

Chapter 23
Metals and Metallurgy

- This chapter reviews some of the chemistry of the metals.
- Where are metals found?
- How do we recover metals?
- What is the chemical behavior of the transition metals?

23.1 Occurrence and Distribution of Metals

- The solid portion of the earth is called the lithosphere.
- Concentrated metal deposits are found beneath the earth's surface.
- Ore: deposit that contains enough metal that we can extract economically.

Occurrence and Distribution of Metals

- Minerals
- Most metals are found in minerals.
- Names of minerals are usually based on the location of their discovery.
- Other minerals are named after their colors: malachite comes from the Greek malache (the name of a tree with very green leaves).
- Most important ores are oxide, sulfide and carbonate minerals.

Metallurgy

- Metallurgy is the science and technology of extracting metals from minerals.
- There are five important steps:
- Mining (getting the ore out of the ground)
- Concentrating (preparing it for further treatment)
- Reduction (to obtain the free metal in the zero oxidation state)
- Refining (to obtain the pure metal)
- Mixing with other metals (to form an alloy)

23.2 Pyrometallurgy

- Pyrometallurgy uses processes at high temperatures to obtain the free metal.
- Several steps are employed:
- Calcination is heating of ore to cause decomposition and elimination of a volatile product:
$$\text{PbCO}_3(\text{s}) \rightarrow \text{PbO}(\text{s}) + \text{CO}_2(\text{g})$$
- Roasting is heating which causes chemical reactions between the ore and the furnace atmosphere:
$$2\text{ZnS}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s}) + 2\text{SO}_2(\text{g})$$
$$2\text{MoS}_2(\text{s}) + 7\text{O}_2(\text{g}) \rightarrow 2\text{MoO}_3(\text{s}) + 4\text{SO}_2(\text{g})$$
- Smelting is a melting process that causes materials to separate into two or more layers.
- Slag consists mostly of molten silicates in addition to aluminates, phosphates, fluorides, and other inorganic materials.
- Refining is a process in which a crude, impure metal is converted into a pure metal.

Pyrometallurgy of Iron

- Most important sources of iron are hematite Fe_2O_3 and magnetite Fe_3O_4 .
- Reduction occurs in a blast furnace.
- The ore, limestone and coke are added to the top of the blast furnace.
- Coke is coal that has been heated to drive off the volatile components.
- Coke reacts with oxygen to form CO (the reducing agent):

$$2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) \quad \Delta\text{H} = -221 \text{ kJ}$$
- CO is also produced by the reaction of water vapor in the air with C:

$$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}) \quad \Delta\text{H} = +131 \text{ kJ}$$
- Since this reaction is endothermic, if the blast furnace gets too hot, water vapor is added to cool it down without interrupting the chemistry.
- At around 250°C limestone is calcined (heated to decomposition and elimination of volatiles).
- Also around 250°C iron oxides are reduced by CO:

$$\text{Fe}_3\text{O}_4(\text{s}) + 4\text{CO}(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{CO}_2(\text{g}) \quad \Delta\text{H} = -15 \text{ kJ}$$

$$\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \quad \Delta\text{H} = +150 \text{ kJ}$$
- Molten iron is produced lower down the furnace and removed at the bottom.
- Slag (molten silicate materials) is removed from above the molten iron.
- If iron is going to be made into steel it is poured directly into a basic oxygen furnace.
- The molten iron is converted to steel, an alloy of iron.
- To remove impurities, O_2 is blown through the molten mixture.
- The oxygen oxidizes the impurities.

Formation of Steel

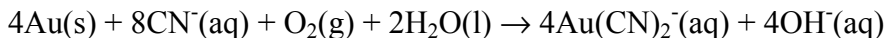
- Steel is an alloy of iron.
- From the blast furnace, the iron is poured into a converter, which consists of a steel shell encasing a refractory brick liner.
- After treatment in the blast furnace, there are impurities in the iron, which must be removed by oxidation.
- Air cannot be present in the converter because the nitrogen will form iron nitride (causes the steel to be brittle).
- Oxygen diluted with Ar is used as the oxidizing agent.
- When oxygen emerges from the converter, then all the impurities have been oxidized and the iron is poured into a ladle.

23.3 Hydrometallurgy

- Hydrometallurgy is the extraction of metals from ores using water. These processes are usually more energy efficient than pyrometallurgical processes.
- Leaching is the selective dissolution of the desired mineral.
- Typical leaching agents are dilute acids, bases, salts, and sometimes water.

Hydrometallurgy

- Gold can be extracted from low-grade ore by cyanidation:
- NaCN solution is sprayed over the crushed ore and the gold is oxidized with air, forming a complex ion in solution:



- The gold is then recovered as a solid by reduction:
 $2\text{Au(CN)}_2^{\ominus}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Zn(CN)}_4^{2-}(\text{aq}) + 2\text{Au(s)}$

The Hydrometallurgy of Aluminum

- Aluminum is the second only to iron in commercial uses.
- Bauxite is a mineral that contains Al as $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. It is treated by the Bayer process:
- The crushed ore is digested in 30% NaOH at 150 to 230°C and up to 30 atm pressure (to prevent boiling).
- The Al_2O_3 dissolves as a complex ion:
 $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O(s)} + 2\text{H}_2\text{O(l)} + 2\text{OH}^{\ominus}(\text{aq}) \rightarrow 2\text{Al(OH)}_4^{\ominus}(\text{aq})$
- The aluminate solution is separated by lowering the pH, then calcined and reduced to produce the metal.

23.4 Electrometallurgy

Electrometallurgy of Sodium

- Electrometallurgy is the process of obtaining metals through electrolysis.
- Two different starting materials: molten salt or aqueous solution.
- Sodium is produced by electrolysis of molten NaCl in a Downs cell.
- CaCl_2 is used to lower the melting point of NaCl from 804°C to 600°C.
- An iron screen is used to separate Na and Cl (so that NaCl is not re-formed).
- At the cathode (iron): $2\text{Na}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Na(l)}$
- At the anode (carbon): $2\text{Cl}^{\ominus}(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

Electrometallurgy of Aluminum

- Hall process electrolysis cell is used to produce aluminum.
- Al_2O_3 melts at 2000°C and it is impractical to perform electrolysis on the molten salt.
- Hall: use purified Al_2O_3 in molten cryolite (Na_3AlF_6 , melting point 1012°C).
- Anode: $\text{C(s)} + 2\text{O}^{2-}(\text{l}) \rightarrow \text{CO}_2(\text{g}) + 4\text{e}^-$
- Cathode: $3\text{e}^- + \text{Al}^{3+}(\text{l}) \rightarrow \text{Al(l)}$
- The graphite rods are consumed in the reaction.
- Bayer process: bauxite (~ 50 % Al_2O_3) is concentrated to produce aluminum oxide.
- To produce 1000 kg of Al, we need 4000 kg of bauxite, 70 kg of cryolite, 450 kg of C anodes and $56 \times 10^9\text{J}$ of energy.
- Requirements for 65,000 beverage cans.

Electrorefining of Copper

- Because of its good conductivity, Cu is used to make electrical wiring.
- Impurities reduce conductivity, therefore pure copper is required in the electronics industry.
- Slabs of impure Cu are used as anodes, thin sheets of pure Cu are the cathodes.
- Acidic copper sulfate is used as the electrolyte.
- The voltage across the electrodes is designed to produce copper at the cathode.
- The metallic impurities do not plate out on the cathode.

- Metal ions are collected in the sludge at the bottom of the cell.
- Copper sludge provides the following amounts of US production of rare elements: Mo (25%), Se (93%), Te (96%), Au (13%), Ag (25%)

23.5 *Metallic Bonding*

Physical Properties of Metals

- Important physical properties of pure metals: malleable, ductile, good conductors, and feel cold.
- Most metals are solids with the atoms in a close packed arrangement.
- In Cu, each atom is surrounded by 12 neighbors.
- There are not enough electrons for the metal atoms to be covalently bonded to each other.

Metallic Bonding

- Electron-Sea Model for Metallic Bonding
- We use a delocalized model for electrons in a metal.
- The metal nuclei are seen to exist in a sea of electrons.
- No electrons are localized between any two metal atoms.
- Therefore, the electrons can flow freely through the metal.
- Without any definite bonds, the metals are easy to deform (and are malleable and ductile).
- Problems with the electron sea model:
 - As the number of electrons increase, the strength of bonding should increase and the melting point should increase.
 - But group 6B metals have the highest melting points (center of the transition metals).

Molecular-Orbital Model for Metals

- Delocalized bonding requires the atomic orbitals on one atom to interact with atomic orbitals on neighboring atoms.
- For example, graphite electrons are delocalized over a whole plane in a molecular orbital, which makes graphite an electrical conductor.
- In metals there is a very large number of orbitals.
- As the number of orbitals increases, their energy spacing decreases and they band together.
- The number of electrons do not completely fill the band of orbitals.
- Therefore, electrons can be promoted to unoccupied energy bands.
- Since the energy differences between orbitals are small, the promotion of electrons occurs at low energy costs.
- As we move across the transition metal series, the antibonding band starts becoming filled.
- Therefore, the first half of the transition metal series have only bonding-bonding interactions, the second half has bonding-antibonding interactions.
- We expect the middle of the transition metal series to have the highest melting points.
- The energy gap between bands is called the band gap.

23.6 Alloys

- Alloys have more than one element with characteristics of metals.
- Pure metals and alloys have different physical properties.
- In jewelry an alloy of gold and copper is used (the alloy is harder than soft gold).
- Solution alloys are homogeneous mixtures.
- Heterogeneous alloys: components are not dispersed uniformly (e.g. pearlite steel has two phases: almost pure Fe and cementite, Fe₃C).
- There are two types of solution alloy:
 - substitutional alloys (the solute atoms take the positions of the solvent);
 - interstitial alloys (the solute occupies interstitial sites in the metallic lattice).
- Substitutional alloys:
 - Atoms must have similar atomic radii.
 - Elements must have similar bonding characteristics.
- Interstitial alloys:
 - One element must have a significantly smaller radius than the other (in order to fit into the interstitial site), e.g. a nonmetal.
 - The alloy is much stronger than the pure metal (increased bonding between nonmetal and metal).
 - Example steel (contains up to 3 % carbon).

23.7 Transition Metals

Physical Properties

- Transition metals occupy the d block of the periodic table.
- Almost all have two s electrons (exceptions group 6B and group 1B).
- Most of these elements are very important in modern technology.
- Physical properties of transition metals can be classified into two groups: atomic properties (e.g. size) and bulk properties (e.g. melting point).
- The atomic trends tend to be smooth for the transition metals.
- Most of the trends in bulk properties are less smooth than the atomic properties.
- The trends in atomic properties of the transition metals can be exemplified with atomic radius.
- Atomic radius decreases and reaches a minimum around group 8B (Fe, Co, Ni) and then increases for groups 1 and 2, with a deviation for groups 6A and 7A.
- This trend is again understood in terms of effective nuclear charge and crystal field stabilization energy.
- The increase in size of the Cu and Zn triads is rationalized in terms of the completely filled d orbital.
- In general atomic size increases down a group.
- An important exception: Hf has almost the same radius as Zr (group 4B): we would expect Hf to be larger than Zr.
- Between La and Hf the 4f shell fills (Lanthanides).
- As 4f orbitals fill, the effective nuclear charge increases and the lanthanides contract smoothly.
- The Lanthanide Contraction balances the increase in size anticipated between Hf and Zr.

- The second and third series are usually about the same size, with the first series being smaller.
- Second and third series metals are very similar in their properties (e.g. Hf and Zr are always found together in ores and are very difficult to separate).
- Electron Configurations and Oxidation States
- Even though the $(n - 1)d$ orbital is filled after the ns orbital, electrons are lost from the orbital with highest n first.
- Transition metals lose s electrons before the d electrons.
- Example: Fe: $[\text{Ar}]3d^64s^2$
 Fe^{2+} : $[\text{Ar}]3d^6$

Electron Configurations and Oxidation States

- d -electrons are responsible for some important properties:
- transition metals have more than one oxidation state
- transition metal compounds are colored (caused by electronic transitions)
- transition metal compounds have magnetic properties
- Note all oxidation states for metals are positive.
- The $2+$ oxidation state is common because it corresponds to the loss of both s electrons. (Exception: Sc where the $3+$ oxidation state is isoelectronic with Ar.)
- The maximum common oxidation state is $+7$ for Mn.
- For the second and third series, the maximum oxidation state is $+8$ for Ru and Os (RuO_4 and OsO_4).

Transition Metals

- Magnetism provides important bonding information.
- Electron spin generates a magnetic field with a magnetic moment.

Magnetism

- There are three types of magnetic behavior:
 - Diamagnetic (no atoms or ions with magnetic moments);
 - Paramagnetic (magnetic moments not aligned outside a magnetic field);
 - Ferromagnetic (coupled magnetic centers aligned in a common direction).
- When two spins are opposing, the magnetic fields cancel (diamagnetic).
- Diamagnetic substances are weakly repelled by external magnetic fields.
- When spins are unpaired, the magnetic fields do not cancel (paramagnetic).
- Generally, the unpaired electrons in a solid are not influenced by adjacent unpaired electrons. That is, the magnetic moments are randomly oriented.
- When paramagnetic materials are placed in a magnetic field, the electrons become aligned.
- Ferromagnetism is a special case of paramagnetism where the magnetic moments are permanently aligned (e.g. Fe, Co and Ni).
- Ferromagnetic oxides are used in magnetic recording tape (e.g. CrO_2 and Fe_3O_4).

*Chemistry of Selected Transition Metals**Chromium*

- In the absence of air, Cr reacts with acid to form a solution of blue Cr^{2+} :
- $\text{Cr(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Cr}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- In the presence of air, the Cr^{2+} readily oxidizes to Cr(III):
- $4\text{Cr}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Cr}(\text{OH})_2\text{Cr}^{4+}(\text{aq})$
- In aqueous solution, Cr is usually present in the 6+ oxidation state.
- In base chromate, CrO_4^{2-} , is the most stable ion.
- In acid dichromate, $\text{Cr}_2\text{O}_7^{2-}$, is the most stable ion.
- Chromate is a much darker yellow than dichromate.

Iron

- In aqueous solution iron is present in the +2 (ferrous) or +3 (ferric oxidation states).
- Iron reacts with nonoxidizing agents to form $\text{Fe}^{2+}(\text{aq})$.
- In the presence of air, Fe^{2+} is oxidized to Fe^{3+} .
- As with most metal ions, in water iron forms complex ions, $\text{Fe}(\text{H}_2\text{O})_6^{n+}$.
- In acidic solution $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is stable, but in base $\text{Fe}(\text{OH})_3$ precipitates.
- If NaOH is added to a solution of $\text{Fe}^{3+}(\text{aq})$ and the brownish $\text{Fe}(\text{OH})_3$ precipitate is formed.

Copper

- In aqueous solution copper has two dominant oxidation states: +1 (cuprous) and +2 (cupric).
- Cu^+ has a $3d^{10}$ electronic configuration.
- Cu(I) salts tend to be white and insoluble in water.
- Cu(I) disproportionates:

$$2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$$
- Cu(II) is the more common oxidation state.
- Blue vitriol is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
- In aqueous solution, four water molecules are coordinated to the Cu and one is hydrogen bonded to the sulfate.
- Water soluble copper(II) salts include $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , and CuCl_2 .
- However, $\text{Cu}(\text{OH})_2$ is insoluble and can be precipitated by adding NaOH to a solution containing Cu^{2+} ions.