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

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
<tr>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Rg</td>
<td>Cn</td>
</tr>
</tbody>
</table>

#### f-block transition elements

* **Lanthanides**

| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |

| 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
    - \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3\) contains \(\text{Co(NH}_3\text{)}_6^{3+}\) cations and \(\text{Cl}^-\) anions
A Complex Ion - $\text{Co(NH}_3\text{)}_6^{3+}$
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

- $3d$ orbitals begin to fill after the $4s$ orbital is complete

- Exceptions
  - Chromium (Cr) - [Ar]$4s^13d^5$
  - Copper - [Ar]$4s^13d^{10}$

- A set of orbitals with the same energy is said to be degenerate
First-row transition metal ions do not have 4s electrons

- Energy of the 3d orbitals is significantly less than that of the 4s orbital

Example

- Configuration of neutral titanium - [Ar]4s²3d²
- Configuration of Ti³⁺ - [Ar]3d¹
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 4s and 3d 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 3d orbitals while going across the period
Section 21.1

The Transition Metals: A Survey

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
  \[ M \rightarrow M^{n+} + ne^- \]
  - This is the reverse of the conventional half-reactions
- The metal with most positive potential is the best reducing agent
Section 21.1
The Transition Metals: A Survey

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc → Sc^{3+} + 3e^-</td>
<td>2.08</td>
</tr>
<tr>
<td>Ti → Ti^{2+} + 2e^-</td>
<td>1.63</td>
</tr>
<tr>
<td>V → V^{2+} + 2e^-</td>
<td>1.2</td>
</tr>
<tr>
<td>Mn → Mn^{2+} + 2e^-</td>
<td>1.18</td>
</tr>
<tr>
<td>Cr → Cr^{2+} + 2e^-</td>
<td>0.91</td>
</tr>
<tr>
<td>Zn → Zn^{2+} + 2e^-</td>
<td>0.76</td>
</tr>
<tr>
<td>Fe → Fe^{2+} + 2e^-</td>
<td>0.44</td>
</tr>
<tr>
<td>Co → Co^{2+} + 2e^-</td>
<td>0.28</td>
</tr>
<tr>
<td>Ni → Ni^{2+} + 2e^-</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu → Cu^{2+} + 2e^-</td>
<td>-0.34</td>
</tr>
</tbody>
</table>
Standard Reduction Potentials (Continued)

\[ 2H^+ + 2e^- \rightarrow H_2 \]

- For this reaction, \( E^\circ = 0 \)
  - 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
Section 21.1

The Transition Metals: A Survey

Figure 21.3 - Atomic Radii of the 3\textit{d}, 4\textit{d}, and 5\textit{d} Transition Series
4d and 5d Transition Series - Trends

- 4d and 5d 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
Differences in size between 4d and 5d transition elements in a group increase gradually from left to right.

Useful properties of 4d and 5d metals:
- Zirconium and zirconium oxide are highly resistant to high temperatures.
  - Used along with niobium and molybdenum alloys in space vehicle parts.
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(H₂O)₆³⁺ 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 TiX₂
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

<table>
<thead>
<tr>
<th>Oxidation State of Vanadium</th>
<th>Species in Aqueous Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>+5</td>
<td>$\text{VO}_2^+$ (yellow)</td>
</tr>
<tr>
<td>+4</td>
<td>$\text{VO}^2+$ (blue)</td>
</tr>
<tr>
<td>+3</td>
<td>$\text{V}^{3+}(aq)$ (blue-green)</td>
</tr>
<tr>
<td>+2</td>
<td>$\text{V}^{2+}(aq)$ (violet)</td>
</tr>
</tbody>
</table>
Chromium

- Rare element and an important industrial material
- Chief ore - Chromite (FeCr$_2$O$_4$)
  - Reduced by carbon to produce ferrochrome, which can be added to iron for making steel

$$\text{FeCr}_2\text{O}_4(s) + 4\text{C}(s) \rightarrow \text{Fe}(s) + 2\text{Cr}(s) + 4\text{CO}(g)$$

Ferrochrome
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 (VI) species are excellent oxidizing agents in acidic solution

- Reduction of dichromate ion (Cr$_2$O$_7^{2-}$) to the Cr$^{3+}$ ion
  - Oxidizing ability of dichromate ion is pH-dependent
  - Exists as the chromate ion in a basic solution
  - Less powerful as an oxidizing agent

$$\text{Cr}_2\text{O}_7^{2-} (aq) + 14\text{H}^+ (aq) + 6e^- \rightarrow 2\text{Cr}^{3+} (aq) + 7\text{H}_2\text{O}(l) \quad E^\circ = 1.33 \text{ V}$$

$$\text{Cr}_2\text{O}_4^{2-} (aq) + 4\text{H}_2\text{O}(l) + 3e^- \rightarrow \text{Cr(OH)}_3 (s) + 5\text{OH}^- (aq) \quad E^\circ = -0.13 \text{ V}$$
Chromium (Continued 3)

- Red chromium(VI) oxide dissolves in H₂O
  - Product is a strongly acidic, red-orange solution
    \[ 2\text{CrO}_3(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}^+(aq) + \text{Cr}_2\text{O}_7^{2-}(aq) \]
  - When made basic, the solution turns yellow
    - Chromate salts can be obtained
- Cleaning solution - Mixture of chromium(VI) oxide and concentrated H₂SO₄
  - Powerful oxidizing medium that can remove organic materials from analytical glassware
**Figure 21.4** - Structures of the Chromium(VI) Anions

- $\text{Cr}_2\text{O}_7^{2-}$ exists in acidic solution
- $\text{CrO}_4^{2-}$ 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

<table>
<thead>
<tr>
<th>Oxidation State of Manganese</th>
<th>Examples of Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>Mn(OH)$_2$ (pink)</td>
</tr>
<tr>
<td></td>
<td>MnS (salmon)</td>
</tr>
<tr>
<td></td>
<td>MnSO$_4$ (reddish)</td>
</tr>
<tr>
<td></td>
<td>MnCl$_2$ (pink)</td>
</tr>
<tr>
<td>+4</td>
<td>MnO$_2$ (dark brown)</td>
</tr>
<tr>
<td>+7</td>
<td>KMnO$_4$ (purple)</td>
</tr>
</tbody>
</table>
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**

<table>
<thead>
<tr>
<th>Oxidation State of Iron</th>
<th>Examples of Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>FeO (black)</td>
</tr>
<tr>
<td></td>
<td>FeS (brownish black)</td>
</tr>
<tr>
<td></td>
<td>FeSO$_4$ · 7H$_2$O (green)</td>
</tr>
<tr>
<td></td>
<td>K$_4$Fe(CN)$_6$ (yellow)</td>
</tr>
<tr>
<td>+3</td>
<td>FeCl$_3$ (brownish black)</td>
</tr>
<tr>
<td></td>
<td>Fe$_2$O$_3$ (reddish brown)</td>
</tr>
<tr>
<td></td>
<td>K$_3$Fe(CN)$_6$ (red)</td>
</tr>
<tr>
<td></td>
<td>Fe(SCN)$_3$ (red)</td>
</tr>
<tr>
<td>+2, +3 (mixture)</td>
<td>Fe$_3$O$_4$ (black)</td>
</tr>
<tr>
<td></td>
<td>KFe[Fe(CN)$_6$] (deep blue, “Prussian blue”)</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Oxidation State of Cobalt</th>
<th>Examples of Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>CoSO$_4$ (dark blue)</td>
</tr>
<tr>
<td></td>
<td>[Co(H$_2$O)$_6$]Cl$_2$ (pink)</td>
</tr>
<tr>
<td></td>
<td><a href="NO$_3$">Co(H$_2$O)$_6$</a>$_2$ (red)</td>
</tr>
<tr>
<td></td>
<td>CoS (black)</td>
</tr>
<tr>
<td></td>
<td>CoO (greenish brown)</td>
</tr>
<tr>
<td>+3</td>
<td>CoF$_3$ (brown)</td>
</tr>
<tr>
<td></td>
<td>Co$_2$O$_3$ (charcoal)</td>
</tr>
<tr>
<td></td>
<td>K$_3$[Co(CN)$_6$] (yellow)</td>
</tr>
<tr>
<td></td>
<td>[Co(NH$_3$)$_6$]Cl$_3$ (yellow)</td>
</tr>
</tbody>
</table>
Section 21.2
The First-Row Transition Metals

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

<table>
<thead>
<tr>
<th>Oxidation State of Nickel</th>
<th>Examples of Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>NiCl₂ (yellow)</td>
</tr>
<tr>
<td></td>
<td>[Ni(H₂O)₆]Cl₂ (green)</td>
</tr>
<tr>
<td></td>
<td>NiO (greenish black)</td>
</tr>
<tr>
<td></td>
<td>NiS (black)</td>
</tr>
<tr>
<td></td>
<td>[Ni(H₂O)₆]SO₄ (green)</td>
</tr>
<tr>
<td></td>
<td><a href="NO%E2%82%83">Ni(NH₃)₆</a>₂ (blue)</td>
</tr>
</tbody>
</table>
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

\[
3\text{Cu}(s) + 2\text{H}_2\text{O}(l) + \text{SO}_2(g) + 2\text{O}_2(g) \rightarrow \text{Cu}_3(\text{OH})_4\text{SO}_4(s)
\]

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

<table>
<thead>
<tr>
<th>Oxidation State of Copper</th>
<th>Examples of Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>Cu$_2$O (red)</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$S (black)</td>
</tr>
<tr>
<td></td>
<td>CuCl (white)</td>
</tr>
<tr>
<td>+2</td>
<td>CuO (black)</td>
</tr>
<tr>
<td></td>
<td>CuSO$_4$ $\cdot$ 5H$_2$O (blue)</td>
</tr>
<tr>
<td></td>
<td>CuCl$_2$ $\cdot$ 2H$_2$O (green)</td>
</tr>
<tr>
<td></td>
<td><a href="NO$_3$">Cu(H$_2$O)$_6$</a>$_2$ (blue)</td>
</tr>
</tbody>
</table>
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$_3$)$_5$Cl]Cl$_2$
  - Brackets indicate the complex ion composition
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

<table>
<thead>
<tr>
<th>M</th>
<th>Coordination Numbers</th>
<th>Coordination Numbers</th>
<th>Coordination Numbers</th>
<th>Coordination Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺</td>
<td>2, 4</td>
<td>Mn²⁺</td>
<td>4, 6</td>
<td>Sc³⁺</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>2</td>
<td>Fe²⁺</td>
<td>6</td>
<td>Cr³⁺</td>
</tr>
<tr>
<td>Au⁺</td>
<td>2, 4</td>
<td>Co²⁺</td>
<td>4, 6</td>
<td>Co³⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni²⁺</td>
<td>4, 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu²⁺</td>
<td>4, 6</td>
<td>Au³⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn²⁺</td>
<td>4, 6</td>
<td></td>
</tr>
</tbody>
</table>
Typical Geometries of Coordination Numbers

- **Linear**
  - Produced by two ligands

- **Tetrahedral or square planar**
  - Produced by four ligands

- **Octahedral**
  - Produced by six ligands
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)
Section 21.3
Coordination Compounds

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)
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 - H₂O, NH₃, 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:
  - \([\text{Fe(en)}_2(\text{NO}_2)_2]_2\text{SO}_4\)
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 $\text{NO}_2^-$ as a ligand is nitro, and the prefix di- indicates the presence of two $\text{NO}_2^-$ ligands
- Since the anion is sulfate, the compound’s name is:

  $$\text{Bis(ethylenediamine)dinitroiron(III) sulfate}$$

  - **Cation**
  - **Anion**
Exercise

- Give formulas for the following:
  - a. Potassium tetrachlorocobaltate(II)
    \[ \text{K}_2[\text{CoCl}_4] \]
  - b. Aquatricarbonylplatinum(II) bromide
    \[ [\text{Pt(H}_2\text{O})(\text{CO})_3]\text{Br}_2 \]
  - c. Triamminechloroethylenediaminechromium(III) iodide
    \[ [\text{Cr(NH}_3)_3\text{Cl(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)]\text{I}_2 \]
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)
  - Geometric (cis-trans) isomerism
  - Optical isomerism

Coordination isomerism
Linkage isomerism
Section 21.4

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
Section 21.4

Isomerism

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
Section 21.4
Isomerism

Figure 21.11 - *Cis* and *Trans* Isomers of the Complex Compound $[\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+$
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
Section 21.4

Isomerism

**Figure 21.12** - Unpolarized Light and Plane-Polarized Light
Section 21.4
Isomerism

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
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
Section 21.4

Isomerism

Geometric Isomers and Optical Isomers

- Geometric isomers are not necessarily optical isomers
  - Example - The *trans* isomer of \([\text{Co(en)}_2\text{Cl}_2]^+\) 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
Example - The cis isomer of \([\text{Co(en)}_2\text{Cl}_2]^+\) 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
Section 21.4

Isomerism

Example 21.3 - Geometrical and Optical Isomerism

- Does the complex ion \([\text{Co(NH}_3\text{)Br(en)}_2]^2+\) 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.

\[
\begin{align*}
&\text{NH}_3 \\
\text{en} & \quad \text{Co} \quad \text{en} \\
\quad & \quad \text{Br} \quad \text{en} \\
\end{align*}
\]
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
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
Section 21.5
Bonding in Complex Ions: The Localized Electron Model

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 3d 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 3d Orbitals for a Metal Ion in an Octahedral Complex
Splitting of 3$d$ Orbital Energies ($\Delta$)

- 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 3d Orbital Energies ($\Delta$) (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
Section 21.6

The Crystal Field Model

Figure 21.22 - Possible Electron Arrangements in the Split 3d 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 3\(d^5\) electron configuration
  - There are two possible arrangements of the five electrons in the \(d\) orbitals split by the octahedrally arranged ligands
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

\[
\text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-
\]

- Magnitude of \( \Delta \) for a given ligand increases as the charge on the metal ion increases

- Strong-field ligands (large \( \Delta \))
- Weak-field ligands (small \( \Delta \))
Interactive Example 21.5 - Crystal Field Model II

- Predict the number of unpaired electrons in the complex ion \( \text{Cr(CN)}_6^{4-} \)
Interactive Example 21.5 - Solution

- The net charge of $4^-$ means that the metal ion present must be $\text{Cr}^{2+}$ ($-6 + 2 = -4$), which has a $3d^4$ electron configuration.
- Since $\text{CN}^-$ is a strong-field ligand, the correct crystal field diagram for $\text{Cr(CN)}_6^{4-}$ 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(H₂O)₆³⁺
### Table 21.16 - Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed

<table>
<thead>
<tr>
<th>Absorbed Wavelength in nm (Color)</th>
<th>Observed Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 (violet)</td>
<td>Greenish yellow</td>
</tr>
<tr>
<td>450 (blue)</td>
<td>Yellow</td>
</tr>
<tr>
<td>490 (blue-green)</td>
<td>Red</td>
</tr>
<tr>
<td>570 (yellow-green)</td>
<td>Violet</td>
</tr>
<tr>
<td>580 (yellow)</td>
<td>Dark blue</td>
</tr>
<tr>
<td>600 (orange)</td>
<td>Blue</td>
</tr>
<tr>
<td>650 (red)</td>
<td>Green</td>
</tr>
</tbody>
</table>
Wavelength absorbed by a molecule is determined by the following relationship:

\[ \Delta E = \frac{hc}{\lambda} \]

- \( \Delta E \) - Energy spacing in the molecule
- \( \lambda \) - 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 $\Delta$ 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 $3d$ 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$_4^{2-}$
The complex ion contains Co$^{2+}$, which has a 3$d^7$ 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.
Section 21.6
The Crystal Field Model

Figure 21.27 - Crystal Field Diagrams for Octahedral and Tetrahedral Complexes

- $\Delta_{\text{oct}} > \Delta_{\text{tet}}$
- $d_{z^2}$ and $d_{x^2-y^2}$ orbitals point their lobes directly at the point charges, making them relatively high in energy
Section 21.6
The Crystal Field Model

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

<table>
<thead>
<tr>
<th>First-Row Transition Metal</th>
<th>Biological Function(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium</td>
<td>None known.</td>
</tr>
<tr>
<td>Titanium</td>
<td>None known.</td>
</tr>
<tr>
<td>Vanadium</td>
<td>None known in humans.</td>
</tr>
<tr>
<td>Chromium</td>
<td>Assists insulin in the control of blood sugar; may also be involved in the control of cholesterol.</td>
</tr>
<tr>
<td>Manganese</td>
<td>Necessary for a number of enzymatic reactions.</td>
</tr>
<tr>
<td>Iron</td>
<td>Component of hemoglobin and myoglobin; involved in the electron-transport chain.</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Component of vitamin B12, which is essential for the metabolism of carbohydrates, fats, and proteins.</td>
</tr>
<tr>
<td>Nickel</td>
<td>Component of the enzymes urease and hydrogenase.</td>
</tr>
<tr>
<td>Copper</td>
<td>Component of several enzymes; assists in iron storage; involved in the production of color pigments of hair, skin, and eyes.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Component of insulin and many enzymes.</td>
</tr>
</tbody>
</table>
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 tetradeutate ligands for many metal ions
    - Example - Chlorophyll is a magnesium–porphyrin complex
Section 21.7
The Biological Importance of Coordination Complexes

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 $\alpha$ chains and two $\beta$ 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 $\text{Fe}^{2+}$
Section 21.7

The Biological Importance of Coordination

Complexes

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
Effect of High Altitudes on Humans

- Reaction between hemoglobin and oxygen

\[
\text{Hb}(aq) + 4\text{O}_2(g) \rightleftharpoons \text{Hb}(\text{O}_2)_4(aq)
\]

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

Impurities are concentrated in the molten zone here.

Impure solid

Purified solid
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 \( \text{Au} (CN)_2^- \)
    
    \[
    4\text{Au} (s) + 8\text{CN}^- (aq) + \text{O}_2 (g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Au} (CN)_2^- (aq) + 4\text{OH}^- (aq)
    \]

  - Pure gold is then recovered by reaction of the \( \text{Au} (CN)_2^- \) solution with zinc powder to reduce \( \text{Au}^+ \) to \( \text{Au} \)
    
    \[
    2\text{Au} (CN)_2^- (aq) + \text{Zn} (s) \rightarrow 2\text{Au} (s) + \text{Zn} (CN)_4^{2-} (aq)
    \]
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

\[
\text{Al}_2\text{O}_3(s) + 2\text{OH}^- (aq) \rightarrow 2\text{AlO}_2^- (aq) + \text{H}_2\text{O}(l)
\]

- Leaves behind solid impurities such as SiO\(_2\), Fe\(_2\)O\(_3\), 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$_2$O$_3$)
  - Magnetite (FeO · Fe$_2$O$_3$)
  - Taconite ores
- Iron is reduced in a **blast furnace**
Figure 21.36 - The Blast Furnace

- Iron ore, limestone, and coke enter the blast furnace.
- Exhaust gases exit at the top.
- Oxygen-enriched air is injected at the bottom.
- Pig iron is produced at the bottom.
- Slag is formed at the top.
- Reactions:
  - $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$
  - $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$
  - $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
  - $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$
  - $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
  - $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
  - $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
  - $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$

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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
    \[
    \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3
    \]

- **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

\[
\text{Acidic flux: } \text{MnO}(s) + \text{SiO}_2(s) \xrightarrow{\text{Heat}} \text{MnSiO}_3(l) \\
\text{Basic flux: } \text{SiO}_2(s) + \text{MgO}(s) \xrightarrow{\text{Heat}} \text{MgSiO}_3(l) \\
\text{P}_4\text{O}_{10}(s) + 6\text{CaO}(s) \xrightarrow{\text{Heat}} 2\text{Ca}_3(\text{PO}_4)_2(l)
\]
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
  - $\alpha$-iron - Body-centered cubic structure of iron when the temperature is less than $912^\circ$ C
  - Austenite or $\gamma$-iron - Iron has a face-centered cubic structure when temperature is between $912^\circ$ C and $1394^\circ$ C
  - $\delta$-iron - Body-centered cubic structure identical to $\alpha$-iron at $1394^\circ$ C
Alloying Iron with Carbon

- Forms the interstitial alloy carbon steel
- The temperature at which $\alpha$-iron is converted to austenite falls by 200°C
  - At high temperatures, iron and carbon can react to form cementite, an iron carbide
    \[3 \text{Fe} + C + \text{energy} \rightleftharpoons \text{Fe}_3\text{C}\]
  - 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