*Chemistry, The Central Science*, 10th edition
Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten

# Chapter 23
# Metals and Metallurgy

John D. Bookstaver
St. Charles Community College
St. Peters, MO

# Minerals

- Most metals are found in solid inorganic compounds known as minerals.
- Minerals are named by common, not chemical, names.

# Minerals

Most important metals are found in minerals as oxides, sulfides, or carbonates.

| Metal | Mineral | Composition |
|---|---|---|
| Aluminum | Corundum | $Al_2O_3$ |
| Chromium | Chromite | $FeCr_2O_4$ |
| Copper | Chalcocite | $Cu_2S$ |
| | Chalcopyrite | $CuFeS_2$ |
| | Malachite | $Cu_2CO_3(OH)_2$ |
| Iron | Hematite | $Fe_2O_3$ |
| | Magnetite | $Fe_3O_4$ |
| Lead | Galena | $PbS$ |
| Manganese | Pyrolusite | $MnO_2$ |
| Mercury | Cinnabar | $HgS$ |
| Molybdenum | Molybdenite | $MoS_2$ |
| Tin | Cassiterite | $SnO_2$ |
| Titanium | Rutile | $TiO_2$ |
| | Ilmenite | $FeTiO_3$ |
| Zinc | Sphalerite | $ZnS$ |

# Metallurgy

The science and technology of extracting metals from their natural sources and preparing them for practical use.

# Metallurgy

- It involves
  - Mining.
  - Concentrating ores.
  - Reducing ores to obtain free metals.
  - Purifying metals.
  - Mixing metals to form alloys that have the properties desired.

# Pyrometallurgy

The use of high temperature to alter or reduce minerals.

# Calcination

Heating an ore to bring about its decomposition and elimination of a volatile product.

$$\mathrm{PbCO_3}(s) \xrightarrow{\Delta} \mathrm{PbO}(s) + \mathrm{CO_2}(g)$$

# Roasting

A thermal reaction between ore and the furnace atmosphere (often oxygen).

$$2\ MoS_2(s) + 7\ O_2(g) \longrightarrow 2\ MoO_3(s) + 4\ SO_2(g)$$

$$HgS(s) + O_2(g) \longrightarrow Hg(g) + SO_2(g)$$

# Smelting

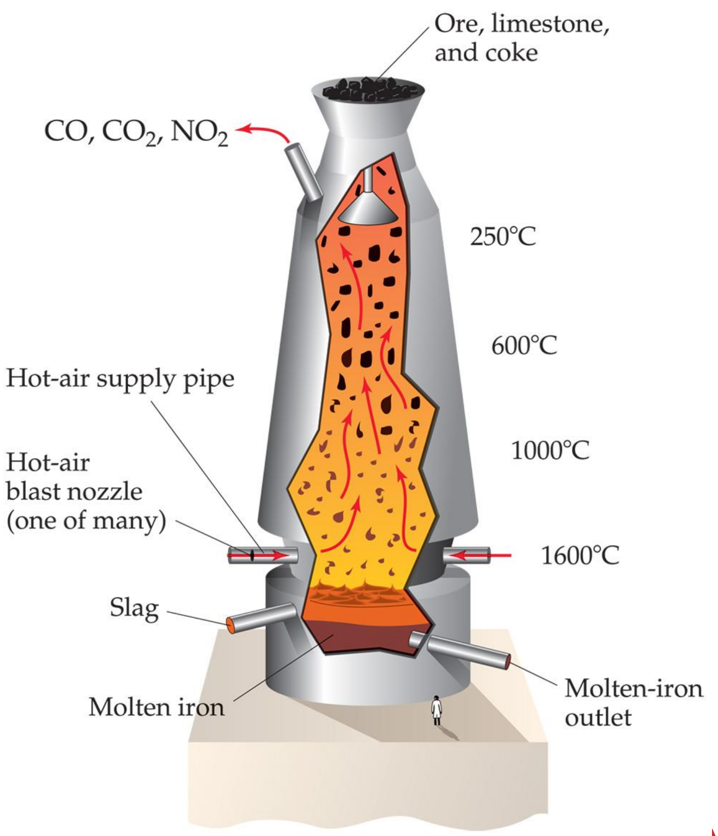
A melting process in which materials formed during reactions separate into two or more layers.

# Refining

The treatment of a crude, relatively impure metal to improve its purity and better define its composition.

# Reduction of Iron

- Hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), and other iron oxides are reduced in blast furnaces.
- Purified iron exits the furnace at the bottom.



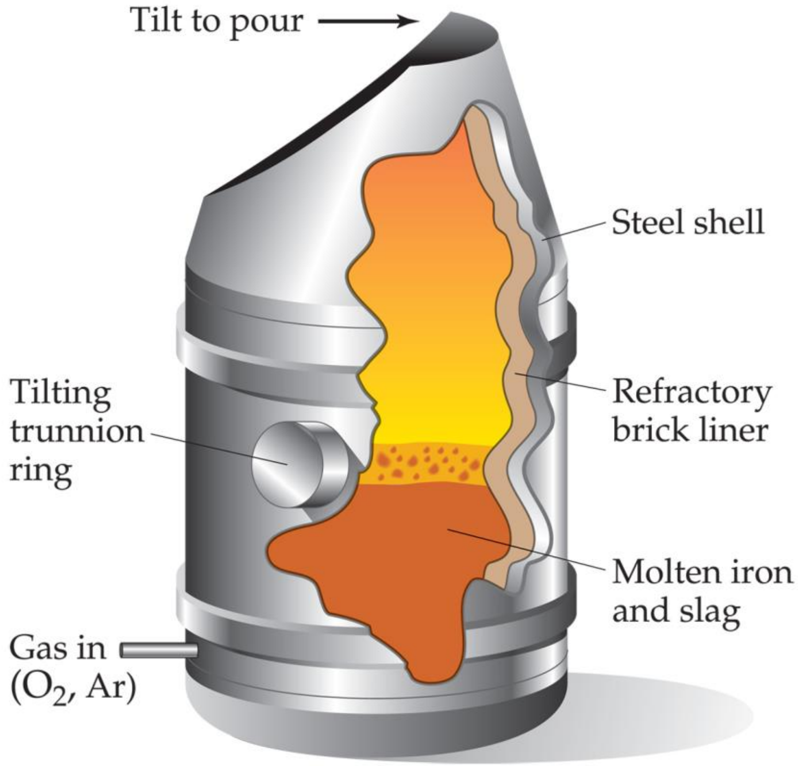

Metals and Metallurgy

# Steel

- Crude molten iron contains many impurities:
  - Silicon
  - Manganese
  - Phosphorus
  - Sulfur
  - Carbon

# Steel

- The impurities are oxidized by $O_2$ (except phosphorus, which reacts with CaO) to compounds easily separated from the molten iron.
- Purified molten steel is poured into molds.



# Hydrometallurgy

These are techniques in which metal is extracted from ore via the use of aqueous reactions.

# Leaching

- Process in which metal-containing compound is selectively dissolved.
- Can use water if metal-containing compound is water soluble, but more often must use acid, base, or a salt solution.

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

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

# Bayer Process

- Method of purifying bauxite (aluminum ore).

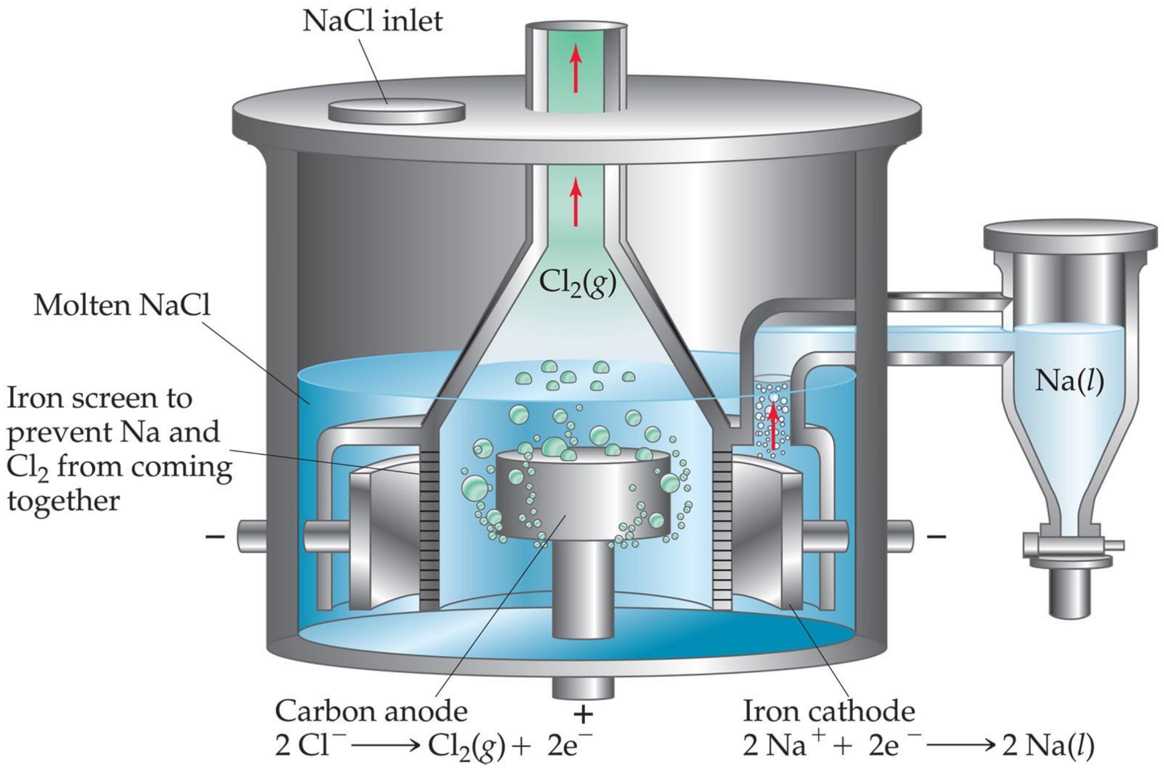
$$Al_2O_3 \cdot H_2O(s) + 2\ H_2O(l) + 2\ OH^-(aq) \longrightarrow 2\ Al(OH)_4^-(aq)$$

- The soluble aluminate ion is separated from the insoluble impurities ($SiO_2$ and $Fe_3O_3$) by filtration.

# Electrometallurgy

The reduction of metal ores or refining of metals by use of electricity.

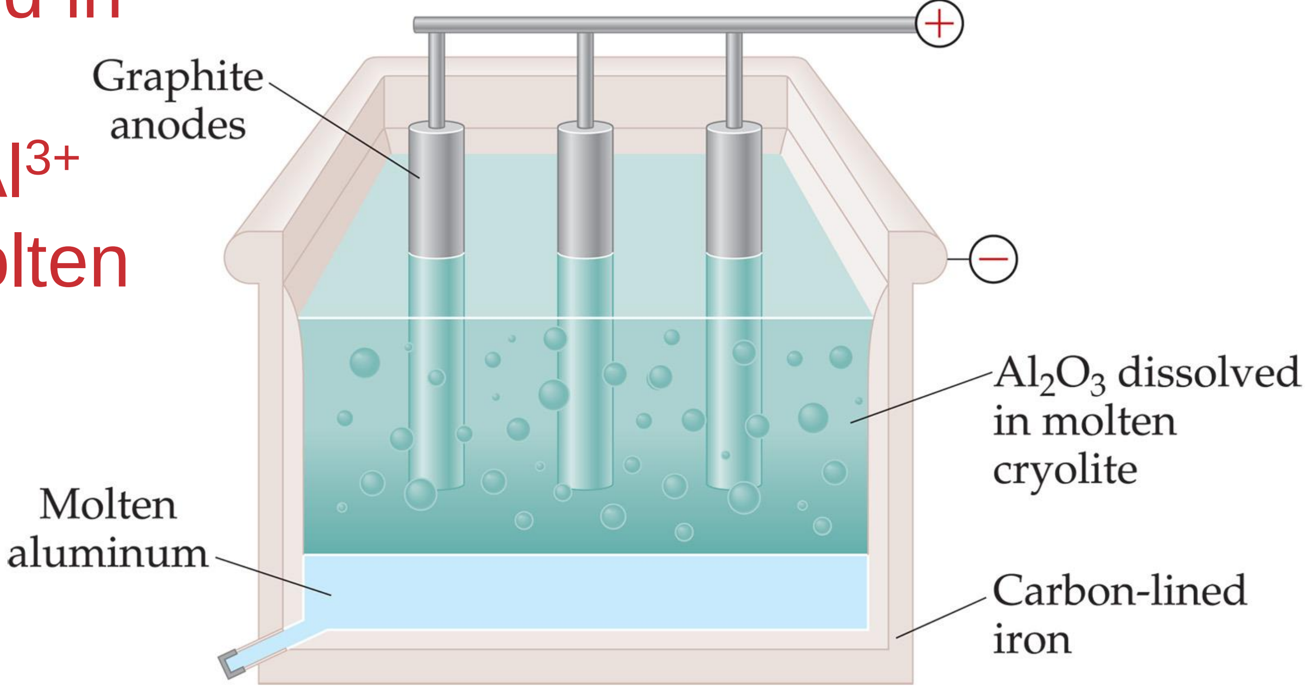
# Sodium




- NaCl is electrolyzed in a Downs cell.
  - Gaseous $Cl_2$ allowed to disperse
  - Molten Na siphoned off

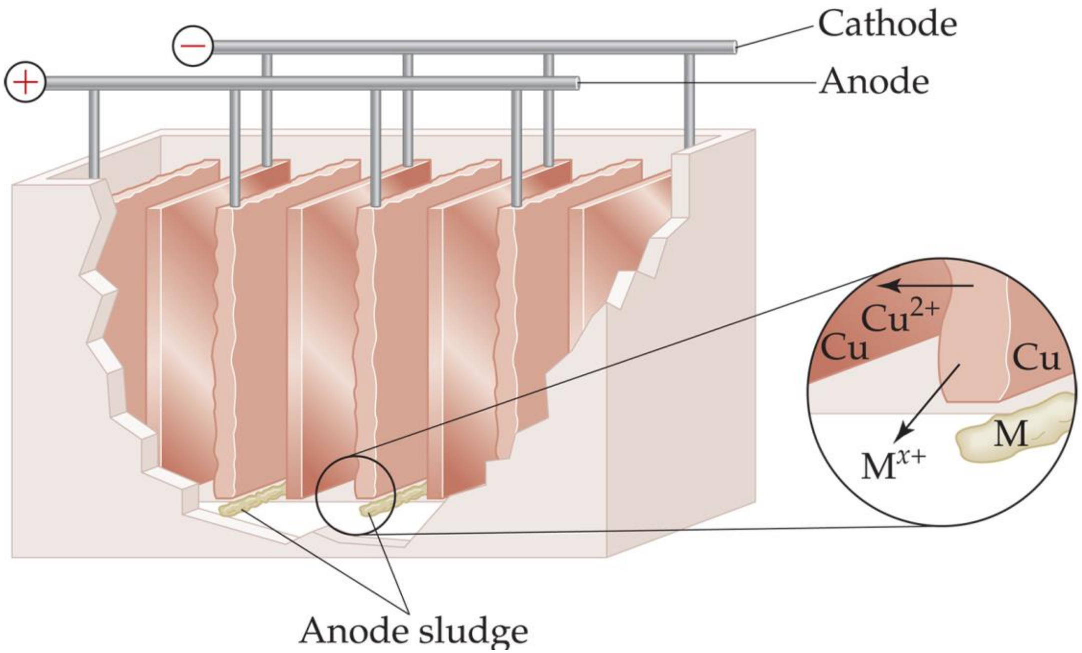
# Aluminum

In the Hall process, $Al_2O_3$ is dissolved in molten cryolite ($Na_2AlF_6$), and $Al^{3+}$ is reduced to molten Al.




Metals and Metallurgy

# Copper

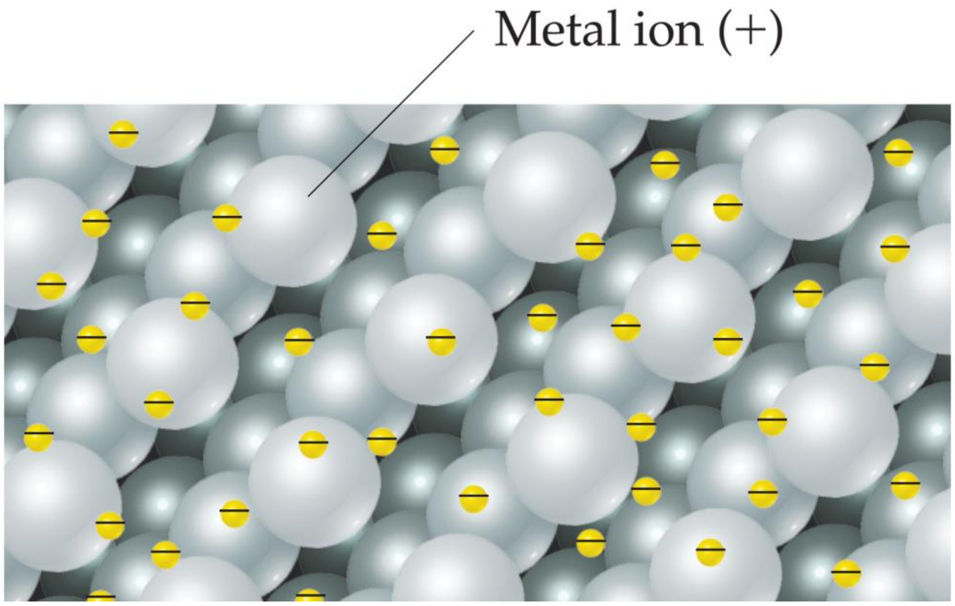



- Active metal impurities oxidized at anode, but don't plate out at cathode.
  - $Cu^{2+}$ more easily reduced
- Less active metals deposit as sludge below anode.

# Physical Properties of Metals

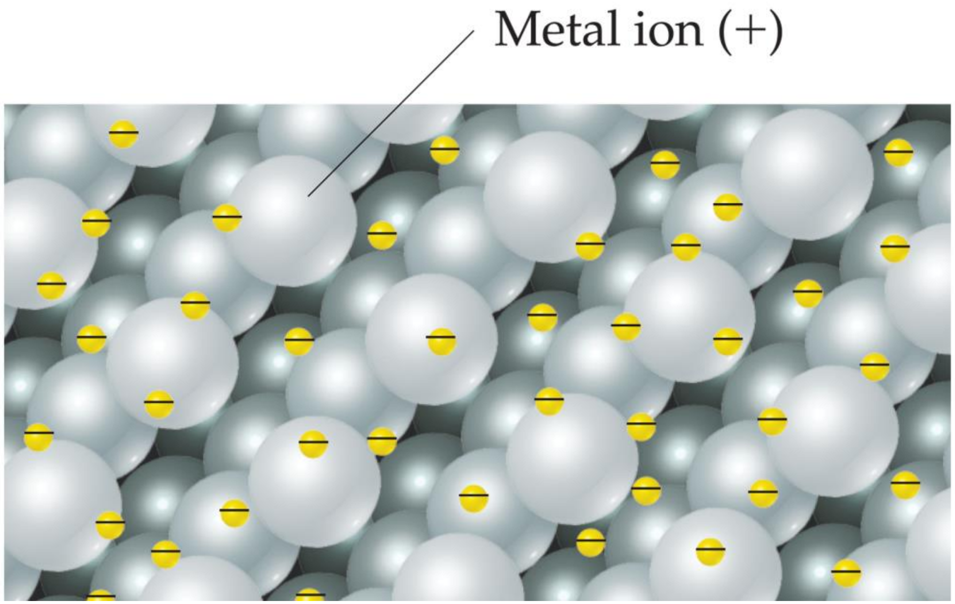
- Conduct heat and electricity.
- Malleable (can be pressed or hammered into sheets).
- Ductile (can be drawn into wire).
- Atoms can slip past each other.
  - So metals aren't as brittle as other solids.

# Electron-Sea Model




- Metals can be thought of as cations suspended in "sea" of valence electrons.
- Attractions hold electrons near cations, but not so tightly as to impede their flow.

# Electron-Sea Model



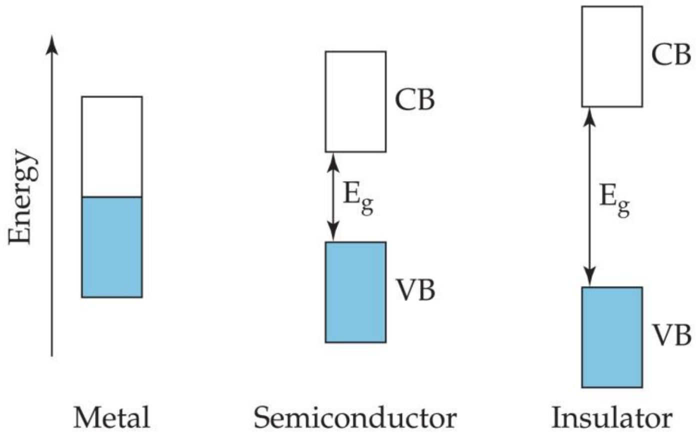

- This explains properties of metals—
  - Conductivity of heat and electricity
  - Deformation

# Molecular Orbital Model

- Electron-sea model does not explain observed trends in melting point, boiling point, heat of fusion, etc.
  - Suggests these properties should increase with increasing number of valence electrons.

| | Group 3B | Group 6B | Group 8B |
|---|---|---|---|
| **Metal** | Sc | Cr | Ni |
| **Melting point (°C)** | 1541 | 1857 | 1455 |
| **Metal** | Y | Mo | Pd |
| **Melting point (°C)** | 1522 | 2617 | 1554 |
| **Metal** | La | W | Pt |
| **Melting point (°C)** | 918 | 3410 | 1772 |

# Molecular Orbital Model

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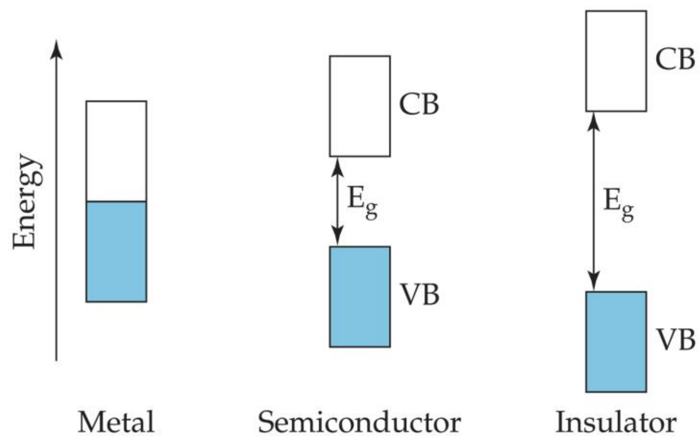
These trends can be explained by energy bands created by large number of molecular orbitals formed as metal atoms bond with each other.

# Molecular Orbital Model

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- As with nonmetals, bond order apexes in center of row, then decreases.
- Thus, attractions (and melting point, etc.) apex in center of transition metals. (Group 6B)

Metals and Metallurgy

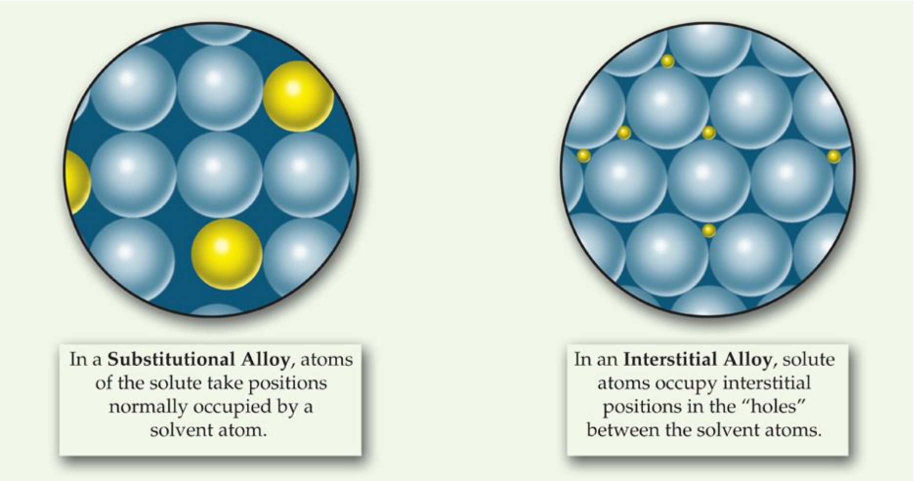
# Alloys

| Primary Element | Name of Alloy | Composition by Mass | Properties | Uses |
|---|---|---|---|---|
| Bismuth | Wood's metal | 50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd | Low melting point (70°C) | Fuse plugs, automatic sprinklers |
| Copper | Yellow brass | 67% Cu, 33% Zn | Ductile, takes polish | Hardware items |
| Iron | Stainless steel | 80.6% Fe, 0.4% C, 18% Cr, 1% Ni | Resists corrosion | Tableware |
| Lead | Plumber's solder | 67% Pb, 33% Sn | Low melting point (275°C) | Soldering joints |
| Silver | Sterling silver | 92.5% Ag, 7.5% Cu | Bright surface | Tableware |
| | Dental amalgam | 70% Ag, 18% Sn, 10% Cu, 2% Hg | Easily worked | Dental fillings |

- Mixtures of elements that have properties characteristic of metals.
- Many ordinary uses of metals involve alloys.

# Solution Alloys

- Components of alloys are dispersed uniformly—
  - ➢ In substitutional alloys, solute particles take place of solvent metal atoms.
  - ➢ Particles close in size.

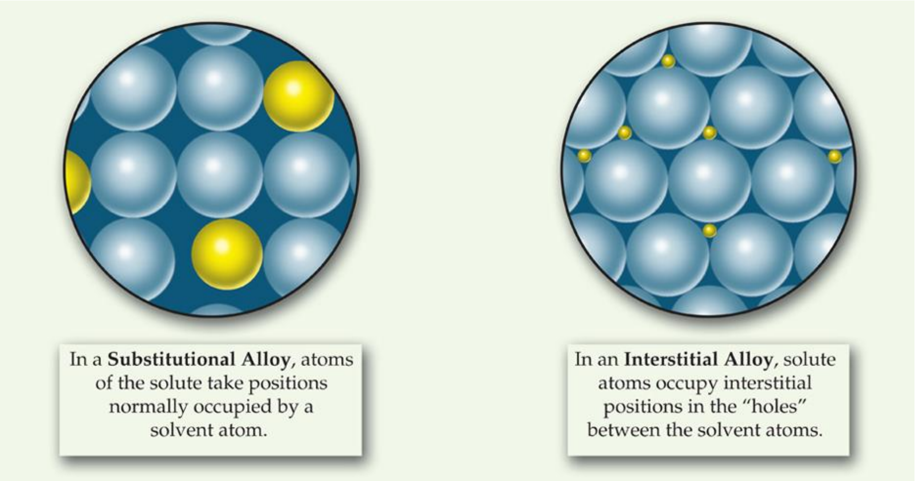


In a **Substitutional Alloy**, atoms of the solute take positions normally occupied by a solvent atom.

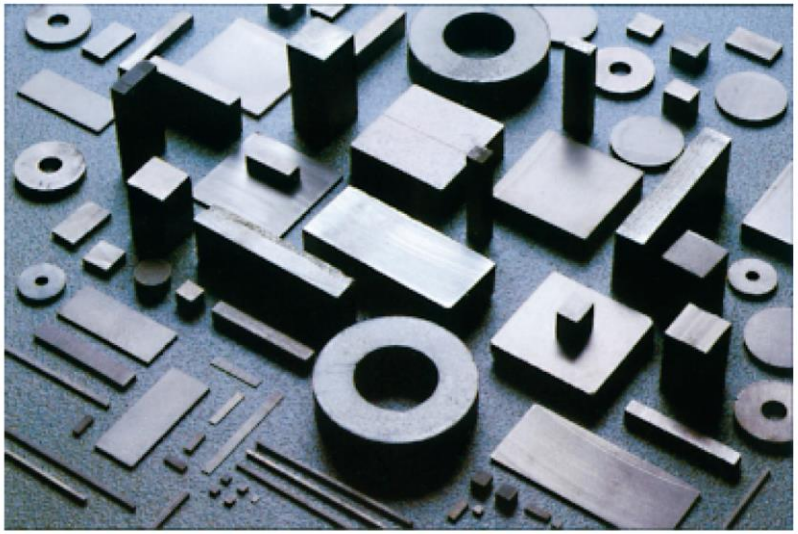
In an **Interstitial Alloy**, solute atoms occupy interstitial positions in the "holes" between the solvent atoms.

# Solution Alloys

- Components of alloys are dispersed uniformly.
  - In interstitial alloys, solute particles find their way into holes between solvent metal atoms.
  - Solute particles smaller than solvent.



# Intermetallic Compounds

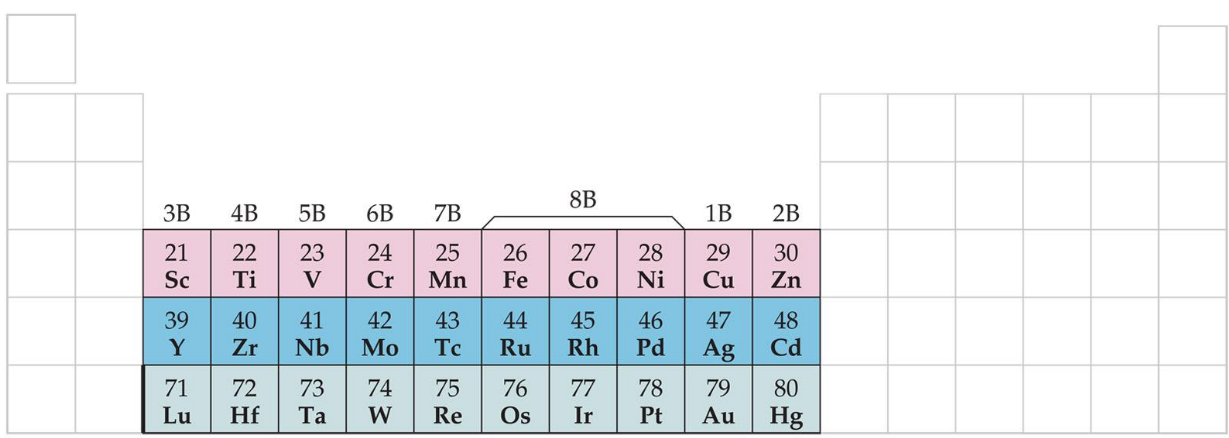


- Homogeneous alloys with definite properties and compositions.
- $Co_5Sm$
  - Used for permanent magnets in headsets and speakers.

Metals and Metallurgy

# Transition Metals

- Many important metals are included in this group.
- Comprised of elements in *d* block of periodic table.



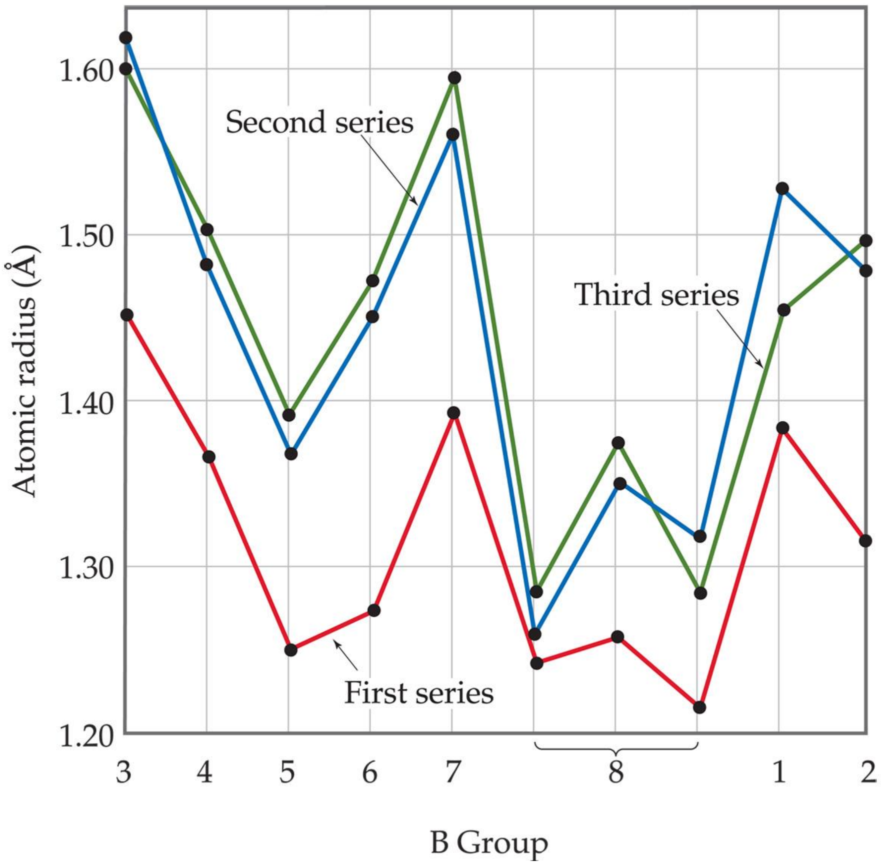
# Physical Properties of Transition Metals

| Group: | 3B | 4B | 5B | 6B | 7B | 8B | | | 1B | 2B |
|---|---|---|---|---|---|---|---|---|---|---|
| Element: | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| Electron configuration | $3d^1 4s^2$ | $3d^2 4s^2$ | $3d^3 4s^2$ | $3d^5 4s^1$ | $3d^5 4s^2$ | $3d^6 4s^2$ | $3d^7 4s^2$ | $3d^8 4s^2$ | $3d^{10} 4s^1$ | $3d^{10} 4s^2$ |
| First ionization energy (kJ/mol) | 631 | 658 | 650 | 653 | 717 | 759 | 758 | 737 | 745 | 906 |
| Bonding atomic radius (Å) | 1.44 | 1.36 | 1.25 | 1.27 | 1.39 | 1.25 | 1.26 | 1.21 | 1.38 | 1.31 |
| Density ($g/cm^3$) | 3.0 | 4.5 | 6.1 | 7.9 | 7.2 | 7.9 | 8.7 | 8.9 | 8.9 | 7.1 |
| Melting point (°C) | 1541 | 1660 | 1917 | 1857 | 1244 | 1537 | 1494 | 1455 | 1084 | 420 |

- Some of their properties (such as ionization energy, atomic radius, etc.) are suggestive of isolated atoms.
- Others (such as density, melting point, etc.) suggest bulk solid metal.

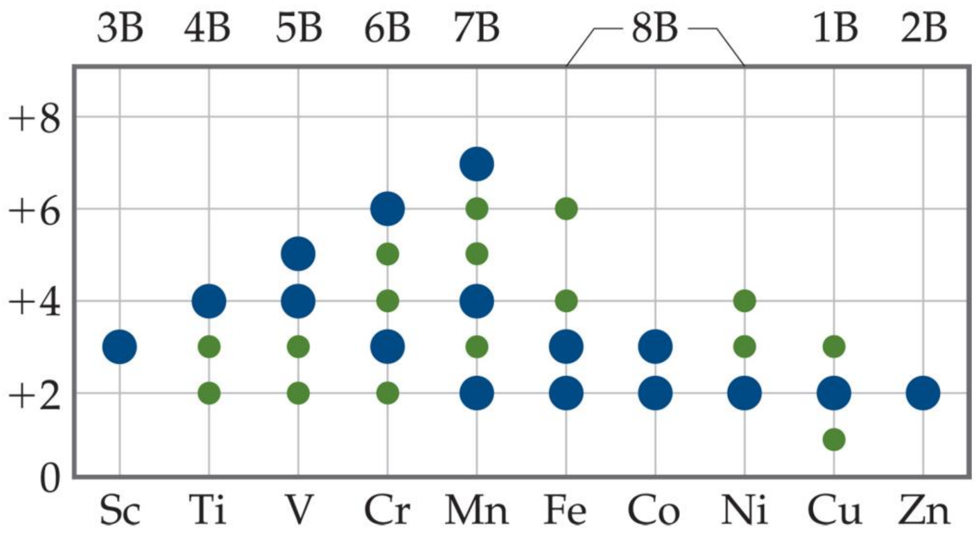
# Atomic Radii

- Trends are similar across all three rows of transition metals.
- While $Z_{eff}$ increases across row, so does number of nonbonding electrons.
  - These repel each other and increase radius.




Metals and Metallurgy

# Electron Configurations and Oxidation States




- Transition metals often have more than one common oxidation state.
  - Most have +2 state due to loss of *s* electrons.
  - Oxidation numbers greater than 2 are due to loss of *d* electrons as well as *s*.

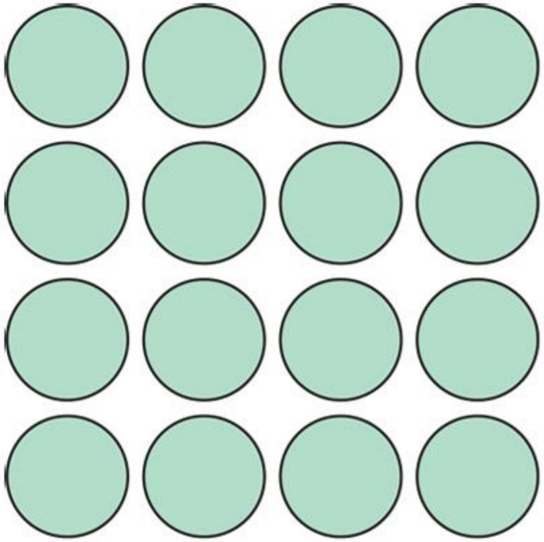
# Electron Configurations and Oxidation States

Many form compounds that have colors.

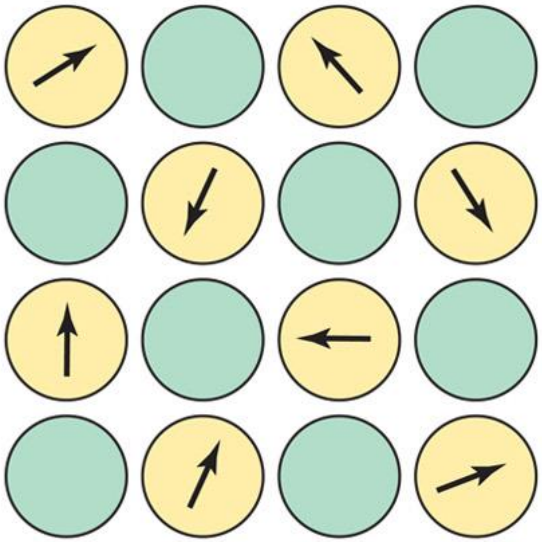
Metals and Metallurgy

# Electron Configurations and Oxidation States

- Many have significant magnetic properties.
  - In diamagnetic elements, all electron spins are paired.
  - Therefore, there is no net magnetic moment.



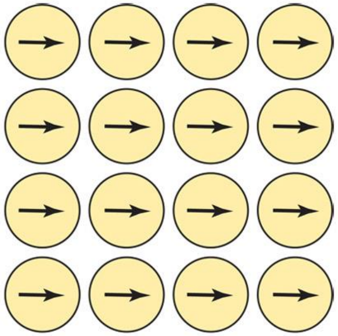
# Electron Configurations and Oxidation States



- In paramagnetic atoms and ions, there are unpaired spins.
- The magnetic fields are randomly arranged, though, unless placed in an external magnetic field.

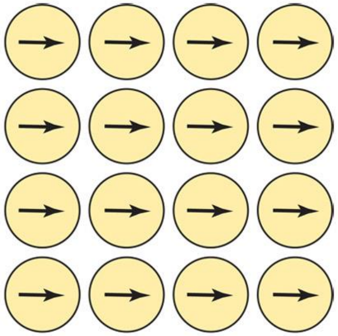
# Electron Configurations and Oxidation States

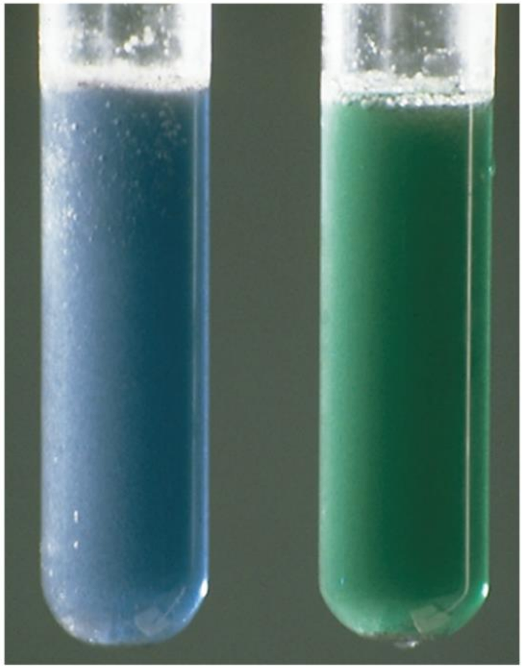
In ferromagnetic substances the orientations of magnetic fields from unpaired electrons are affected by spins from electrons around them.



# Electron Configurations and Oxidation States

When an external field is applied and then removed, the substance maintains the magnetic moment and becomes a permanent magnet.





# Chromium

- Oxidized by HCl or $H_2SO_4$ to form blue $Cr^{2+}$ ion.
- $Cr^{2+}$ oxidized by $O_2$ in air to form green $Cr^{3+}$.

- Cr also found in +6 state as in $CrO_4^{2-}$ and the strong oxidizer $Cr_2O_7^{2-}$.

# Iron

- Exists in solution in +2 or +3 state.
- Elemental iron reacts with non-oxidizing acids to form $Fe^{2+}$, which oxidizes in air to $Fe^{3+}$.

# Iron

- Brown water running from a faucet is caused by insoluble $Fe_2O3$.
- $Fe^{3+}$ soluble in acidic solution, but forms a hydrated oxide as red-brown gel in basic solution.

# Copper

- In solution exists in +1 or +2 state.
- +1 salts generally white, insoluble.
- +2 salts commonly blue, water-soluble.