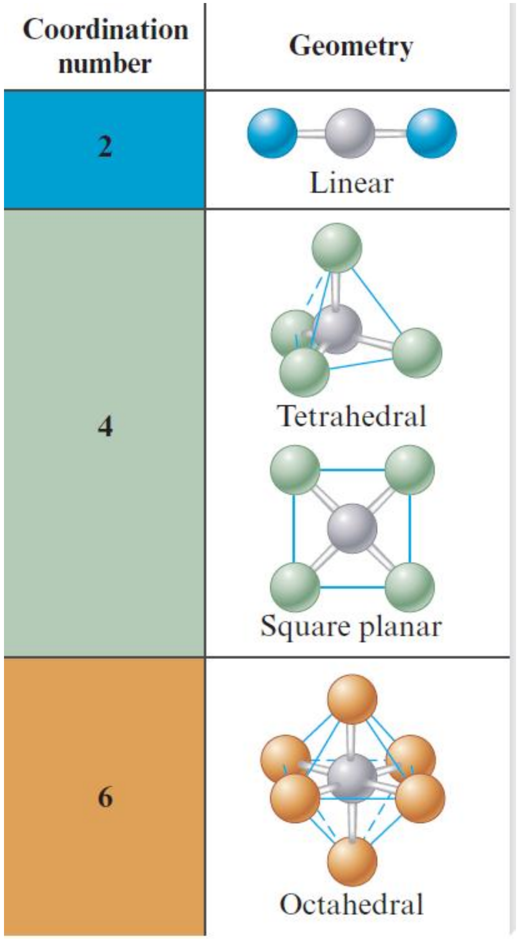
- Number of bonds formed by metal ions to ligands in complex ions
    - Varies from two to eight based on the size, charge, and electron configuration of the transition metal ion
- Metal ions can have more than one coordination number

Table 21.12 - Typical Coordination Numbers for Some Common Metal Ions

M	Coordination Numbers	M^{2+}	Coordination Numbers	M^{3+}	Coordination Numbers
Cu^{+}	2, 4	Mn^{2+}	4, 6	Sc^{3+}	6
Ag^{+}	2	Fe^{2+}	6	Cr^{3+}	6
Au^{+}	2, 4	Co^{2+}	4, 6	Co^{3+}	6
		Ni^{2+}	4, 6		
		Cu^{2+}	4, 6	Au^{3+}	4
		Zn^{2+}	4, 6		

Typical Geometries of Coordination Numbers

- Linear
    - Produced by two ligands
- Tetrahedral or square planar
    - Produced by four ligands
- Octahedral
    - Produced by six ligands



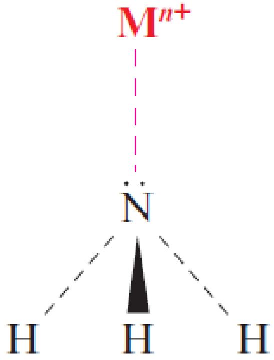
Coordination number	Geometry
2	Linear
4	Tetrahedral Square planar
6	Octahedral

Ligands

- Neutral molecule or ion having a lone electron pair that is used to form a bond to a metal ion
  - **Coordinate covalent bond**: Metal–ligand bond resulting from the interaction between a Lewis base (the ligand) and a Lewis acid (the metal ion)

Types of Ligands

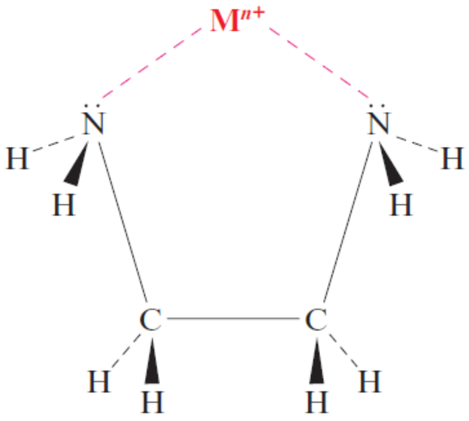
- **Monodentate (unidentate) ligand**
  - Can form one bond to a metal ion
- **Chelating ligand (chelate)**
  - Has more than one atom with a lone pair that can bond to a metal ion



Ammonia (NH_3) is a unidentate ligand

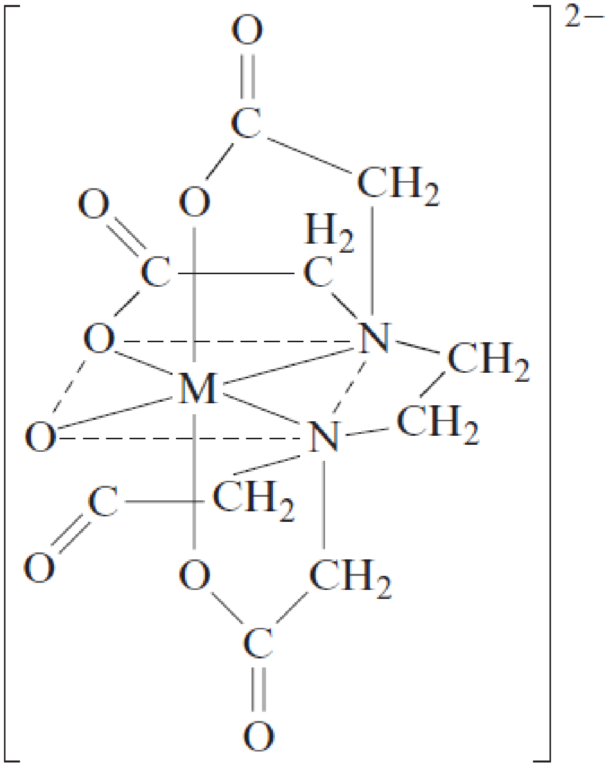
Chelating Ligands

- **Bidentate ligand**
  - Can form two bonds to a metal ion
- Polydentate ligand
  - Can form more than two bonds to a metal ion
- Hexadentate ligand
  - Can form as many as six bonds to a metal ion
    - Example - Ethylenediaminetetraacetate (EDTA)



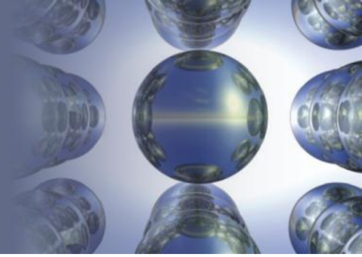
Bidentate ligand ethylenediamine

Figure 21.7 - The Coordination of EDTA with a 2+ Metal Ion



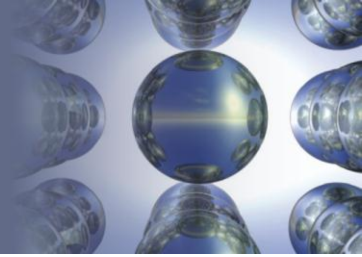
Rules for Naming Coordination Compounds

- Ionic compound
    - Cation is named before the anion
- Complex ion
    - Ligands are named before the metal ion
- Ligands
    - An ‘o’ is added to the root name of the anion
    - For a neutral ligand, the name of the molecule is used
        - Exception - H_2O, NH_3, CO, and NO



Rules for Naming Coordination Compounds (Continued 1)

- Number of simple ligands are denoted by prefixes mono-, di-, tri-, tetra-, penta-, and hexa-
    - Prefixes bis-, tris-, tetrakis-, and so on are used for more complicated ligands or ones that already contain di-, tri-, and so on
- The oxidation state of the central metal ion is designated by a Roman numeral in parentheses



Rules for Naming Coordination Compounds (Continued 2)

- When more than one type of ligand is present, they are named alphabetically
    - Prefixes have no effect on the order
- If the complex ion has a negative charge, the suffix -ate is added to the name of the metal

Interactive Example 21.1 - Naming Coordination Compounds I

- Give the systematic name for the following coordination compound:
    - $[Fe(en)_2(NO_2)_2]_2SO_4$

Interactive Example 21.1 - Solution

- First determine the oxidation state of the iron by looking at the other charged species
    - Four NO_2^- ions and one SO_4^{2-} ion
    - The ethylenediamine is neutral
        - Thus, the two iron ions must carry a total positive charge of 6 to balance the six negative charges, which means that each iron has a +3 oxidation state and is designated as iron(III)

Interactive Example 21.1 - Solution (Continued)

- Since the name ethylenediamine already contains di, we use bis- instead of di- to indicate the two en ligands
- The name for NO_2^- as a ligand is nitro, and the prefix di- indicates the presence of two NO_2^- ligands
- Since the anion is sulfate, the compound’s name is:

$$\underbrace{\text{Bis(ethylenediamine)dinitroiron(III)}}_{\text{Cation}}\ \underbrace{\text{sulfate}}_{\text{Anion}}$$

Exercise

- Give formulas for the following:
  a. Potassium tetrachlorocobaltate(II)

  $K_2[CoCl_4]$

  b. Aquatricarbonylplatinum(II) bromide

  $[Pt(H_2O)(CO)_3]Br_2$

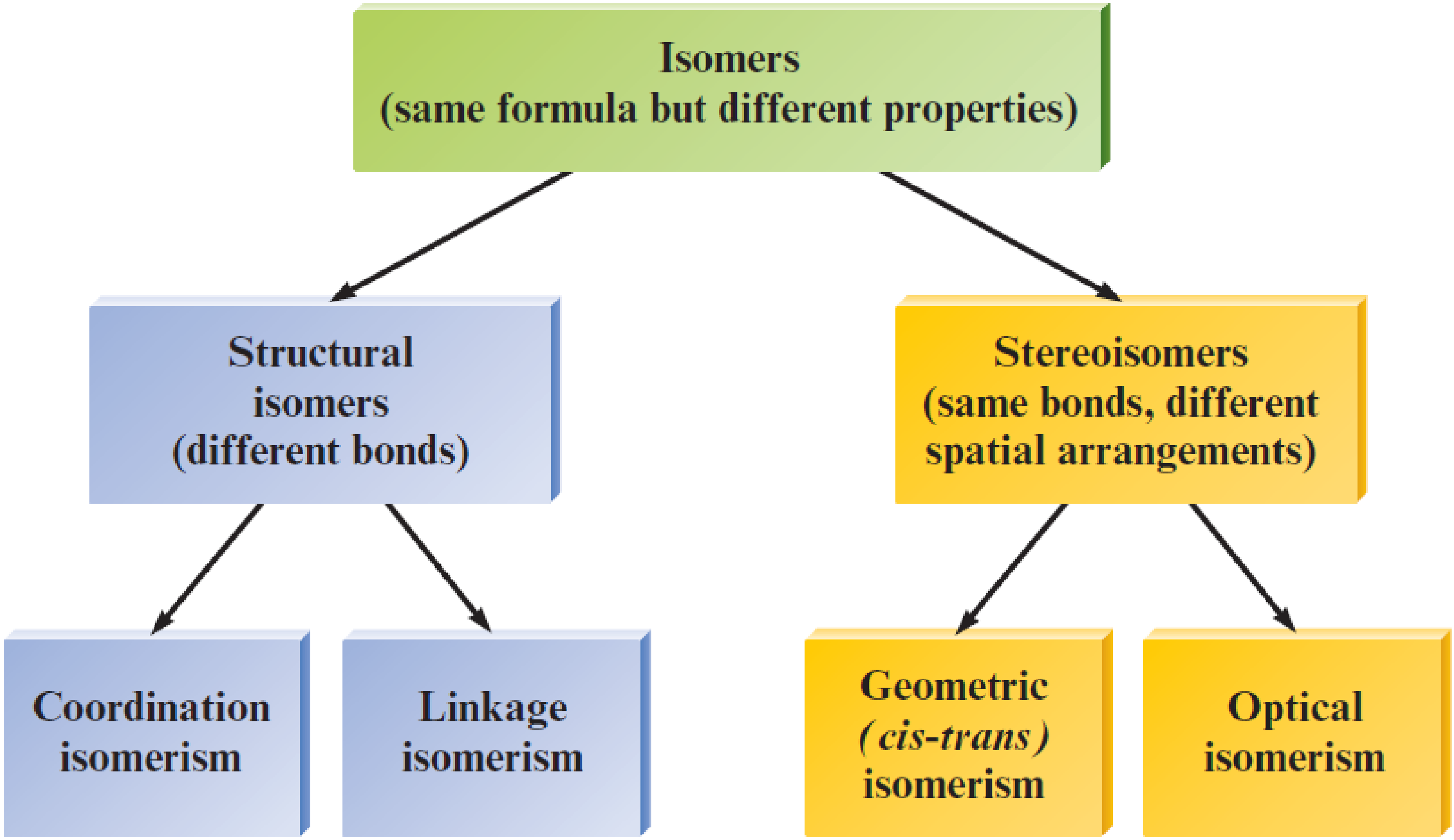
  c. Triamminechloroethylenediaminechromium(III) iodide

  $[Cr(NH_3)_3Cl(H_2NCH_2CH_2NH_2)]I_2$

Concept of Isomerism

- **Isomers**: Two or more species with the same formula but different properties
- Types
  - **Structural isomerism**: Isomers contain the same atoms
    - Only one or more bonds differ
  - **Stereoisomerism**: All bonds in the isomers are the same
    - Spatial arrangements of the atoms are different

Figure 21.8 - Some Classes of Isomers



Isomers
(same formula but different properties)

Structural isomers
(different bonds)

Stereoisomers
(same bonds, different spatial arrangements)

Coordination isomerism

Linkage isomerism

Geometric (*cis-trans*) isomerism

Optical isomerism

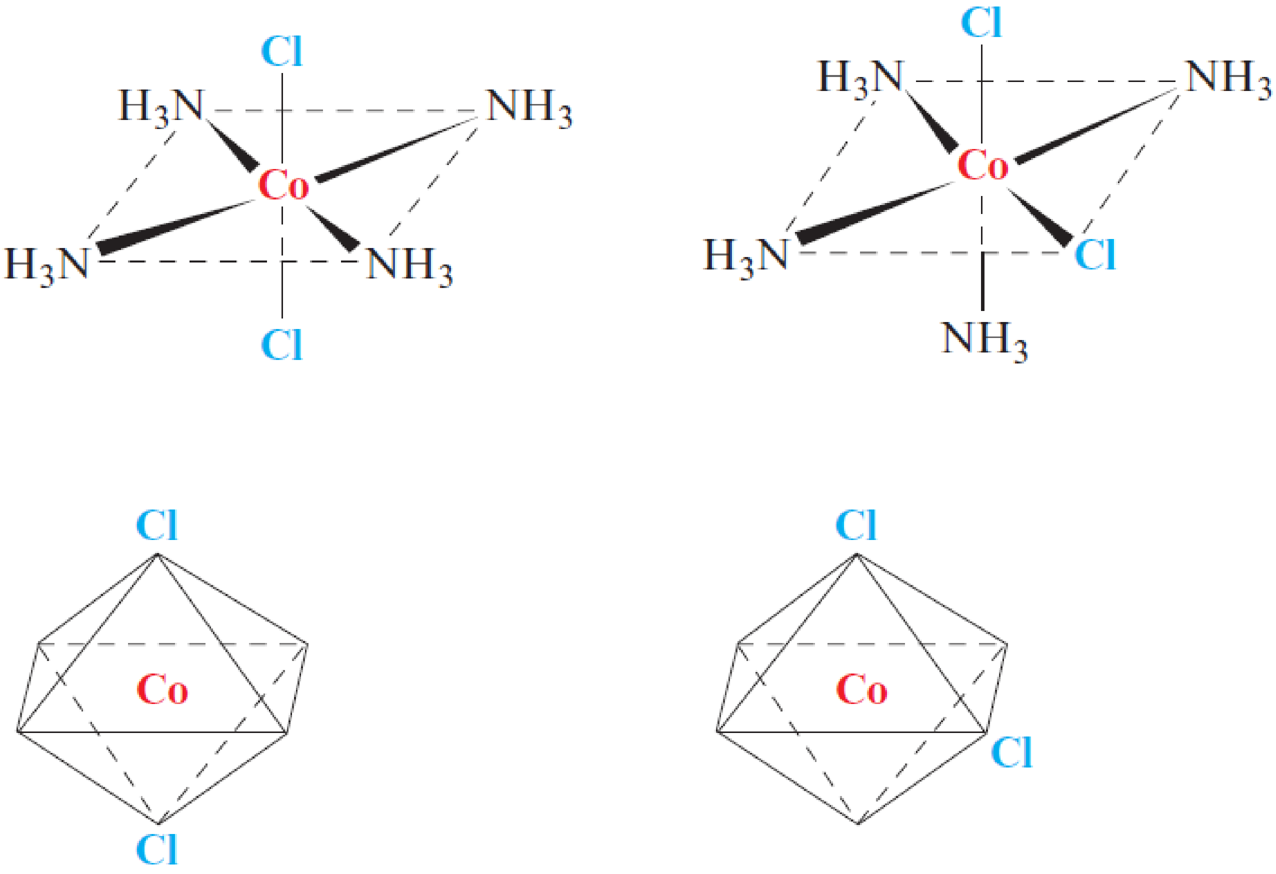
Structural Isomerism

- **Coordination isomerism**: Composition of the complex ion varies
- **Linkage isomerism**: Composition of the complex ion is the same, but the point of attachment of at least one of the ligands differs

Stereoisomerism

- **Geometrical (*cis–trans*) isomerism**: Atoms or groups of atoms can assume different positions around a rigid ring or bond
  - ***Cis* isomer**: Molecules are next to each other
  - ***Trans* isomer**: Molecules are across from each other

Figure 21.11 - *Cis* and *Trans* Isomers of the Complex Compound $[Co(NH_3)_4Cl_2]^+$



Stereoisomerism (Continued)

- **Optical isomerism**: Isomers have opposite effects on plane-polarized light
  - When light is emitted from a source, the oscillating electric fields of the photons in the beam are oriented randomly
    - Plane-polarized light constitutes photons with electric fields that oscillate in a single plane

Figure 21.12 - Unpolarized Light and Plane-Polarized Light

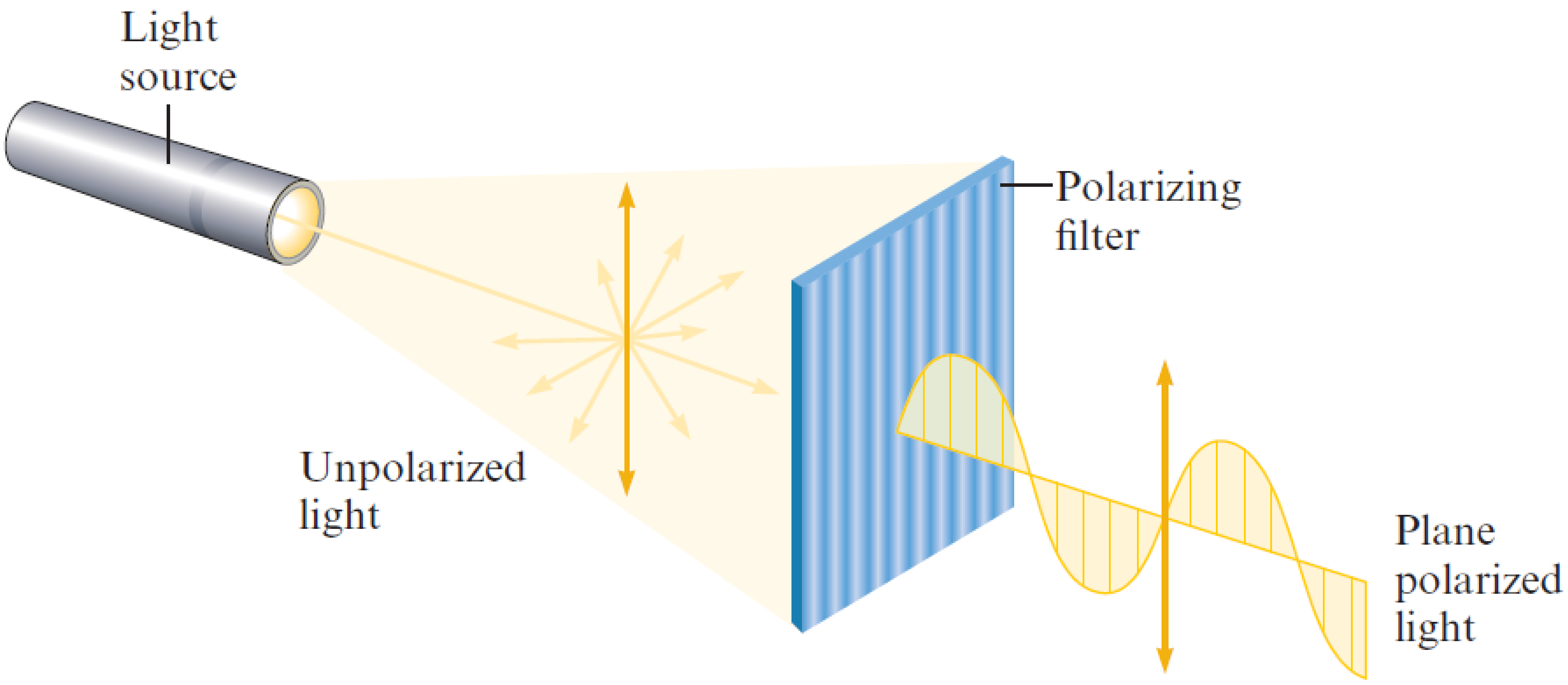
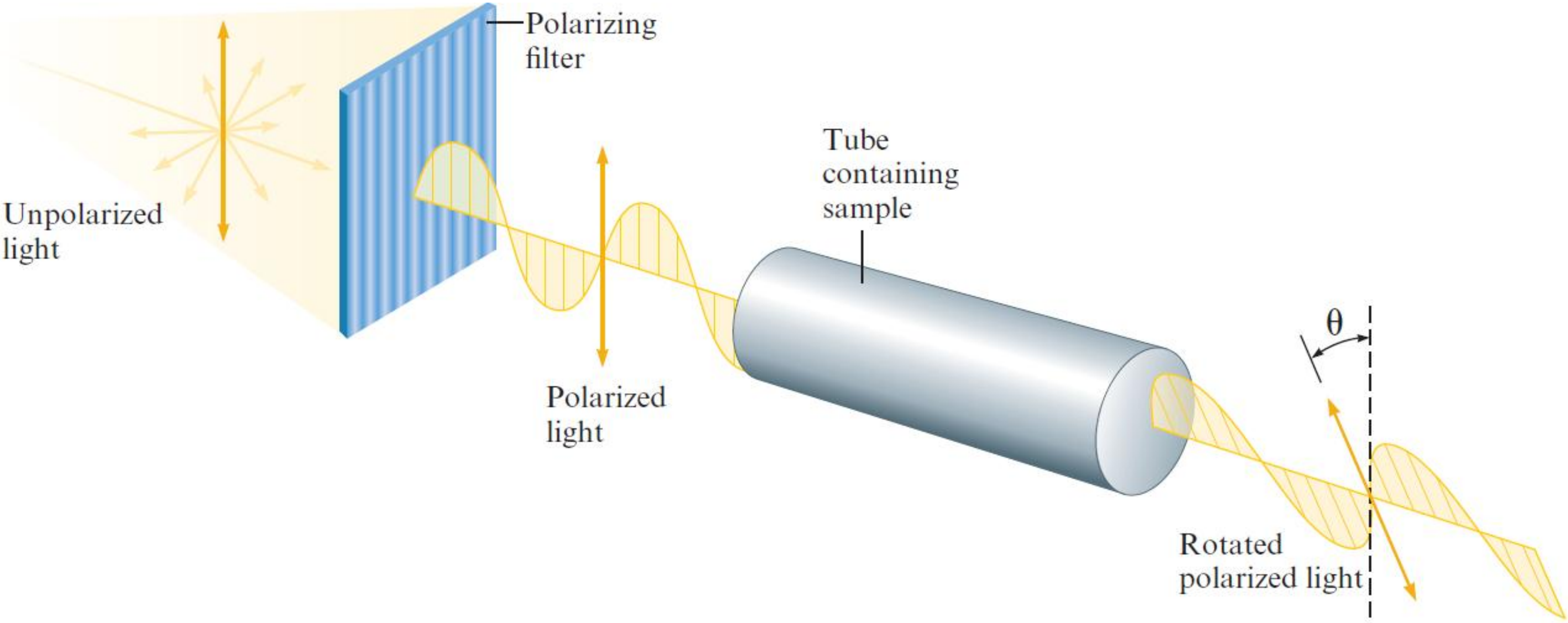


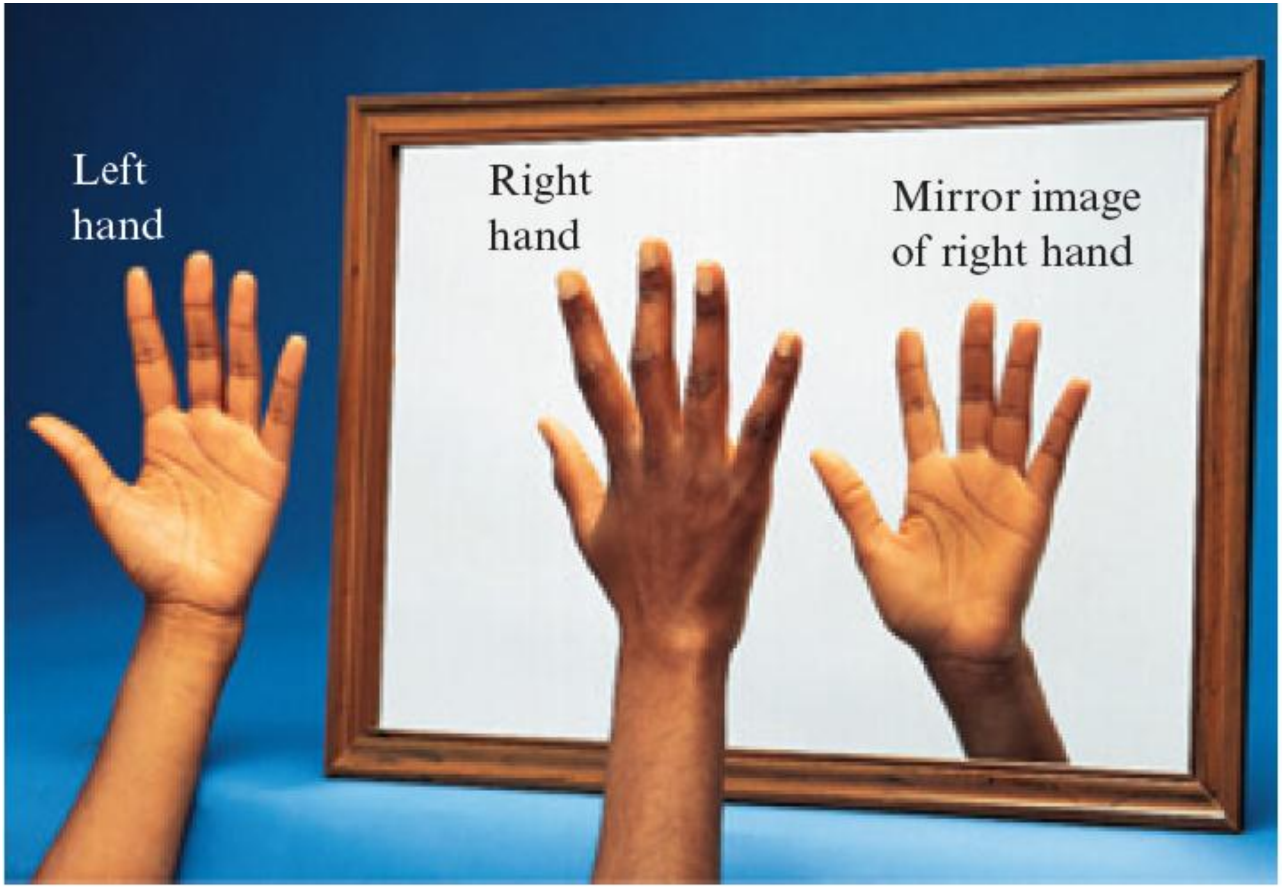
Figure 21.13 - Rotation of the Plane of Polarized Light by an Optically Active Substance



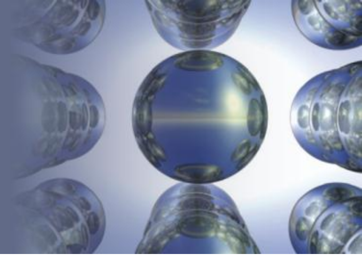
Optical Activity

- Exhibited by molecules that have nonsuperimposable mirror images
    - Considered to be **chiral**
- **Enantiomers**: Isomers that are nonsuperimposable mirror images of each other
    - Rotate plane-polarized light in opposite directions
        - Hence, they are optical isomers

Figure 21.15 - The Human Hand, a Nonsuperimposable Mirror Image



Martin Bough/Fundamental Photographs © Cengage Learning

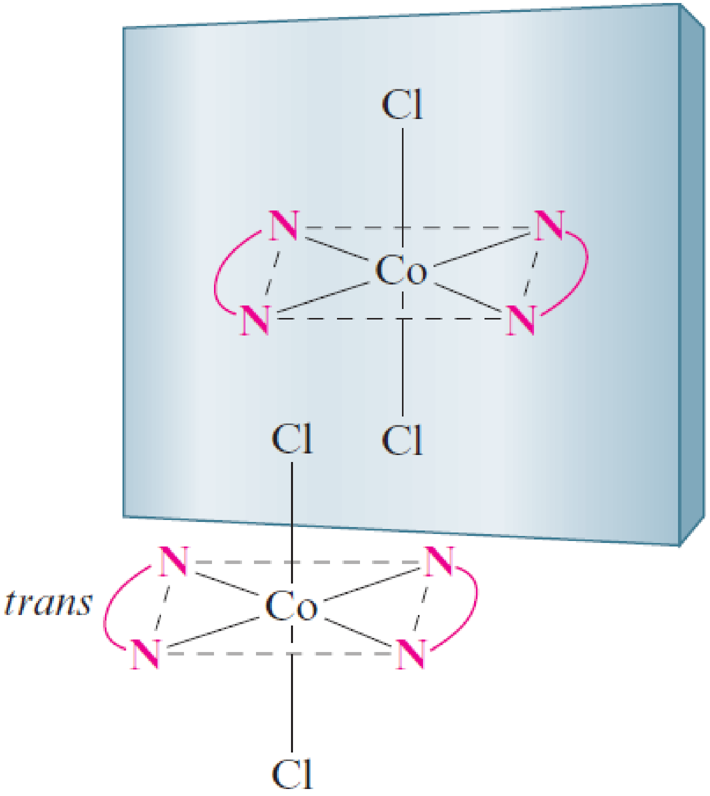


Enantiomers

- Dextrorotatory (*d*)
  - Isomer that rotates the plane of light to the right
- Levorotatory (*l*)
  - Isomer that rotates the plane of light to the left
- Racemic mixture
  - Solution containing an equal mixture of *d* and *l* forms
    - Does not rotate the plane of the polarized light as the opposite effects cancel each other

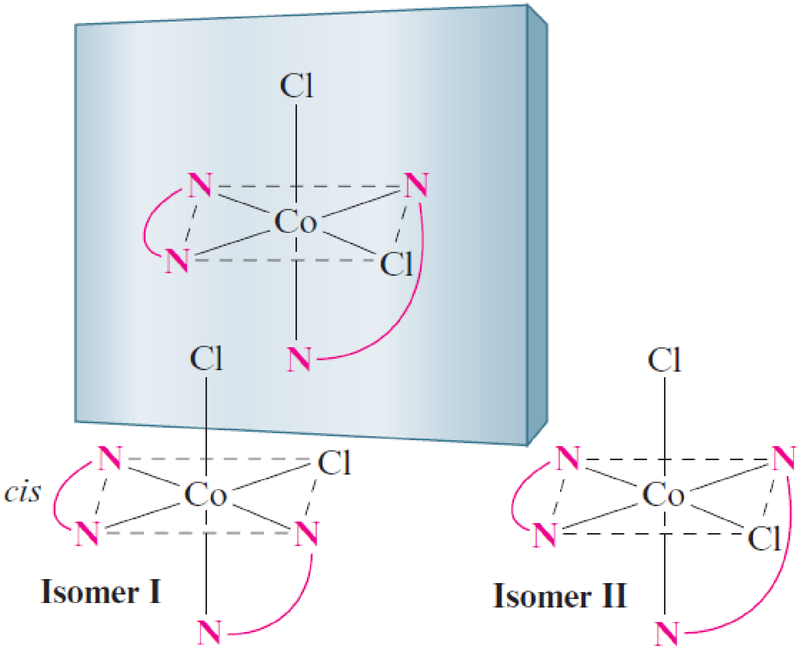
Geometric Isomers and Optical Isomers

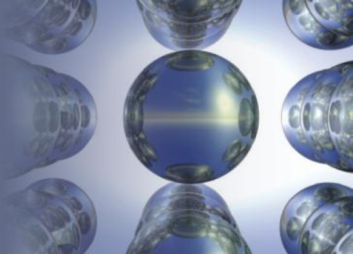
- Geometric isomers are not necessarily optical isomers
  - Example - The *trans* isomer of $[Co(en)_2Cl_2]^+$ and its mirror image are identical
    - Since the isomer is superimposable on its mirror image, it does not exhibit optical isomerism and is not chiral



Geometric Isomers and Optical Isomers (Continued)

- Example - The *cis* isomer of $[Co(en)_2Cl_2]^+$ and its mirror image are not superimposable
  - Thus, they are a pair of optical isomers
  - Isomer II has the same structure as the mirror image of isomer I



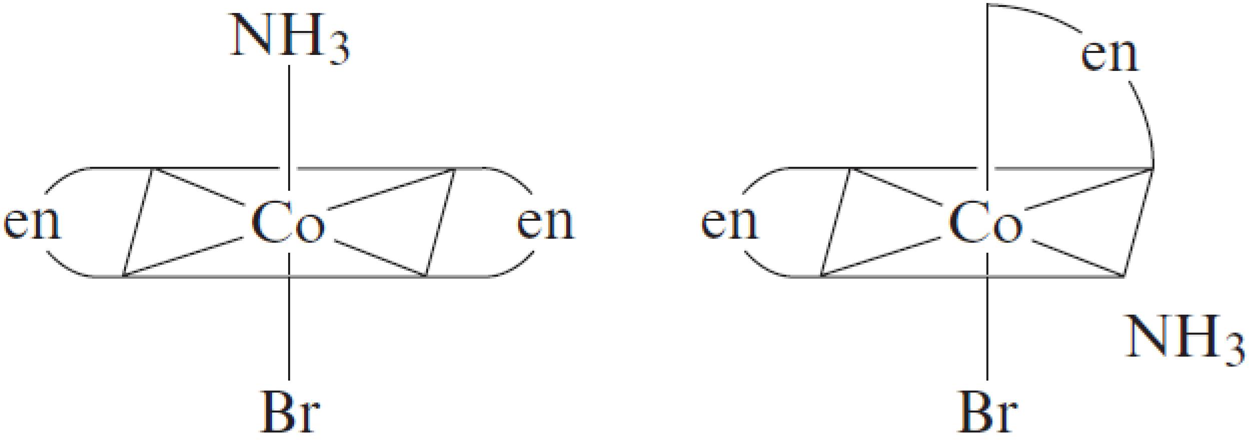


Example 21.3 - Geometrical and Optical Isomerism

- Does the complex ion $[Co(NH_3)Br(en)_2]^{2+}$ exhibit geometrical isomerism?
  - Does it exhibit optical isomerism?

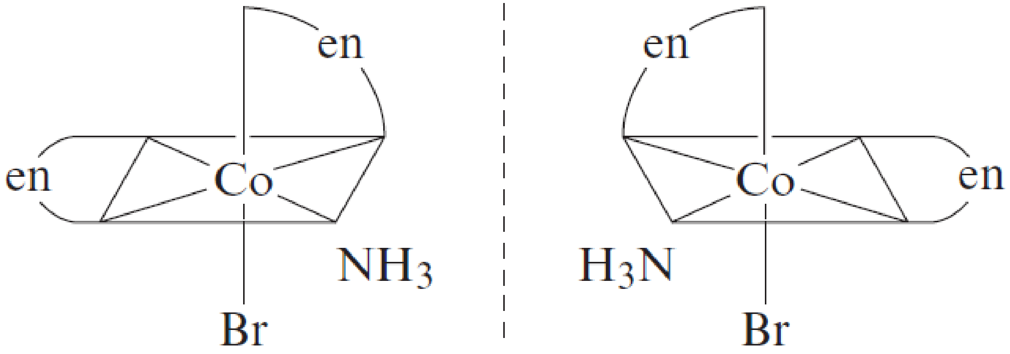
Example 21.3 - Solution

- The complex ion exhibits geometrical isomerism because the ethylenediamine ligands can be across from or next to each other



Example 21.3 - Solution (Continued)

- The *cis* isomer of the complex ion also exhibits optical isomerism because its mirror images cannot be turned in any way to make them superimposable



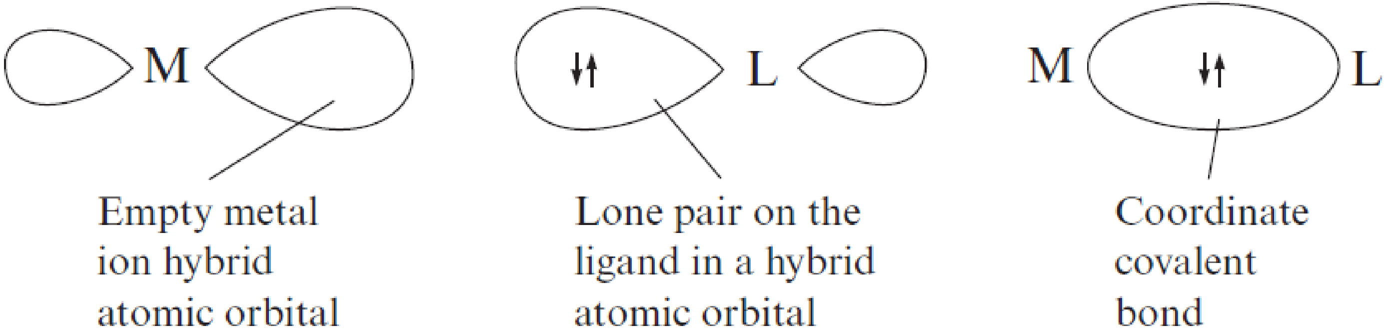
  - Thus, these mirror-image isomers of the *cis* complex are shown to be enantiomers that will rotate plane-polarized light in opposite directions

Key Points

1. The VSEPR model does not help determine the structure of complex ions
   - It is safe to assume that:
     - A complex ion with a coordination number of 6 will have octahedral arrangement of ligands
     - Complexes with two ligands will be linear
   - Complex ions with a coordination number of 4 can be either tetrahedral or square planar
     - No reliable way exists to predict which will occur

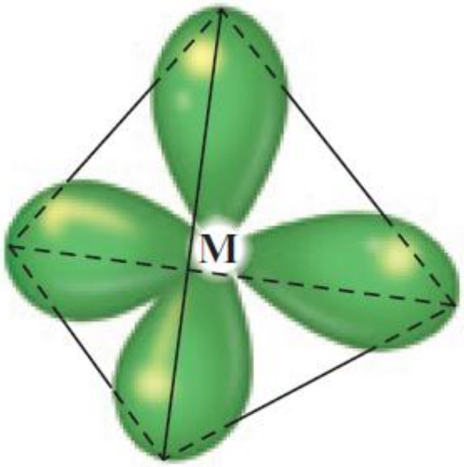
Key Points (Continued)

2. Interaction between a metal ion and a ligand can be viewed as a Lewis acid–base reaction
   - The ligand donates a lone pair of electrons to an empty orbital of the metal ion to form a coordinate covalent bond

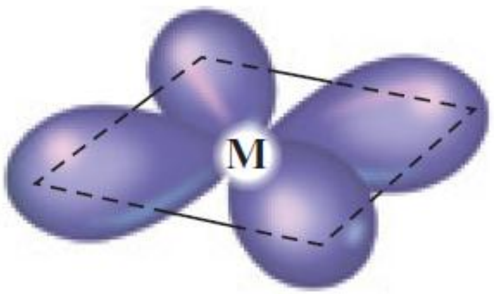


Hybrid Orbitals Required for Complex Ion Formation

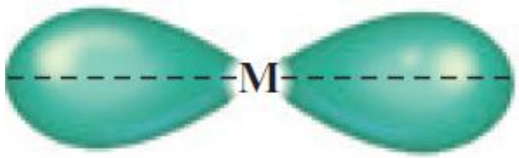
- Based on the number and arrangement of ligands



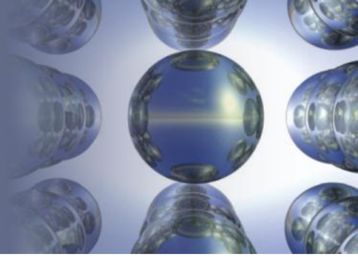
Tetrahedral ligand arrangement; sp^3 hybridization



Square planar ligand arrangement; dsp^2 hybridization



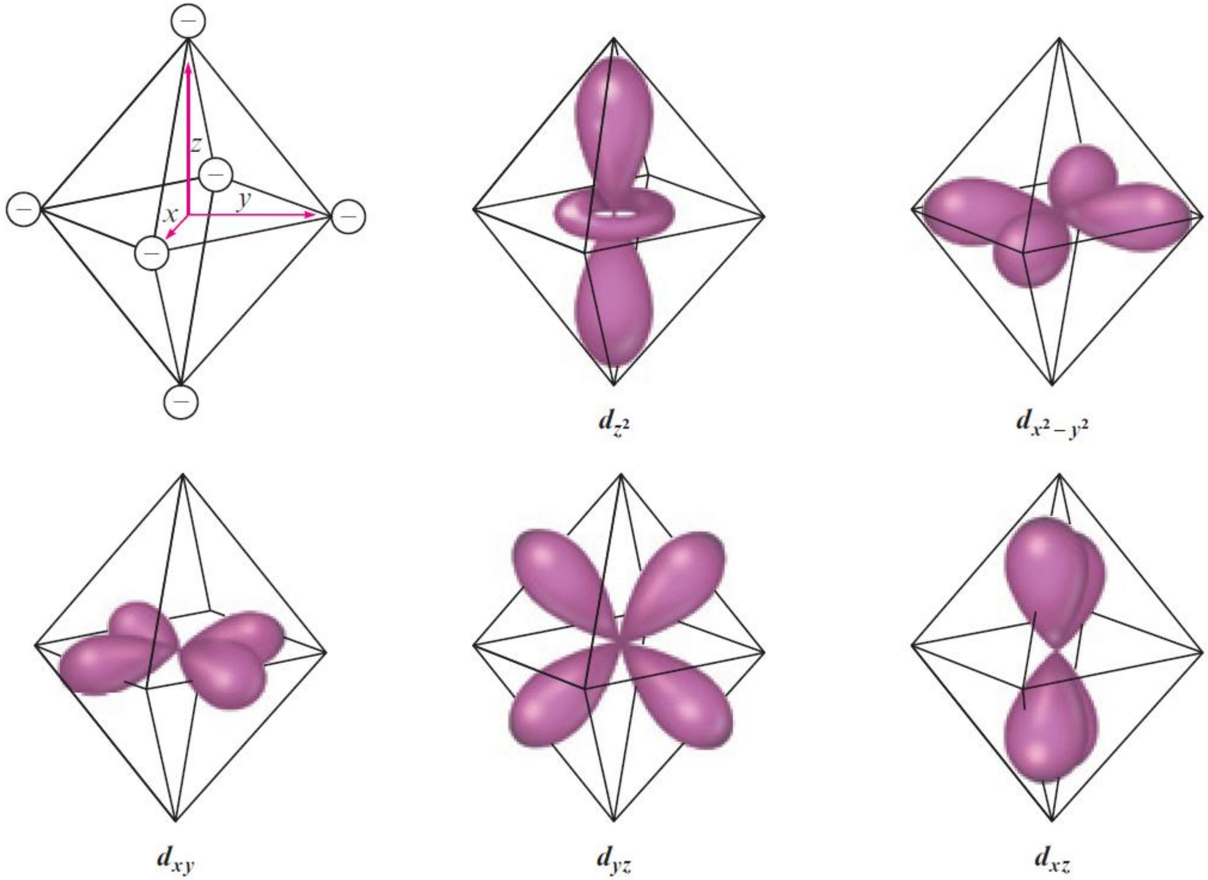
Linear ligand arrangement; sp hybridization



The Crystal Field Model - An Introduction

- Focuses on the energies of the *d* orbitals
- Attempts to account for the magnetic properties and colors of complex ions
- Assumptions
  - Ligands can be approximated by negative point charges
  - Metal–ligand bonding is entirely ionic

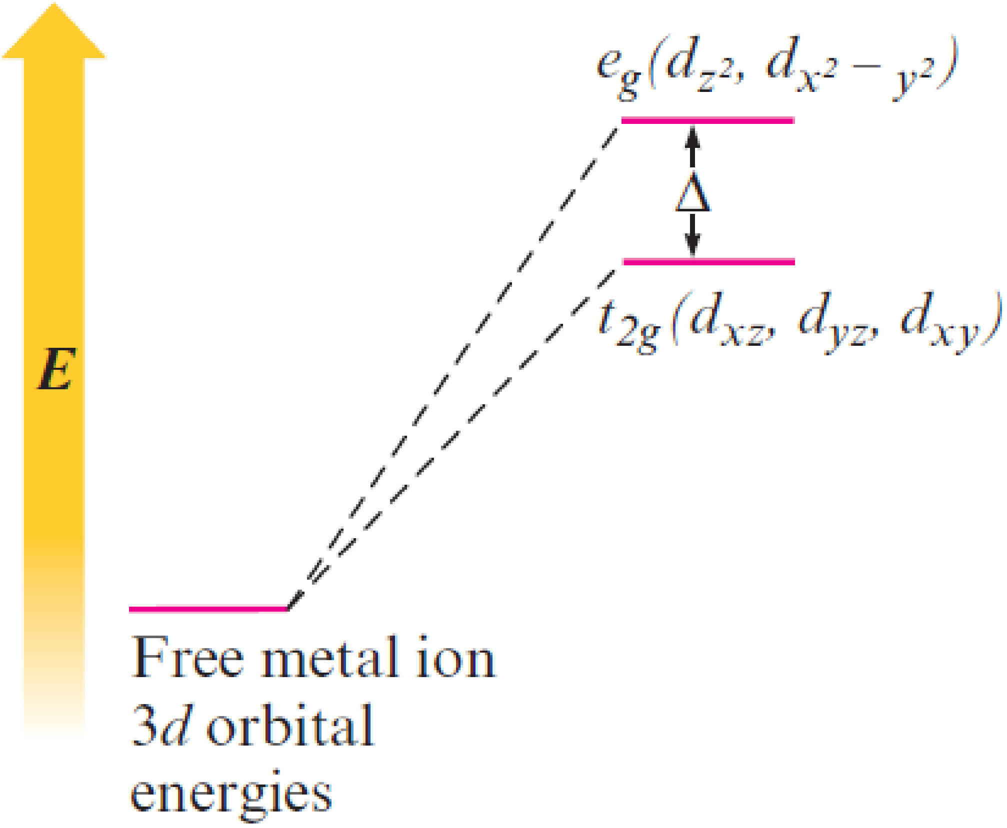
Figure 21.20 - Octahedral Arrangement of Point-Charge Ligands and the Orientation of the 3*d* Orbitals

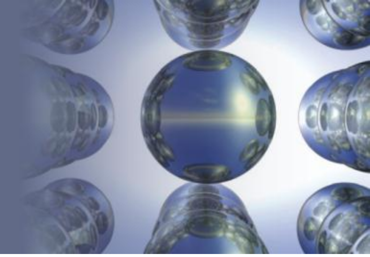


Octahedral Complexes

- d_{z^2} and $d_{x^2-y^2}$ point their lobes directly at the point-charge ligands
- d_{xz}, d_{yz}, and d_{xy} point their lobes between the point charges
- Negative point-charge ligands repel negatively charged electrons
  - Electrons will first fill the *d* orbitals farthest from the ligands to minimize repulsions

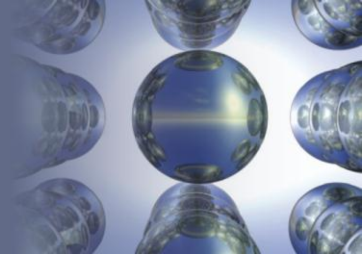
Figure 21.21 - The Energies of the 3*d* Orbitals for a Metal Ion in an Octahedral Complex





Splitting of 3*d* Orbital Energies (Δ)

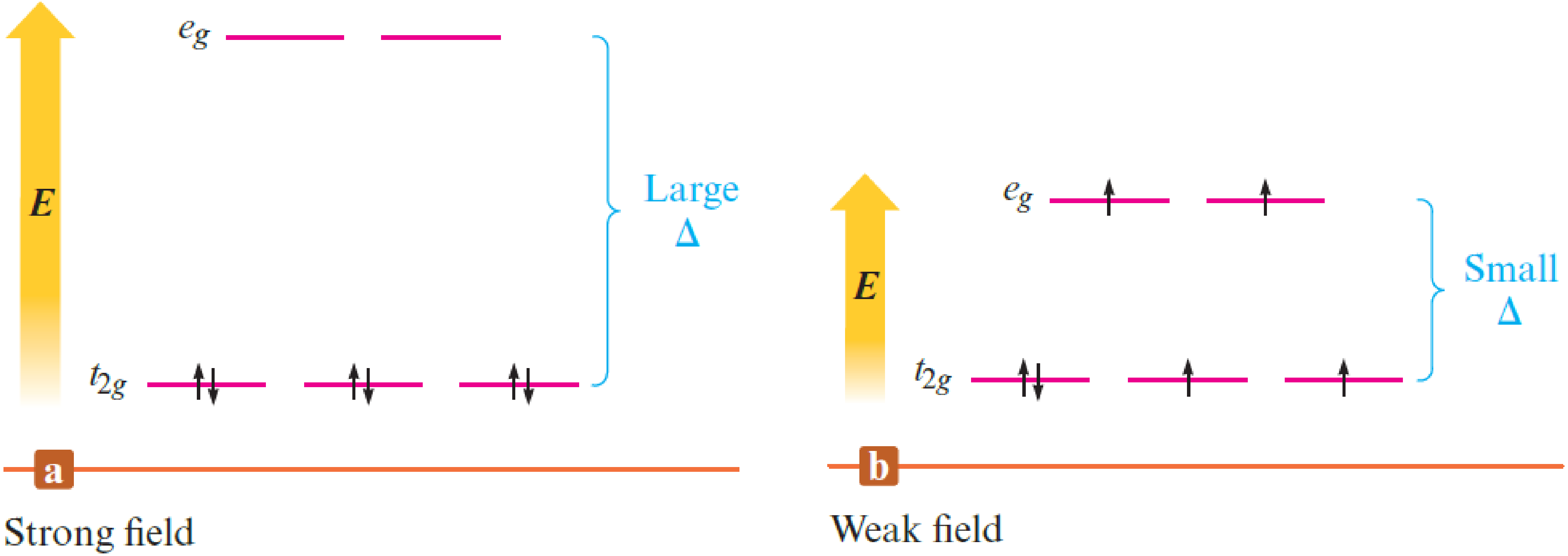
- Explains the color and magnetism of complex ions of the first-row transition metal ions
- **Strong-field case**: Splitting produced by ligands is very large
    - Electrons pair in the lower-energy t_{2g} orbitals
        - Gives a diamagnetic complex in which all the electrons are paired
        - **Low-spin case**: Yields the minimum number of unpaired electrons



Splitting of 3*d* Orbital Energies (Δ) (Continued)

- **Weak-field case**: Splitting is small
    - Causes the electrons to occupy all five orbitals prior to pairing
        - The resulting complex contains four unpaired electrons and will be paramagnetic
        - **High-spin case**: Yields the maximum number of unpaired electrons

Figure 21.22 - Possible Electron Arrangements in the Split 3*d* Orbitals in an Octahedral Complex of Co^{3+}



Critical Thinking

- What if you are told the number of unpaired electrons for a coordinate covalent ion and are asked to tell if the ligand produced a strong or weak field?
    - Give an example of a coordinate covalent ion for which you could decide if it produced a strong or weak field and one for which you couldn’t, and explain your answers

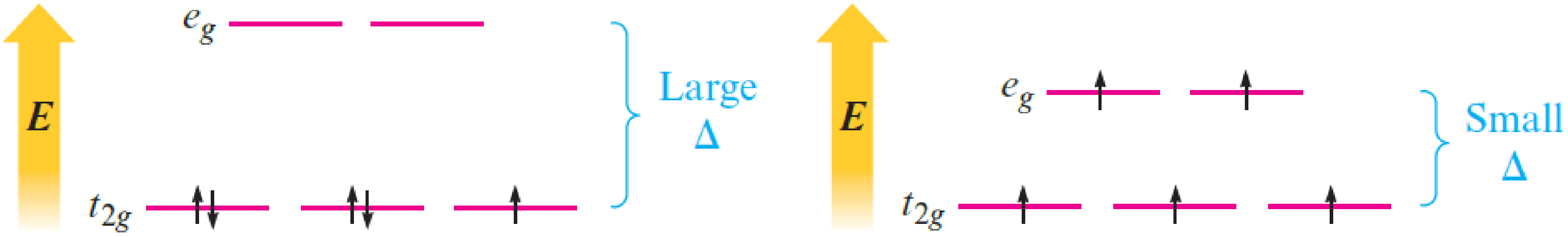
Interactive Example 21.4 - Crystal Field Model I

- The $Fe(CN)_6^{3-}$ ion is known to have one unpaired electron
  - Does the CN^- ligand produce a strong or weak field?

Interactive Example 21.4 - Solution

- The ligand is CN^- and the overall complex ion charge is 3^-
  - The metal ion must be Fe^{3+}, which has a $3d^5$ electron configuration
  - There are two possible arrangements of the five electrons in the *d* orbitals split by the octahedrally arranged ligands

Interactive Example 21.4 - Solution (Continued)



- The strong-field case gives one unpaired electron, which agrees with the experimental observation
- The CN^- ion is a strong-field ligand toward the Fe^{3+} ion

Spectrochemical Series

- Listing of ligands in order based on their ability to produce *d*-orbital splitting

$CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

Strong-field
ligands
(large Δ)

Weak-field ligands
(small Δ)

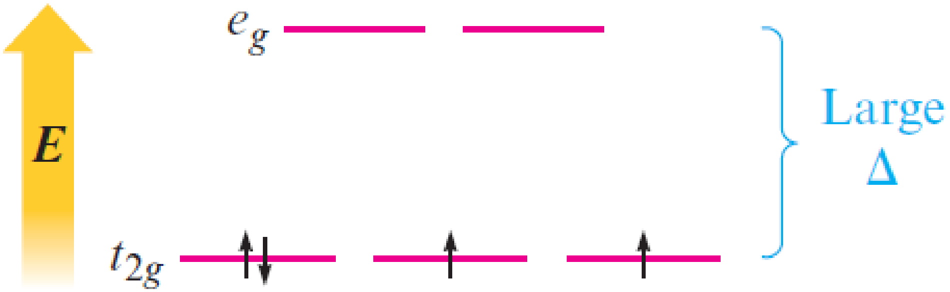
  - Magnitude of Δ for a given ligand increases as the charge on the metal ion increases

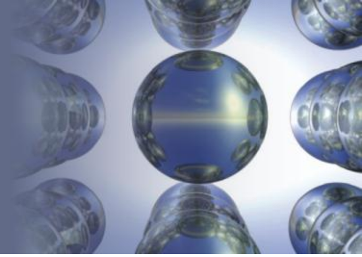
Interactive Example 21.5 - Crystal Field Model II

- Predict the number of unpaired electrons in the complex ion $Cr(CN)_6^{4-}$

Interactive Example 21.5 - Solution

- The net charge of 4⁻ means that the metal ion present must be Cr^{2+} (–6 + 2 = –4), which has a $3d^4$ electron configuration
  - Since CN^- is a strong-field ligand, the correct crystal field diagram for $Cr(CN)_6^{4-}$ is



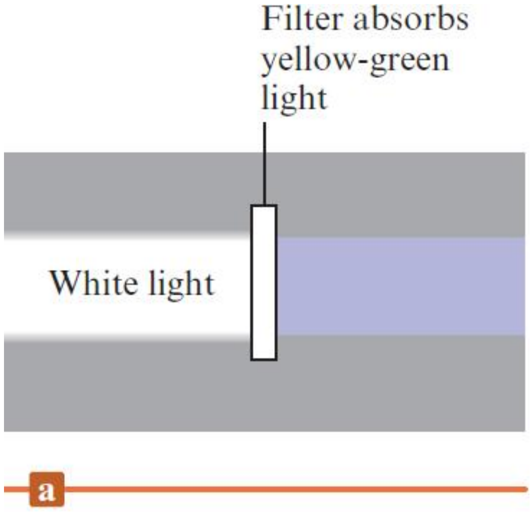


Interactive Example 21.5 - Solution (Continued)

- The complex ion will have two unpaired electrons
- Note that the CN⁻ ligand produces such a large splitting that all four electrons will occupy the t_{2g} set even though two of the electrons must be paired in the same orbital

Complex Ion Colors

- When a substance absorbs certain wavelengths of light in the visible region, its color is determined by the wavelengths of visible light that remain
  - Substance exhibits the color complementary to those absorbed
  - Example - Violet color of $Ti(H_2O)_6^{3+}$



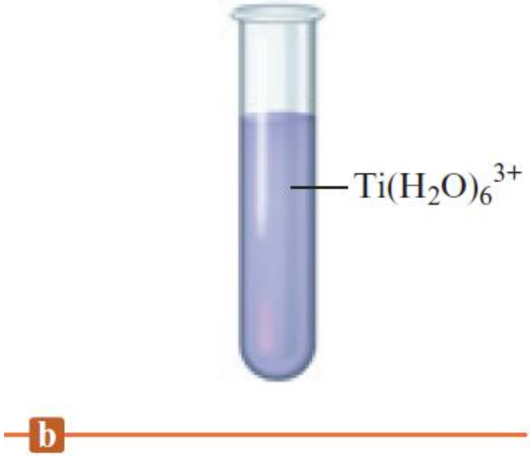


Table 21.16 - Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed

Absorbed Wavelength in nm (Color)	Observed Color
400 (violet)	Greenish yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green

Complex Ion Colors (Continued 1)

- Wavelength absorbed by a molecule is determined by the following relationship:

$$\Delta E = \frac{hc}{\lambda}$$

  - ΔE - Energy spacing in the molecule
  - λ - Wavelength of light required

Complex Ion Colors (Continued 2)

- Ligands coordinated to a given metal ion determine the size of the *d*-orbital splitting
  - Color changes as the ligands are changed
    - Caused by a change in Δ that implies a change in the wavelength of light needed to transfer electrons between the t_{2g} and e_g orbitals

Other Coordination Geometries

- Tetrahedral arrangement
    - None of the 3*d* orbitals point at the ligands
        - Difference in energy between the split *d* orbitals is significantly less
    - Tetrahedral splitting is $\frac{4}{9}$ that of the octahedral splitting for a given ligand and metal ion

Other Coordination Geometries (Continued)

- *d*-orbital splitting will be opposite to that for the octahedral arrangement
    - d_{xy}, d_{xz}, and d_{yz} orbitals are closer to the point charges
    - Weak-field case (high-spin) always applies as the *d*-orbital splitting is relatively small for the tetrahedral case

Interactive Example 21.6 - Crystal Field Model III

- Give the crystal field diagram for the tetrahedral complex ion $CoCl_4^{2-}$

Interactive Example 21.6 - Solution

- The complex ion contains Co^{2+}, which has a $3d^7$ electron configuration
  - The splitting of the *d* orbitals will be small, since this is a tetrahedral complex, giving the high-spin case with three unpaired electrons

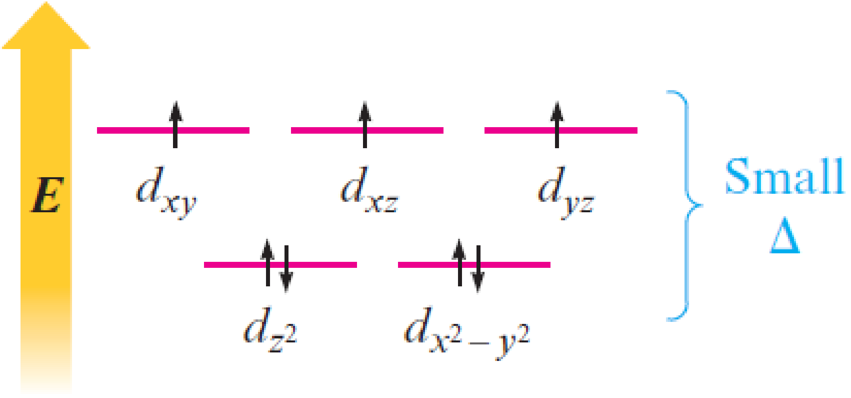
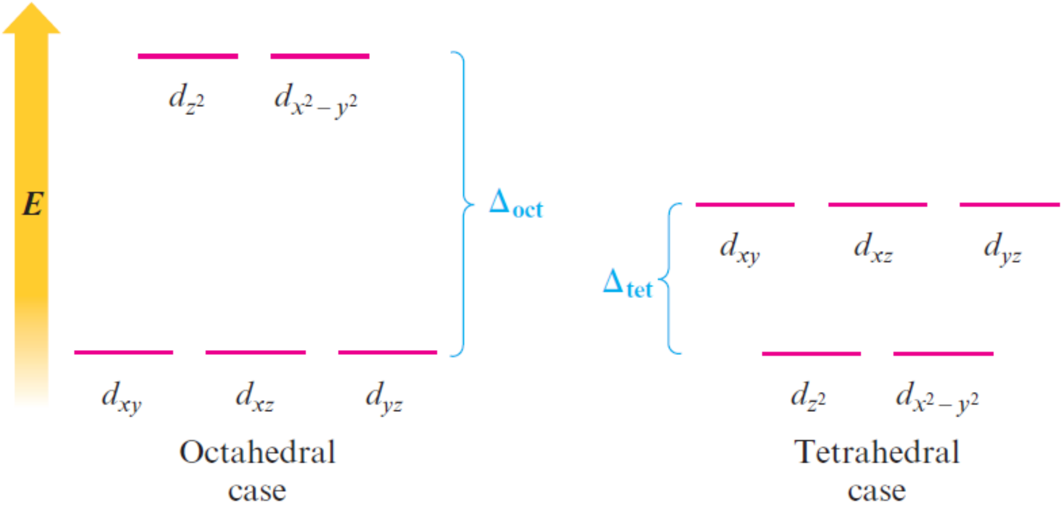


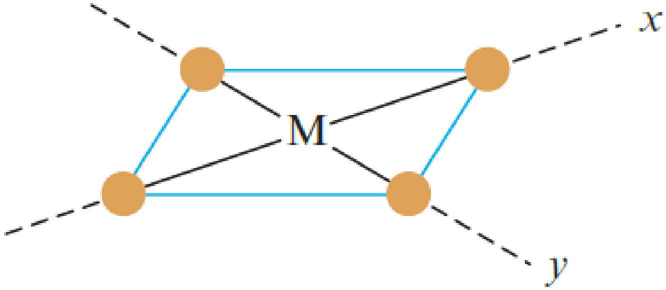
Figure 21.27 - Crystal Field Diagrams for Octahedral and Tetrahedral Complexes

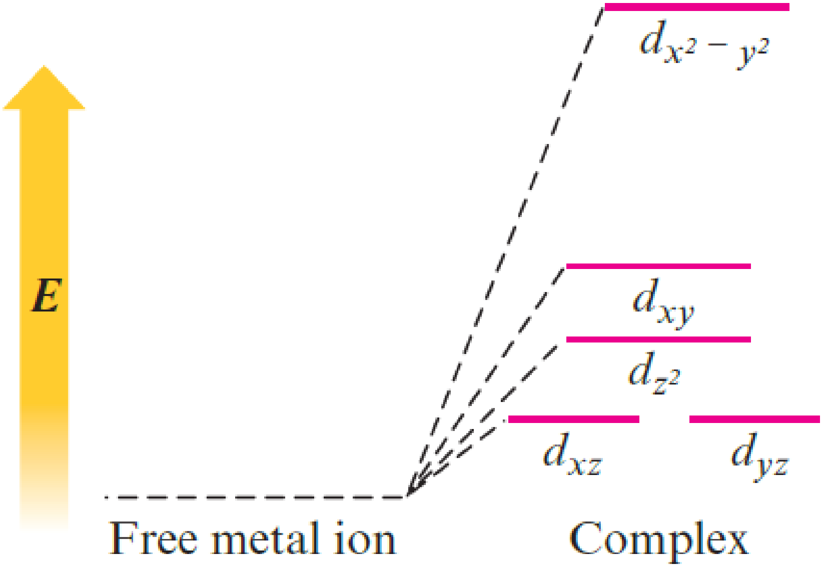
- $\Delta_{oct} > \Delta_{tet}$
    - d_{z^2} and $d_{x^2-y^2}$ orbitals point their lobes directly at the point charges, making them relatively high in energy



Square Planar Complexes

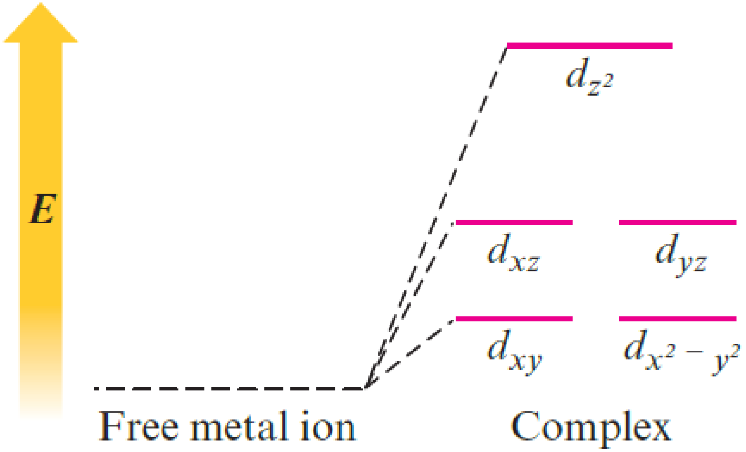
- Obtained from the octahedral arrangement by removing the two point charges along the *z* axis
  - Lowers the energy of d_{z^2}
  - Leaves only $d_{x^2-y^2}$
    - Points at the four remaining ligands





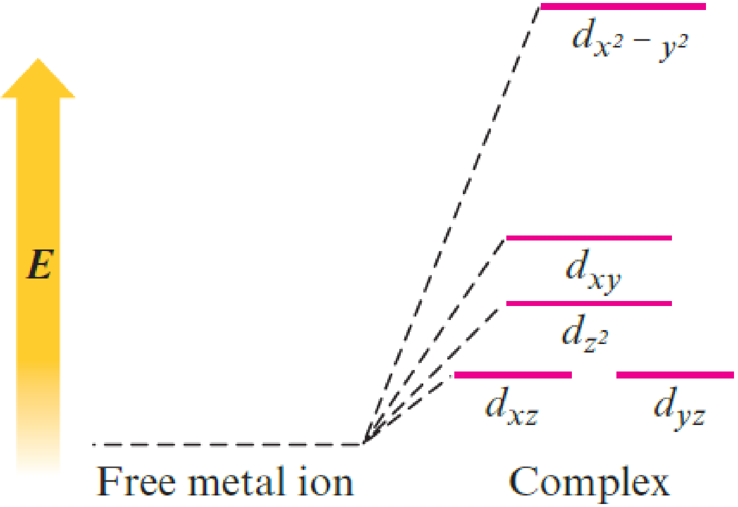
Linear Complexes

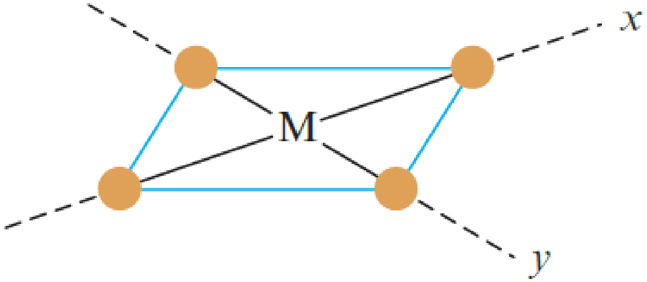
- Obtained from the octahedral arrangement by:
  - Retaining 2 ligands along the *z* axis
  - Removing 4 ligands in the *xy* plane
    - Only d_{z^2} points at the ligands and is highest in energy

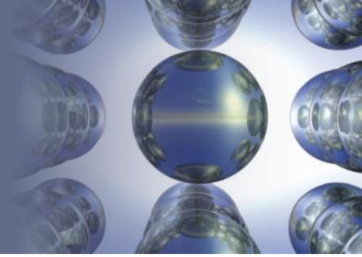


Critical Thinking

- This figure shows a crystal field diagram for a square planar complex oriented in the *xy* plane
    - What if you oriented the complex in the *xz* plane?
        - Sketch the crystal field diagram and contrast it with the figure







Biological Necessity of Metal Ion Complexes

- Used in humans:
  - For the transport and storage of oxygen
  - As electron-transfer agents, catalysts, and drugs
- First-row transition metals are important for human health

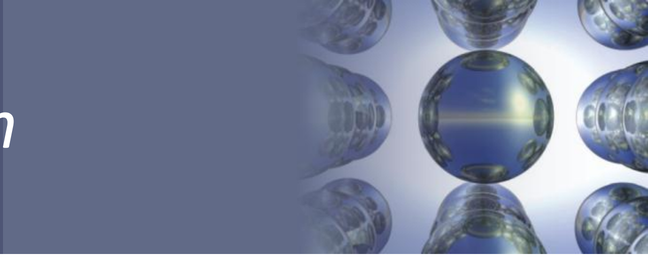


Table 21.18 - First-Row Transition Metals and Their Biological Significance

First-Row Transition Metal	Biological Function(s)
Scandium	None known.
Titanium	None known.
Vanadium	None known in humans.
Chromium	Assists insulin in the control of blood sugar; may also be involved in the control of cholesterol.
Manganese	Necessary for a number of enzymatic reactions.
Iron	Component of hemoglobin and myoglobin; involved in the electron-transport chain.
Cobalt	Component of vitamin B_{12}, which is essential for the metabolism of carbohydrates, fats, and proteins.
Nickel	Component of the enzymes urease and hydrogenase.
Copper	Component of several enzymes; assists in iron storage; involved in the production of color pigments of hair, skin, and eyes.
Zinc	Component of insulin and many enzymes.

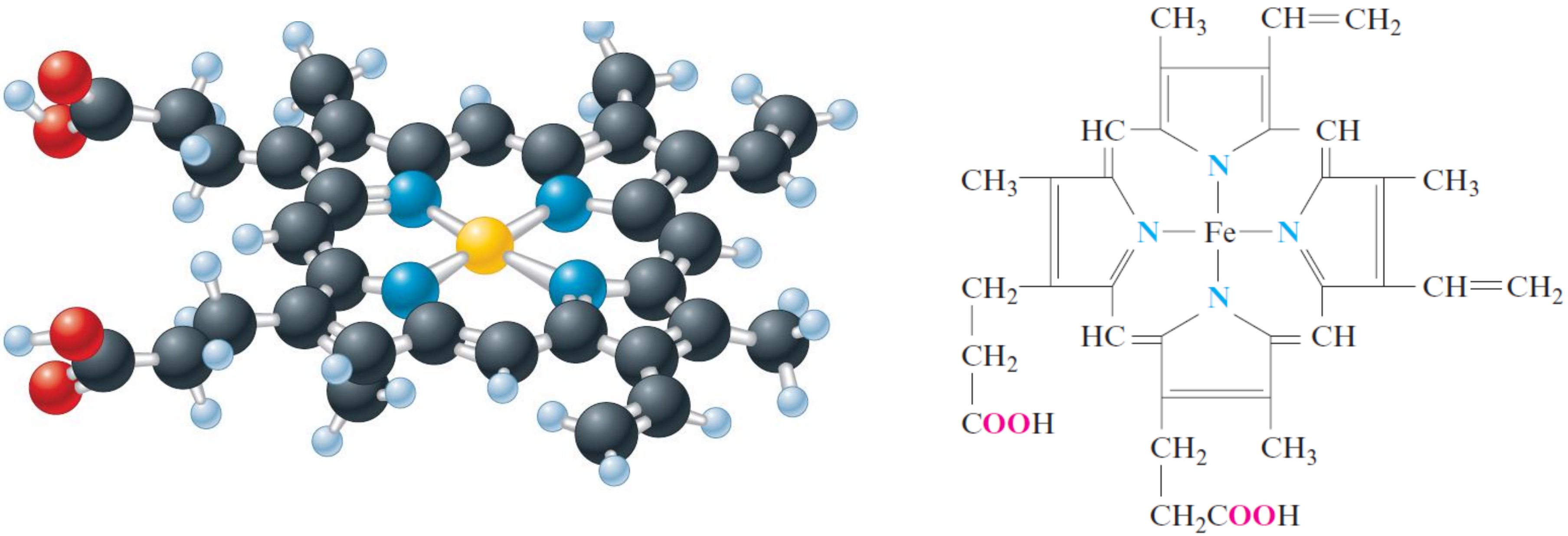
Biological Importance of Iron

- Plays a central role in all living cells
- Mammals gain energy from the oxidation of proteins, carbohydrates, and fats
    - Electrons from the breakdown of the nutrients are passed along the respiratory chain
    - **Cytochromes**: Iron-containing species that are the principal electron-transfer molecules in the respiratory chain
        - Composed of an iron complex (**heme**) and a protein

The Heme Complex

- Contains an Fe^{2+} or Fe^{3+} ion that is coordinated to porphyrin
    - **Porphyrin**: A complicated planar ligand
        - All porphyrins contain the same central ring structure but have different substituent groups at the edges
    - Porphyrin molecules act as tetradentate ligands for many metal ions
        - Example - Chlorophyll is a magnesium–porphyrin complex

Figure 21.29 - The Heme Complex

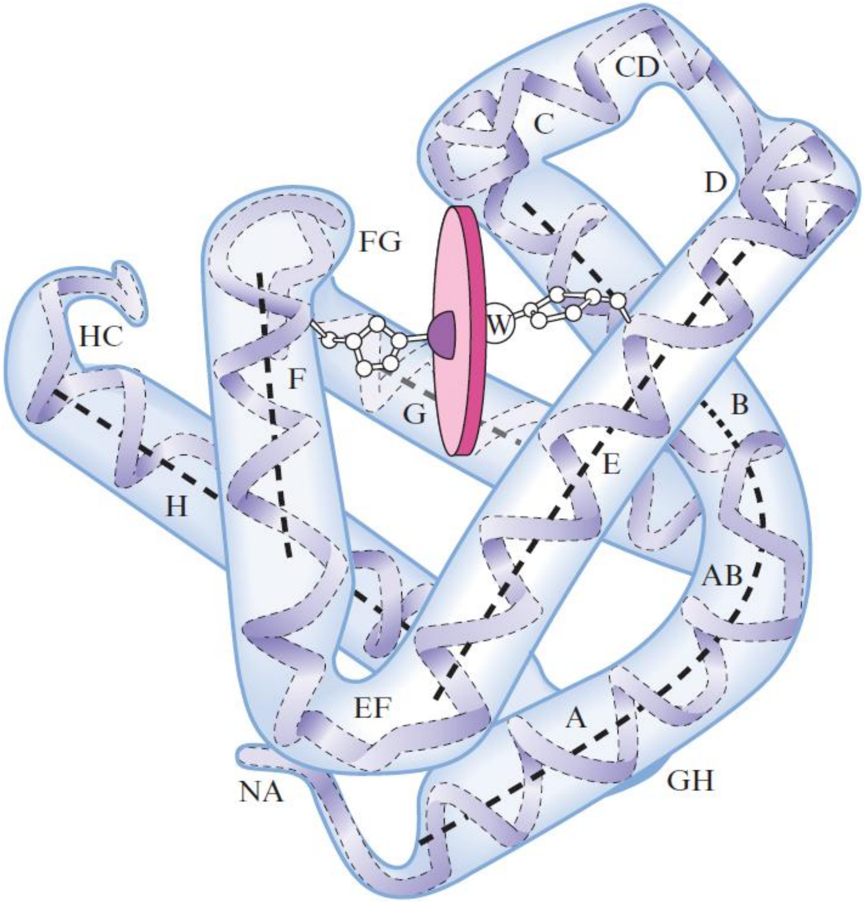


Role of Iron in the Storage of Oxygen in Mammals

- **Myoglobin**: Oxygen storage molecule, which consists of a heme complex and a protein
  - Involves the direct bonding between an O_2 molecule and Fe^{2+}
  - When gaseous O_2 is bubbled in an aqueous solution containing heme, Fe^{2+} is oxidized to Fe^{3+}
    - Oxidation does not occur in myoglobin
    - Involves an O_2 bridge between Fe^{2+} ions

Myoglobin

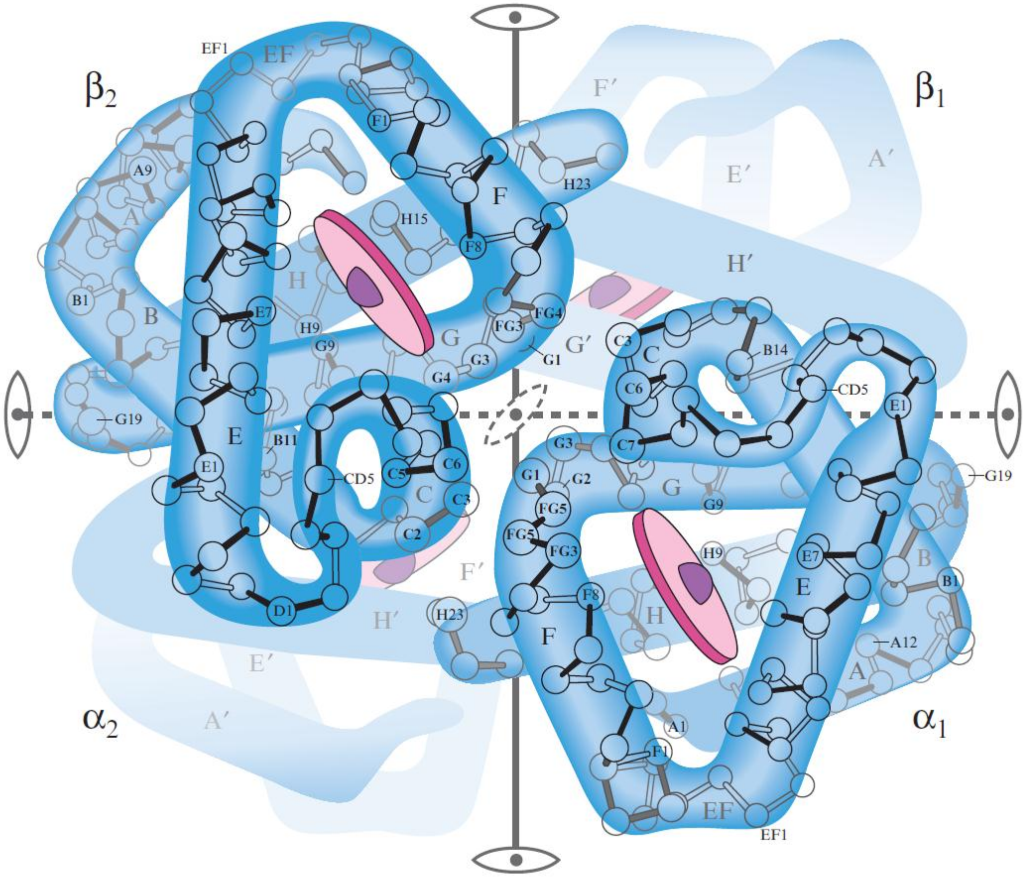
- The Fe^{2+} ion is coordinated to four nitrogen atoms in the porphyrin of the heme and on nitrogen from the protein chain
    - This leaves a sixth coordination position (the W) available for an oxygen molecule



Role of Iron in the Transportation of Oxygen

- **Hemoglobin**: Molecule that contains four myoglobin-like units
  - Helps in the transportation of oxygen in the blood
  - Each hemoglobin contains two α chains and two β chains, each with a heme complex near the center
    - Can bind four oxygen molecules to form a bright red diamagnetic complex
    - When the oxygen molecule is released, water molecules occupy the sixth coordination position around each Fe^{2+}

Figure 21.32 - A Representation of the Hemoglobin Structure



Sickle Cell Anemia

- During protein synthesis for hemoglobin, an improper amino acid is inserted into the protein in two places
  - Due to the nonpolar nature of the incorrect amino acid, the hemoglobin drastically changes its shape

Ingram Publishing/PhotoLibrary/Getty Image

Effect of High Altitudes on Humans

- Reaction between hemoglobin and oxygen

$$\mathrm{Hb}(aq) + 4\mathrm{O}_2(g) \rightleftharpoons \mathrm{Hb(O_2)_4}(aq)$$

Hemoglobin

Oxyhemoglobin

- Oxygen content in high altitudes is low
  - Position of the equilibrium will shift to the left according to Le Châtelier’s principle
  - Lower levels of oxyhemoglobin cause fatigue, dizziness, and high-altitude sickness

Effect of High Altitudes on Humans (Continued)

- The human body is capable of adapting to lower levels of oxygen by making more hemoglobin
  - Causes the equilibrium to shift back to the right
- High-altitude acclimatization
  - Effect of high altitude can be felt for a few weeks, but it disappears as hemoglobin levels in the body increase

Toxicity of Carbon Monoxide and the Cyanide Ion

- **Carboxyhemoglobin**: Stable complex of hemoglobin and carbon monoxide
  - Prevents normal oxygen uptake in the blood
  - Can result in asphyxiation
- Cyanide ion - Respiratory inhibitor
  - Coordinates strongly to cytochrome oxidase, an iron-containing cytochrome enzyme catalyst
    - Prevents the electron-transfer process, and rapid death results

Metallurgy

- Process of separating a metal from its ore and preparing it for use
- Steps
  - Mining
  - Pretreatment of the ore
  - Reduction to the free metal
  - Purification of the metal (refining)
  - Alloying

Extracting a Metal from Its Ore

- Ore is a mixture of **minerals** (pure metal compounds) and **gangue** (sand, clay, and rock)
- Ores must be treated to remove the gangue
  - Ores are pulverized and then processed in various devices
    - Cyclone separators
    - Inclined vibrating tables
    - Flotation tanks

Extracting a Metal from Its Ore (Continued 1)

- **Flotation process**: Method of separating the mineral particles in an ore from the gangue
  - Depends on the greater wettability of the mineral pieces
    - Crushed ore is fed into a tank with a mixture of water, oil, and detergent
    - A stream of air is blown through the mixture to skim the oil-covered pieces

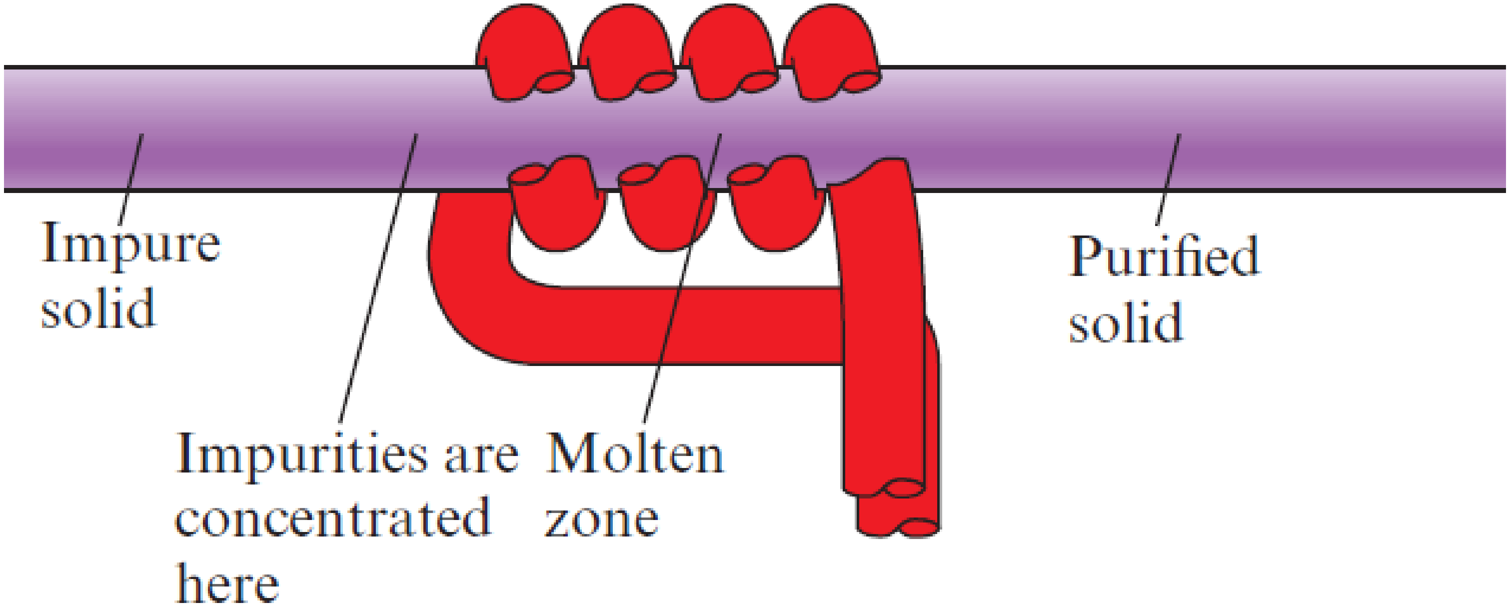
Extracting a Metal from Its Ore (Continued 2)

- After ensuring that the mineral is concentrated, it is chemically altered for the reduction step
  - Carbonates and hydroxides can be converted by simple heating
  - **Roasting**: Sulfide minerals are converted to oxides by heating in air at temperatures below their melting points
  - **Smelting**: Reducing a metal ion to the free metal
    - Depends on the electron affinity of the metal ion

Zone Refining

- Process used for extracting highly pure metals
- Steps
    - A bar of impure metal travels through a heater
        - Causes the metal to melt and recrystallize as it cools
    - Purification of the metal
        - As the crystal re-forms, metal ions are more likely to fit better in the crystal lattice than are the atoms of impurities
        - Impurities are carried to the end of the bar

Figure 21.35 - Schematic Representation of Zone Refining



Pyrometallurgy

- Traditional metallurgical process that requires tremendous amounts of energy
- Drawbacks
  - Leads to atmospheric pollution
  - High costs make it economically unfeasible to treat low-grade ores

Hydrometallurgy

- Uses aqueous chemical solutions to extract metals from their ores through a process called **leaching**
- Uses
  - Extraction of gold from low-grade ores
  - Production of alumina (aluminum oxide) from bauxite

Extraction of Gold from Low-Grade Ores

- **Cyanidation**: Process that treats crushed ore with an aqueous cyanide solution in the presence of air
  - Dissolves gold by forming the complex ion $Au(CN)_2^-$

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4Au(CN)_2^-(aq) + 4OH^-(aq)$$

  - Pure gold is then recovered by reaction of the $Au(CN)_2^-$ solution with zinc powder to reduce Au^+ to Au

$$2Au(CN)_2^-(aq) + Zn(s) \rightarrow 2Au(s) + Zn(CN)_4^{2-}(aq)$$

Extraction of Alumina from Bauxite

- Conducted using the Bayer process
  - The ore is leached with sodium hydroxide at high temperatures and pressures to dissolve the amphoteric aluminum oxide

$$\mathrm{Al_2O_3}(s) + 2\mathrm{OH^-}(aq) \rightarrow 2\mathrm{AlO_2^-}(aq) + \mathrm{H_2O}(l)$$

  - Leaves behind solid impurities such as SiO_2, Fe_2O_3, and TiO_2

Extraction of Alumina from Bauxite (Continued)

- After the impurities are removed, the pH of the solution is lowered, and pure aluminum oxide is formed
- The product is electrolyzed to produce aluminum metal

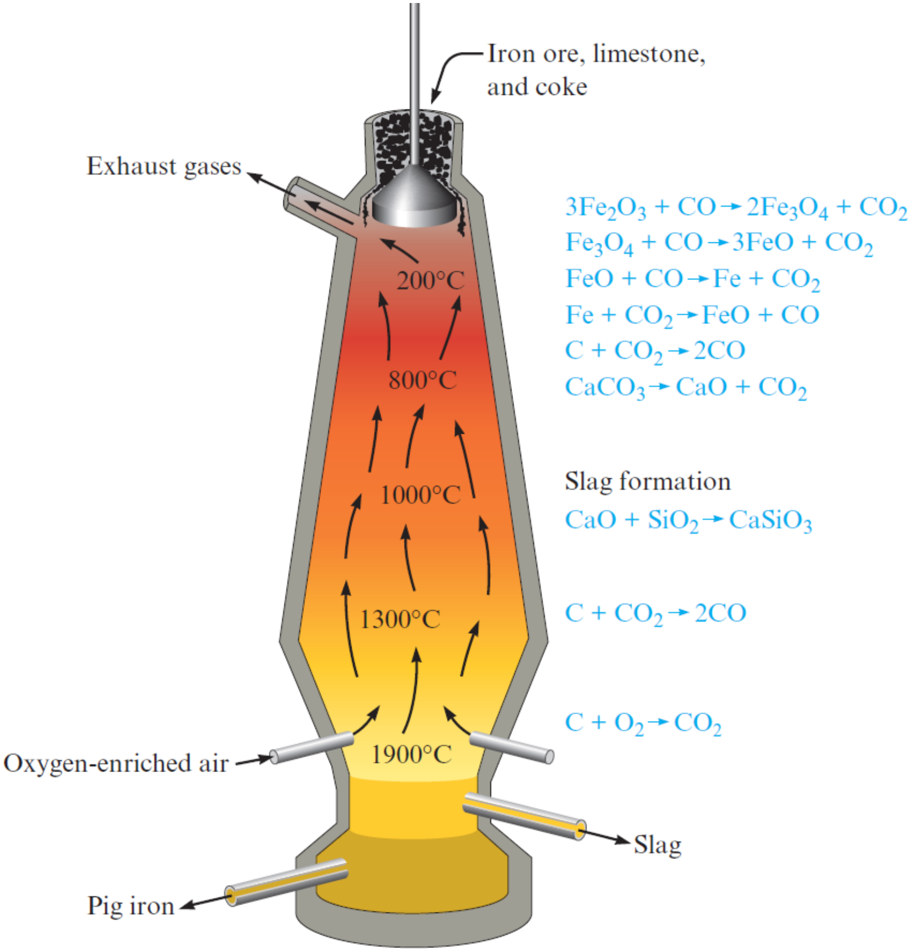
Steps in Hydrometallurgy

- Selective leaching of a metal from its ore
  - Leaching agent
    - Can be water if the metal-containing compound is a water-soluble chloride or sulfate
    - If the metal is present in a water-insoluble substance, aqueous solutions containing acids, bases, oxidizing agents, and salts are used
- Recovering the metal ion from the solution by selective precipitation as an ionic compound

Metallurgy of Iron

- Iron is found in the earth’s crust in many minerals
    - Iron pyrite (FeS_2)
    - Siderite ($FeCO_3$)
    - Hematite (Fe_2O_3)
    - Magnetite ($FeO \cdot Fe_2O_3$)
    - Taconite ores
- Iron is reduced in a **blast furnace**

Figure 21.36 - The Blast Furnace



Metallurgy of Iron - Terms

- **Slag**: Molten calcium silicate and alumina
  - Product of the reaction between $CaCO_3$ that loses CO_2 in the blast furnace and combines with silica and other impurities

$$CaO + SiO_2 \rightarrow CaSiO_3$$

- **Pig iron**: Impure iron that is collected from the blast furnace

Production of Steel

- Steel is an alloy
- Can be classified as:
  - **Carbon steel**: Contains approximately 1.5% carbon
  - **Alloy steel**: Contains carbon and Cr, Co, Mn, or Mo
- Iron is converted to steel by an oxidation process that eliminates unwanted impurities
  - Open hearth process
  - Basic oxygen process

Oxidation Reactions of Steelmaking

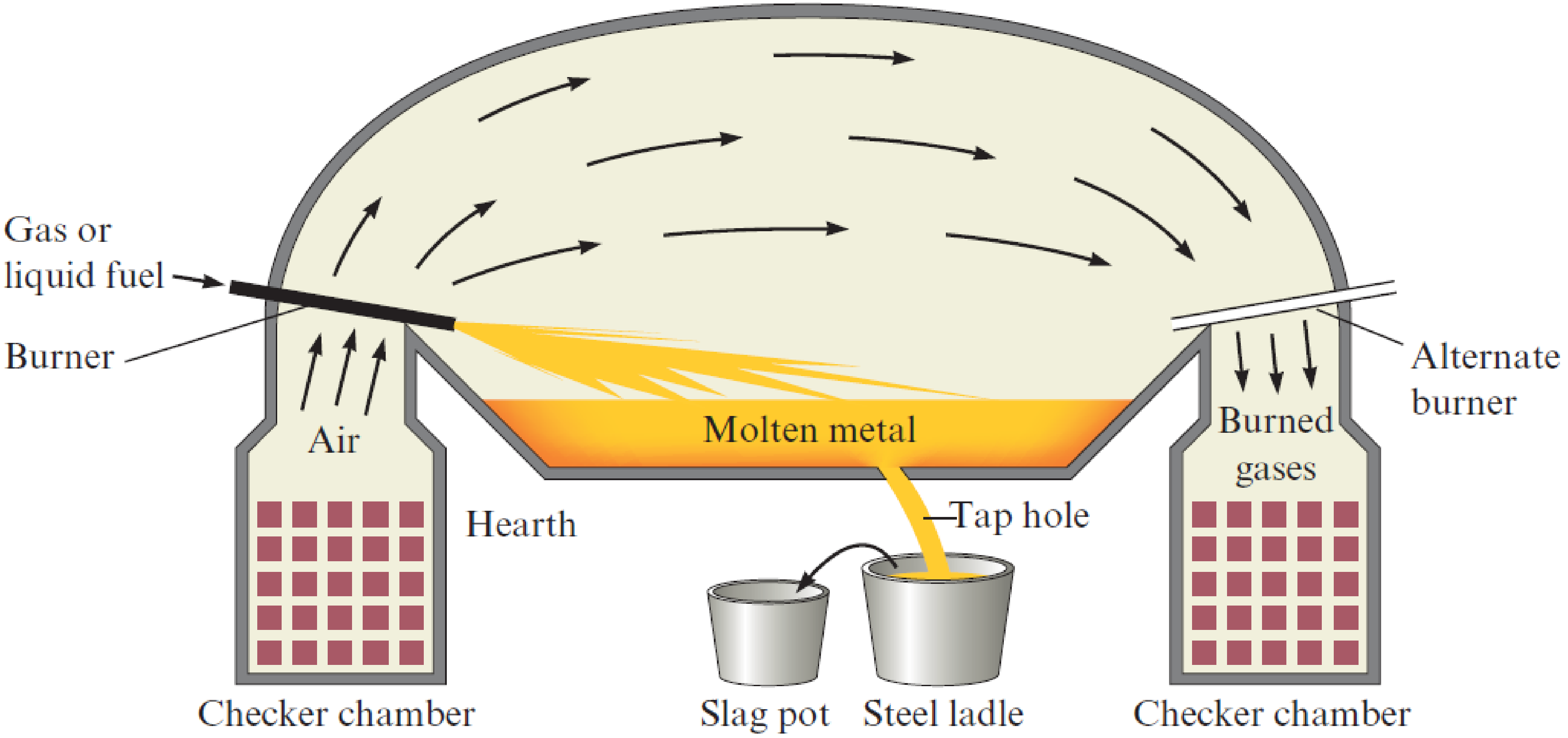
- Manganese, phosphorus, and silicon in the impure iron react with oxygen to form oxides
  - Oxides react with fluxes to form slag
    - Choice of flux depends on the major impurities present

$$\text{Acidic flux: } \mathrm{MnO}(s) + \mathrm{SiO_2}(s) \xrightarrow{\text{Heat}} \mathrm{MnSiO_3}(l)$$

$$\text{Basic flux: } \mathrm{SiO_2}(s) + \mathrm{MgO}(s) \xrightarrow{\text{Heat}} \mathrm{MgSiO_3}(l)$$

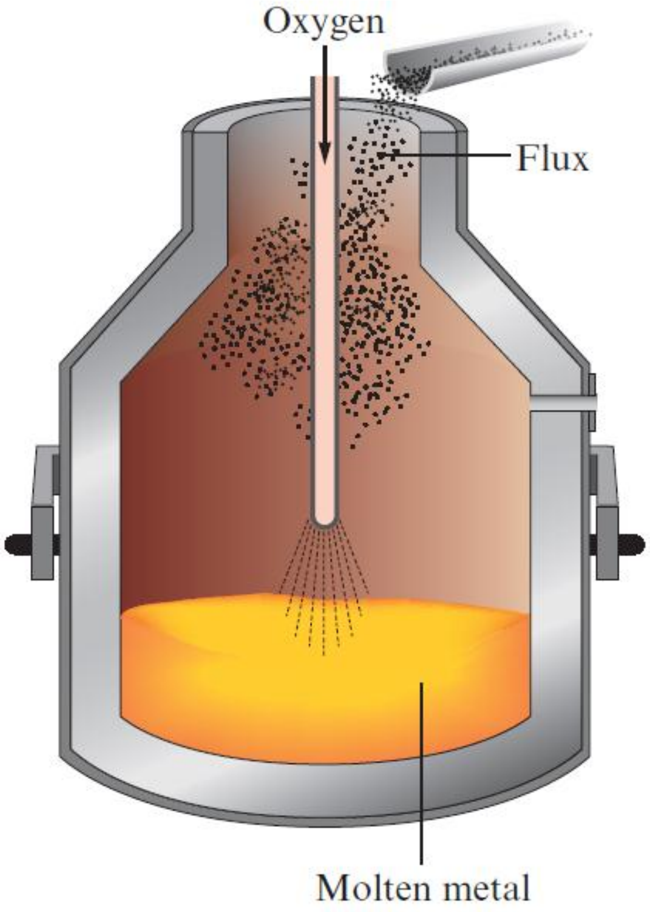
$$\mathrm{P_4O_{10}}(s) + 6\mathrm{CaO}(s) \xrightarrow{\text{Heat}} 2\mathrm{Ca_3(PO_4)_2}(l)$$

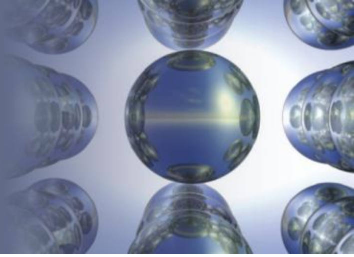
Figure 21.37 - Schematic Diagram of the Open Hearth Process for Steelmaking



Basic Oxygen Process for Steelmaking

- Faster method
- Exothermic oxidation reactions proceed rapidly
  - Produce enough heat to raise the temperature nearly to the boiling point of iron without an external heat source





Electric Arc Method of Steel Making

- An electric arc between carbon electrodes is used to melt the charge
    - No fuel-borne impurities are added to the steel, since no fuel is needed
- Higher temperatures lead to more effective removal of sulfur and phosphorus impurities
- Oxygen is added in the process
    - Helps control oxide impurities in the steel effectively

Heat Treatment of Steel

- Pure iron exists in two crystalline forms based on the temperature
  - α-iron - Body-centered cubic structure of iron when the temperature is less than 912° C
  - Austentite or γ-iron - Iron has a face-centered cubic structure when temperature is between 912° C and 1394° C
  - δ-iron - Body-centered cubic structure identical to α-iron at 1394° C

Alloying Iron with Carbon

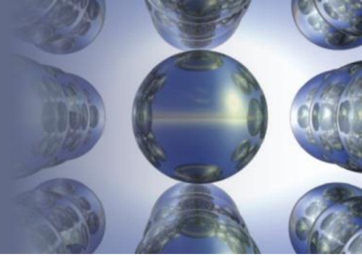
- Forms the interstitial alloy carbon steel
- The temperature at which α-iron is converted to austentite falls by 200° C
  - At high temperatures, iron and carbon can react to form cementite, an iron carbide

$$3\text{Fe} + \text{C} + \underset{\text{Heat}}{\text{energy}} \rightleftharpoons \underset{\text{Cementite}}{\text{Fe}_3\text{C}}$$

  - Thus, steel is a mixture of iron metal in one of its crystal forms, carbon, and cementite

Alloying Iron with Carbon (Continued 1)

- Much of the carbon is converted to cementite when steel is heated to 1000° C
  - The equilibrium shifts to the left if the steel is allowed to cool slowly
    - Small crystals of carbon precipitate
  - The equilibrium does not have time to adjust if the cooling is rapid
    - The cementite is trapped, and the steel has a high cementite content



Alloying Iron with Carbon (Continued 2)

- **Tempering**: Heating a mixture to intermediate temperatures followed by a rapid cooling process
    - Used for fine-tuning the proportions of carbon crystals and cementite in steel to give the desired properties