Chapter 23

Metallurgy and Chemistry of the Metals

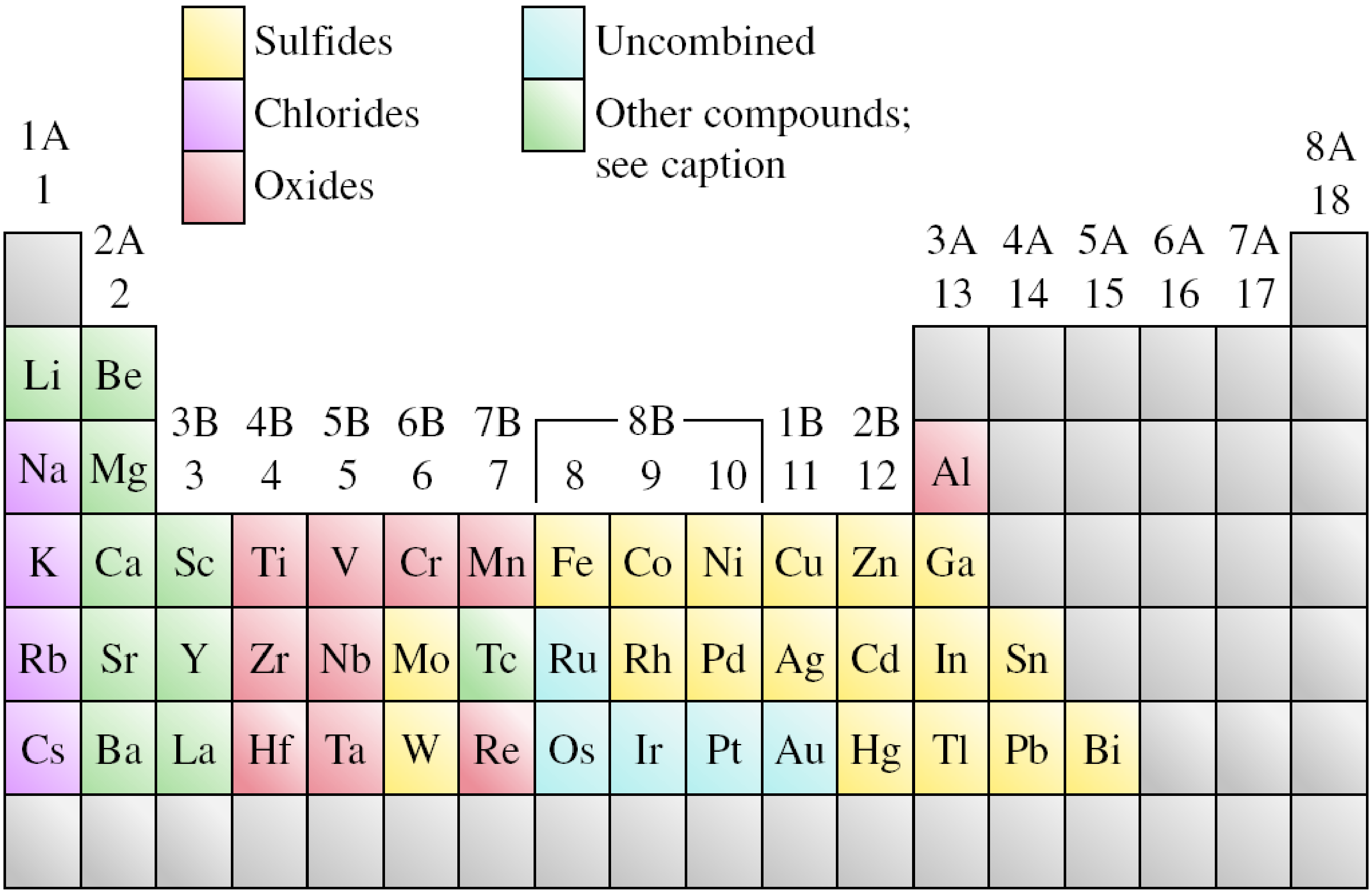
23.1 Occurrence of the Metals

- Most metals come from minerals.
  - A ***mineral*** is a naturally occurring substance with a range of chemical composition.
  - An ***ore*** is a mineral deposit concentrated enough to allow economical recovery of a desired metal***.***
- Metals exist in various forms
  - In the Earth's surface
  - As ions in seawater
  - In the ocean floor

TABLE 23.1 Natural Sources of Common Metals

Type	Minerals
Uncombined metals	Ag, Au, Bi, Cu, Pd, Pt
Carbonates	$BaCO_3$ (witherite), $CaCO_3$ (calcite, limestone), $MgCO_3$ (magnesite), $CaCO_3 \cdot MgCO_3$ (dolomite), $PbCO_3$ (cerussite), $ZnCO_3$ (smithsonite)
Halides	CaF_2 (fluorite), NaCl (halite), KCl (sylvite), Na_3AlF_6 (cryolite)
Oxides	$Al_2O_3 \cdot 2H_2O$ (bauxite), Al_2O_3 (corundum), Fe_2O_3 (hematite), Fe_3O_4 (magnetite), Cu_2O (cuprite), MnO_2 (pyrolusite), SnO_2 (cassiterite), TiO_2 (rutile), ZnO (zincite)
Phosphates	$Ca_3(PO_4)_2$ (phosphate rock), $Ca_5(PO_4)_3OH$ (hydroxyapatite)
Silicates	$Be_3Al_2Si_6O_{18}$ (beryl), $ZrSiO_4$ (zircon), $NaAlSi_3O_8$ (albite), $Mg_3(Si_4O_{10})(OH)_2$ (talc)
Sulfides	Ag_2S (argentite), CdS (greenockite), Cu_2S (chalcocite), FeS_2 (pyrite), HgS (cinnabar), PbS (galena), ZnS (sphalerite)
Sulfates	$BaSO_4$ (barite), $CaSO_4$ (anhydrite), $PbSO_4$ (anglesite), $SrSO_4$ (celestite), $MgSO_4 \cdot 7H_2O$ (epsomite)

Metals and Their Best Known Minerals



23.2 Metallurgical Processes

- ***Metallurgy*** is the science and technology of separating metals from their ores and of compounding alloys.
- An ***alloy*** is a solid solution either of two or more metals, or of a metal or metals with one or more *nonmetals.*
- Preparation, production and purification are principal steps involved in the recovery of a metal from its ore

– Preparation of the ore - desired mineral is separated from waste materials or *gangue* (clay and silicate minerals)
  - Flotation
  - Magnetic separation
  - Amalgamation
– Production of metal – reduction process to isolate metal from the combined form
  - Roasting

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

- Chemical reduction – reducing agent at high temperatures

$$V_2O_5(s) + 5Ca(l) \longrightarrow 2V(l) + 5CaO(s)$$

- Electrolytic reduction – suitable for electropositive metals

$$2MO(l) \longrightarrow 2M \text{ (at cathode)} + O_2 \text{ (at anode)}$$

$$2MCl(l) \longrightarrow 2M \text{ (at cathode)} + Cl_2 \text{ (at anode)}$$

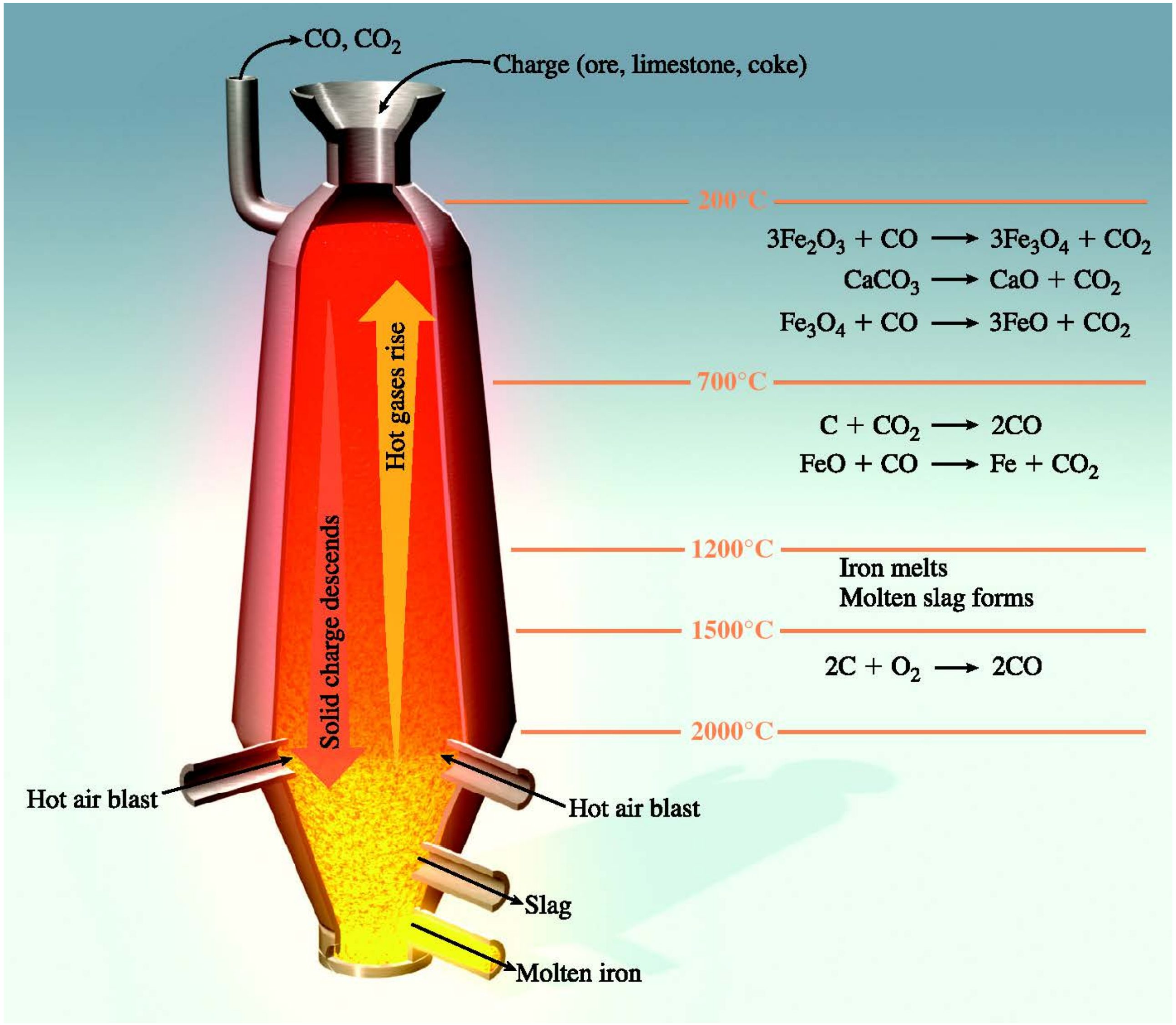
- ***pyrometallurgy,*** procedures carried out at high temperatures
  - Chemical reduction
  - Electrolytic reduction

TABLE 23.2 Reduction Processes for Some Common Metals

	Metal	Reduction Process
Decreasing activity of metals ↓	Lithium, sodium, magnesium, calcium	Electrolytic reduction of the molten chloride
	Aluminum	Electrolytic reduction of anhydrous oxide (in molten cryolite)
	Chromium, manganese, titanium, vanadium, iron, zinc	Reduction of the metal oxide with a more electropositive metal, or reduction with coke and carbon monoxide
	Mercury, silver, platinum, copper, gold	These metals occur in the free (uncombined) state, or they can be obtained by roasting their sulfides

- Metallurgy of iron –
  - Iron exists in Earth's crust in many different minerals and must be isolated
  - Chemical reduction by carbon in a blast furnace
  - Mineral is mixed with carbon and limestone ($CaCO_3$)
  - *Slag* removes sand and aluminum oxide impurites
  - Molten iron is removed at the bottom of the furnace

A Blast Furnace



- Steelmaking
  - Steel is an alloy of iron with a small carbon content plus various other elements
  - Oxidation process to remove unwanted impurities
  - Basic oxygen process – widely used due to its simplicity
    - *Flux* removes oxidized impurities
      - Flux used depends on impurities (CaO versus SiO_2)
    - Rate of cooling of molten steel (*tempering*) helps determine the carbon content and the steel's properties

Basic Oxygen Process

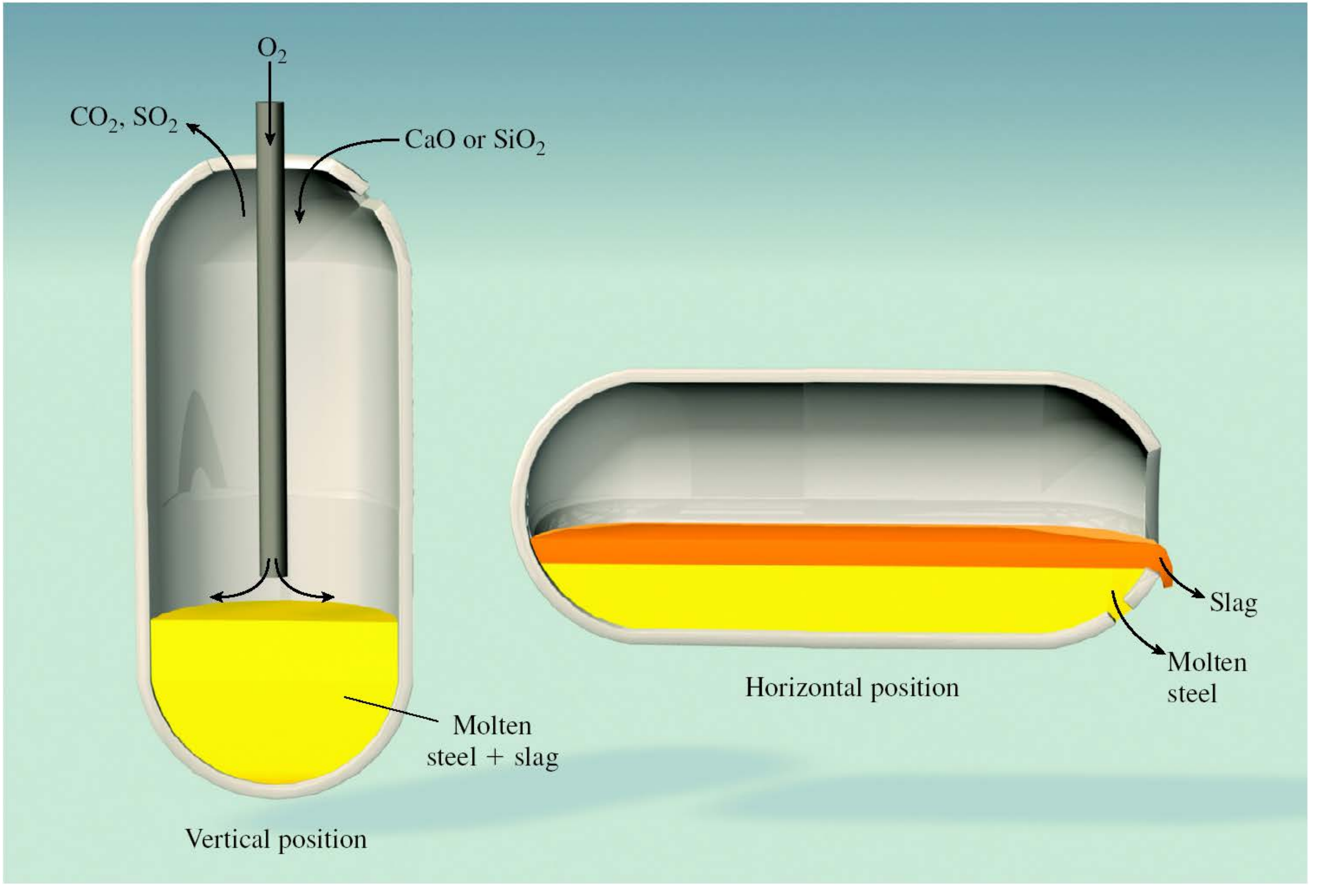


TABLE 23.3 Types of Steel

Type	Composition (Percent by Mass)* C	Mn	P	S	Si	Ni	Cr	Others	Uses
Plain	1.35	1.65	0.04	0.05	0.06	—	—	Cu (0.2–0.6)	Sheet products, tools
High-strength	0.25	1.65	0.04	0.05	0.15−0.9	0.4–1.0	0.3–1.3	Cu (0.01–0.08)	Construction, steam turbines
Stainless	0.03–1.2	1.0–10	0.04–0.06	0.03	1–3	1–22	4.0–27	—	Kitchen utensils, razor blades

*A single number indicates the maximum amount of the substance present.

Steelmaking

- Purification of Metals –
  - Occurs after reduction
  - Extent depends on the usage of the metal
  - Types
    - Distillation – based on boiling points
      - Mond process for nickel

b.p. 43°C

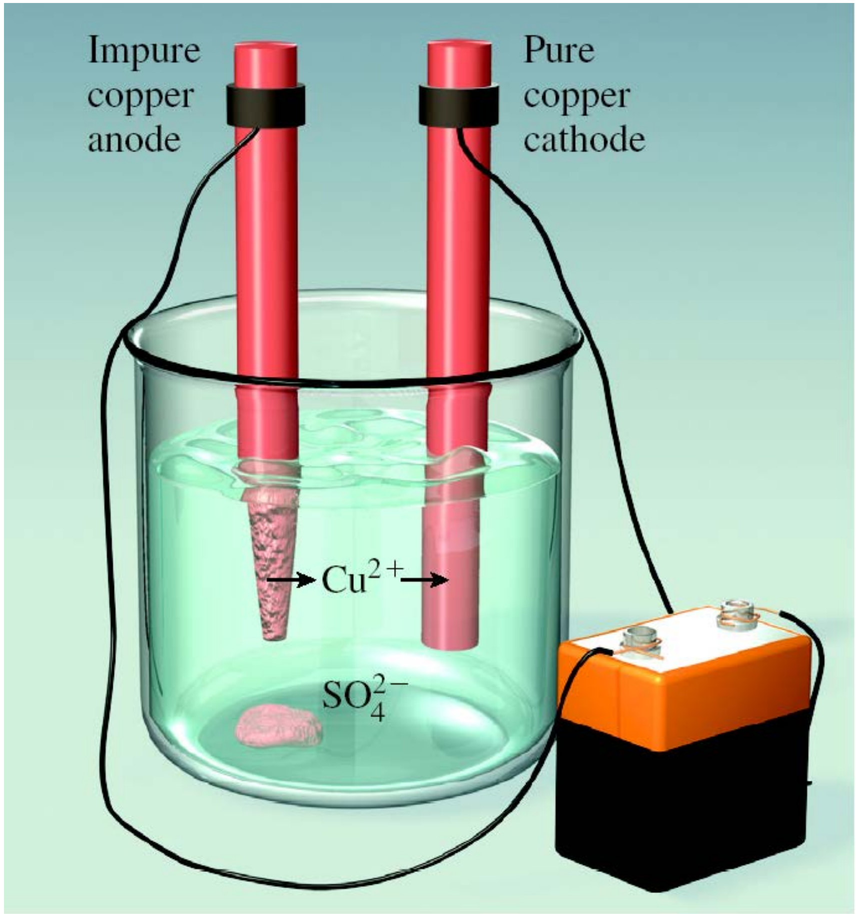
$$Ni(s) + 4CO(g) \longrightarrow Ni(CO)_4(g)$$

At 200 °C

$$Ni(CO)_4(g) \longrightarrow Ni(s) + 4CO(g)$$

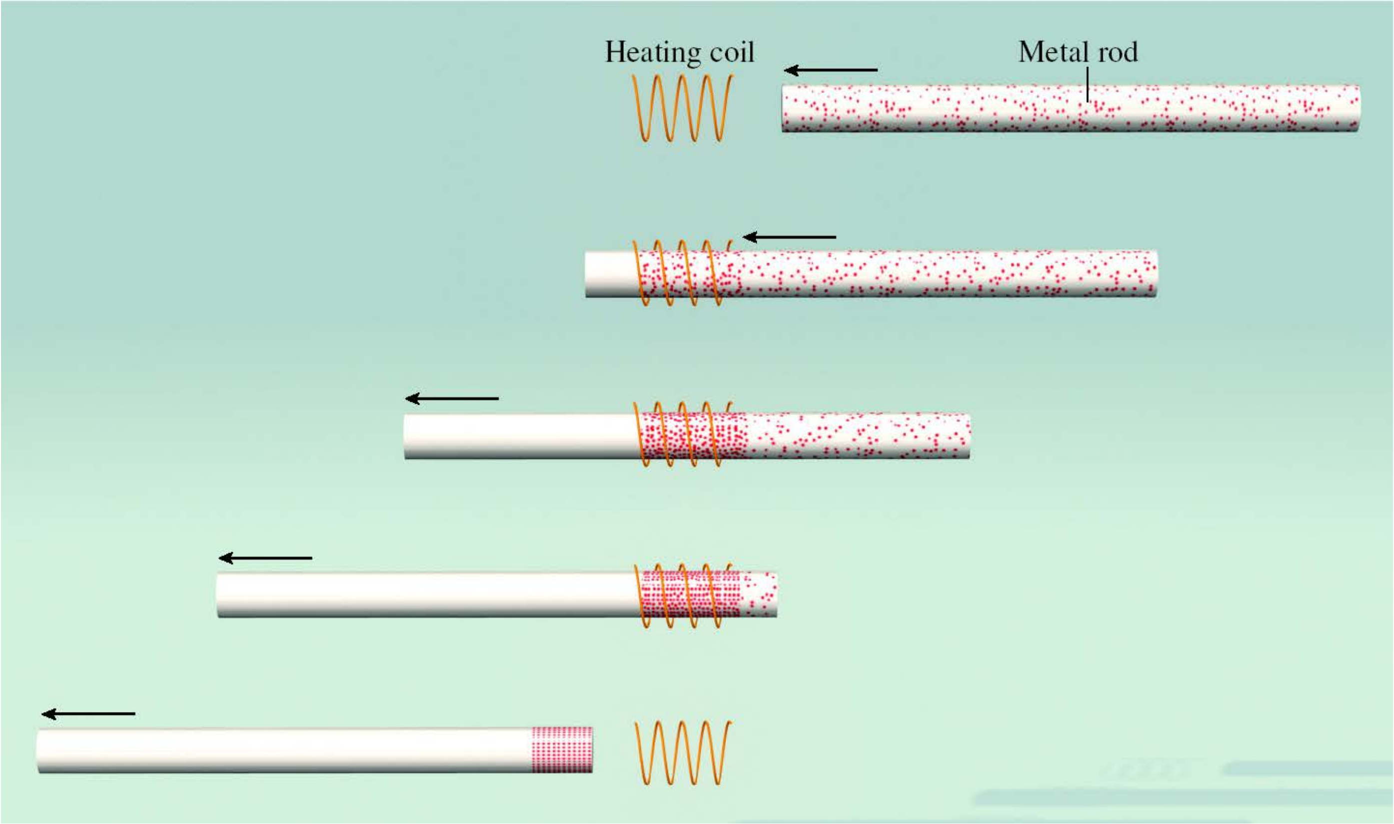
– Electrolysis – an important technique

  - Example for copper purification



– Zone refining

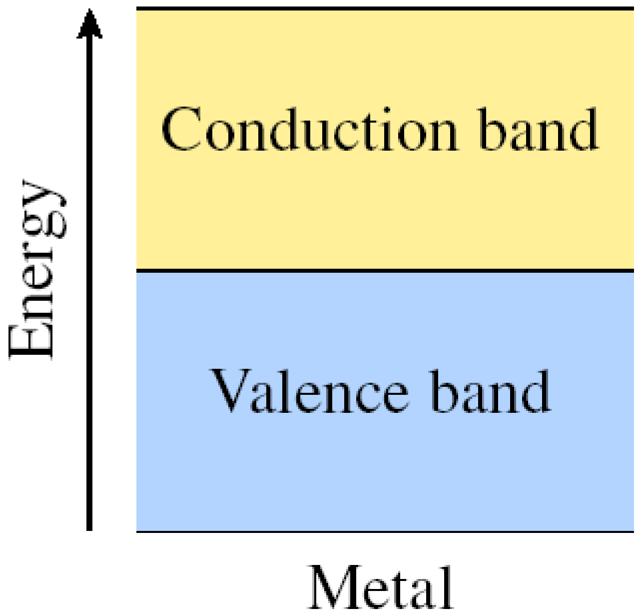
- Produces extremely pure metals



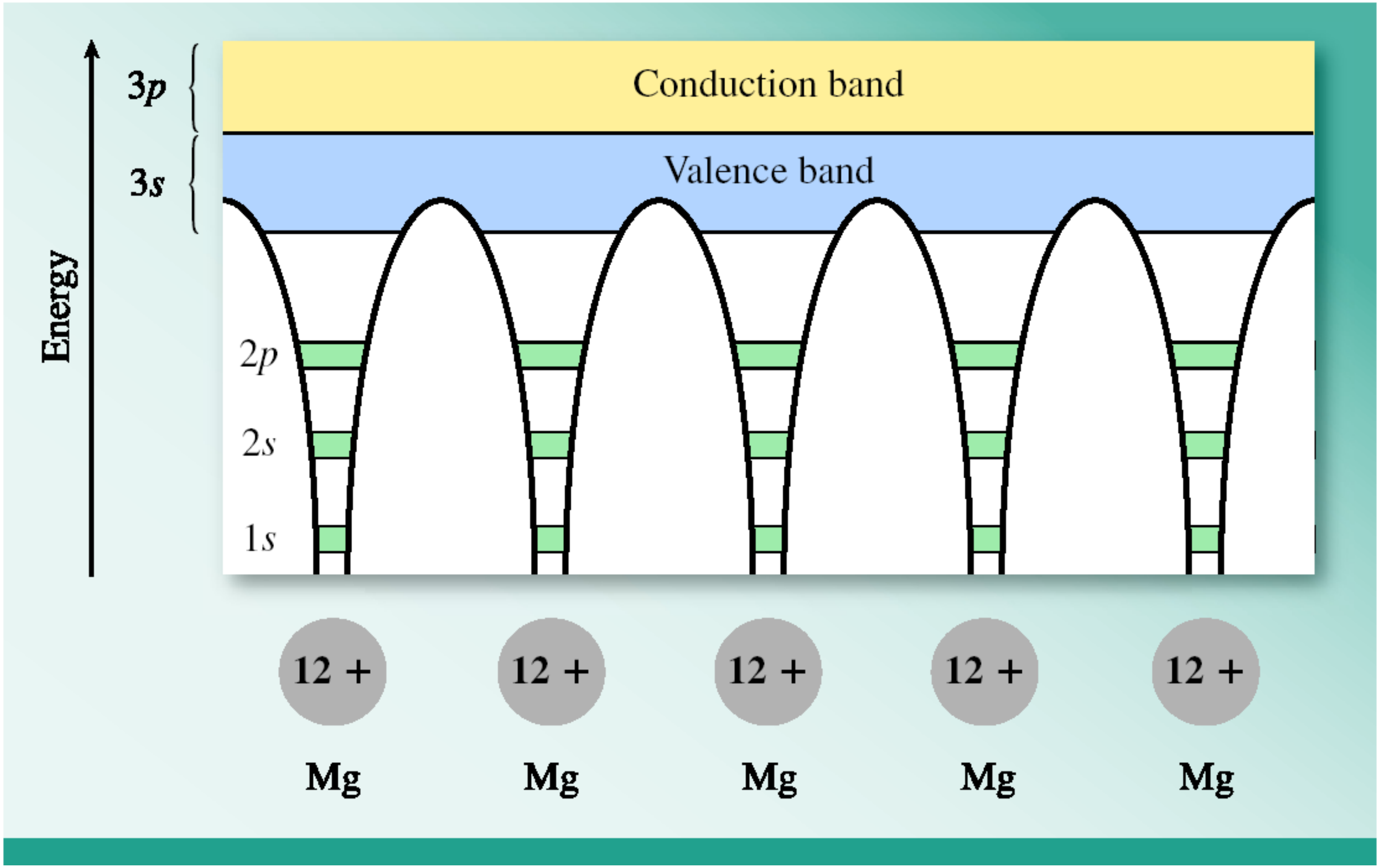
23.3 Band Theory of Conductivity

- ***Band theory*** - model used to study conductivity in metals
  - Delocalized electrons move freely through "bands" formed by overlapping molecular orbitals
- Conductors
  - Metals are good conductors of electricity
  - Explained by band theory

– Overlapping molecular orbitals produce
  - A *valence band* (lower energy)
  - A *conduction band* (higher energy)
  - Bands are separated by an amount of energy called the *band gap*
  - In metals the band gap is negligible

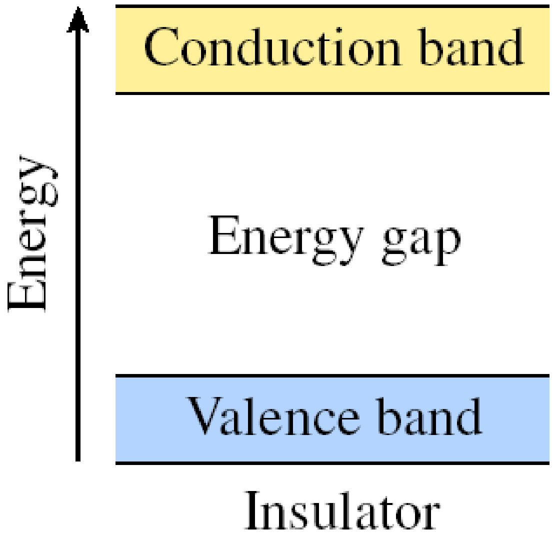


Formation of Conduction Bands in Mg



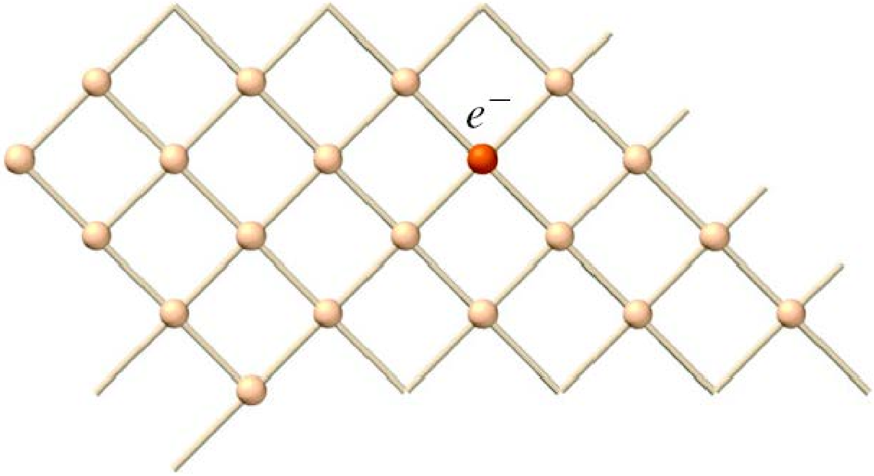
– Metals are viewed as an array of positive charges immersed in a sea of delocalized electrons.

- Insulators – ineffective conductors of electricity
  – Band gap is large
  – Electrons cannot move freely

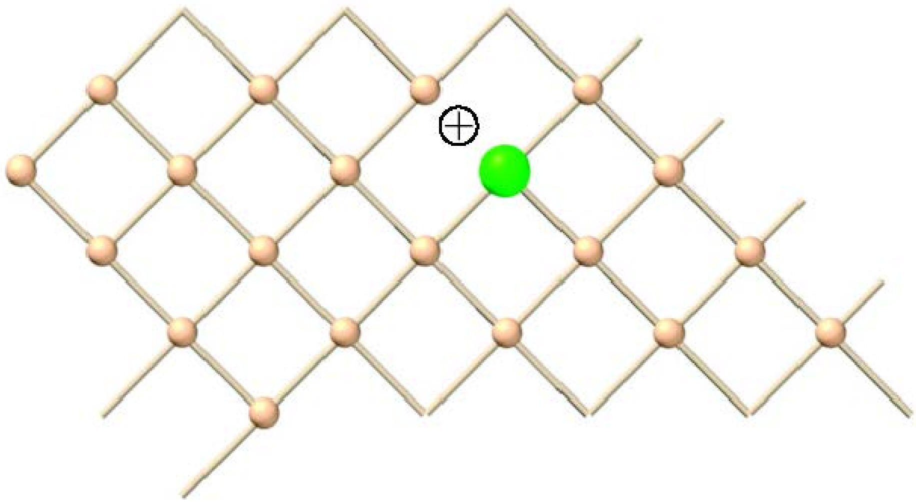


- ***Semiconductors*** are elements that normally are *not* conductors, but will conduct electricity
  - at elevated temperatures
  - or when combined with a small amount of certain other elements.
  - Group 4A elements are semiconductors especially
    - Silicon
    - Germanium

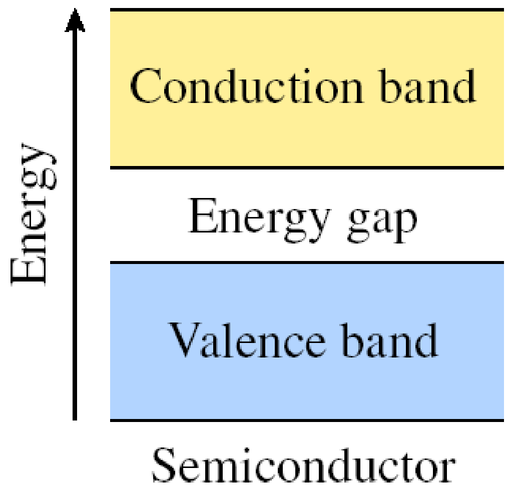
- ***Doping*** can enhance the ability to conduct
  - Addition of small amounts of certain impurities
- Types of impurities
  - Donor impurities – provide additional electrons
    - The doping of silicon ([Ne]$3s^2 3p^{2)}$ with phosphorus ([Ne]$3s^2 3p^3$)
    - Form ***n-type semiconductors*** (*n* for negative from the charge of the "extra" electron)



- Acceptor impurities – electron deficient
  - The doping of silicon ([Ne]$3s^2 3p^2$) with boron [He]$2s^2 2p^1$
  - Form ***p-type semiconductors*** (*p* for positive from the electron deficiency)

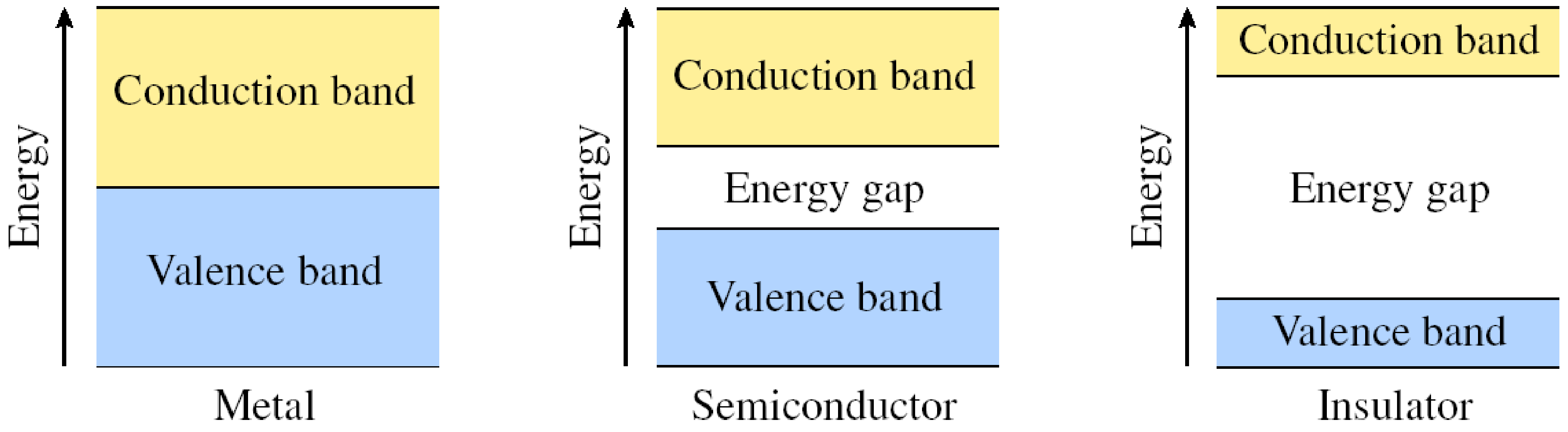


– Energy gap is smaller after doping



– Conductivity increased by a factor of 100,000
– Finds wide application in electronic components

Comparison: Conductors, Semiconductors, Insulators



23.4 Periodic Trends in Metallic Properties

- Metals are generally
  - Lustrous in appearance
  - Solid at room temperature (with the exception of mercury)
  - Good conductors of heat
  - Good conductors of electricity
  - Malleable (can be hammered flat)
  - Ductile (can be drawn into wires)

- Classified as representative (A Groups) or transition (B Groups) based on position on the periodic table

- Periodic trends
  - Electronegativity increases left to right across a period and up a column
  - Metallic character decreases left to right across a period and up a column
  - Form positive ions or cations
  - Have positive oxidation numbers

Metals on the Periodic Table

1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Main group metals coded in green.

23.5 The Alkali Metals

- Group IA on the Periodic Table

TABLE 23.4 Properties of Alkali Metals

	Li	Na	K	Rb	Cs
Valence electron configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$
Density (g/cm^3)	0.534	0.97	0.86	1.53	1.87
Melting point (°C)	179	97.6	63	39	28
Boiling point (°C)	1317	892	770	688	678
Atomic radius (pm)	155	190	235	248	267
Ionic radius (pm)*	60	95	133	148	169
Ionization energy (kJ/mol)	520	496	419	403	375
Electronegativity	1.0	0.9	0.8	0.8	0.7
Standard reduction potential (V)†	3.05	2.71	2.93	2.93	2.92

* Refers to the cation M^+, where M denotes an alkali metal atom.

† The half-reaction is $M^+(aq) + e^- \longrightarrow M(s)$.

- Common properties of the alkali metals
  - Common oxidation state +1
  - Do not occur free in nature, are combined in halides, sulfates, carbonates and silicates
  - Found dissolved in seawater due to geologic erosion of minerals
- Sodium and Potassium
  - Preparation
    - Sodium - obtained from electrolysis of molten salt
    - Potassium – distillation of molten KCl in the presence of sodium vapor

– Reactions

- React with water to from hydroxides
- React with oxygen to form oxides, peroxides, superoxides

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

- Dissolve in liquid ammonia to form powerful reducing agents

$$Na \xrightarrow{NH_3} Na^+ + e^-$$

$$K \xrightarrow{NH_3} K^+ + e^-$$

- Compounds of sodium and potassium
  - Sodium carbonate, Na_2CO_3, or soda ash
    - Important in industrial processes – manufacture of soaps, detergents, medicine, food additives
    - Produced in the Solvay process

$$NH_3(aq) + NaCl(aq) + H_2CO_3(aq) \longrightarrow NaHCO_3(s) + NH_4Cl(aq)$$

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

    - Alternate production – heating the mineral *trona*, $[Na_5(CO_3)_2(HCO_3) \cdot 2H_2O]$

$$2Na_5(CO_3)_2(HCO_3) + 2H_2O(s) \longrightarrow 5Na_2CO_3(s) + CO_2(g) + 3H_2O(g)$$

- Sodium and potassium hydroxides
  - Prepared by electrolysis of chloride salts
  - Strong bases
  - Highly soluble in water
- Sodium nitrate and potassium nitrate
  - Sodium nitrate is found in Chili salt peter and decomposes

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

  - Potassium nitrate (salt peter) is prepared by

$$KCl(aq) + NaNO_3(aq) \longrightarrow KNO_3(aq) + NaCl(aq)$$

23.6 The Alkaline Earth Metals

- Group 2 A on the periodic table

TABLE 23.5 Properties of Alkaline Earth Metals

	Be	Mg	Ca	Sr	Ba
Valence electron configuration	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$
Density (g/cm^3)	1.86	1.74	1.55	2.6	3.5
Melting point (°C)	1280	650	838	770	714
Boiling point (°C)	2770	1107	1484	1380	1640
Atomic radius (pm)	112	160	197	215	222
Ionic radius (pm)*	31	65	99	113	135
First ionization energy (kJ/mol)	899	738	590	548	502
Second ionization energy (kJ/mol)	1757	1450	1145	1058	958
Electronegativity	1.5	1.2	1.0	1.0	0.9
Standard reduction potential (V)†	−1.85	−2.37	−2.87	−2.89	−2.90

* Refers to the cation M^{2+}, where M denotes an alkali earth metal atom.

† The half-reaction is $M^{2+}(aq) + 2e^- \longrightarrow M(s)$.

- Common properties (Except for Be which resembles 3A elements)
  - Somewhat less electropositive than alkali metals
  - Less reactive than the alkali metals.
  - M^{2+} ions attain the stable electron configuration of the preceding noble gas
  - Oxidation number is commonly +2
  - All isotopes of radium are radioactive

- Magnesium
  - Magnesium is the sixth most plentiful element in Earth's crust (about 2.5 percent by mass).
  - principal magnesium ores are brucite [$Mg(OH)_2$], dolomite ($CaCO_3 \cdot MgCO_3$) and epsomite ($MgSO_4 \cdot 7H_2O$).
  - Seawater is a source of magnesium—there are about 1.3 g of magnesium in each kilogram of seawater.
  - Metallic magnesium is obtained by electrolysis, from its molten chloride, $MgCl_2$

– Strongly basic hydroxide

– Reactions of magnesium

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

– Magnesium is essential to plant and animal life

- Calcium
  - Earth's crust contains about 3.4 percent calcium by mass.
  - Calcium occurs in limestone, calcite, chalk, and marble as $CaCO_3$; in dolomite as $CaCO_3 \cdot MgCO_3$, gypsum as $CaSO_4 \cdot 2H_2O$; and in fluorite as CaF_2
  - Metallic calcium is best prepared by the electrolysis of molten calcium chloride ($CaCl_2$).

- Reactions of calcium and calcium compounds

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

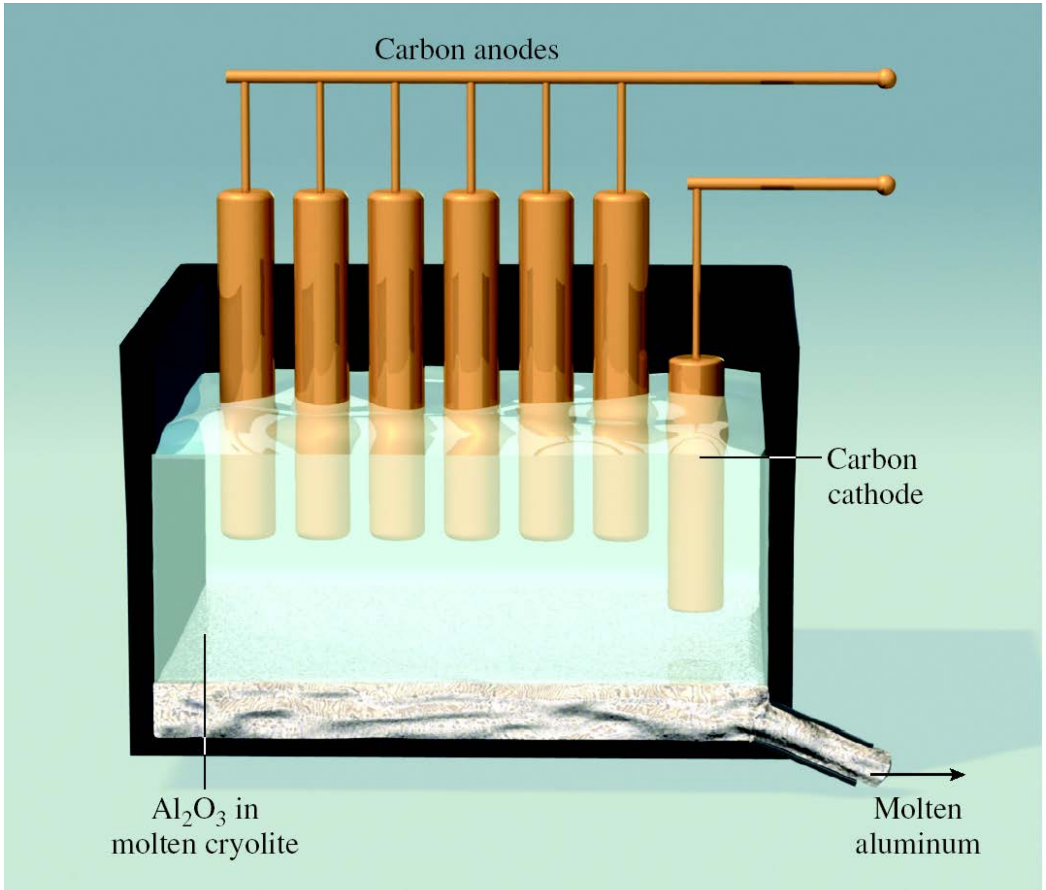
- Metallic calcium serves mainly as an alloying agent
- Essential for living systems

23.7 Aluminum

- Most abundant metal and the third most plentiful element in Earth's crust (7.5 percent by mass).
- Elemental form does not occur in nature
- Principal ore is bauxite ($Al_2O_3 \cdot 2H_2O$)
- Other minerals containing aluminum are orthoclase ($KAlSi_3O_8$), beryl ($Be_3Al_2Si_6O_{18}$), cryolite (Na_3AlF_6), and corundum (Al_2O_3)
- Aluminum used to be considered a precious metal until Hall developed a method of aluminum production.

- Preparation – Hall process

Anode (oxidation):	$3[2O^{2-} \longrightarrow O_2(g) + 4e^-]$
Cathode (reduction):	$4[Al^{3+} + 3e^- \longrightarrow Al(l)]$
Overall:	$2Al_2O_3 \longrightarrow 4Al(l) + 3O_2(g)$



- Reactions of the element
  - Amphoteric –reacts with acid or base

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow 2NaAlO_2(aq) + 3H_2(g)$$

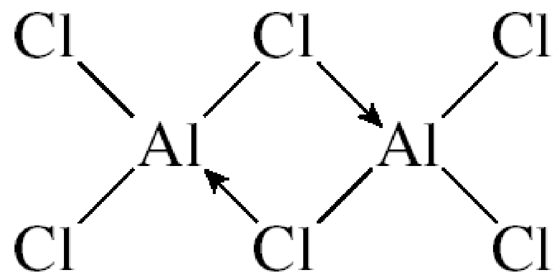
  - Oxide formation

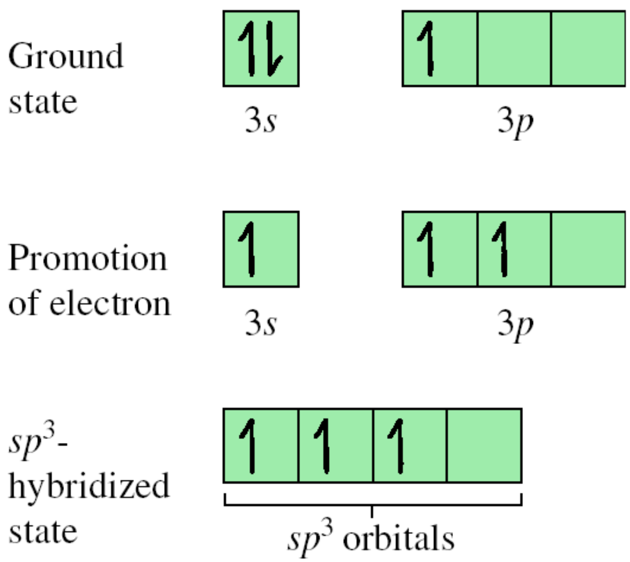
$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

  - With metal oxides

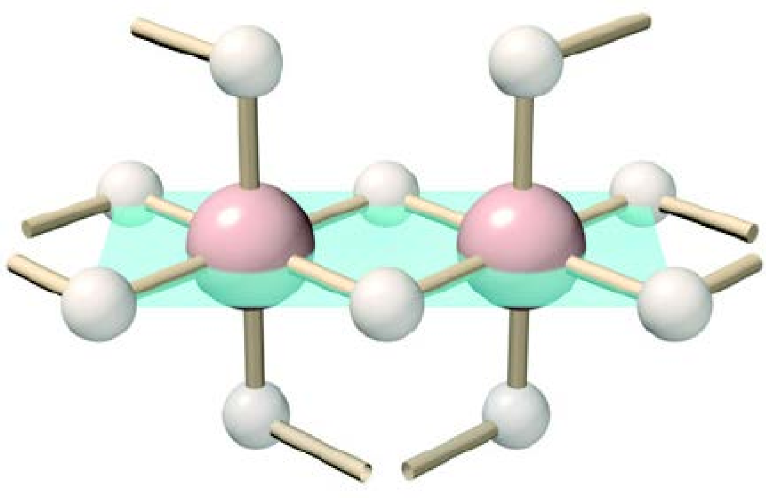
$$2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(l) + 2Fe(l)$$

- Aluminum chloride
  - Exists as a dimer – Al_2Cl_6





- Aluminum hydrides
  - well-defined series of compounds
  - aluminum hydride is a polymer in which each aluminum atom is surrounded octahedrally by bridging hydrogen atoms



- Other important reactions
  - Hydrolysis

$$AlCl_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3HCl(aq)$$

  - Amphoterism

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O(l)$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)_4^-(aq)$$

  - Formation of alums

$$M^+M^{3+}(SO_4)_2 \cdot 12H_2O$$

M^+: K^+, Na^+, NH_4^+

M^{3+}: Al^{3+}, Cr^{3+}, Fe^{3+}

Key Points

- Occurrence of metals
  - Minerals
  - Ores
- Metallurgical processes
  - Preparation of ores
  - Production of metal
    - Chemical reduction
    - Electrolytic reduction

- Metallurgy of iron
- Steelmaking
- Purification
  - Distillation
  - Electrolysis
  - Zone refining
- Band Theory of Conductivity
  - Conductors
  - Insulators
  - Semiconductors

- Donor impurities
- *n*-type semiconductors
- Acceptor impurities
- *p*-type semiconductors

- Periodic trends in metallic properties
- The alkali metals
  - Properties and reactions of the metals
    - Sodium
    - Potassium
  - Important compounds

- The alkaline earth metals
  - Properties and reactions of the metals
  - Calcium and magnesium
- Aluminum
  - Properties and reactions
  - Important compounds