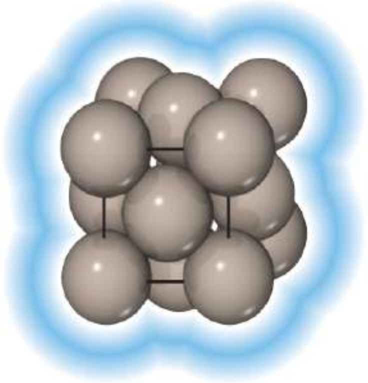
CHAPTER 12

Solids and Modern Materials

12.1: CLASSIFICATION OF SOLIDS

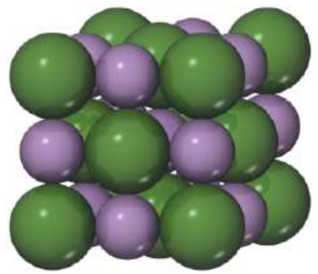
CLASSIFYING SOLIDS BASED ON BONDS

- **Metallic solids** are held together by a “sea” of collectively shared electrons.
- **Ionic solids** are sets of cations and anions mutually attracted to one another.
- **Covalent-network solids** are joined by an extensive network of covalent bonds.
- **Molecular solids** are discrete molecules held together by weak forces.



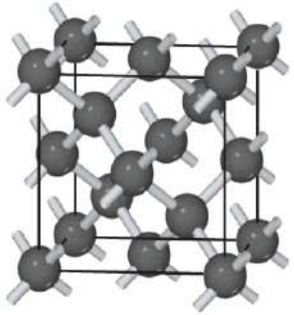
Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



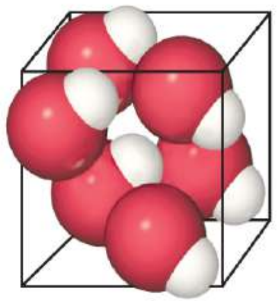
Ionic solids

Extended networks of ions held together by ion–ion interactions (NaCl, MgO)



Covalent-network solids

Extended networks of atoms held together by covalent bonds (C, Si)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H_2O)

TWO OTHER TYPES OF SOLIDS

- **Polymers** contain long chains of atoms connected by covalent bonds; the chains can be connected to other chains by weak forces. These molecules have different properties than small molecules or metallic or ionic compounds.
- **Nanomaterials** are crystalline compounds with the crystals on the order of 1–100 nm; this gives them very different properties than larger crystalline materials.

12.2 STRUCTURES OF SOLIDS

ONE ORGANIZATION OF SOLIDS

- Solids with a regular repeating pattern of atoms are **crystalline**.
- **Amorphous** solids are characterized by a distinct lack of order in the arrangement of atoms.
- Since crystalline solids have a regular pattern, they are of more interest to most chemists.

Iron pyrite (FeS_2), a crystaline solid

Obsidian (typically $KAlSi_3O_8$), an amorphous solid

UNIT CELL

- The basis of a repeating pattern is the unit cell.
- The structure of a crystalline solid is defined by
  - the size and shape of the unit cell.
  - the locations of atoms within the unit cell.

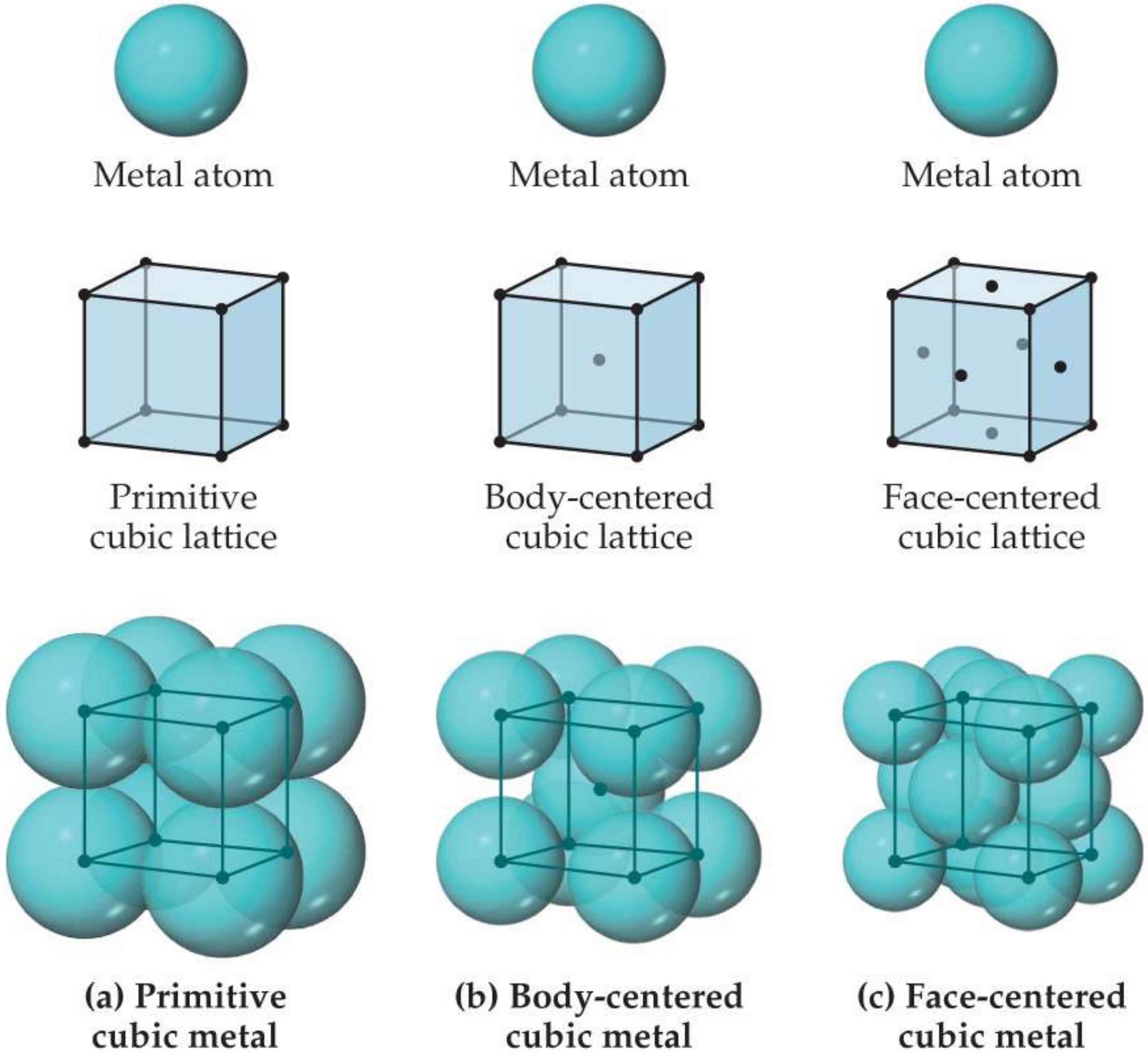
12.3 METALLIC SOLIDS

Atoms in metals easily slip past one another as mechanical force is applied; can you think of why this would not be true for ionic solids?

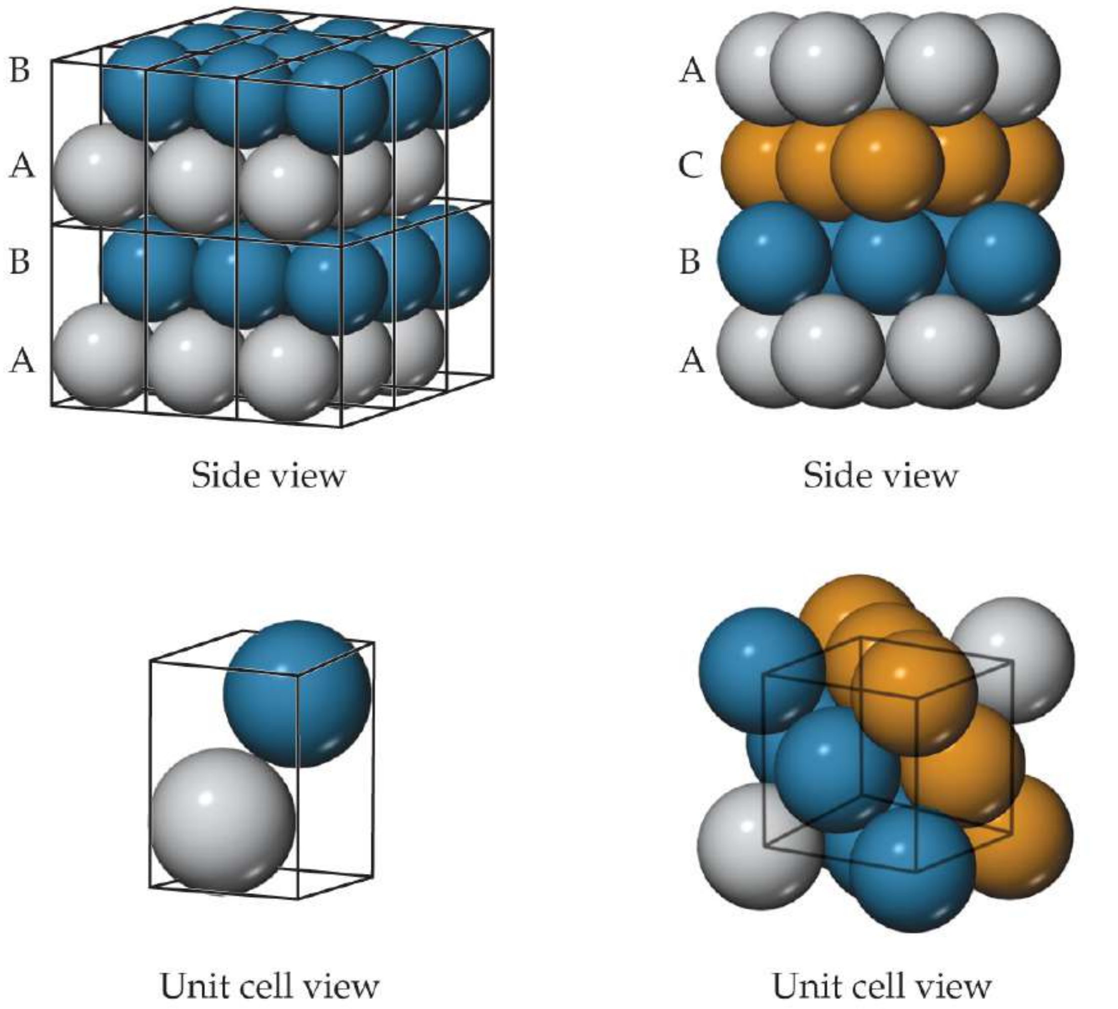
a. Ionic solids have less efficient packing that makes the slipping motion difficult, causing the solid to be brittle.
b. When ions slip past each other, like charges experience repulsions, causing the solid to be brittle.

METALLIC STRUCTURE

- The structures of many metals conform to one of the cubic unit cells: simple cubic, body-centered cubic, or face-centered cubic.



CLOSE PACKING



(a) Hexagonal close-packed metal (b) Cubic close-packed metal

- Nature does not like empty space!
- The atoms in a crystal pack as close together as they can.
- The two common types of packing seen are
  - cubic close-packed.
  - hexagonal close-packed.

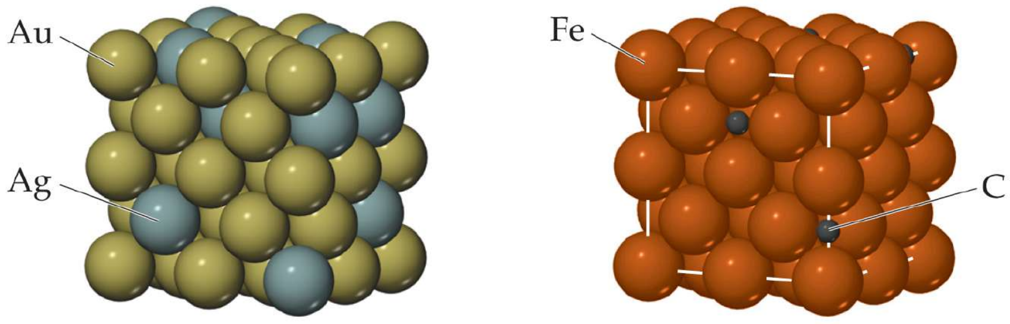
ALLOYS

- **Alloys** are materials that contain more than one element and have the characteristic properties of metals.
- It is an important means employed to change the properties of certain metals.

Table 12.2 Some Common Alloys

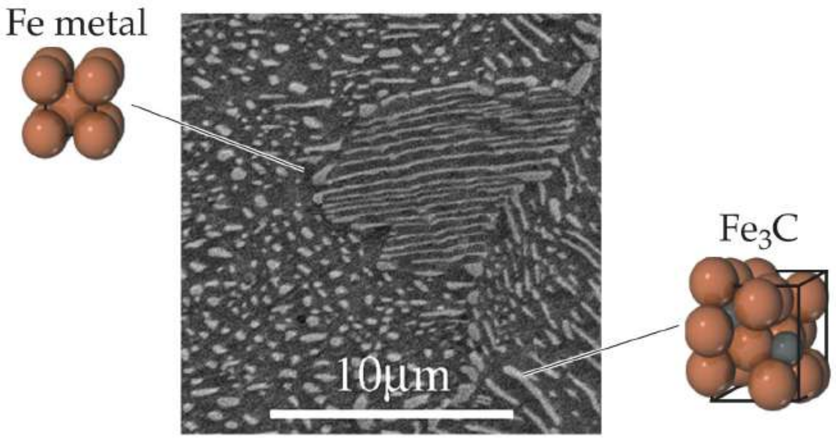
Name	Primary Element	Typical Composition (by Mass)	Properties	Uses
Wood's metal	Bismuth	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70 °C)	Fuse plugs, automatic sprinklers
Yellow brass	Copper	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for early civilizations
Stainless steel	Iron	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Cookware, surgical instruments
Plumber's solder	Lead	67% Pb, 33% Sn	Low melting point (275 °C)	Soldering joints
Sterling silver	Silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Dental amalgam	Silver	70% Ag, 18% Sn, 10% Cu, 2% Hg	Easily worked	Dental fillings
Pewter	Tin	92% Sn, 6% Sb, 2% Cu	Low melting point (230 °C)	Dishes, jewelry

TYPES OF ALLOYS

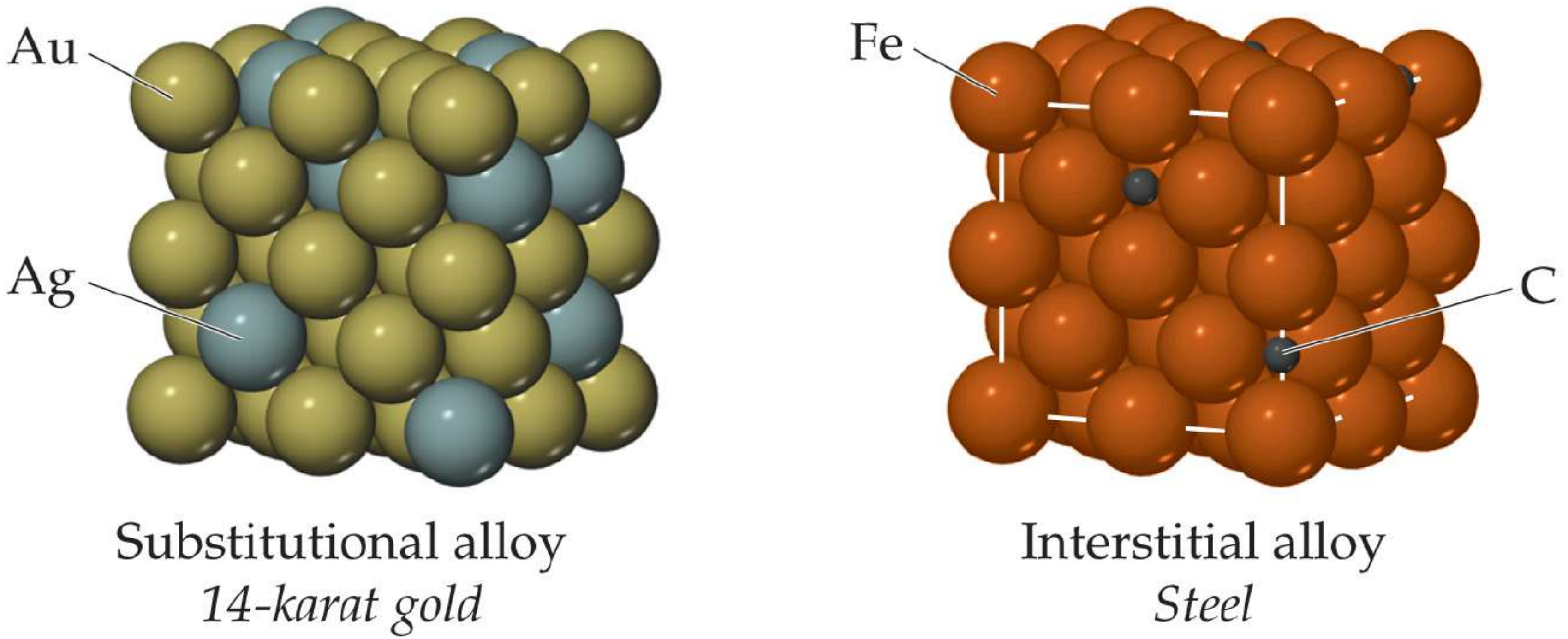


Substitutional alloy
14-karat gold

Interstitial alloy
Steel



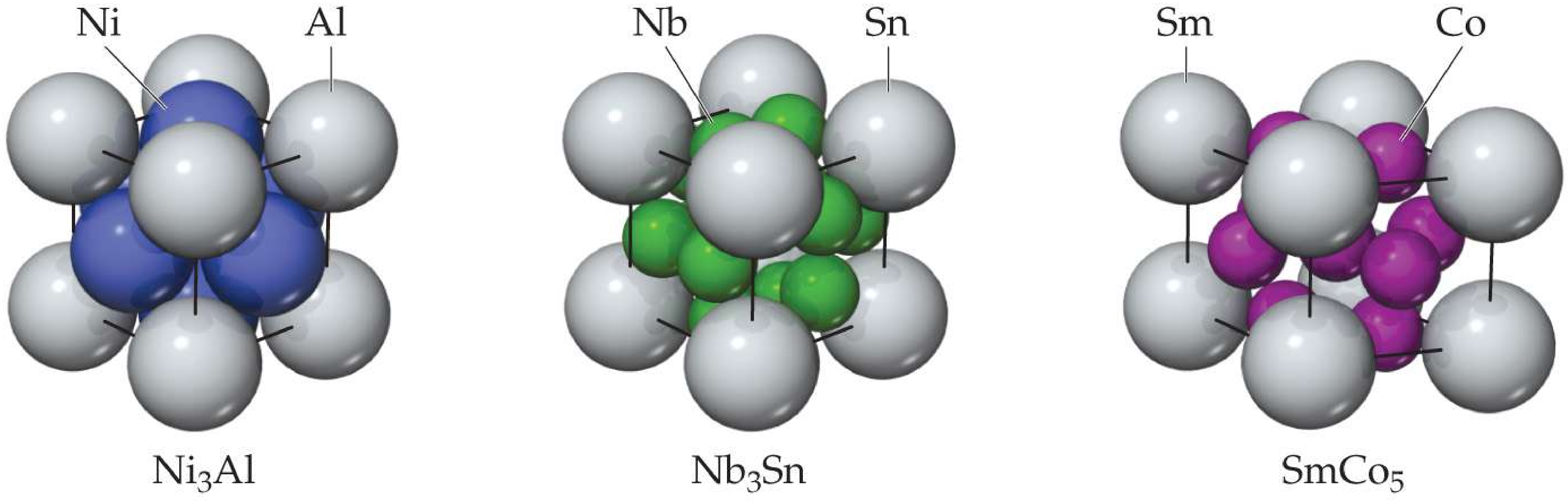
- **Substitutional alloys**: A second element takes the place of a metal atom.
- **Interstitial alloys**: A second element fills a space in the lattice of metal atoms.
- **Heterogeneous alloys**: components not dispersed uniformly



- What determines which species in a solid solution is the solute and which is the solvent?

INTERMETALLIC COMPOUNDS

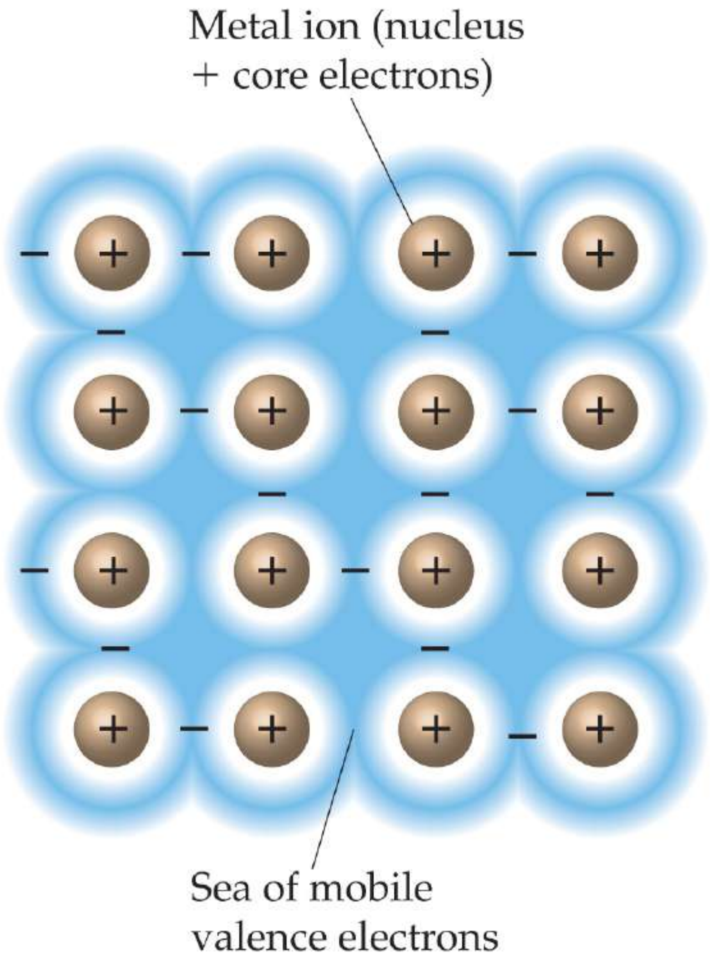
- compounds, *not* mixtures
- distinct properties, definite composition (since they are compounds)
- ordered, rather than randomly distributed



12.4 METALLIC BONDING

METALLIC BONDING

- One can think of a metal as a group of cations suspended in a sea of electrons.
- The electrical and thermal conductivity, ductility, and malleability of metals is explained by this model.



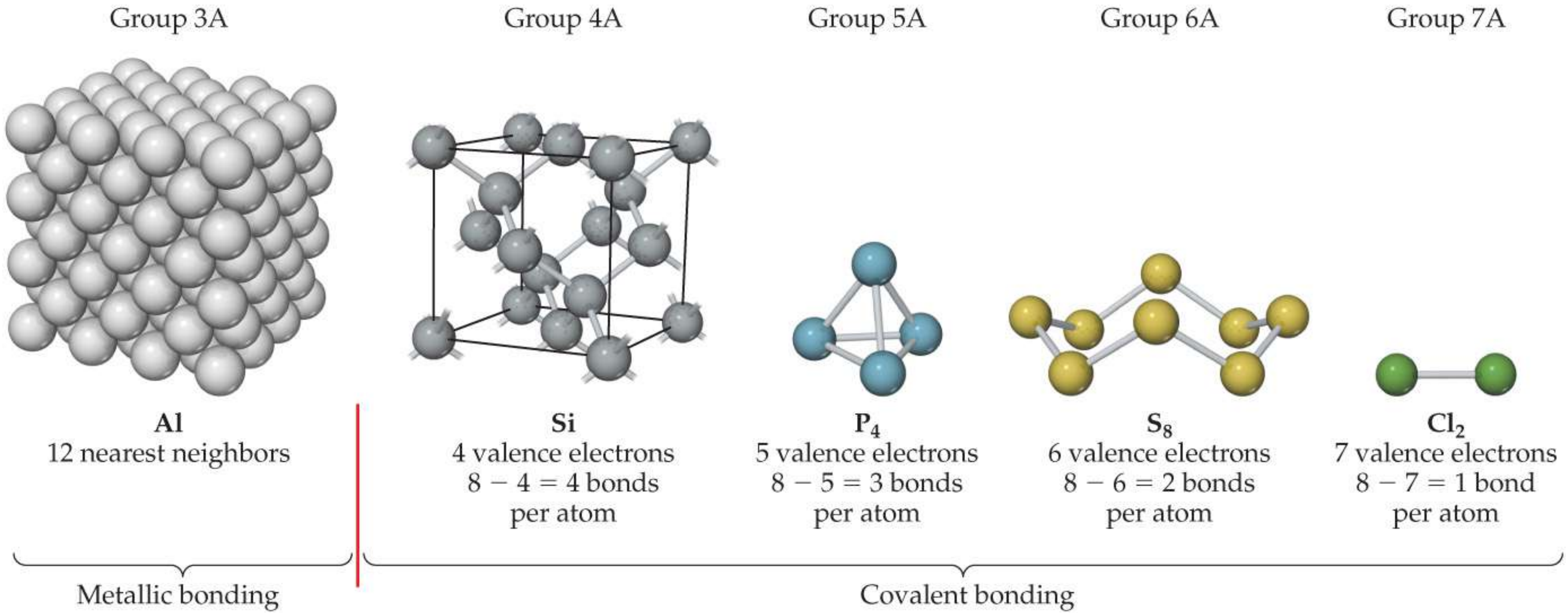
Which of these drawings represent molecules?

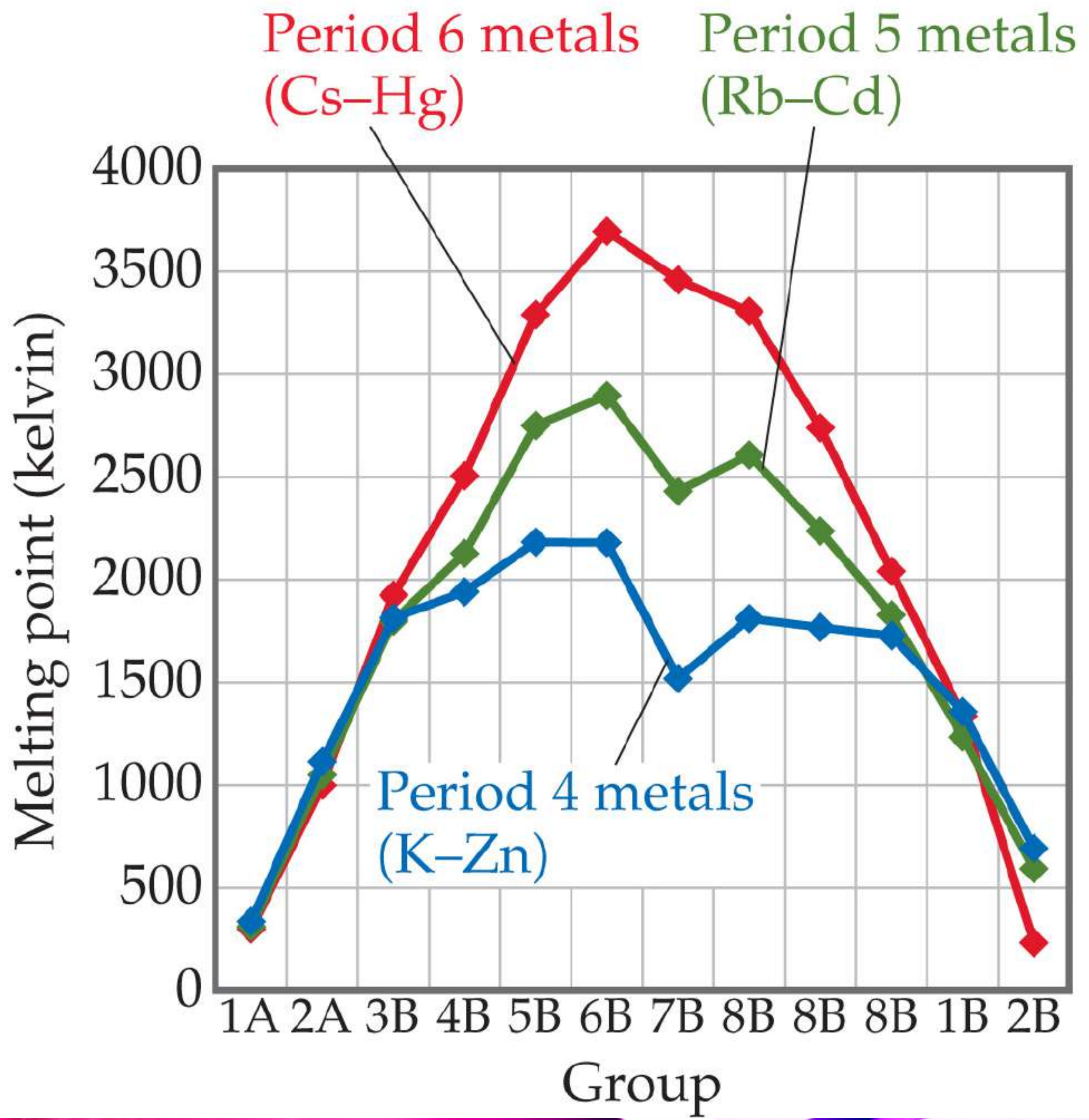
a. Al, Si, and P_4

b. Si, P_4, and S_8

c. P_4, S_8, and Cl_2

d. S_8 and Cl_2



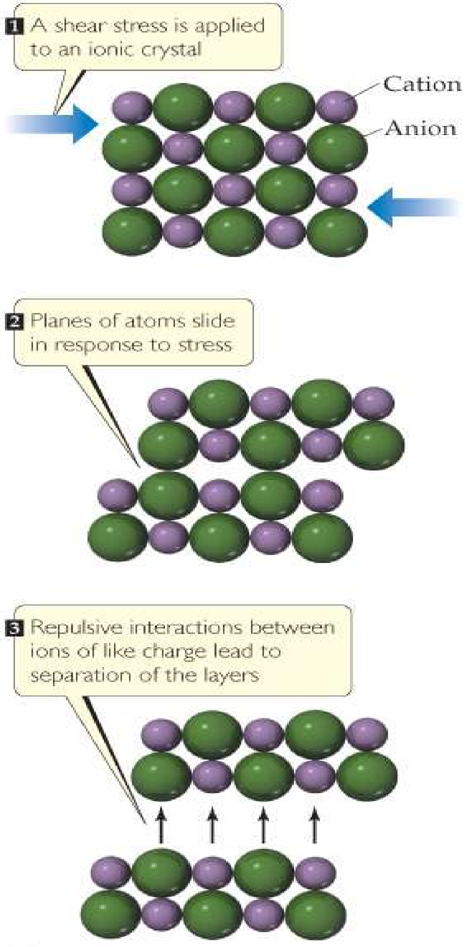


Which element in each period has the highest melting point? In each case, is the element you named at the beginning, middle, or end of its period?

12.5 IONIC SOLIDS

IONIC SOLIDS

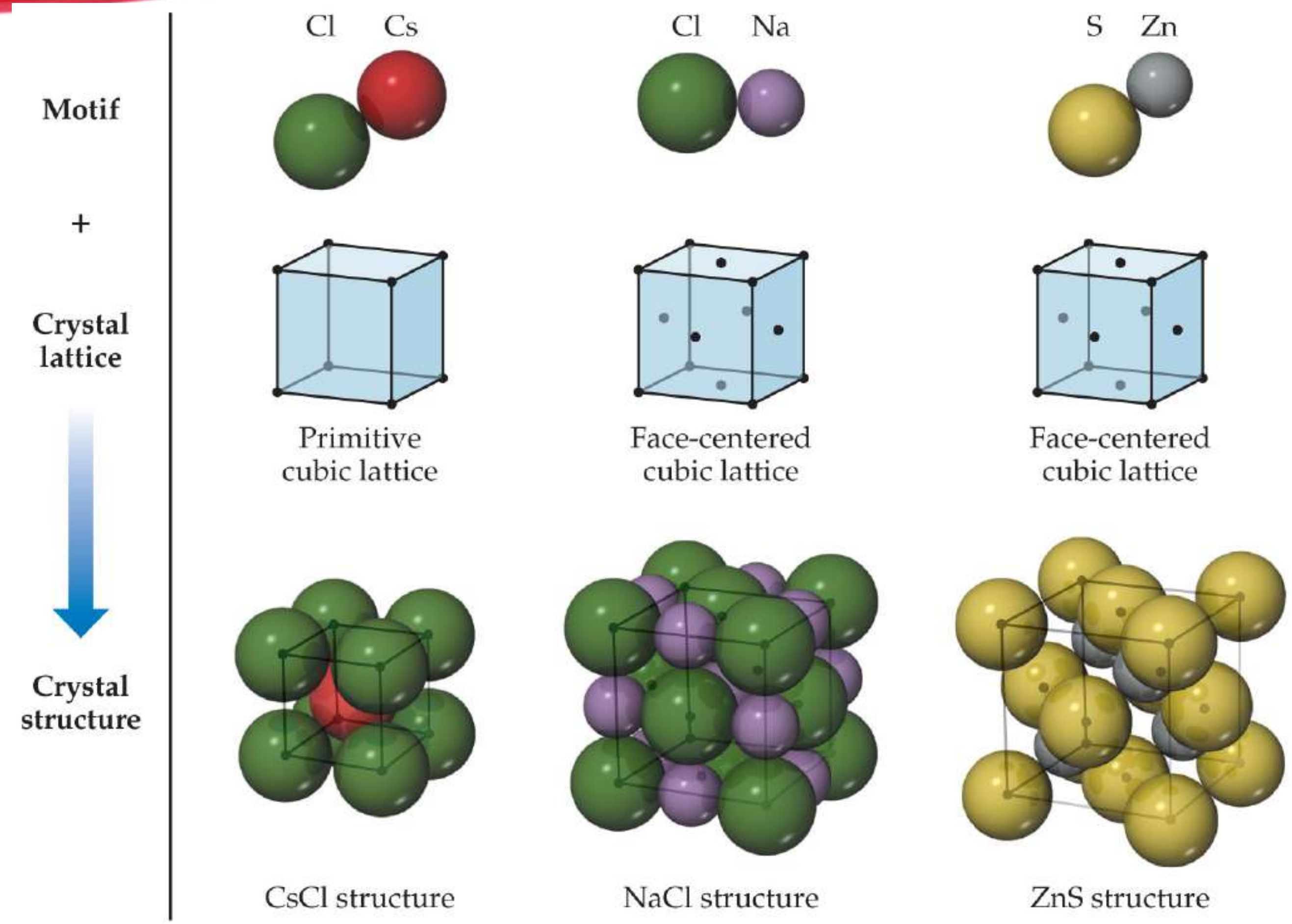
- In ionic solids, the lattice comprises alternately charged ions.
- Ionic solids have very high melting and boiling points and are quintessential crystals.



(a)

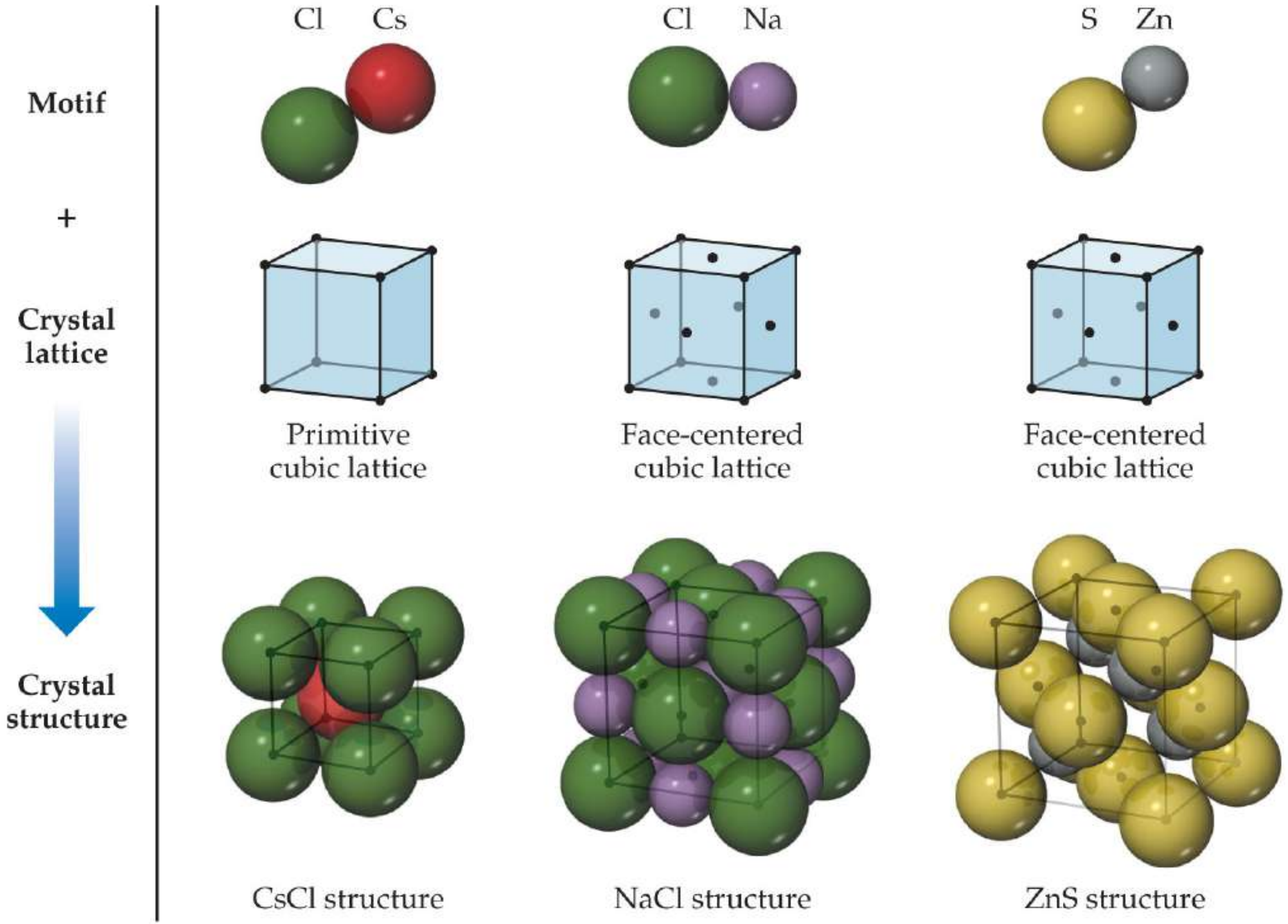

(b)

IONIC SOLIDS



- Most favorable structures have cation–anion distances as close as possible, but the anion–anion and cation–cation distances are maximized.
- Three common structures for 1:1 salts:
  - CsCl structure
  - NaCl (rock salt) structure
  - zinc blende (ZnS) structure

Do the anions touch each other in any of these three structures? If not, which ions do touch each other?

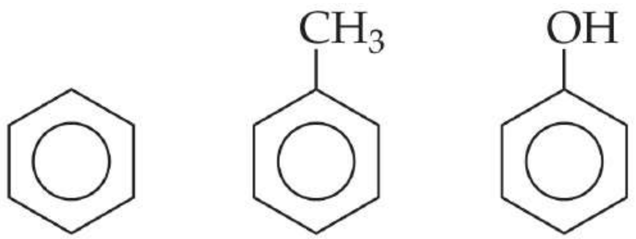


a. Yes, if the anions are sufficiently large.
b. Yes, if the anions are sufficiently small.
c. No, because anions repel one another.
d. No, because each anion adopts different lattice points in the unit cell.

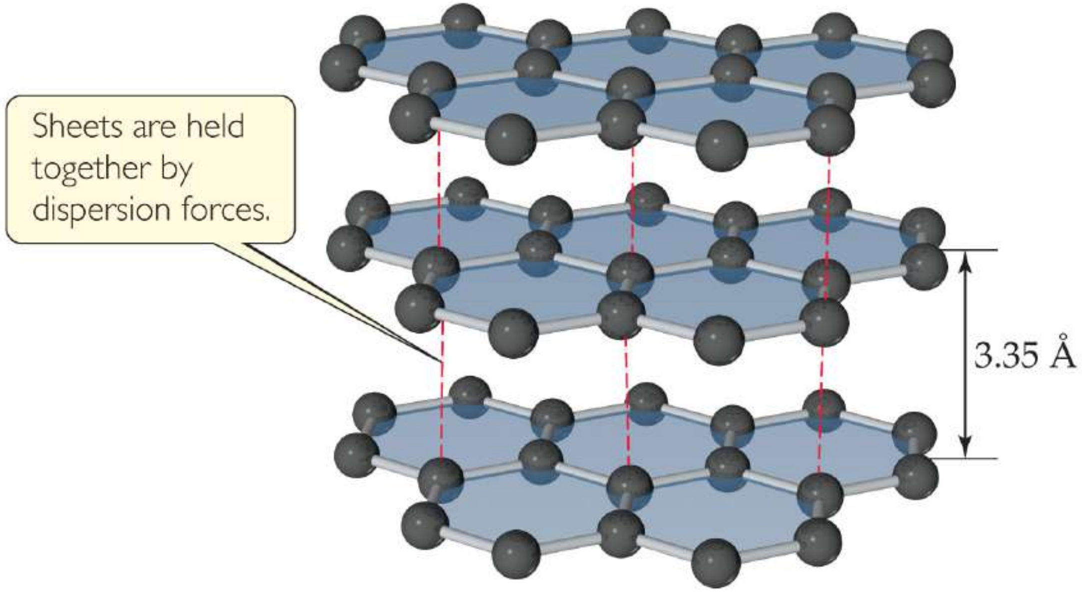
12.6 MOLECULAR SOLIDS

MOLECULAR SOLIDS

- Consist of atoms or molecules held together by weaker forces (dispersion, dipole–dipole, or hydrogen bonds).
- Shape (ability to stack) matters for some physical properties, like boiling point.
- Graphite is an example.



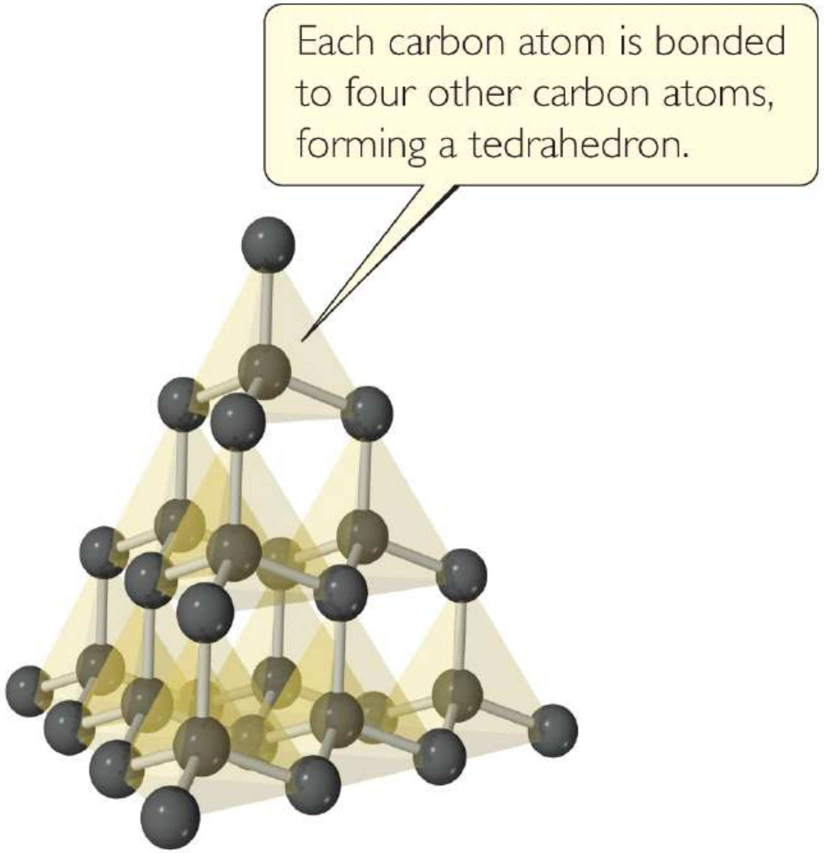
	Benzene	Toluene	Phenol
Melting point (°C)	5	−95	43
Boiling point (°C)	80	111	182



(b) Graphite

12.7 COVALENT-NETWORK SOLIDS

COVALENT-NETWORK SOLIDS



(a) Diamond

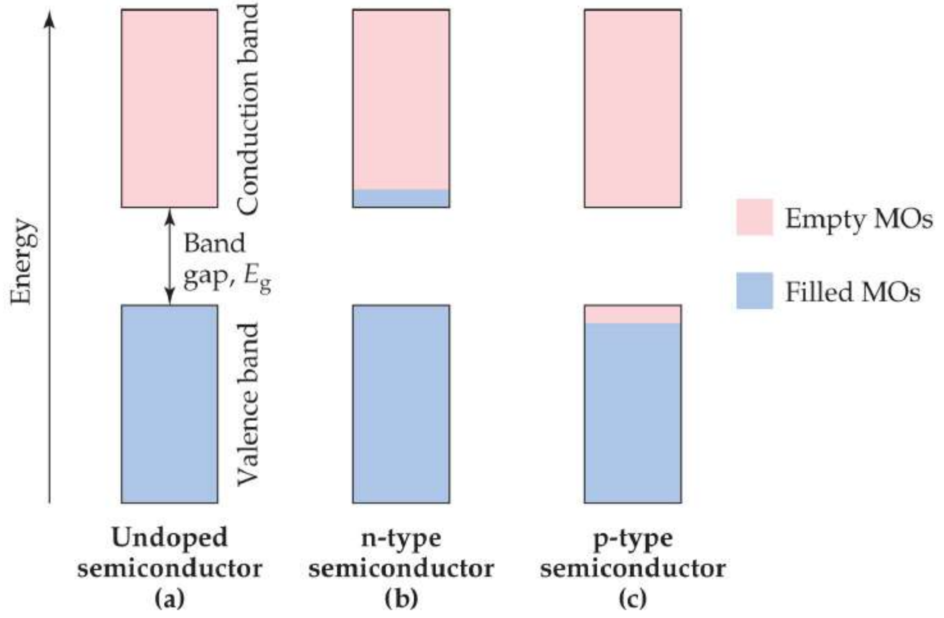
- Atoms are covalently bonded over large network distances with regular patterns of atoms.
- Tend to have higher melting and boiling points.
- Diamond is an example.

WHAT FORMS A SEMICONDUCTOR?

- Among elements, only Group IVA, all of which have 4 valence electrons, are semiconductors.
- Inorganic semiconductors (like GaAs) tend to have an average of 4 valence electrons (3 for Ga, 5 for As).

DOPING

- changing the conductivity of semiconductors by adding an element with more or fewer electrons
- **n-type semiconductors** have more electrons, so the negative charge travels in the conductance band.
- **p-type semiconductors** have fewer electrons, so the "hole" travels in the valence band.

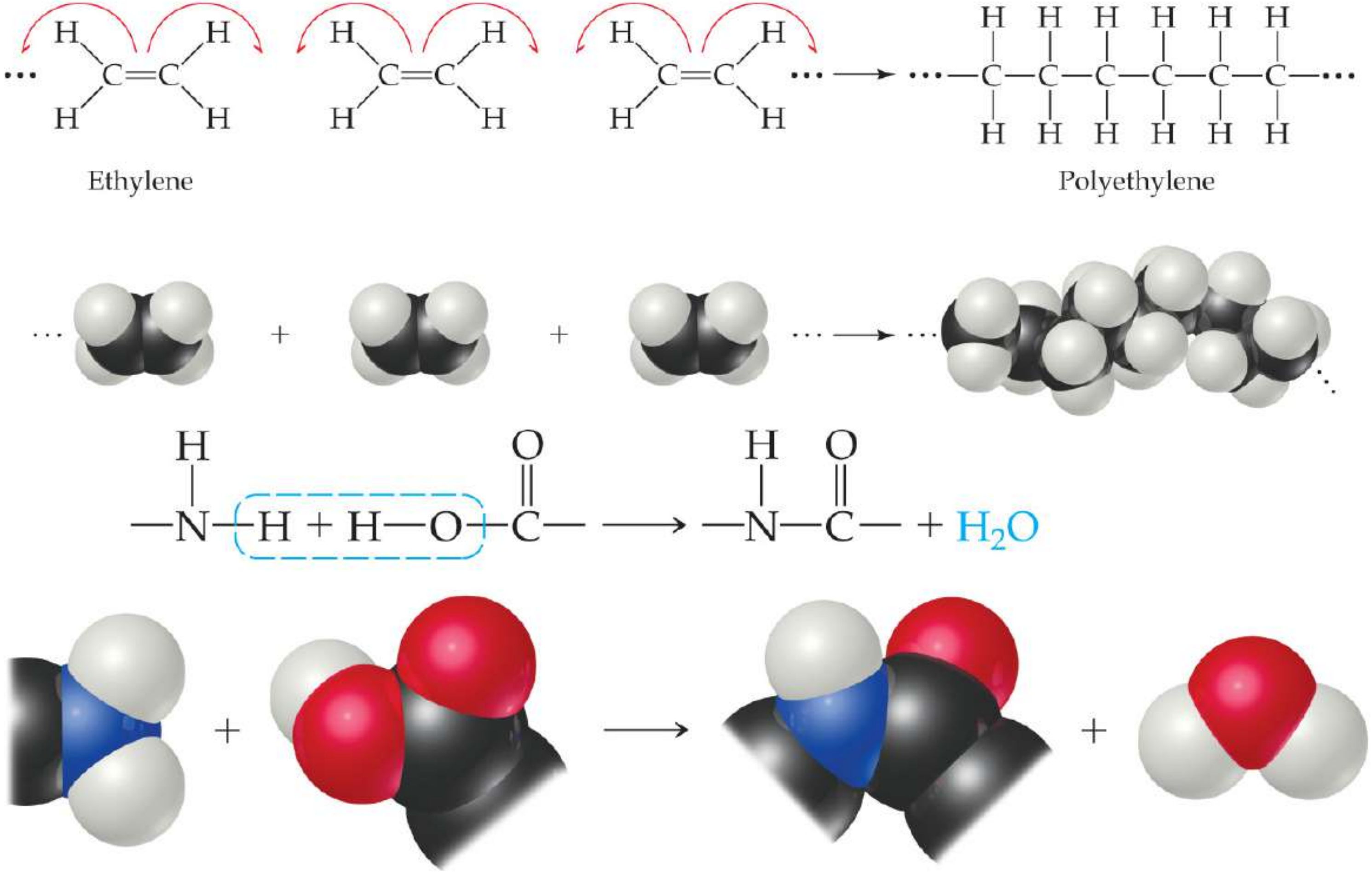


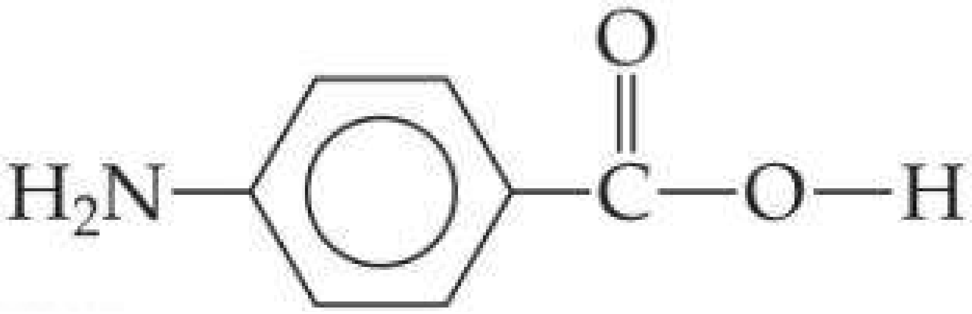
12.8 POLYMERS

POLYMERS

- **Polymers** are molecules of high molecular weight made by joining smaller molecules, called **monomers.**
- There are two primary types of polymers:
  - **Addition polymers** are formed when a bond breaks, and the electrons in that bond make two new bonds.
  - **Condensation polymers** are formed when a small molecule is removed between two large molecules.

ADDITION VS. CONDENSATION POLYMERIZATION





Is this molecule a better starting material for an addition polymer or a condensation polymer?

a. An addition polymer, because it has no C=C bond available for a polymer reaction.

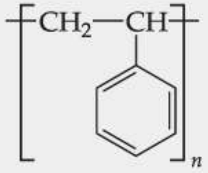
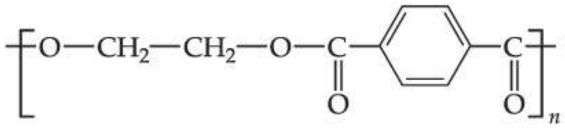
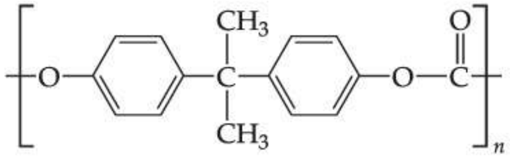
b. An addition polymer, because it has a C=C bond available for a polymer reaction.

c. A condensation polymer, because it has one reactive site H_2N- that can react with H_2N on another molecule.

d. A condensation polymer because it has a reactive site H_2N- that can react with a —COOH site on another molecule with water also forming.

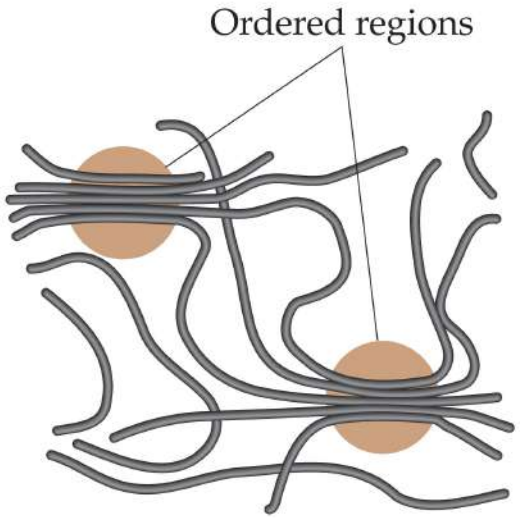
SOME COMMON POLYMERS

Table 12.5 Polymers of Commercial Importance

Polymer	Structure	Uses
Addition Polymers		
Polyethylene	$-(CH_2-CH_2)_n-$	Films, packaging, bottles
Polypropylene	$-[CH_2-CH(CH_3)]_n-$	Kitchenware, fibers, appliances
Polystyrene		Packaging, disposable food containers, insulation
Polyvinyl chloride (PVC)	$-[CH_2-CH(Cl)]_n-$	Pipe fittings, plumbing
Condensation Polymers		
Polyurethane	$-[NH-R-NH-C(=O)-O-R'-O-C(=O)]_n-$ R, R′ = $-CH_2-CH_2-$ (for example)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethylene terephthalate (a polyester)		Tire cord, magnetic tape, apparel, soft-drink bottles
Nylon 6,6	$-[NH-(CH_2)_6-NH-C(=O)-(CH_2)_4-C(=O)]_n-$	Home furnishings, apparel, carpet, fishing line, toothbrush bristles
Polycarbonate		Shatterproof eyeglass lenses, CDs, DVDs, bulletproof windows, greenhouses

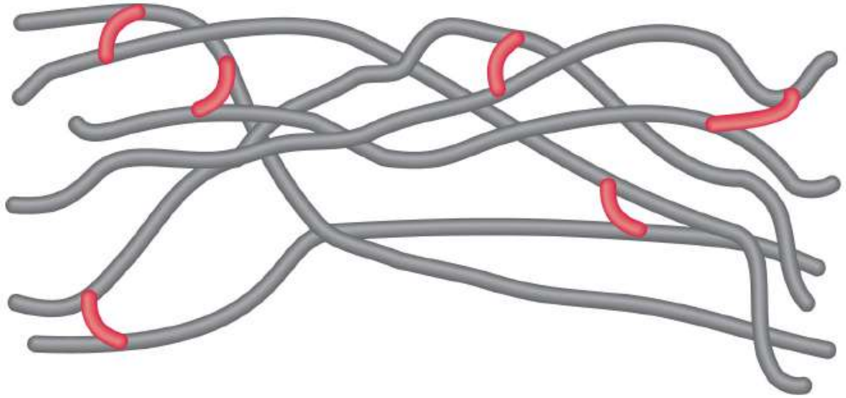
BULK PROPERTIES OF POLYMERS

- The molecules are *not* straight lines—the longer the chain, the more twisting happens.
- Chains can have a variety of lengths, and therefore a variety of molecular weights.
- The material can be very flexible (plastics).
- Short range order can lead to **crystallinity** in the solid.



CHANGING THE POLYMER'S PHYSICAL PROPERTIES

- Chemically bonding chains of polymers to each other can stiffen and strengthen the substance.
- In **vulcanization**, chains are cross-linked by short chains of sulfur atoms, making the rubber stronger.



(b)