Chemistry: A Molecular Approach, 1st Ed.
Nivaldo Tro

Chapter 23 Metals & Metallurgy

Roy Kennedy
Massachusetts Bay Community College
Wellesley Hills, MA
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General Properties and Structure of Metals

- opaque
- good conductors of heat and electricity
- high malleability and ductility
- in the electron sea model, each metal atom releases its valence electrons to be shared by all the atoms in the crystal
- the valence electrons occupy an energy band called the valence band that is delocalized over the entire solid
- however, each metal has its own unique properties to be accounted for

Properties of Some Metals

TABLE 23.1 Thermal Conductivity and Electrical Resistivity of Several Metals

Metal	Thermal Conductivity (W/cm · K)	Electrical Resistivity (Ω · cm)
Ag, silver	4.29	1.59
Cu, copper	4.01	1.67
Fe, iron	0.804	9.71
V, vanadium	0.307	24.8

Distribution of Metals in Earth

- metals make up about 25% of the Earth's crust
- aluminum is the most abundant
- alkali and alkali earth metals make up about 1%
- iron is only transition metal > 5%
- only Ni, Cu, Ag, Au, Pd, Pt found in native form
  - ✓noble metals
- most metals found in **minerals**
  - ✓natural, homogeneous crystalline inorganic solids

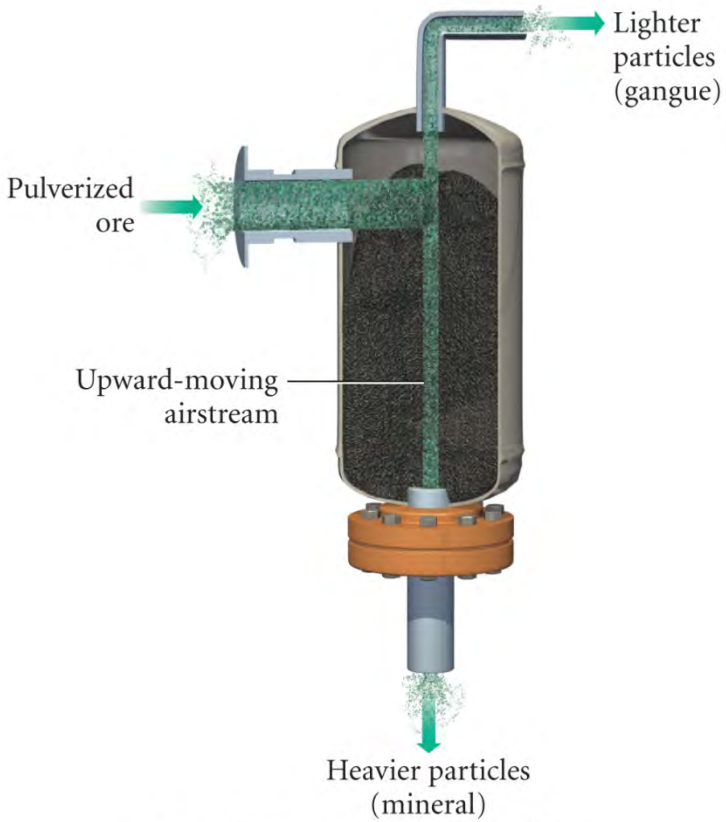
Metallurgy

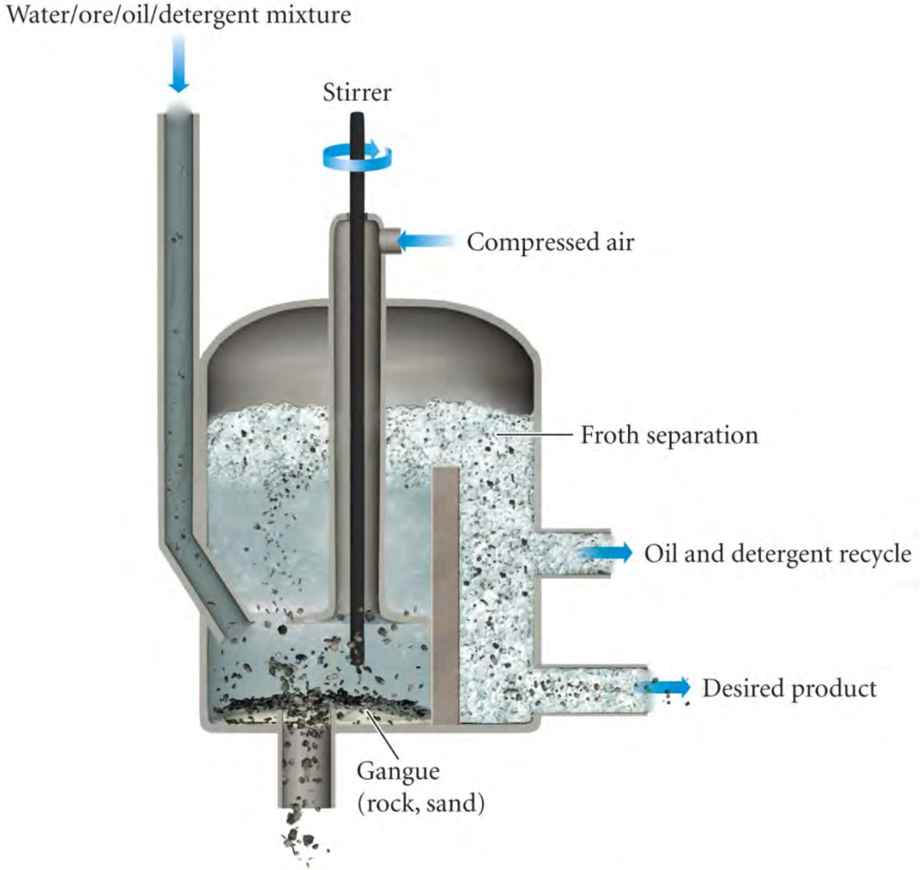
- the mineral must first be separated from the surrounding ore material by physical means
- **extractive metallurgy** are the chemical processes that separate a metal from its mineral
- **refining** are the processes that purify the metal for use

Separation

- first step is to crush the ore into small particles
- the mineral is then separated from the gangue by physical means
  - ✓ using cyclonic winds to separate by density
  - ✓ froth flotation in which the mineral is treated with a wetting agent to make it more attracted to the froth

Separation Methods





Pyrometallurgy

- in **pyrometallurgy**, heat is used to extract the metal from the mineral
- some minerals can be decomposed on heating into volatile materials that will vaporize easily, leaving the metal behind – this is called **calcination**
  - ✓ or drive off water of hydration

$$PbCO_{3\,(s)} \xrightarrow{\Delta} PbO_{(s)} + CO_{2\,(g)}$$

$$Fe_2O_3 \bullet 2\,Fe(OH)_{3\,(s)} \xrightarrow{\Delta} 2\,Fe_2O_{3(s)} + 3\,H_2O_{(g)}$$

Pyrometallurgy

- heating a mineral so that it will react with furnace gases is called **roasting**
  - ✓ if the roast product is a liquid, it's called **smelting**
- if some byproduct of the roasting doesn't volatilize and escape, a **flux** can be added to react with the nonvolatile gangue to create a low-melting waste product easy to separate
  - ✓ the waste liquid is called the **slag**
  - ✓ the slag separates from the molten metal by density

Roasting

$$2\,PbS_{(s)} + 3\,O_{2(g)} \xrightarrow{heat} 2\,PbO_{(s)} + SO_{2(g)}$$

$$HgS_{(s)} + O_{2(g)} \xrightarrow{heat} Hg_{(l)} + SO_{2(g)}$$

Smelting

$$ZnO_{(s)} + C_{(s)} \xrightarrow{heat} Zn_{(l)} + CO_{(g)}$$

$$\underset{\text{gangue}}{SiO_{2(s)}} + \underset{\text{flux}}{CaCO_{3(s)}} \xrightarrow{heat} \underset{\text{slag}}{CaSiO_{3(l)}} + CO_{2(g)}$$

Hydrometallurgy

- the use of aqueous solutions to extract the metal from its mineral is called **hydrometallurgy**
- gold is often extracted by dissolving it in NaCN(*aq*)

$$4\ Au_{(s)} + 8\ CN^{-}_{(aq)} + O_{2\ (g)} + 2\ H_2O_{(l)} \rightarrow 4\ Au(CN)_2^{-}{}_{(aq)} + 4\ OH^{-}_{(aq)}$$

  - ✓ **leaching**
  - ✓ after the impurities are filtered off, the Au is reduced back to the metallic form

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

- some minerals dissolve in acidic, basic, or salt solutions

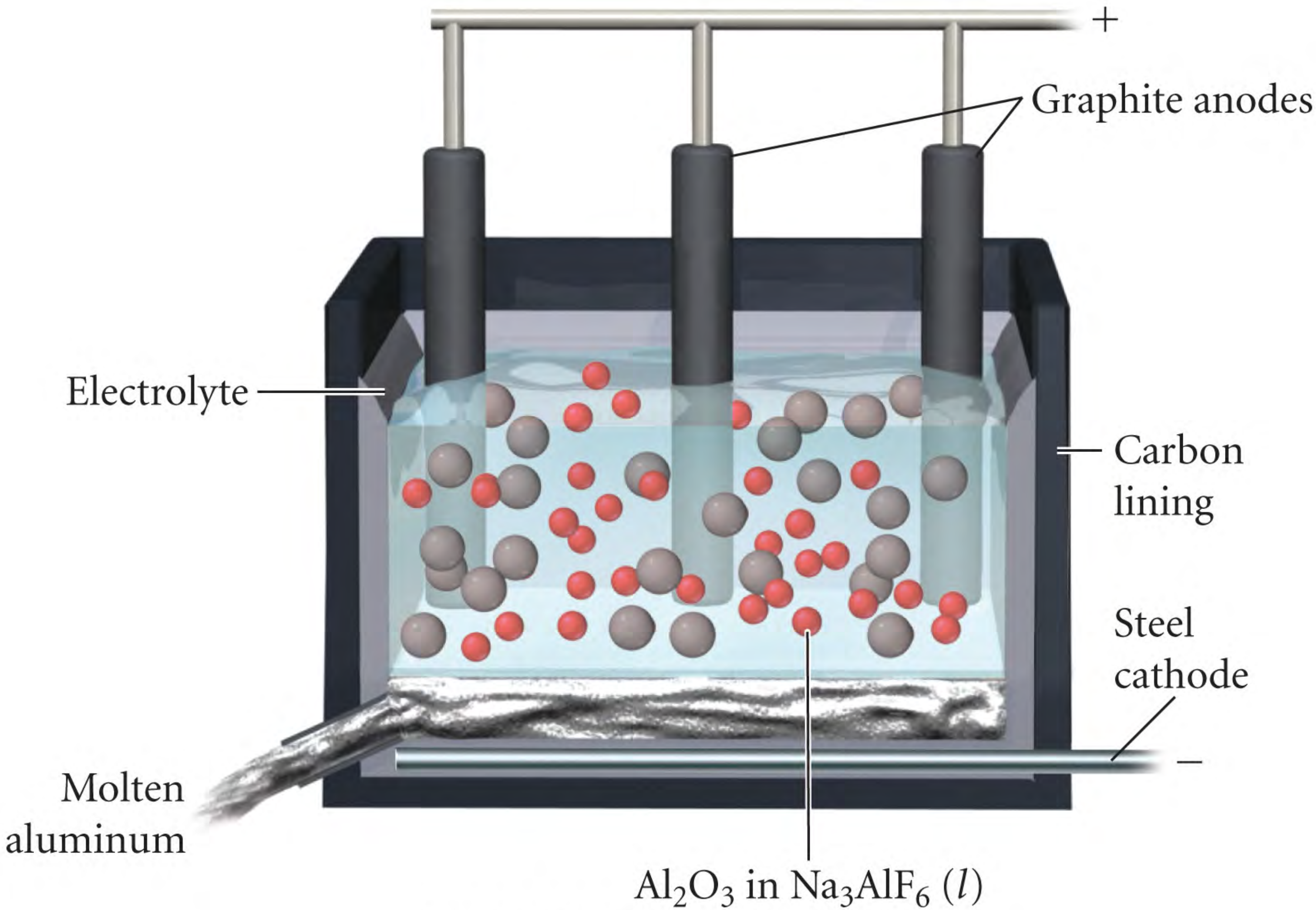
$$2\,CuFeS_{2\,(s)} + H_2SO_{4\,(aq)} + 4\,O_{2\,(g)} \longrightarrow 2\,CuSO_{4\,(aq)} + Fe_2O_{3\,(aq)} + 3\,S_{(s)} + H_2O_{(l)}$$

$$PbSO_{4\,(s)} + 4\,NaCl_{(aq)} \longrightarrow Na_2(PbCl_4)_{(aq)} + Na_2SO_{4\,(aq)}$$

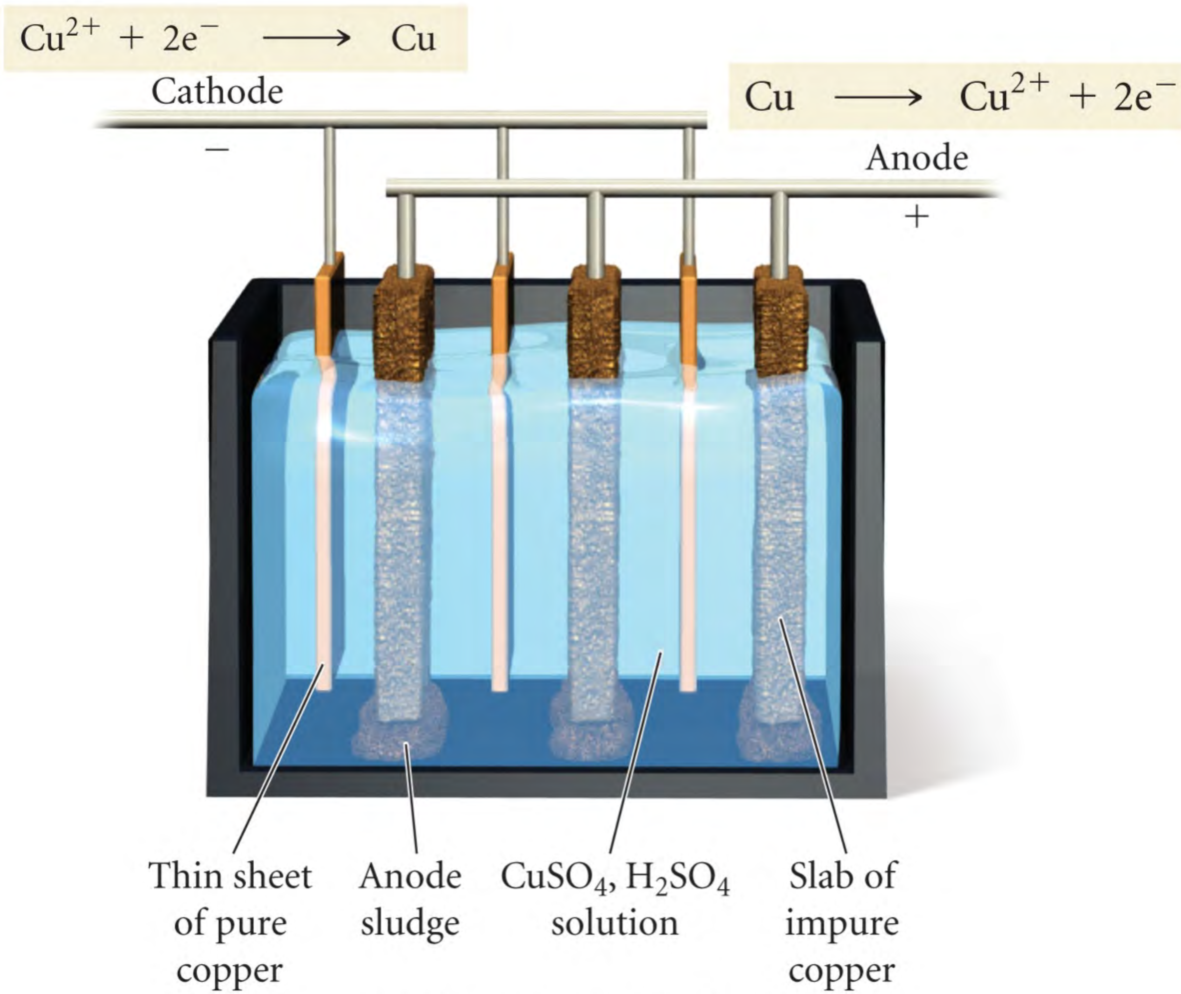
Electrometallurgy

- using electrolysis to reduce the metals from the mineral is called **electrometallurgy**
- the Hall Process is a method for producing aluminum metal by reducing it from its mineral bauxite ($Al_2O_3 \bullet nH_2O$)
  - ✓ bauxite melts at a very high temperature, to reduce the energy cost, bauxite is dissolved in the molten mineral cryolite (Na_3AlF_3)
  - ✓ electrolysis of the solution produces molten Al
- electrolysis is also used to refine metals extracted by other methods
  - ✓ e.g., copper

Hall Process



Electrolytic Refining of Cu



Powder Metallurgy

- powdered metal particles are compressed into a component
- the component is heated until the metal particles fuse – called **sintering**
  - ✓ but not melt
- advantages over milling or casting
  - ✓ no scrap
  - ✓ intricate pieces can be made that would be difficult to cast
  - ✓ allows making pieces from high melting metals that would require very high heat to cast

Structures of Alloys

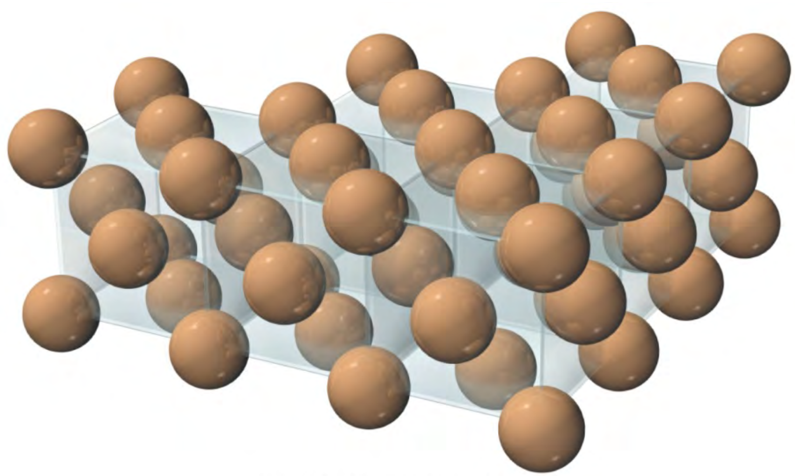
- metals generally closest packing of spheres
- exact crystal structure may change with temperature
- **alloys** are metals that contain more than one type of material
  - ✓ some are solid solutions
  - ✓ some have fixed composition like a compound

TABLE 23.2 The Crystal Structures of the 3*d* Elements

Metal	Natural Crystal Structure at Room Temperature	Other Crystal Structures at Different Temperatures and Pressures
Sc	Hexagonal closest packed	Face-centered cubic, body-centered cubic
Ti	Hexagonal closest packed	Body-centered cubic above 882 °C
V	Body-centered cubic	
Cr	Body-centered cubic	Hexagonal closest packed
Mn	Alpha complex body-centered cubic form	Beta simple cubic form above 727 °C
		Face-centered cubic above 1095 °C
		Body-centered cubic above 1133 °C
Fe	Body-centered cubic	Face-centered cubic above 909 °C
		Body-centered cubic above 1403 °C
Co	Hexagonal closest packed	Face-centered cubic above 420 °C
Ni	Face-centered cubic	
Cu	Face-centered cubic	
Zn	Hexagonal closest packed	

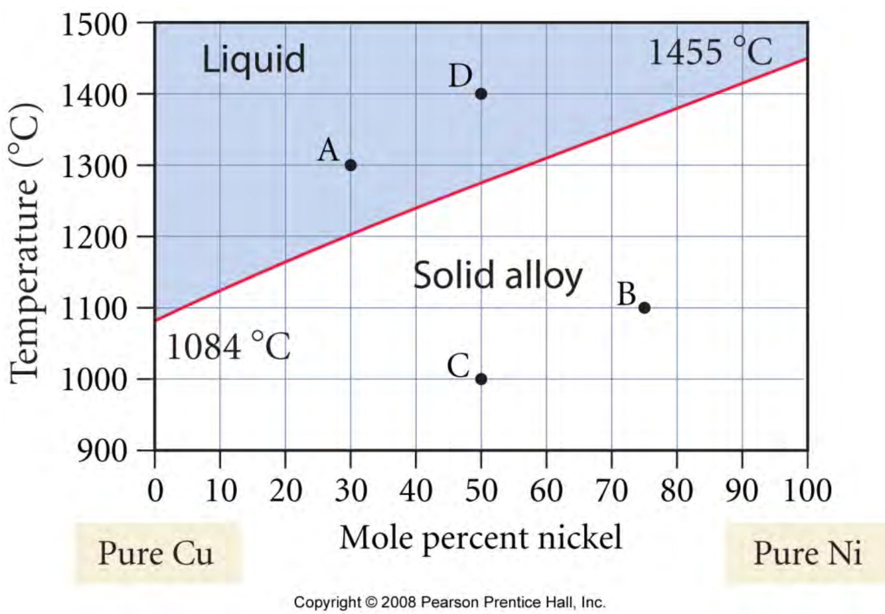
Types of Alloys

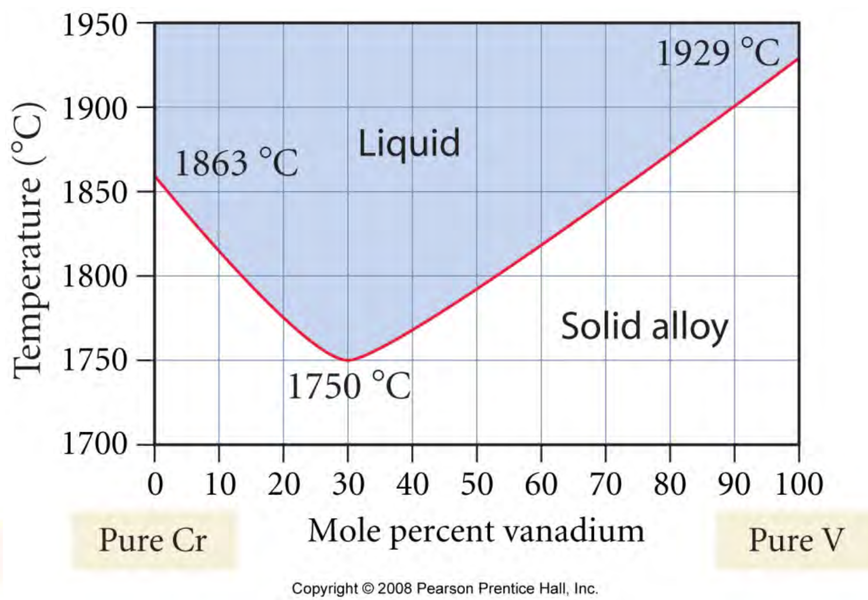
- in **substitutional alloys,** one metal atom substitutes for another
  - ✓crystal structure may stay the same or change
- in **interstitial alloys,** an atom fits in between the metal atoms in the crystal
  - ✓usually a small nonmetal atom



Substitutional Alloys
Miscible Solid Solutions

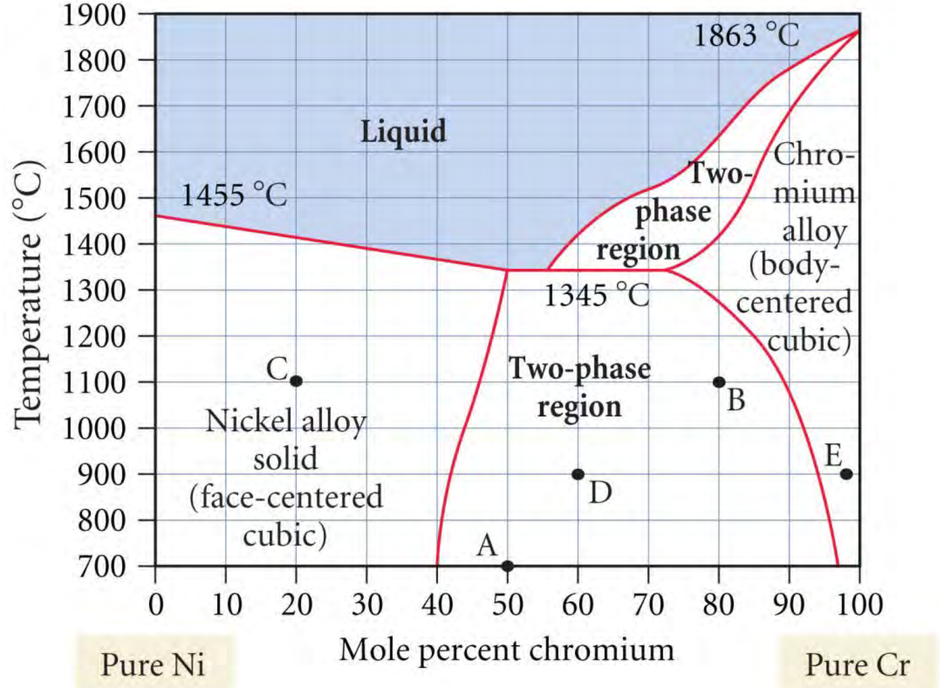
- phase-composition diagram





Substitutional Alloys
Limited Solubility Solid Solutions

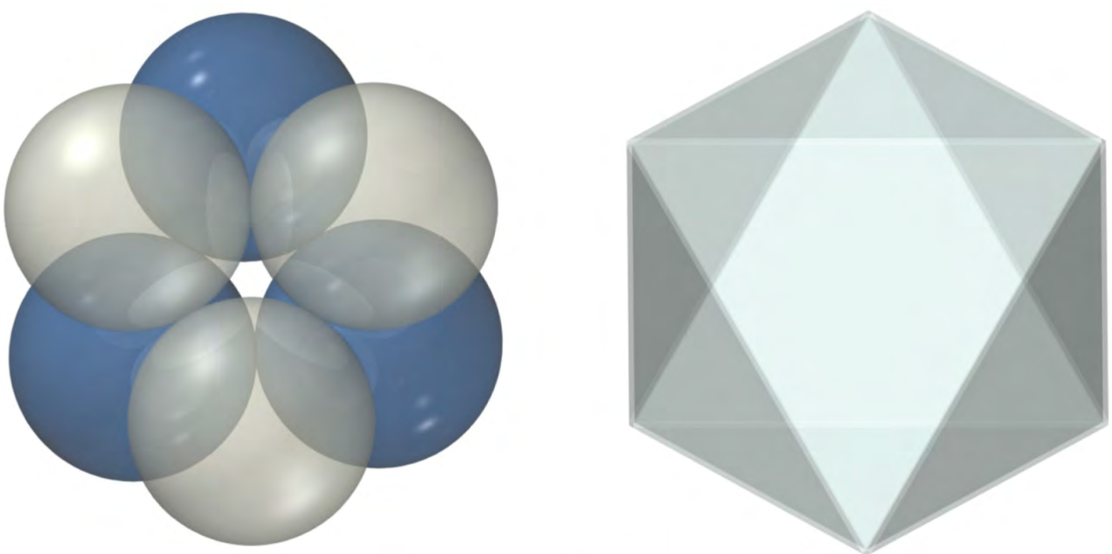
- because of their different crystal structures, some metals are not miscible
- phase-composition diagram

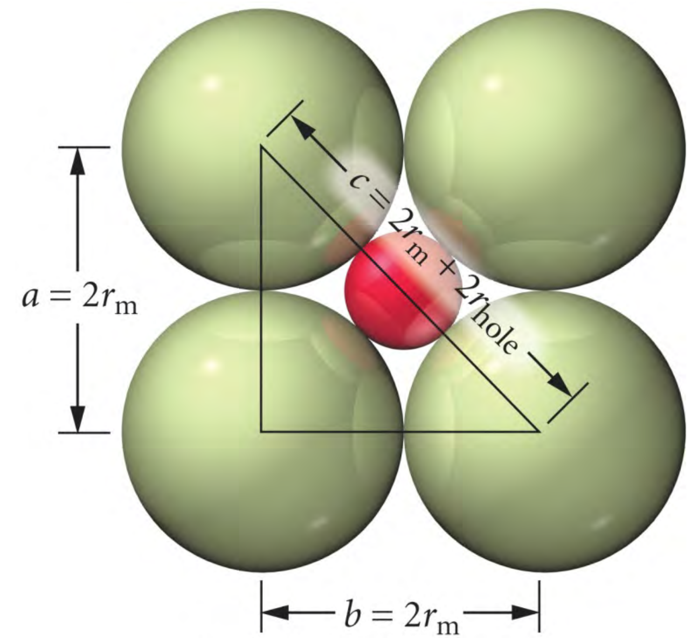


Interstitial Alloys

- H, B, N, C can often fit in the holes in a closest packed structure
- an atom with maximum radius 41.4% of the metal atom's can fit in an octahedral hole
- an atom with maximum radius 23% of the metal atom's can fit in an tetrahedral hole
- formula of alloy depends on the number and type of holes occupied

Octahedral Hole





Tetrahedral Holes

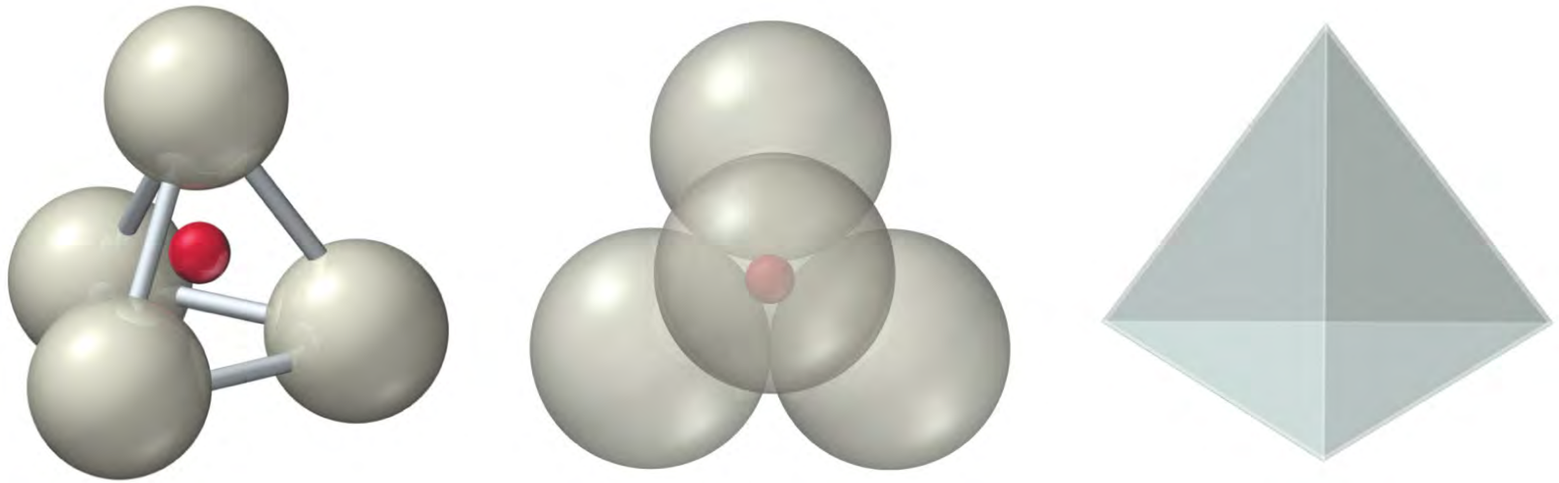


TABLE 23.3 Formulas of Several Interstitial Alloys

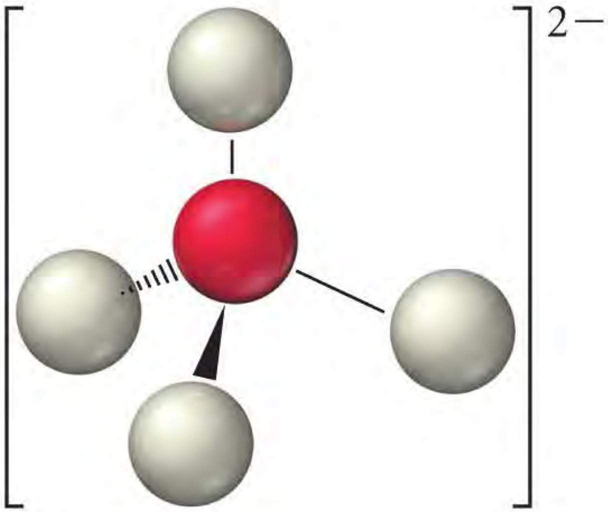
Compound	Type of Interstitial Hole Occupied	Fraction of Holes Occupied	Formula
Titanium carbide	Octahedral	All	TiC
Molybdenum nitride	Octahedral	One-half	Mo_2N
Tungsten nitride	Octahedral	One-half	W_2N
Manganese nitride	Octahedral	One-quarter	Mn_4N
Palladium hydride	Tetrahedral	One-quarter	Pd_2H
Titanium hydride	Tetrahedral	All	TiH_2

Titanium

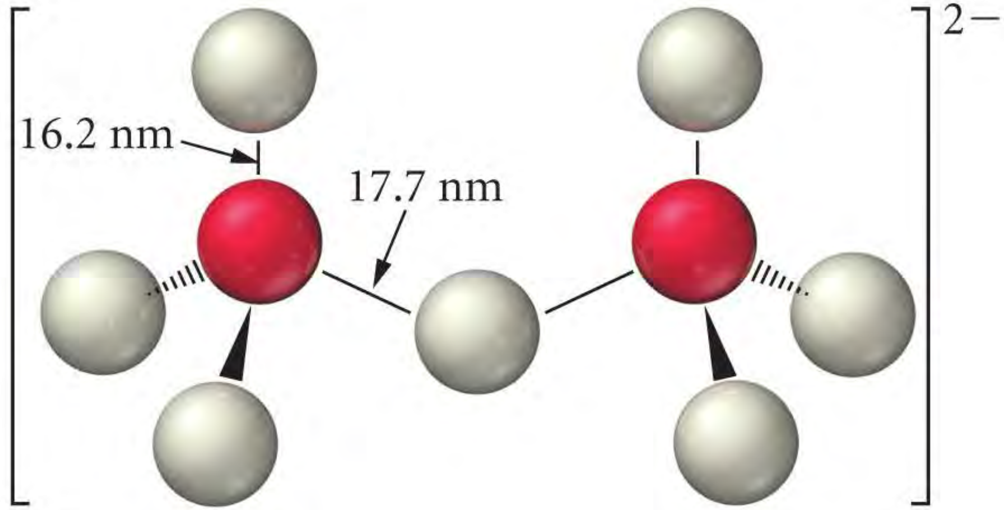
- 9th most abundant element on Earth
- 4th most abundant metal
- minerals rutile (TiO_2) and ilmenite ($FeTiO_3$)
- very reactive
- oxidizes in the presence of O_2 and N_2
  - ✓ needs to be **arc-welded** under inert atmosphere
- resists corrosion because of a tightly held oxide coat
- stronger than steel, but half the density
- denser than aluminum, but twice as strong
- alloyed with 5% Al
- most common use is as TiO_2 in paint

Chromium

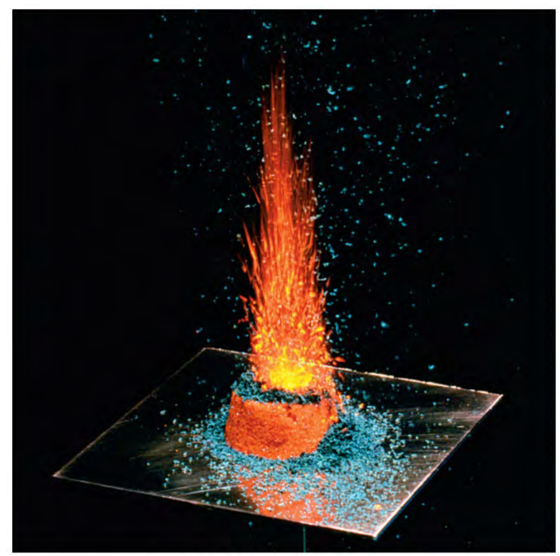
- forms many compounds with different colors
- mineral chromite ($FeCr_2O_4$)
  - ✓ which is reduced with Al
- white, hard, lustrous, brittle
- Cr dissolves in HCl and H_2SO_4 but not HNO_3
- mainly used as alloy to make stainless steel
- compounds used as pigments and wood preservatives
- toxic and carcinogenic
- oxidation states +1 to +6



Chromate (CrO_4^{2-})



Dichromate ($Cr_2O_7^{2-}$)



Manganese

- mineral pyrolusite (MnO_2), hausmannite (Mn_3O_4), and rhodochrosite $MnCO_3$
  - ✓ which is reduced with Al or Na
  - ✓ heating impure pyrolusite with C produces alloy ferromanganese
- Mn very reactive, dissolves in acids
- used as alloy to make stainless steel
- compounds used as glass additives
- oxidation states +1 to +7

Cobalt

- mineral cobaltite (CoAsS),
- ferromagnetic
- Mn very reactive, dissolves in acids
- used as alloy to make high-strength steels
  - ✓ carbaloy
- used to make magnets
- compounds with deep blue colors, used in pigments and inks
- covitamin of B_{12}

Copper

- found in its native form
- minerals are chalcopyrite ($CuFeS_2$), malachite ($Cu_2(OH)_2CO_3$)
- reddish color
    - ✓ used in ornamentation and jewelry
- high abundance and concentration = useful industrially
- easy to recycle
- second best electrical conductor – used in electrical wiring and devices
- high heat conductivity – used in heat exchangers
- used in water piping because of its resistance to corrosion
- long exposure to environment produces a green patina – mainly malachite and brohchanite ($Cu_4SO_4(OH)_6$)
- strong metal – so used to alloy with metals where strength is needed
    - ✓ bronze = Cu and Sn
    - ✓ brass = Cu and Zn

Brass – a Mixture

Type	Color	% Cu	% Zn	Density g/cm^3	MP °C	Tensile Strength psi	Uses
Gilding	redish	95	5	8.86	1066	50K	pre-83 pennies, munitions, plaques
Commercial	bronze	90	10	8.80	1043	61K	door knobs, grillwork
Jewelry	bronze	87.5	12.5	8.78	1035	66K	costume jewelry
Red	golden	85	15	8.75	1027	70K	electrical sockets, fasteners & eyelets
Low	deep yellow	80	20	8.67	999	74K	musical instruments, clock dials
Cartridge	yellow	70	30	8.47	954	76K	car radiator cores
Common	yellow	67	33	8.42	940	70K	lamp fixtures, bead chain
Muntz metal	yellow	60	40	8.39	904	70K	nuts & bolts

Nickel

- comes from meteor crater in Ontario
- nickel sulfides are roasted in air to form oxides, then reduced with carbon
- separated by converting to volatile $Ni(CO)_4$, which is later heated to decompose back to Ni
- Ni not very reactive and resistant to corrosion
- used as an alloying metal in stainless steel, especially where corrosion resistance is important
  - ✓ Monel metal
  - ✓ used in armor plating
- Ni metal plated onto other metals as protective coat

Zinc

- minerals sphalerite (ZnS), smithsonite ($ZnCO_3$), and franklinite (Zn, Fe, and Mn oxides)
- minerals are roasted in air to form oxides, then reduced with carbon
- used in alloys with Cu (brass) and Cu and Ni (German brass)
- reactive metal
- resists corrosion because it forms an oxide coat
- **galvinizing** is plating Zn onto other metals to protect them from corrosion
  - ✓ both coating and sacrificial anode
- zinc compounds used in paints for metals
  - ✓ if scratched, becomes sacrificial anode
- zinc phosphate used to coat steel so that it may be painted
- considered safe – used to replace Cr and Pb additives
  - ✓ though some evidence it may be an environmental hazard

zinc phosphate adhering to steel surface