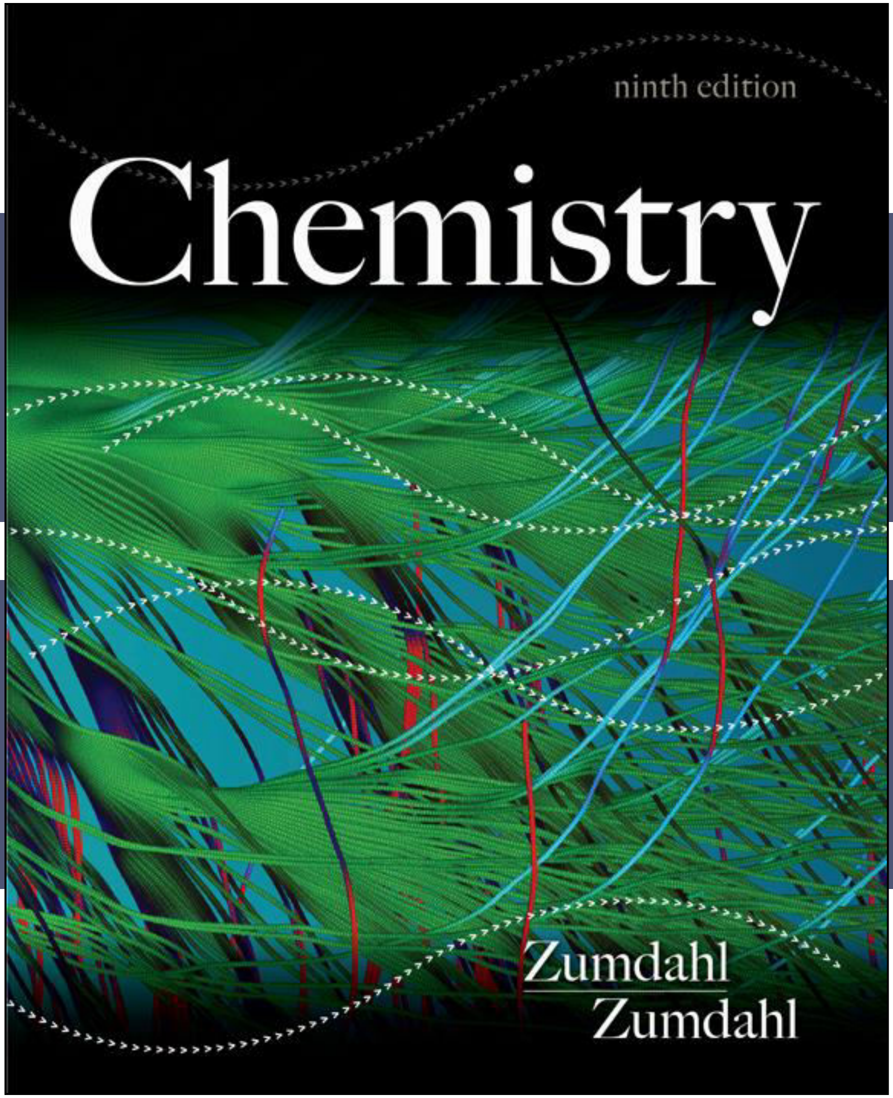


Chapter 10

Liquids and Solids

Intramolecular Bonding

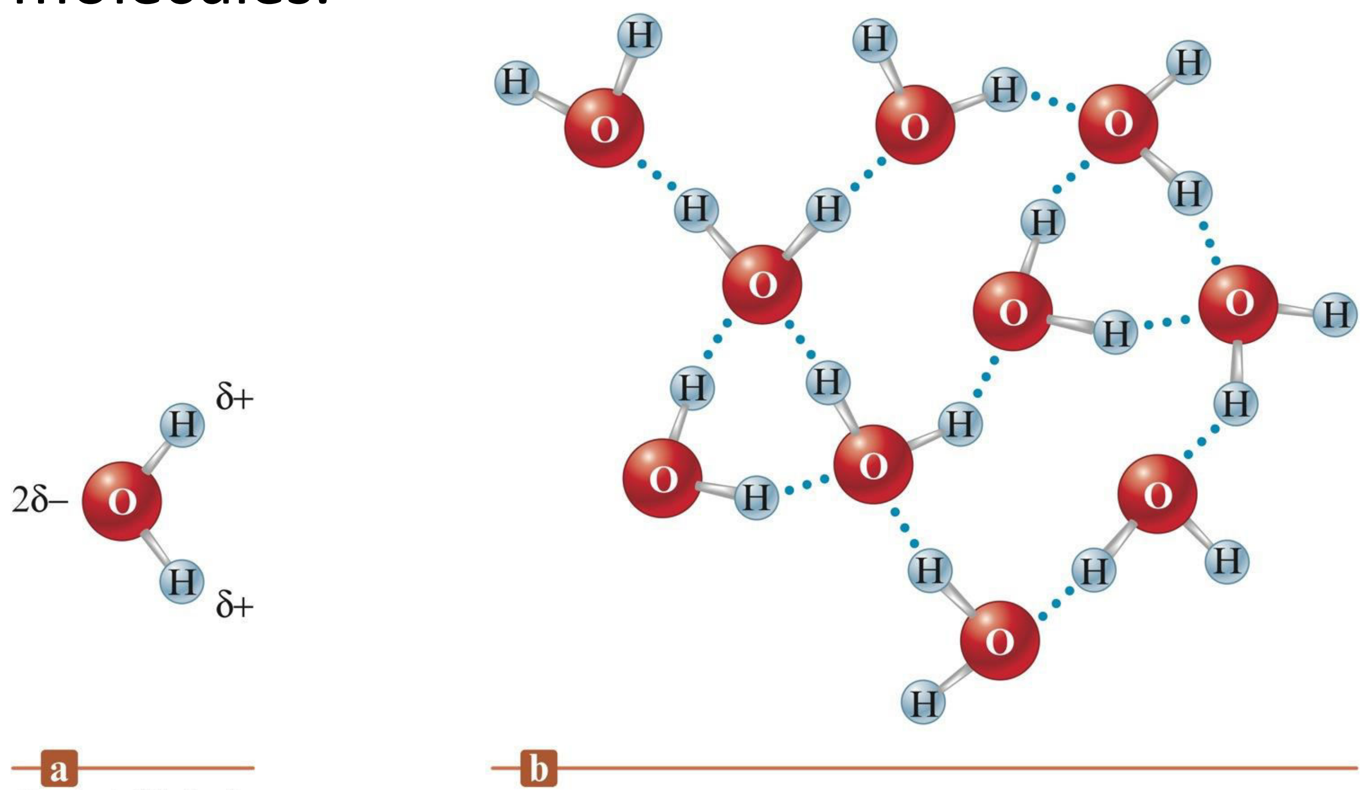
- "Within" the molecule.
- Molecules are formed by sharing electrons between the atoms.

Intermolecular Forces

- Forces that occur between molecules.
  - Dipole–dipole forces
    - Hydrogen bonding
  - London dispersion forces
- Intramolecular bonds are stronger than intermolecular forces.

Hydrogen Bonding in Water

- Blue dotted lines are the intermolecular forces between the water molecules.



CONCEPT CHECK!

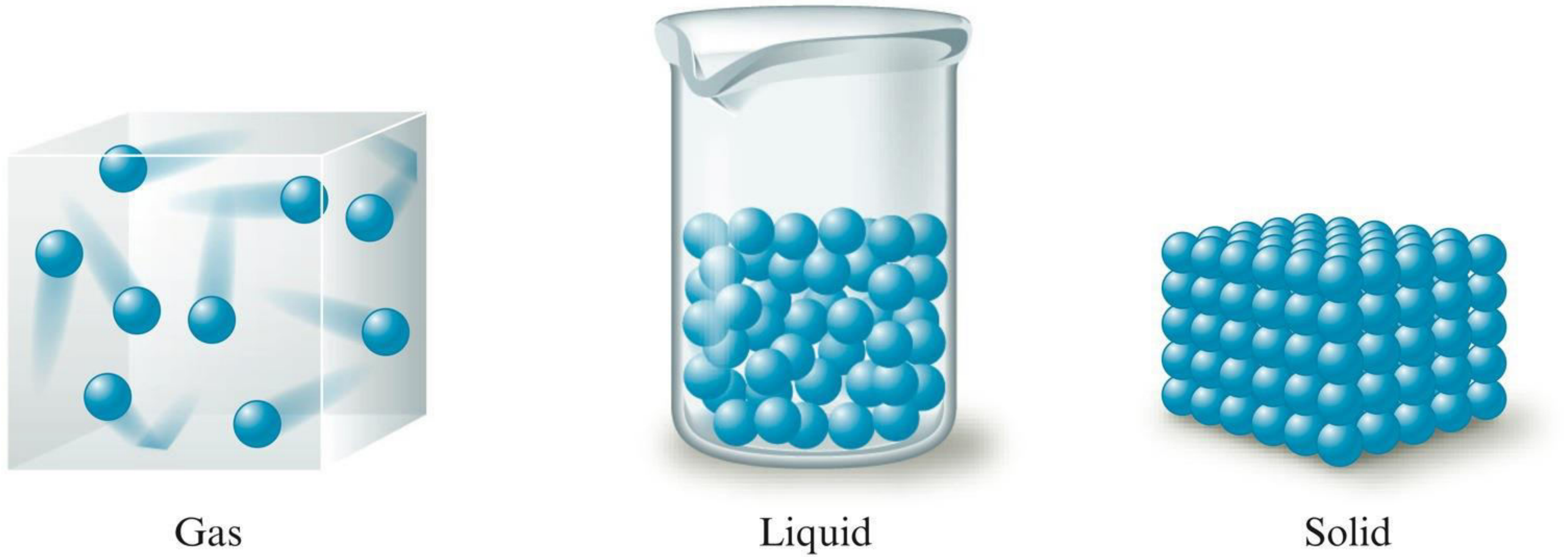
Which are stronger, intramolecular bonds or intermolecular forces?

How do you know?

Phase Changes

- When a substance changes from solid to liquid to gas, the molecules *remain intact*.
- The changes in state are due to changes in the forces *among* molecules rather than in those *within* the molecules.

Schematic Representations of the Three States of Matter



Phase Changes

- Solid to Liquid
  - As energy is added, the motions of the molecules increase, and they eventually achieve the greater movement and disorder characteristic of a liquid.
- Liquid to Gas
  - As more energy is added, the gaseous state is eventually reached, with the individual molecules far apart and interacting relatively little.

Densities of the Three States of Water

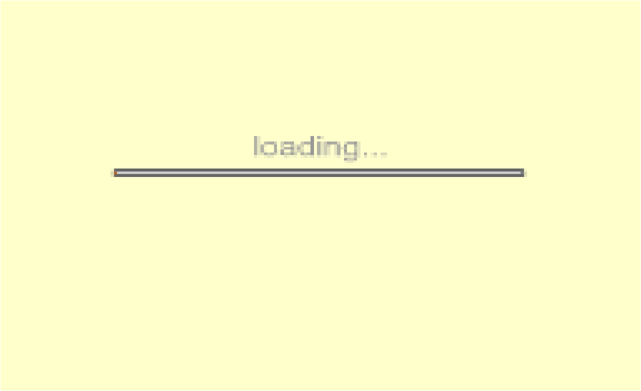
Table 10.1 | Densities of the Three States of Water

State	Density (g/cm^3)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

Dipole-Dipole Forces

- Dipole moment – molecules with polar bonds often behave in an electric field as if they had a center of positive charge and a center of negative charge.
- Molecules with dipole moments can attract each other electrostatically. They line up so that the positive and negative ends are close to each other.
- Only about 1% as strong as covalent or ionic bonds.

Dipole-Dipole Forces



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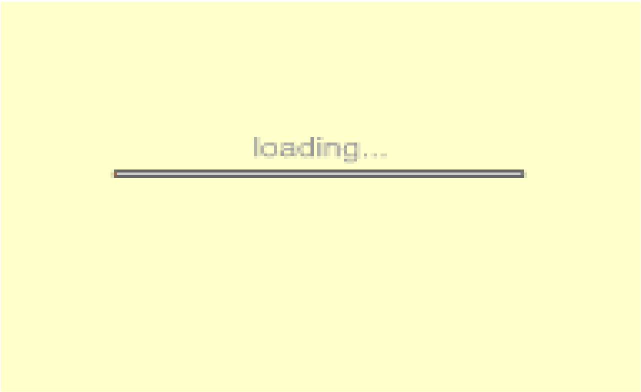
Hydrogen Bonding



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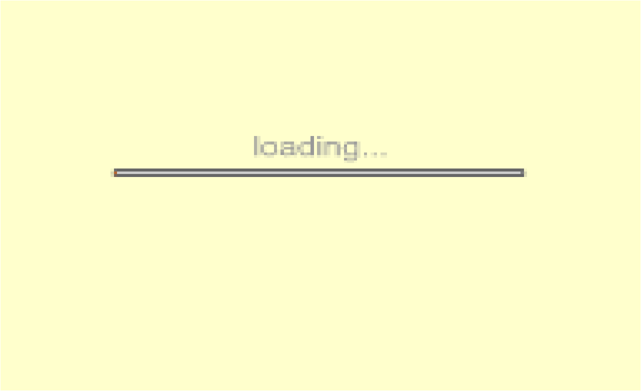
Hydrogen Bonding

- Strong dipole-dipole forces.
- Hydrogen is bound to a highly electronegative atom – nitrogen, oxygen, or fluorine.
- That same hydrogen is then electrostatically attracted to a lone pair on the nitrogen, oxygen or fluorine on adjacent molecules.

London Dispersion Forces



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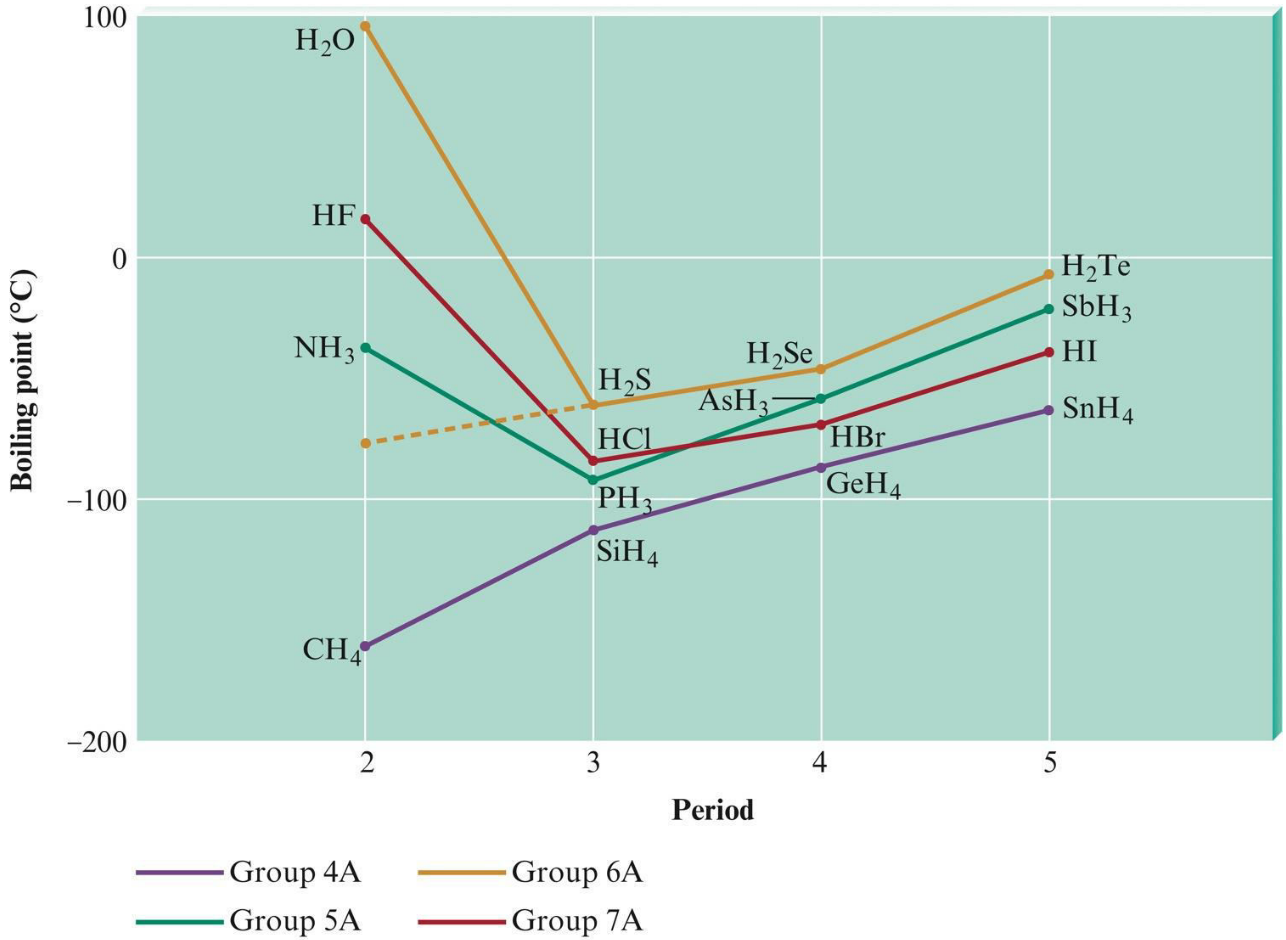
London Dispersion Forces

- Instantaneous dipole that occurs accidentally in a given atom induces a similar dipole in a neighboring atom.
- Significant in large atoms/molecules.
- Occurs in *all molecules*, including nonpolar ones.

Melting and Boiling Points

- In general, the stronger the intermolecular forces, the higher the melting and boiling points.

The Boiling Points of the Covalent Hydrides of the Elements in Groups 4A, 5A, 6A, and 7A



CONCEPT CHECK!

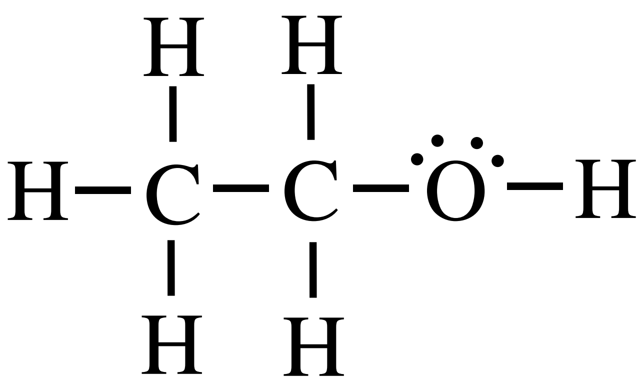
Which molecule is capable of forming stronger intermolecular forces?

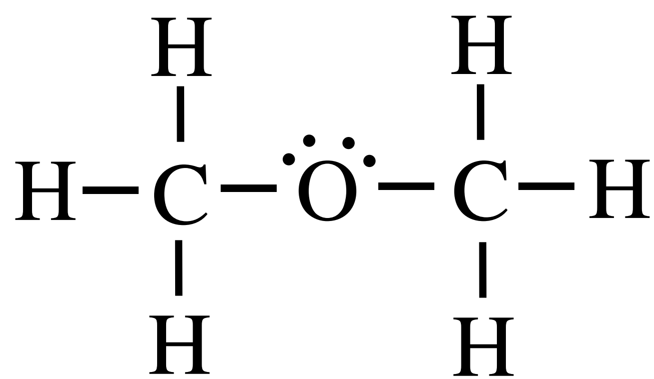
N_2 H_2O

Explain.

CONCEPT CHECK!

Draw two Lewis structures for the formula C_2H_6O and compare the boiling points of the two molecules.





CONCEPT CHECK!

Which gas would behave more ideally at the same conditions of P and T?

CO or N_2

Why?

Liquids

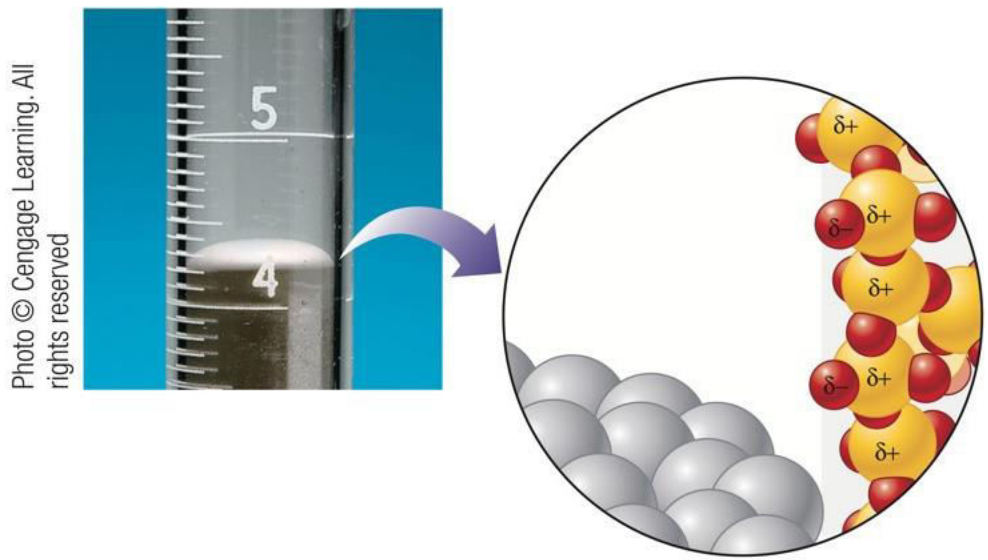
- Low compressibility, lack of rigidity, and high density compared with gases.
- Surface tension – resistance of a liquid to an increase in its surface area:
  - Liquids with large intermolecular forces tend to have high surface tensions.

Liquids

- Capillary action – spontaneous rising of a liquid in a narrow tube:
  - Cohesive forces – intermolecular forces among the molecules of the liquid.
  - Adhesive forces – forces between the liquid molecules and their container.

Convex Meniscus Formed by Nonpolar Liquid Mercury

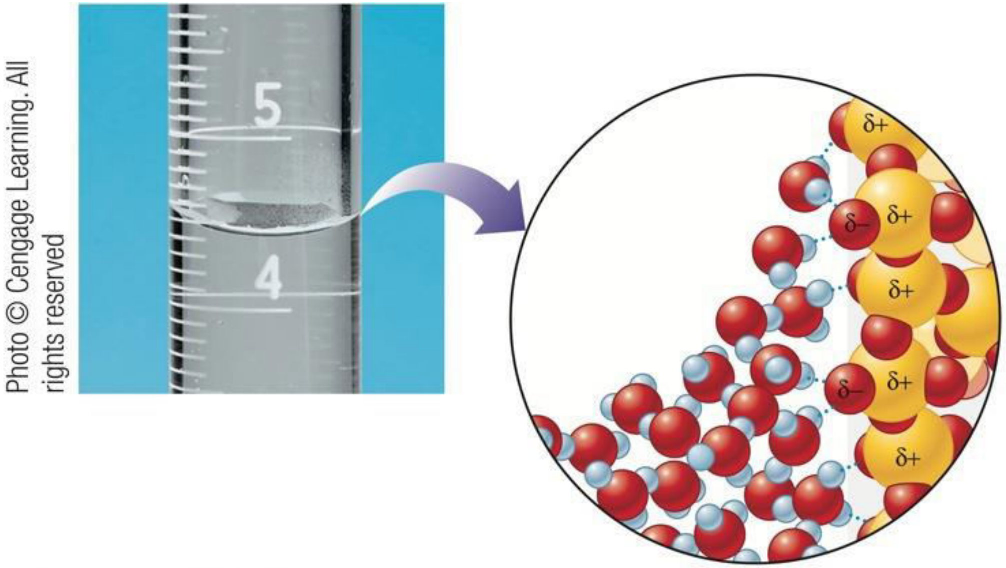
- Which force dominates alongside the glass tube – cohesive or adhesive forces?



cohesive forces

Concave Meniscus Formed by Polar Water

- Which force dominates alongside the glass tube – cohesive or adhesive forces?



adhesive forces

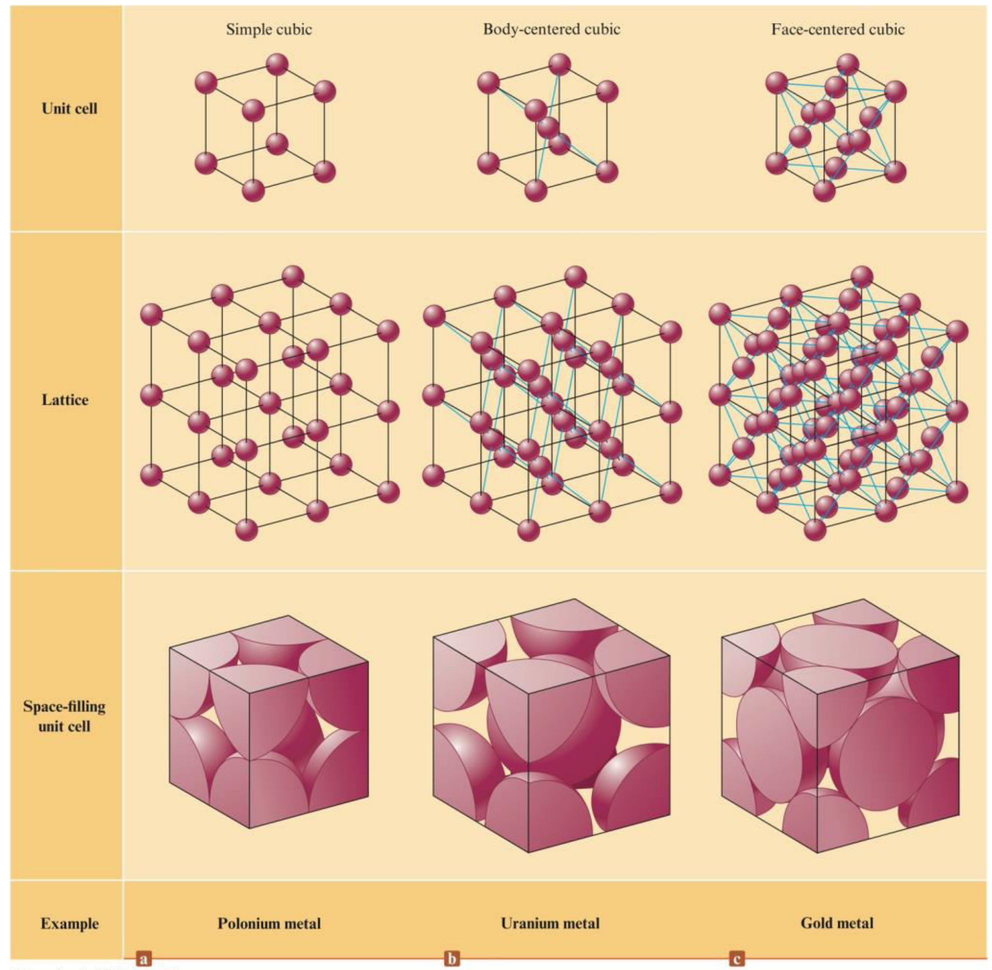
Liquids

- Viscosity – measure of a liquid's resistance to flow:
  - Liquids with large intermolecular forces or molecular complexity tend to be highly viscous.

Solids

- Amorphous Solids:
  - Disorder in the structures
  - Glass
- Crystalline Solids:
  - Ordered Structures
  - Unit Cells

Three Cubic Unit Cells and the Corresponding Lattices



Bragg Equation

- Used to determine the interatomic spacings.

$$n\lambda = 2d \sin \theta$$

n = integer

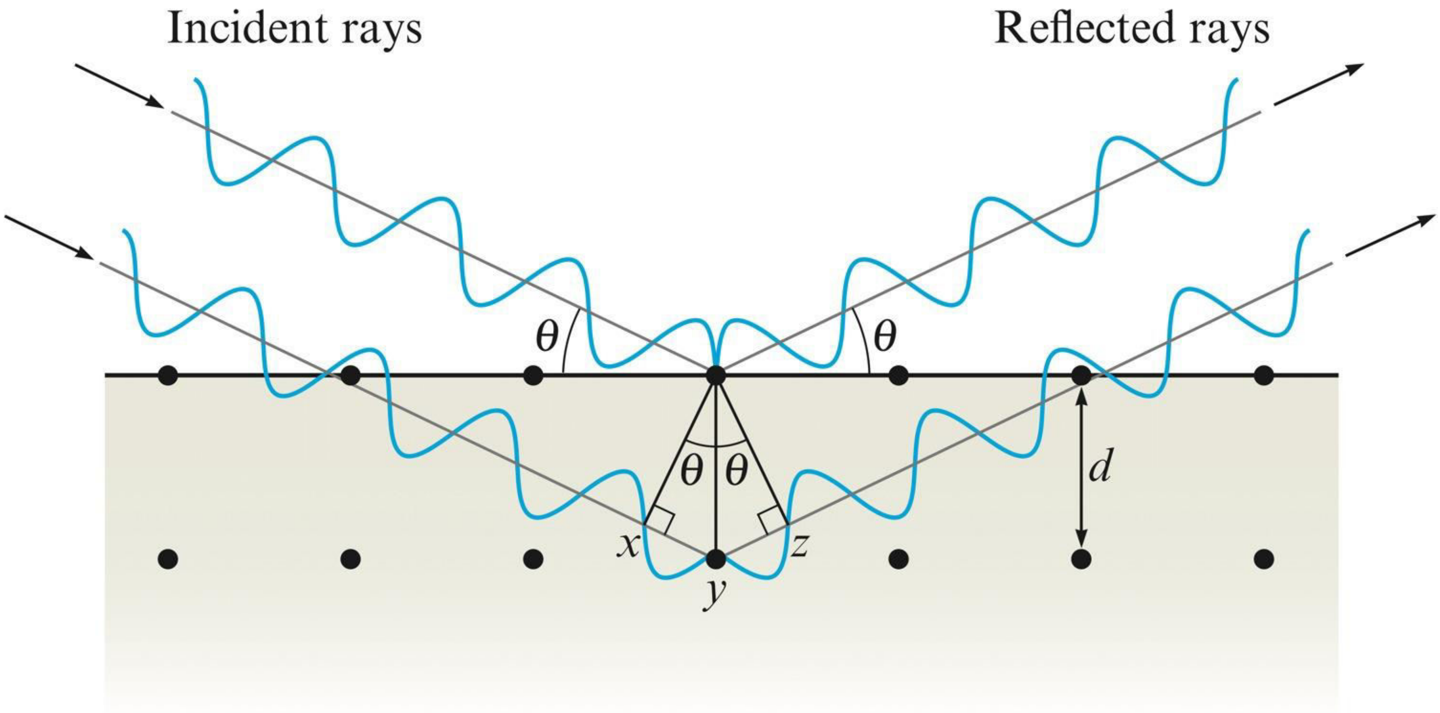
λ = wavelength of the X rays

d = distance between the atoms

θ = angle of incidence and reflection

Bragg Equation

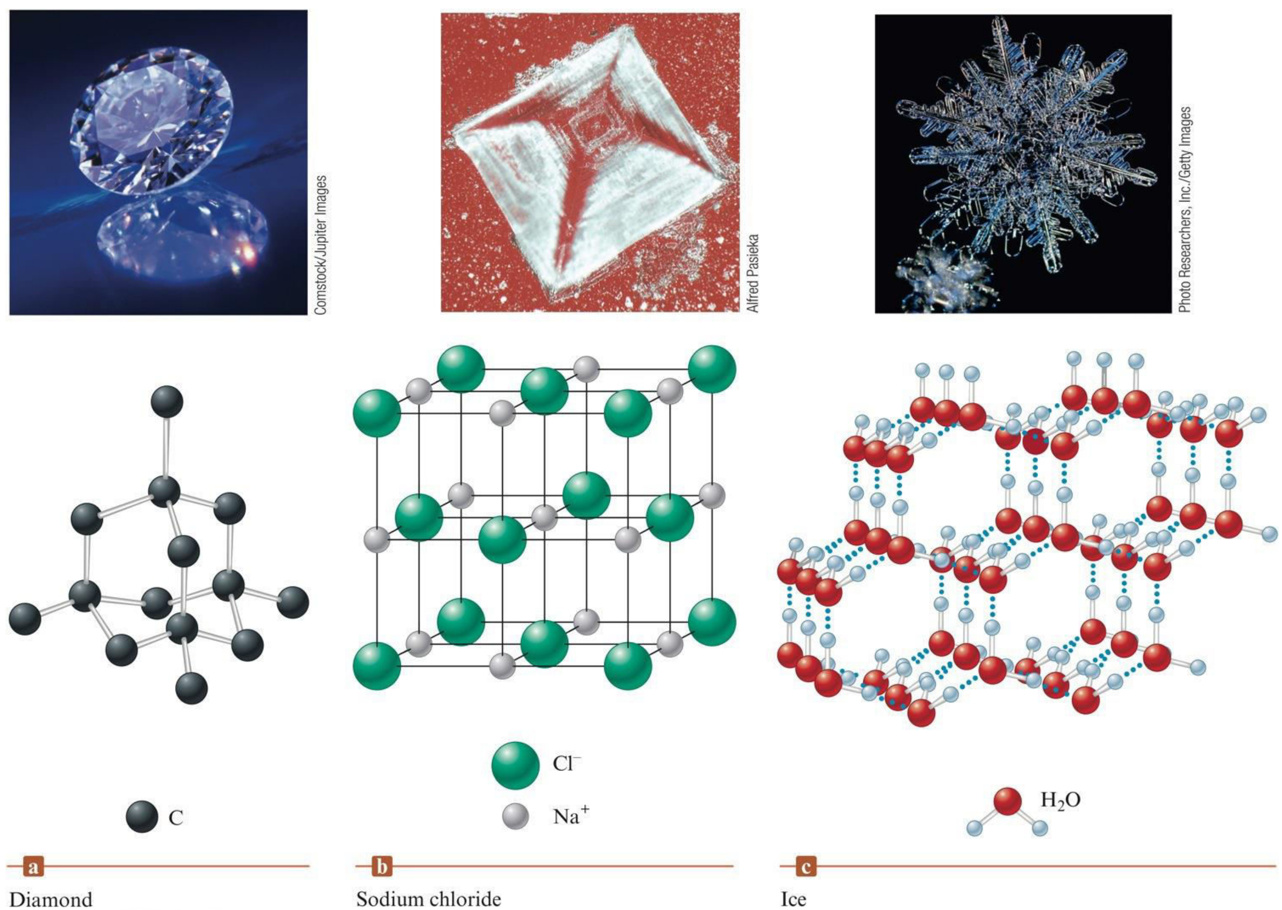
$$n\lambda = 2d \sin \theta$$



Types of Crystalline Solids

- *Ionic Solids* – ions at the points of the lattice that describes the structure of the solid.
- *Molecular Solids* – discrete covalently bonded molecules at each of its lattice points.
- *Atomic Solids* – atoms at the lattice points that describe the structure of the solid.

Examples of Three Types of Crystalline Solids



Classification of Solids

Table 10.3 | Classification of Solids

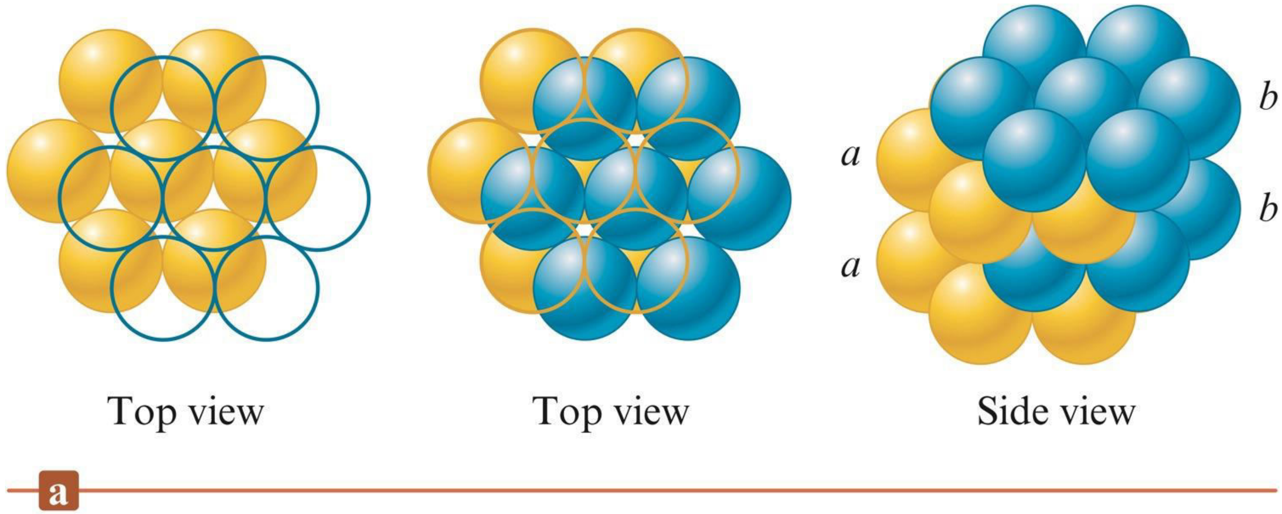
	Atomic Solids				
	Metallic	**Network**	**Group 8A**	**Molecular Solids**	**Ionic Solids**
Components That Occupy the Lattice Points	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

Closest Packing Model

- Closest Packing:
  - Assumes that metal atoms are uniform, hard spheres.
  - Spheres are packed in layers.

The Closest Packing Arrangement of Uniform Spheres

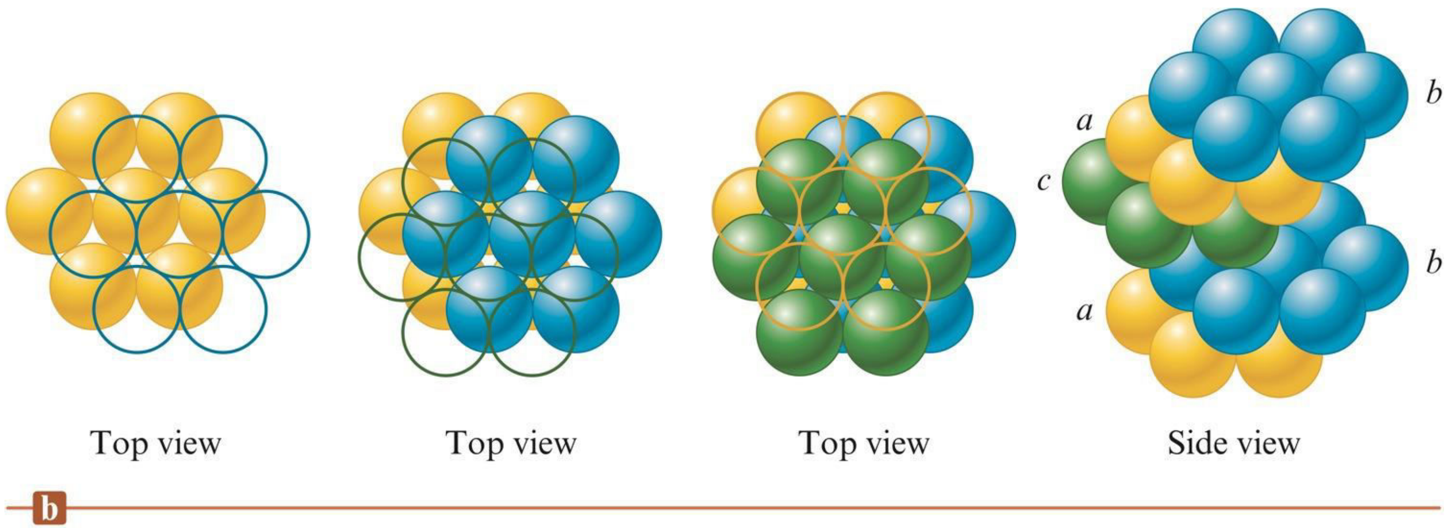
- *abab* packing – the 2nd layer is like the 1st but it is displaced so that each sphere in the 2nd layer occupies a dimple in the 1st layer.
- The spheres in the 3rd layer occupy dimples in the 2nd layer so that the spheres in the 3rd layer lie directly over those in the 1st layer.



abab — Closest packing

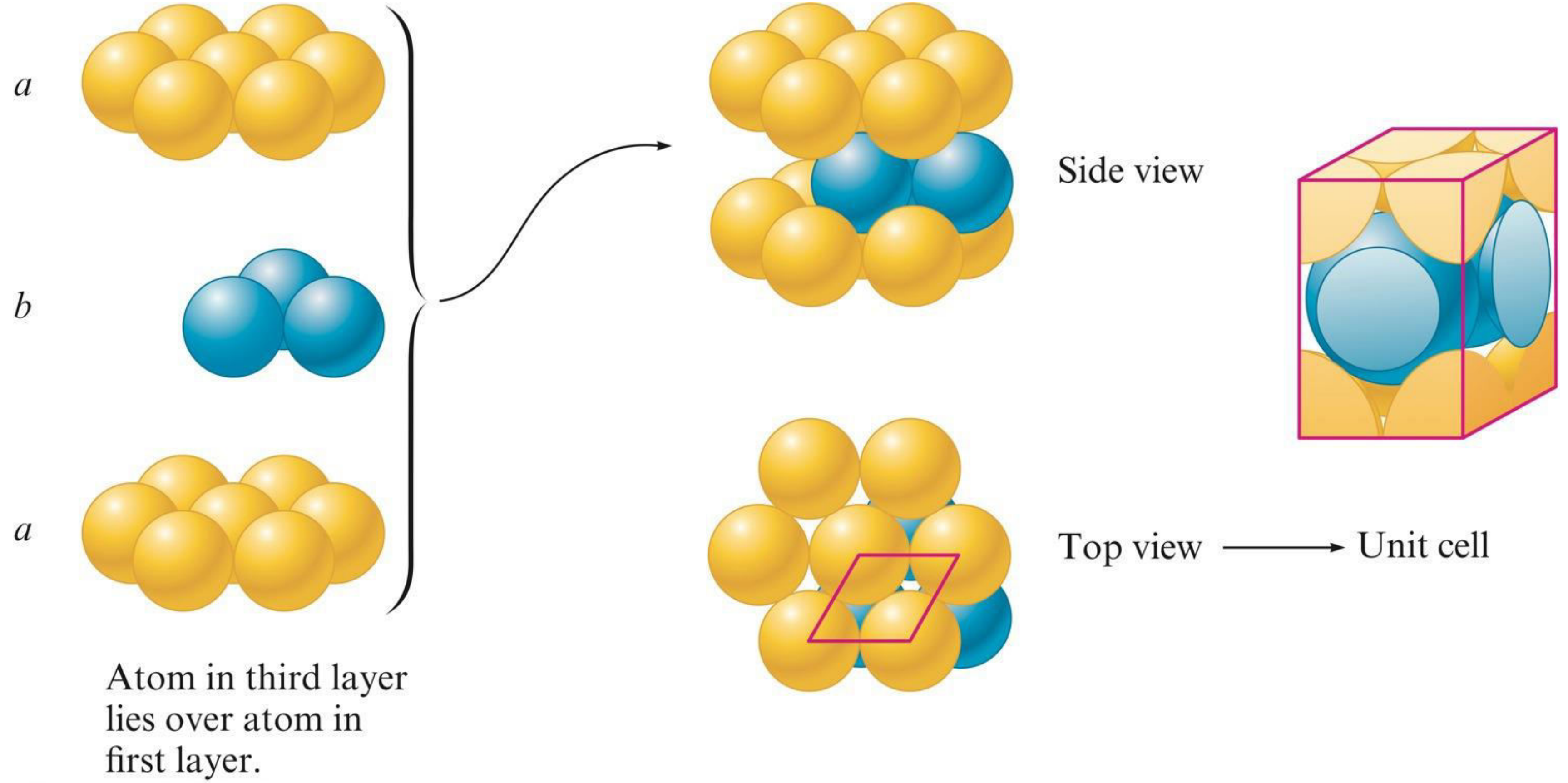
The Closest Packing Arrangement of Uniform Spheres

- *abca* packing – the spheres in the 3rd layer occupy dimples in the 2nd layer so that no spheres in the 3rd layer lie above any in the 1st layer.
- The 4th layer is like the 1st.

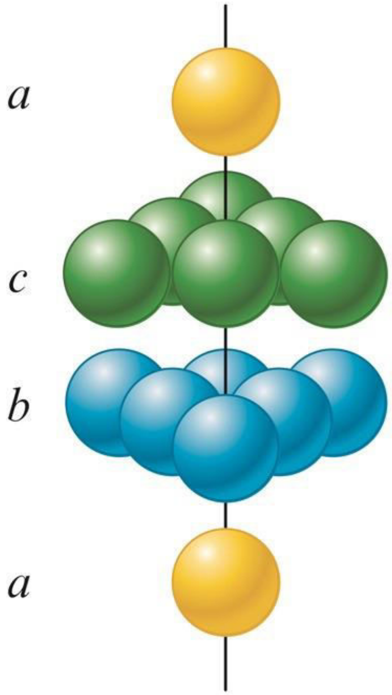


abca — Closest packing

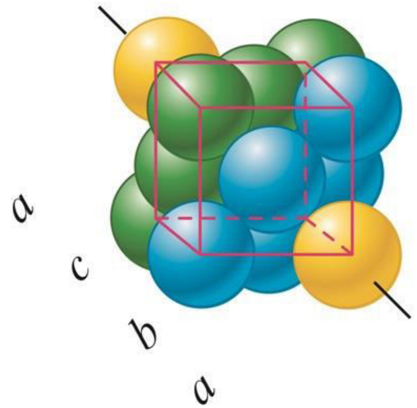
Hexagonal Closest Packing

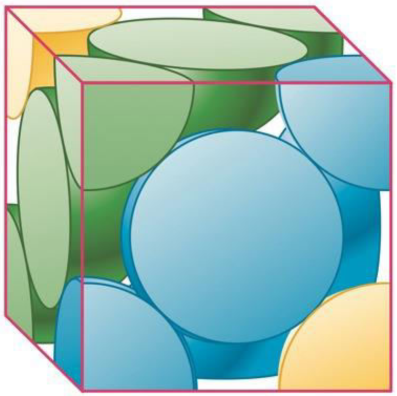


Cubic Closest Packing



An atom in every fourth layer lies over an atom in the first layer.

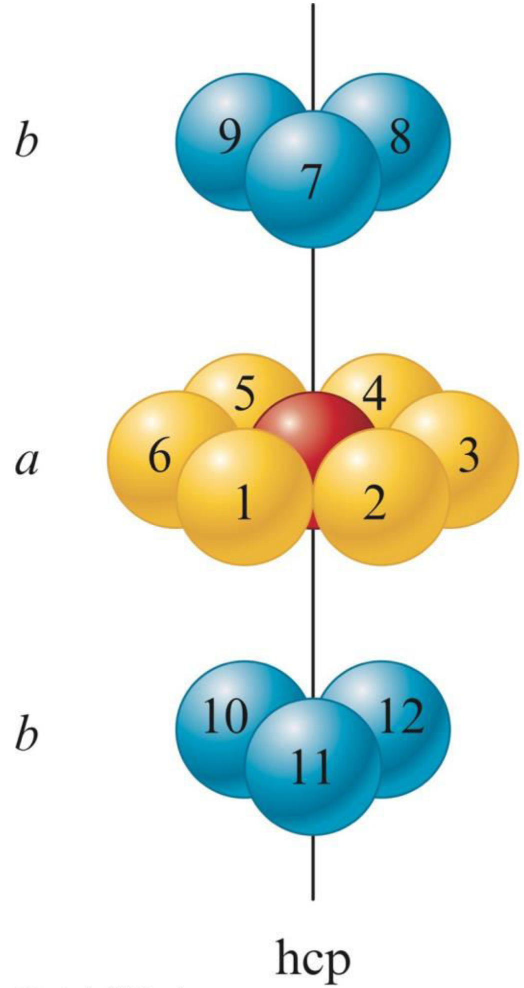




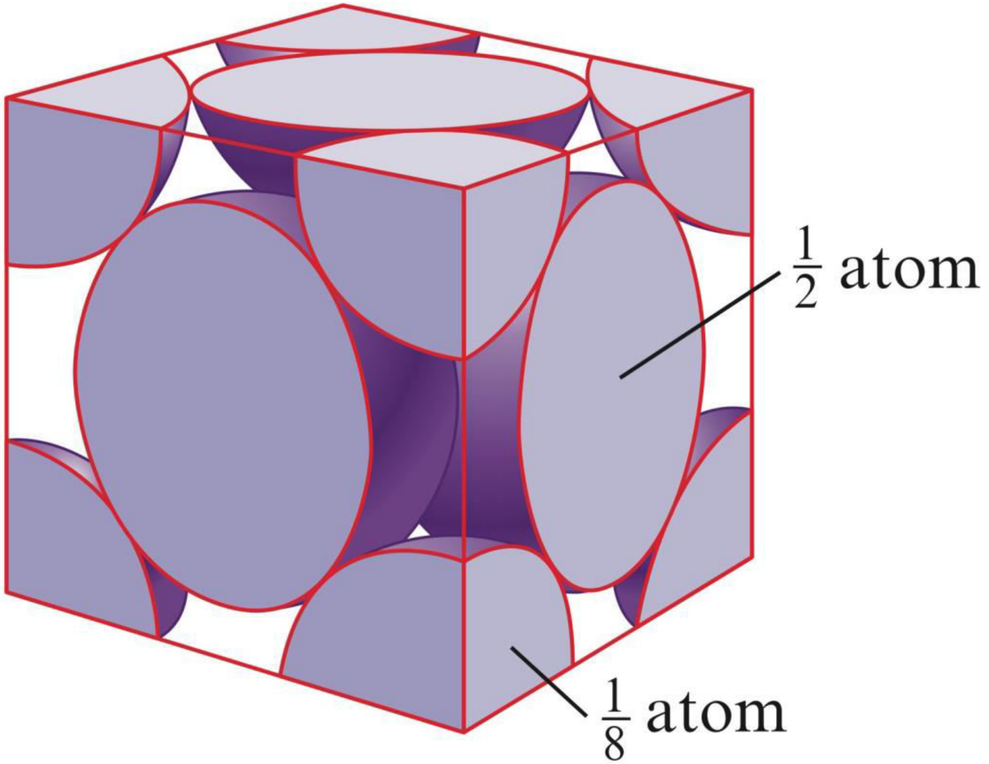
Unit cell

The Indicated Sphere Has 12 Nearest Neighbors

- Each sphere in both ccp and hcp has 12 equivalent nearest neighbors.



The Net Number of Spheres in a Face-Centered Cubic Unit Cell



CONCEPT CHECK!

Determine the number of metal atoms in a unit cell if the packing is:

a) Simple cubic
b) Cubic closest packing

a) 1 metal atom
b) 4 metal atoms

CONCEPT CHECK!

A metal crystallizes in a face-centered cubic structure.

Determine the relationship between the radius of the metal atom and the length of an edge of the unit cell.

$$\text{Length of edge} = r \times \sqrt{8}$$

CONCEPT CHECK!

Silver metal crystallizes in a cubic closest packed structure. The face centered cubic unit cell edge is 409 pm.

Calculate the density of the silver metal.

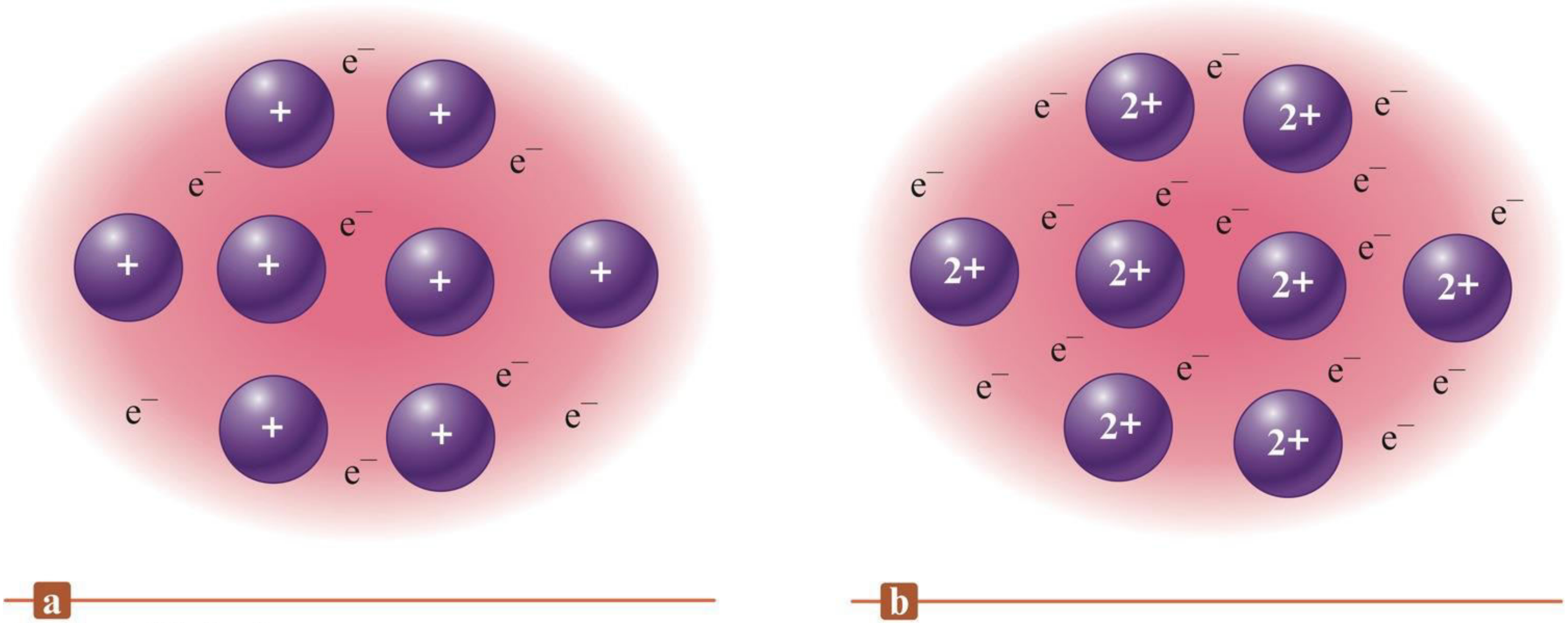
Density = 10.5 g/cm^3

Bonding Models for Metals

- Electron Sea Model
- Band Model (MO Model)

The Electron Sea Model

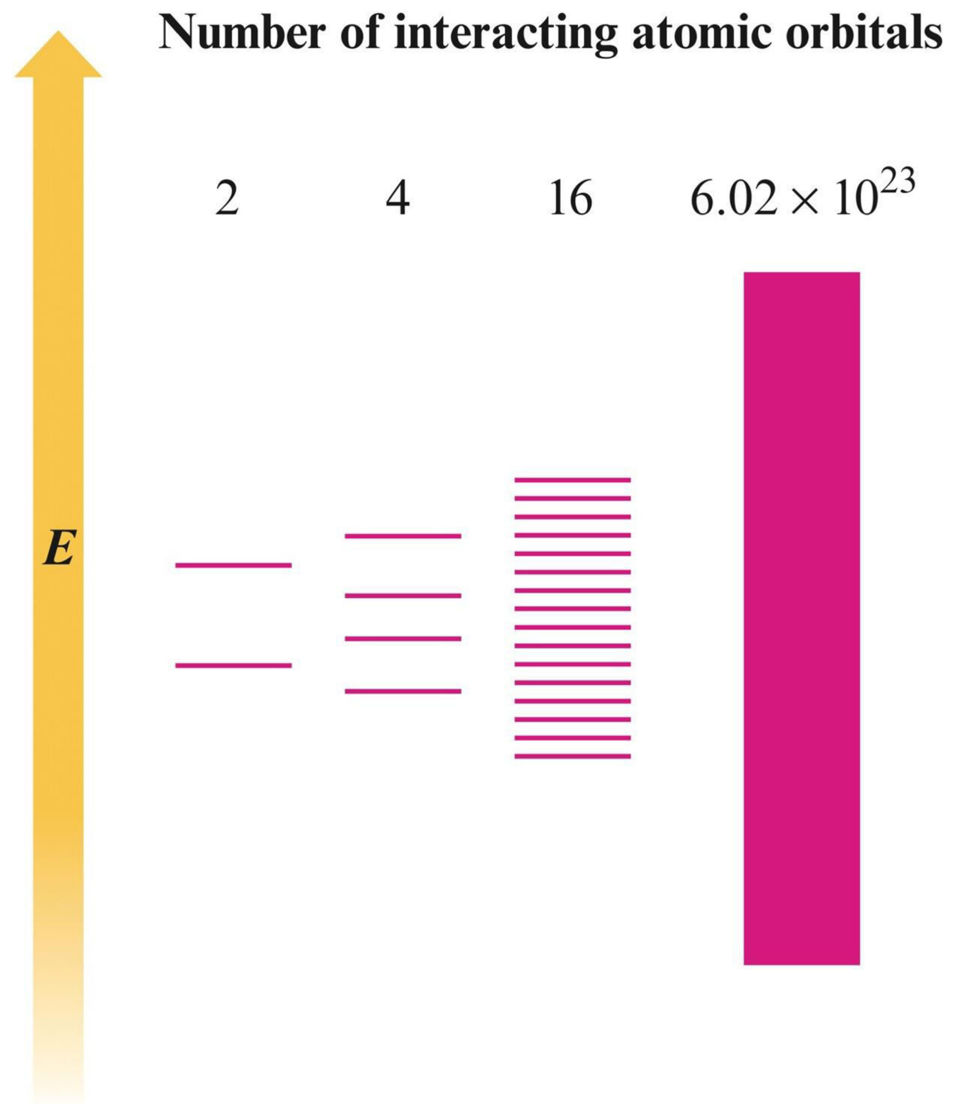
- A regular array of cations in a “sea” of mobile valence electrons.



Band or Molecular Orbital (MO) Model

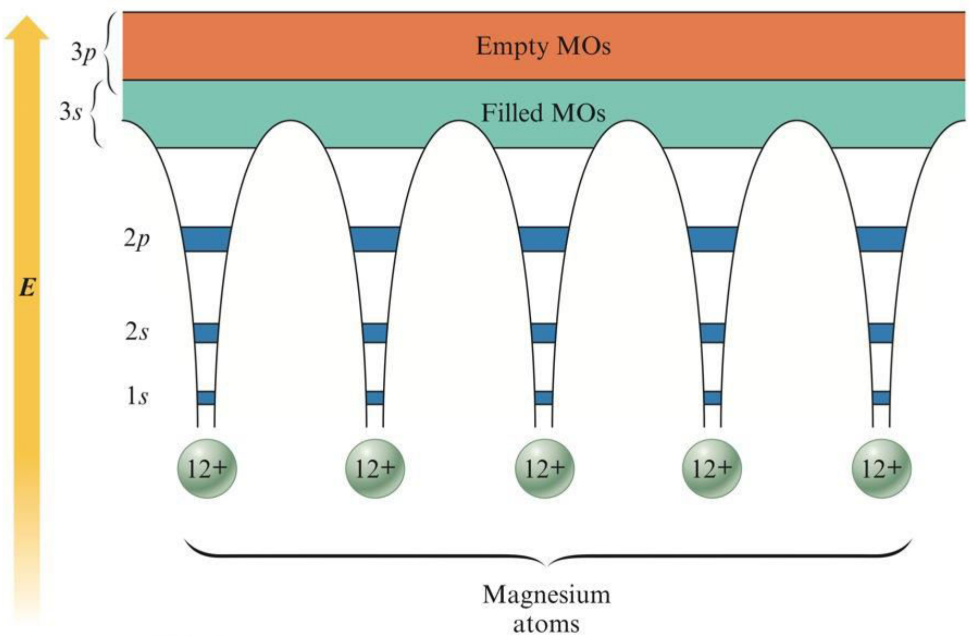
- Electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms.

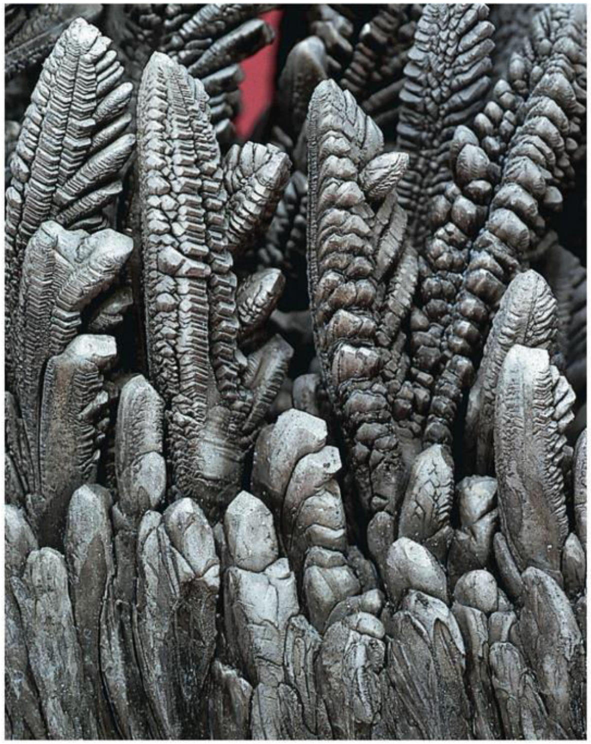
Molecular Orbital Energy Levels Produced When Various Numbers of Atomic Orbitals Interact



The Band Model for Magnesium

- Virtual continuum of levels, called bands.





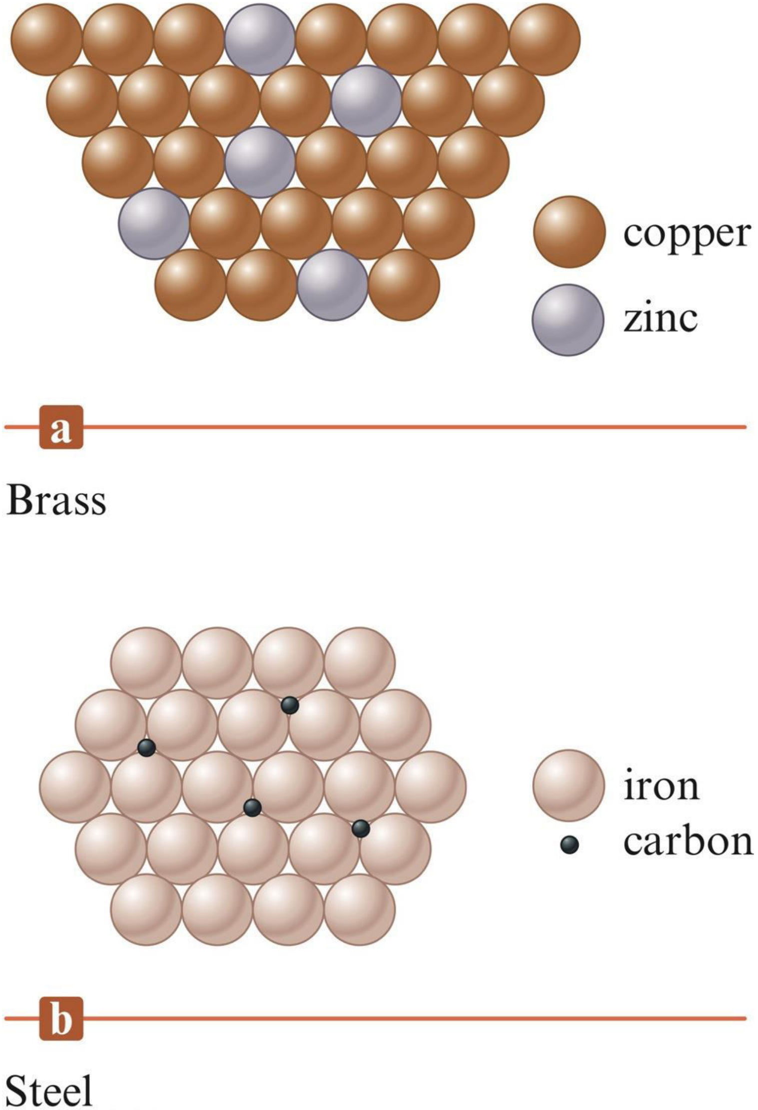
Chip Clark/Fundamental Photographs

Metal Alloys

- Substitutional Alloy – some of the host metal atoms are *replaced* by other metal atoms of similar size.
- Interstitial Alloy – some of the holes in the closest packed metal structure are occupied by small atoms.

Two Types of Alloys

- Brass is a substitutional alloy.
- Steel is an interstitial alloy.



Network Solids

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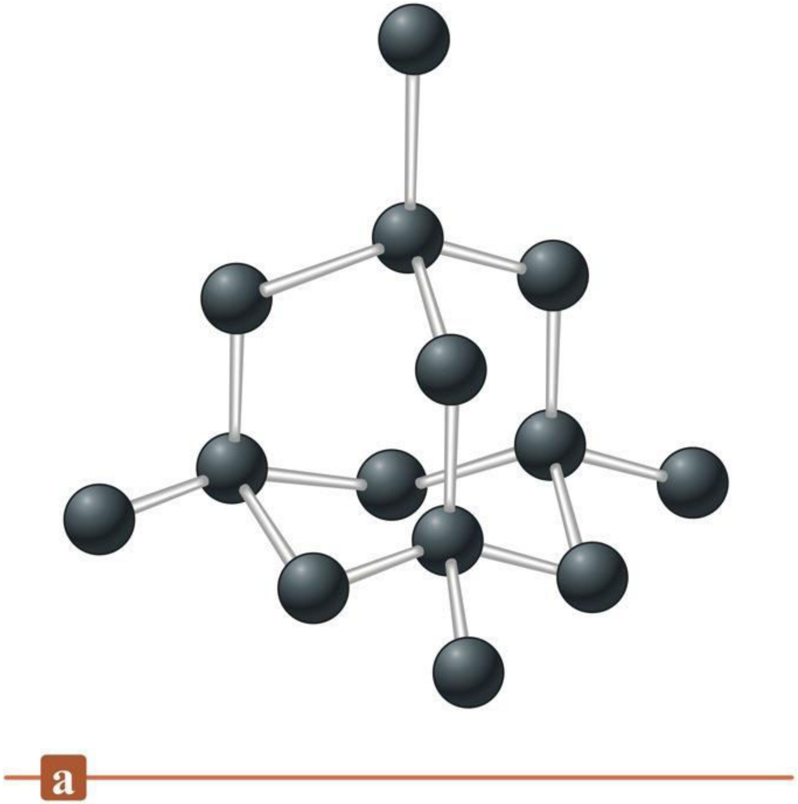
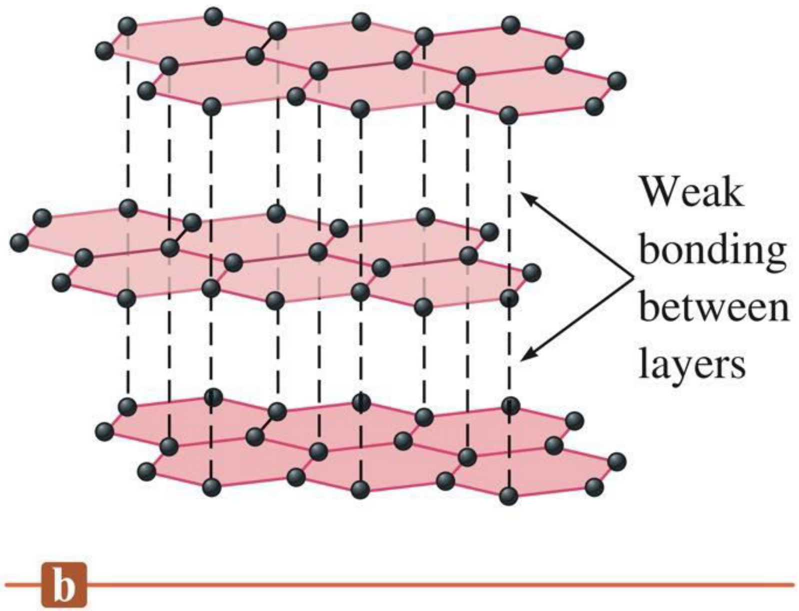
The Structures of Diamond and Graphite



Diamond

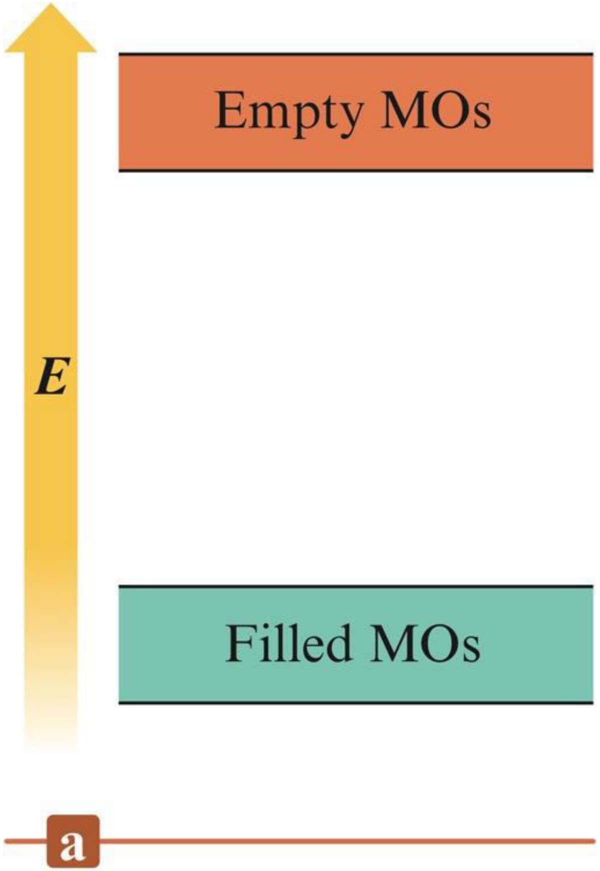


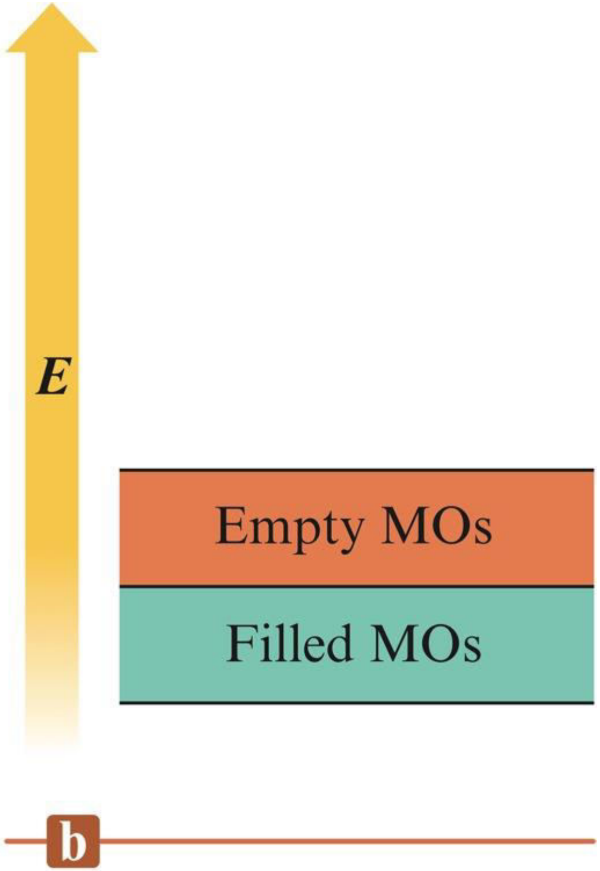
Graphite

Partial Representation of the Molecular Orbital Energies in

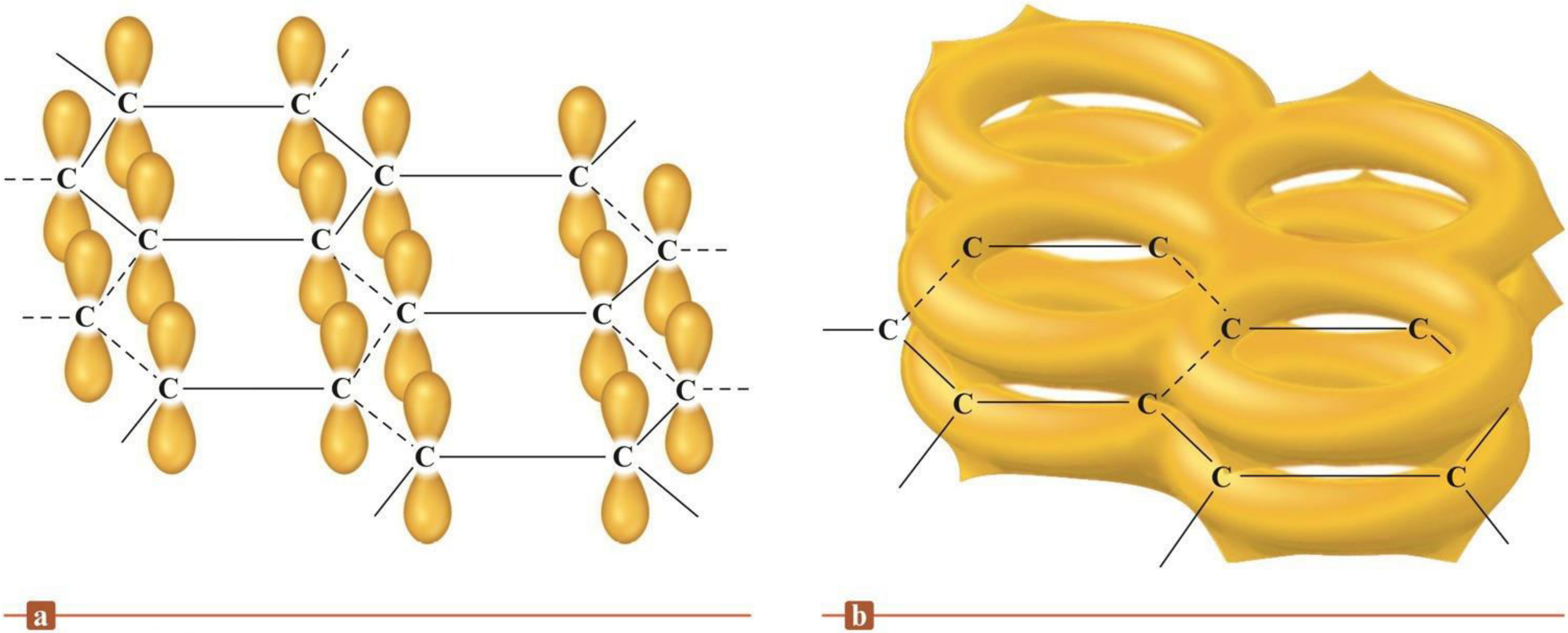
a) Diamond

b) a Typical Metal





The *p* Orbitals and Pi-system in Graphite



Ceramics

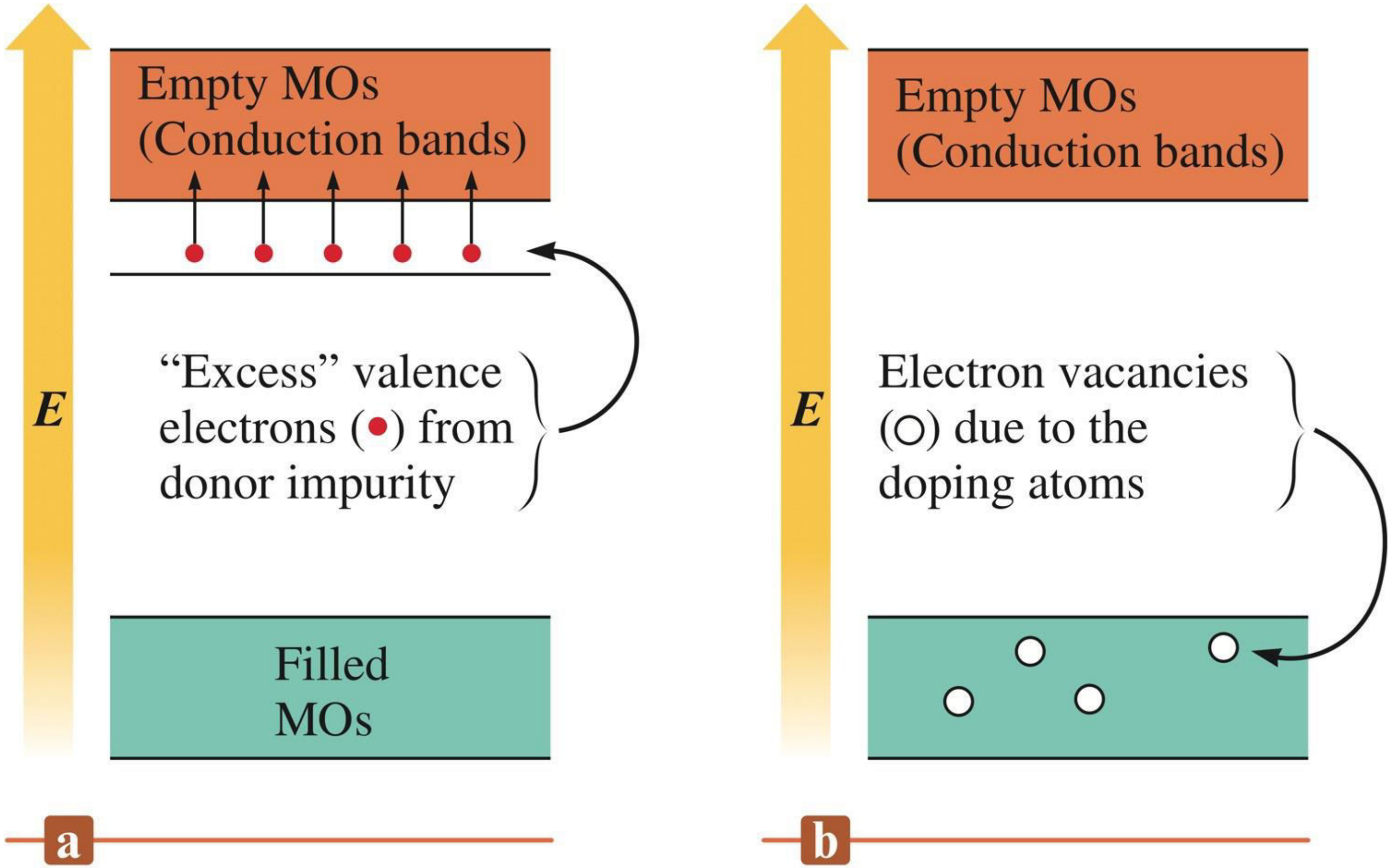
- Typically made from clays (which contain silicates) and hardened by firing at high temperatures.
- Nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals.

Semiconductors

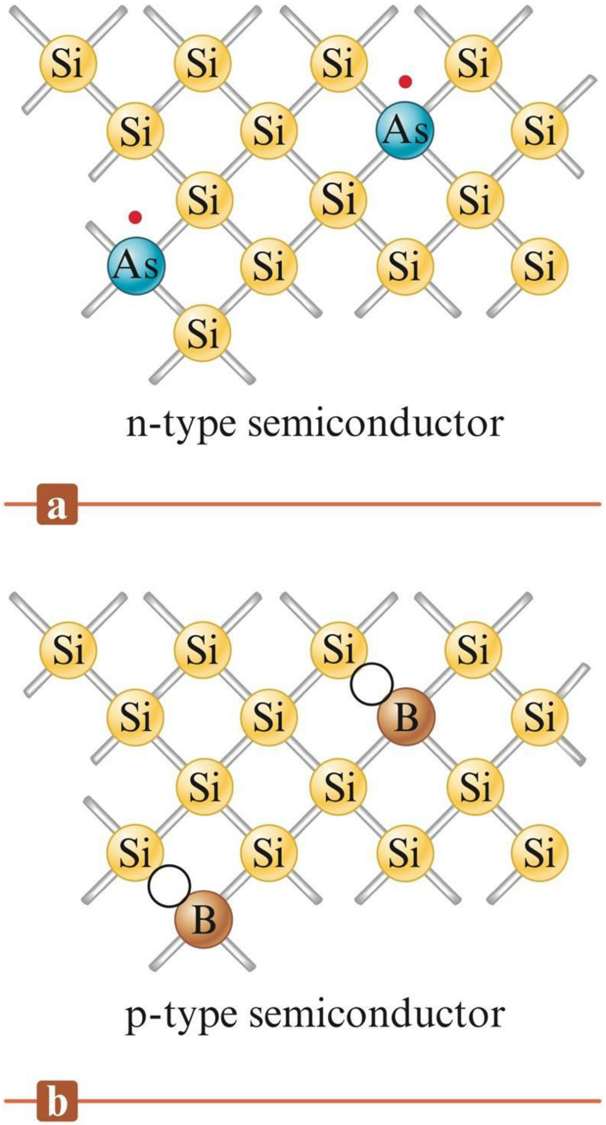
- n-type semiconductor – substance whose conductivity is increased by doping it with atoms having more valence electrons than the atoms in the host crystal.
- p-type semiconductor – substance whose conductivity is increased by doping it with atoms having fewer valence electrons than the atoms of the host crystal.

Energy Level Diagrams for

(a) an *n*-type Semiconductor (b) a *p*-type Semiconductor



Silicon Crystal Doped with
(a) Arsenic and
(b) Boron



Section 10.6
Molecular Solids

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Section 10.7
Ionic Solids

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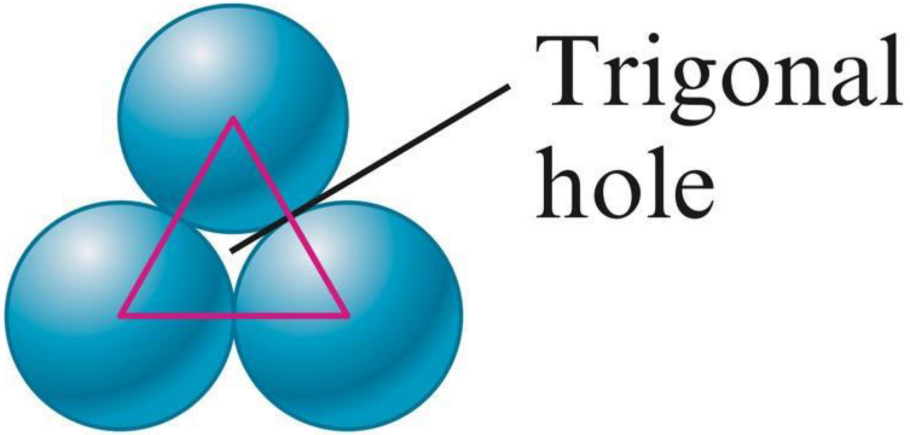
Ionic Solids

- Ionic solids are stable, high melting substances held together by the strong electrostatic forces that exist between oppositely charged ions.

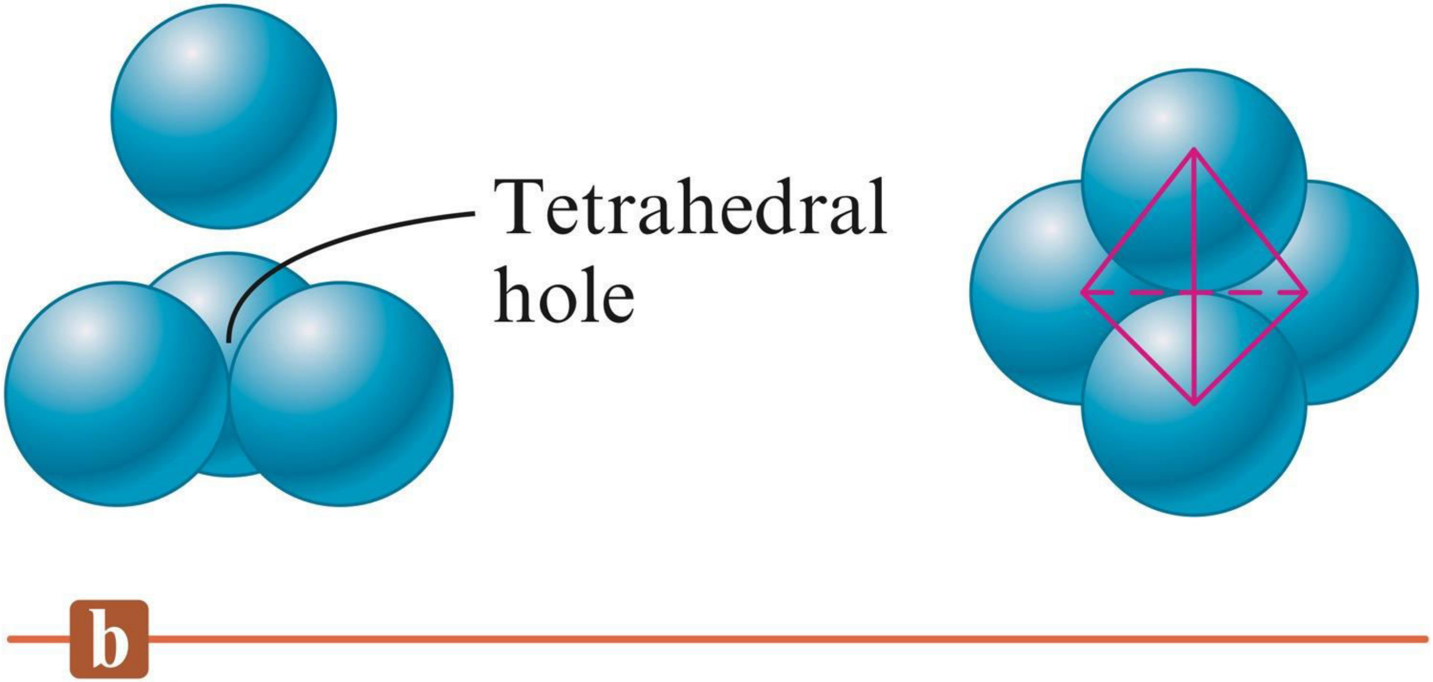
Three Types of Holes in Closest Packed Structures

1) Trigonal holes are formed by three spheres in the same layer.



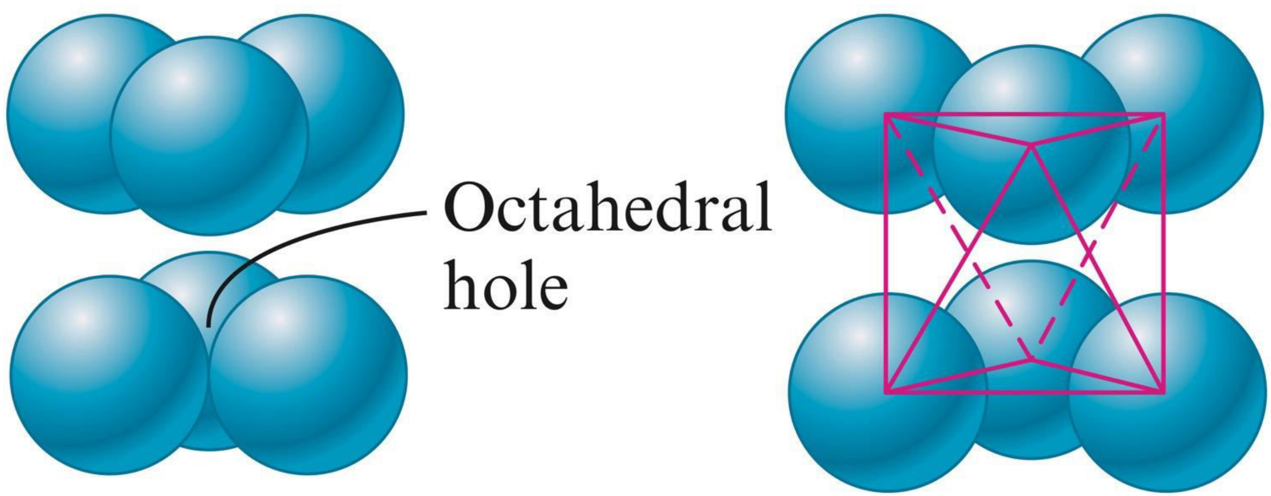
Three Types of Holes in Closest Packed Structures

2) Tetrahedral holes are formed when a sphere sits in the dimple of three spheres in an adjacent layer.



Three Types of Holes in Closest Packed Structures

3) Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures.



- For spheres of a given diameter, the holes increase in size in the order:

trigonal < tetrahedral < octahedral

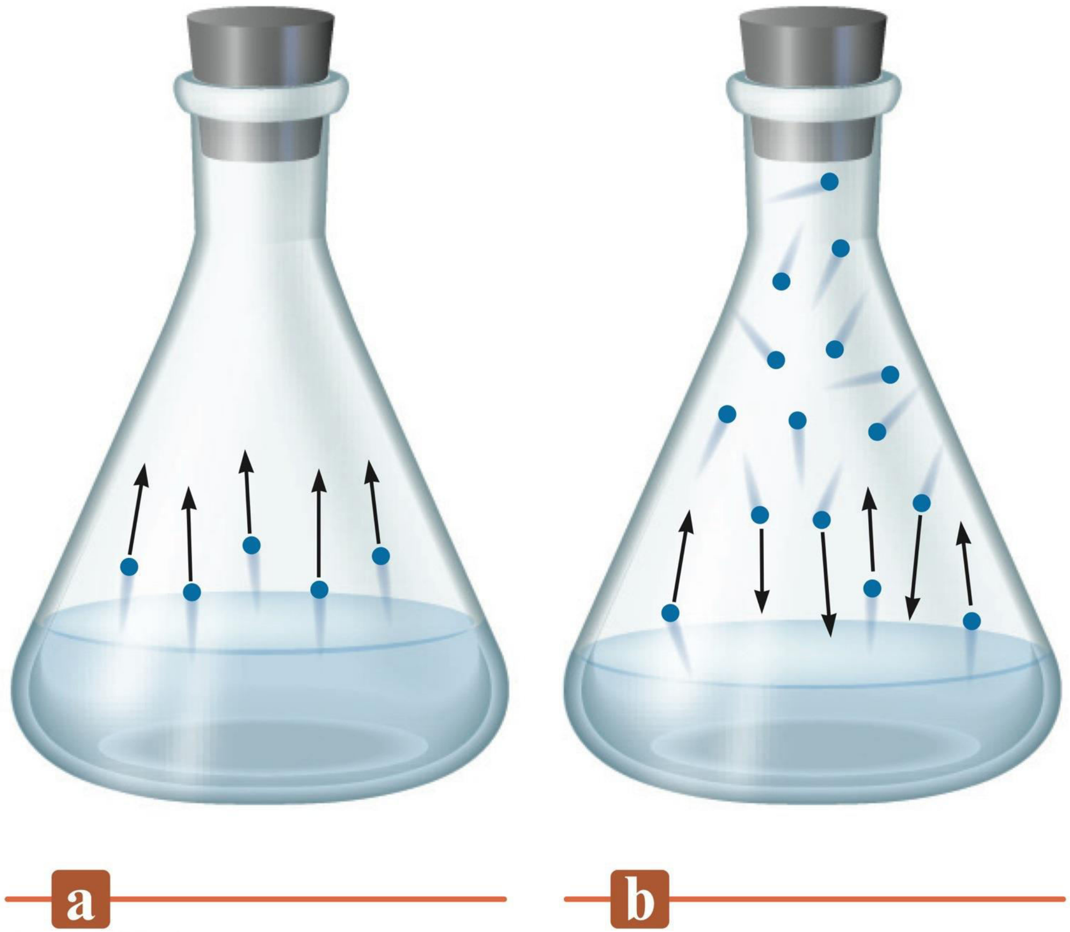
Types and Properties of Solids

Table 10.7 | Types and Properties of Solids

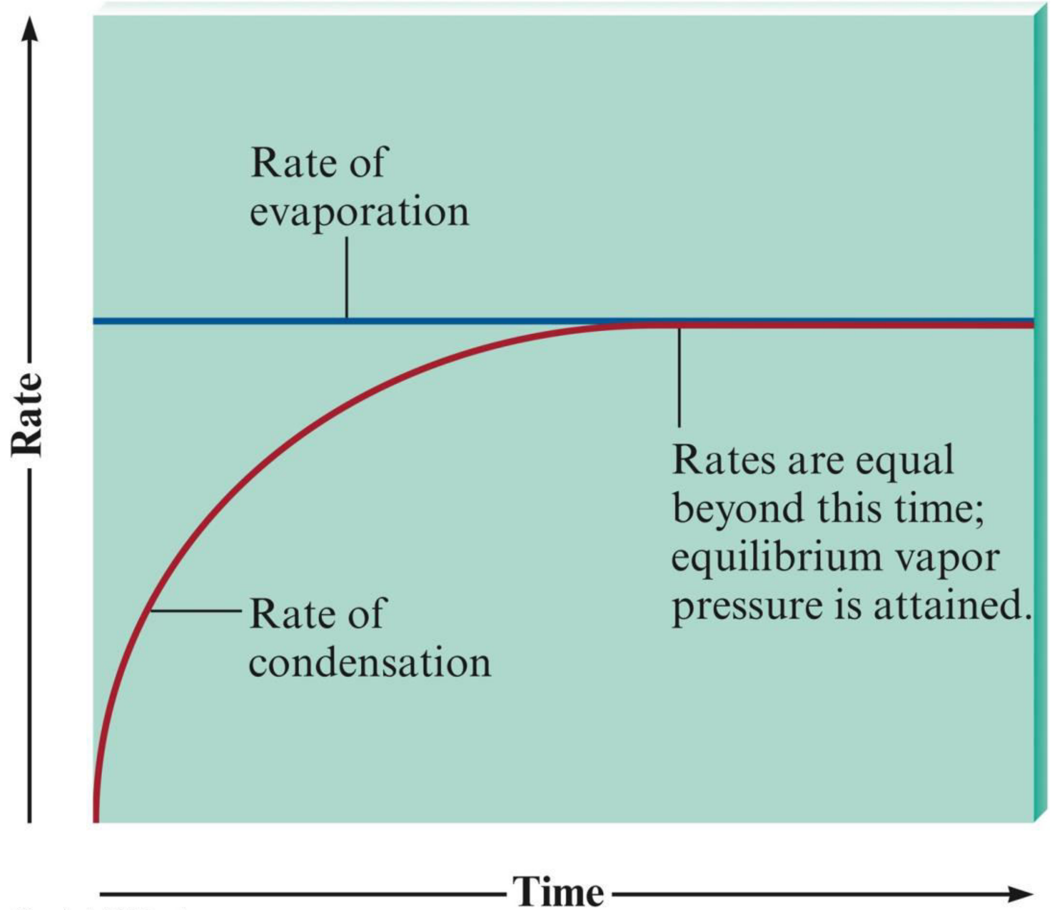
Type of Solid	Atomic			Molecular	Ionic
	Network	**Metallic**	**Group 8A**		
Structural Unit	Atom	Atom	Atom	Molecule	Ion
Type of Bonding	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties	Hard	Wide range of hardness		Soft	Hard
	High melting point	Wide range of melting points	Very low melting point	Low melting point	High melting point
	Insulator	Conductor		Insulator	Insulator
Examples	Diamond	Silver Iron Brass	Argon(*s*)	Ice (solid H_2O) Dry ice (solid CO_2)	Sodium chloride Calcium fluoride

Behavior of a Liquid in a Closed Container

a) Initially b) at Equilibrium



The Rates of Condensation and Evaporation



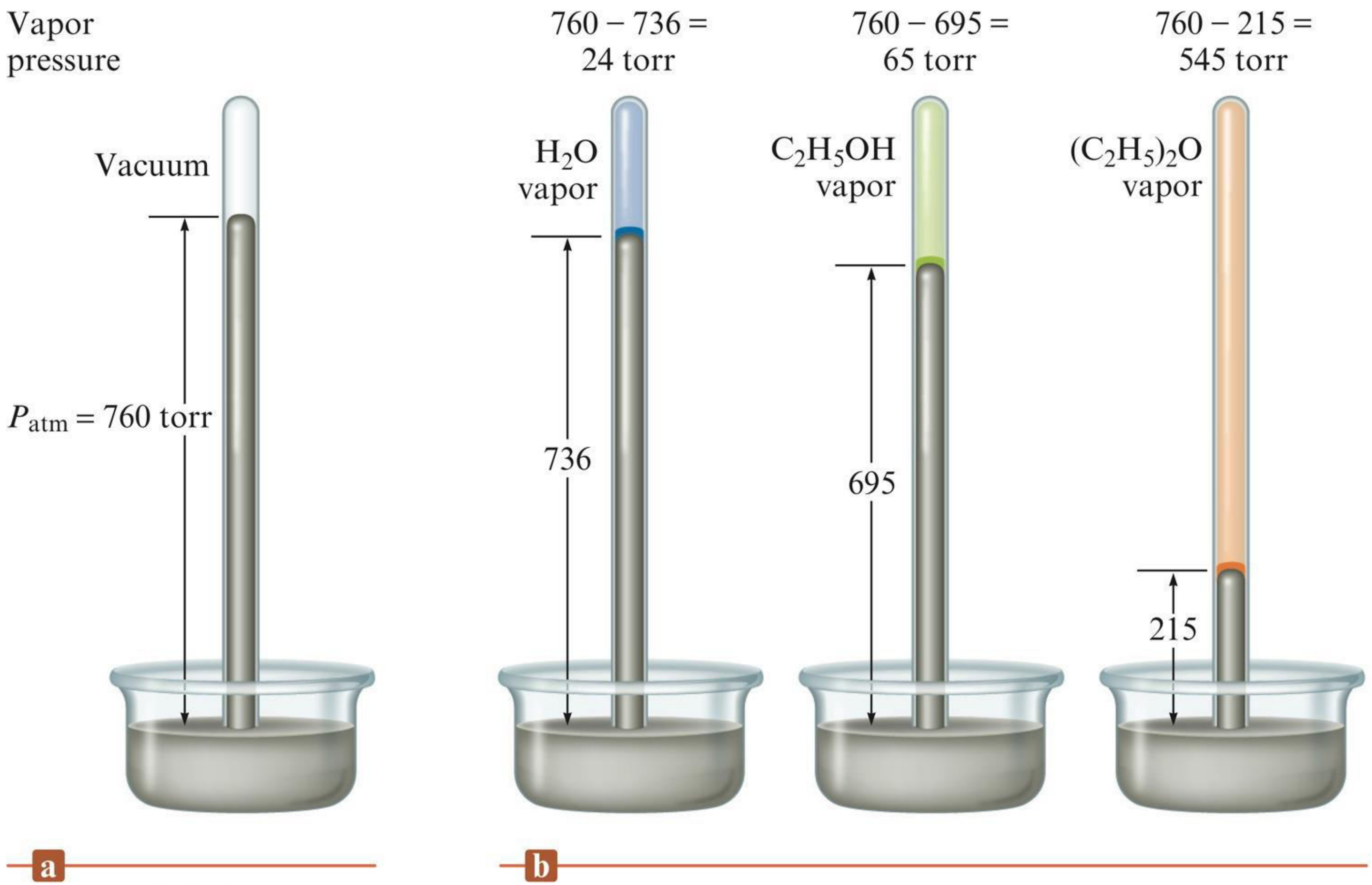
Vapor Pressure

- Pressure of the vapor present at equilibrium.
- The system is at equilibrium when no net change occurs in the amount of liquid or vapor because the two opposite processes exactly balance each other.

What is the vapor pressure of water at 100° C? How do you know?

1 atm

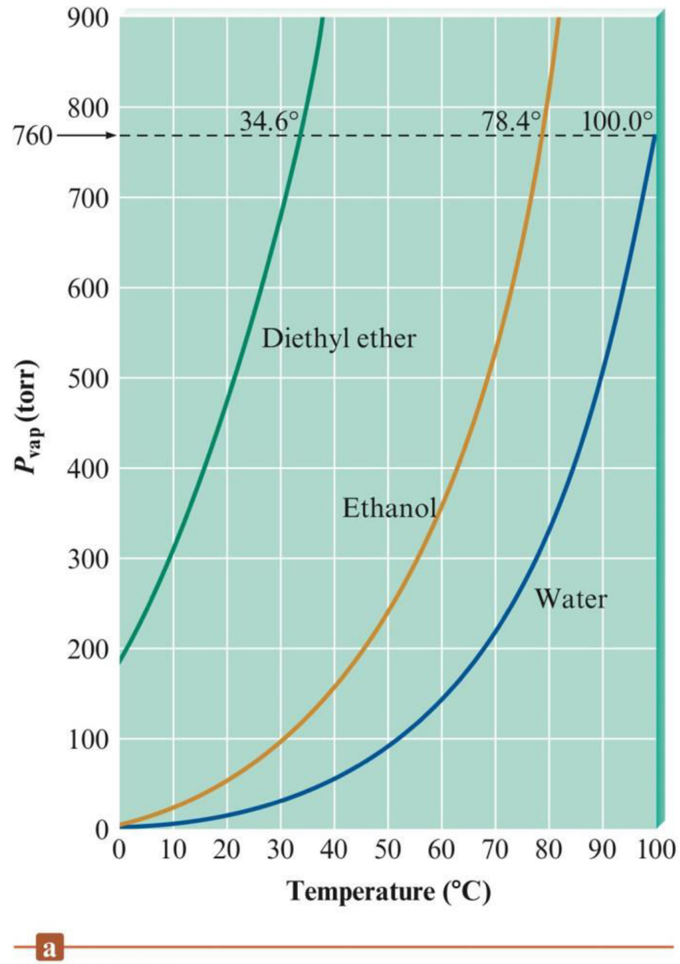
Vapor Pressure



Vapor Pressure

- Liquids in which the intermolecular forces are large have relatively low vapor pressures.
- Vapor pressure increases significantly with temperature.

Vapor Pressure vs. Temperature



Clausius–Clapeyron Equation

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

P_{vap} = vapor pressure

ΔH_{vap} = enthalpy of vaporization

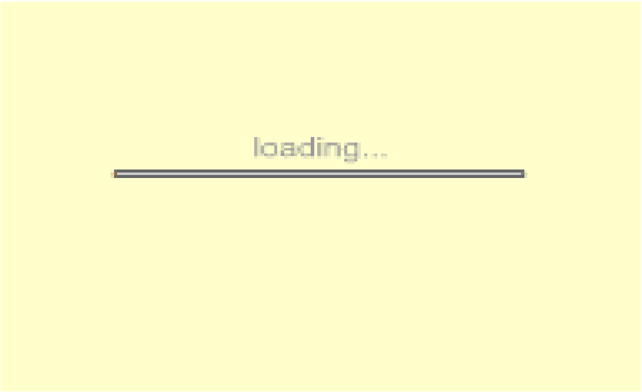
R = 8.3145 J/K·mol

T = temperature (in kelvin)

The vapor pressure of water at 25° C is 23.8 torr, and the heat of vaporization of water at 25° C is 43.9 kJ/mol. Calculate the vapor pressure of water at 65° C.

194 torr

Changes of State



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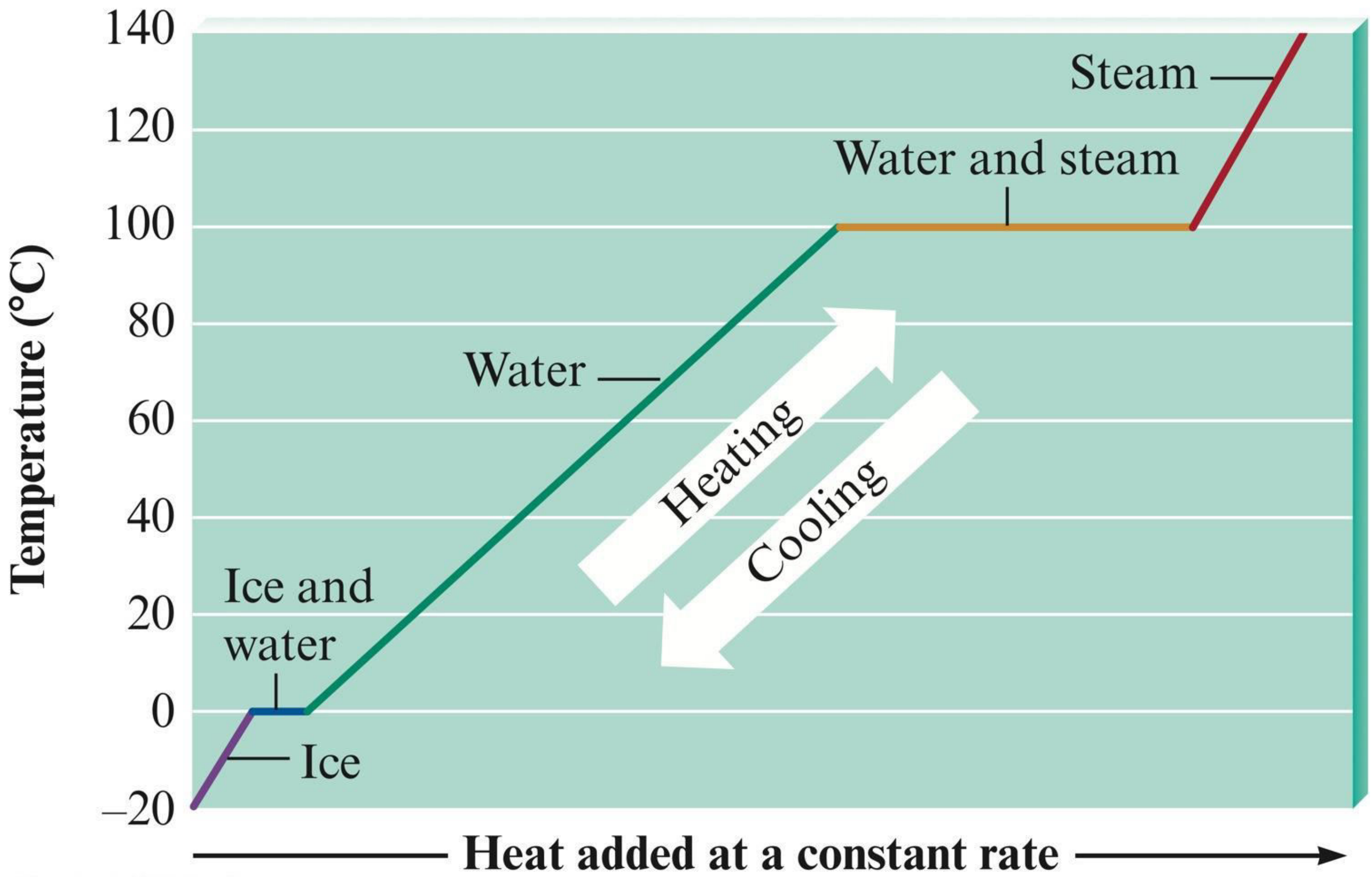
Heating Curve for Water



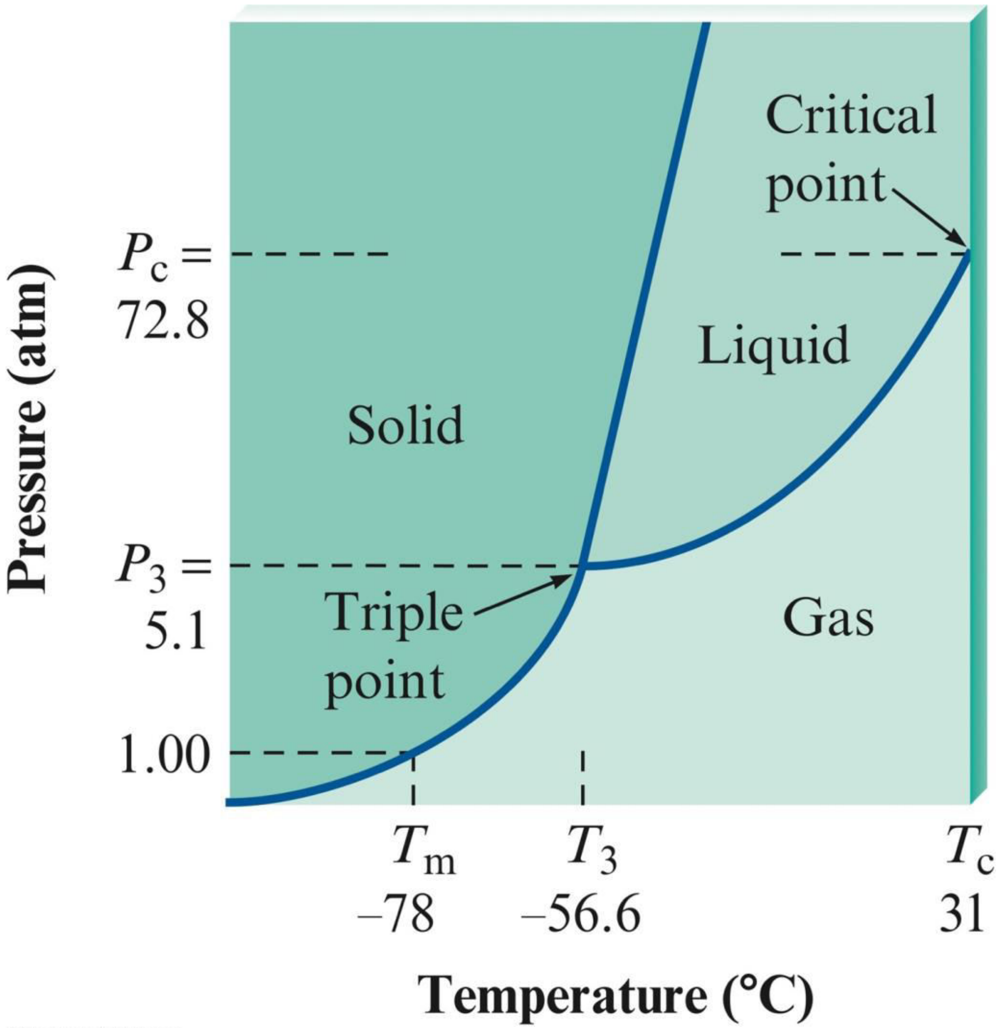
CONCEPT CHECK!

Which would you predict should be larger for a given substance: ΔH_{vap} or ΔH_{fus}?

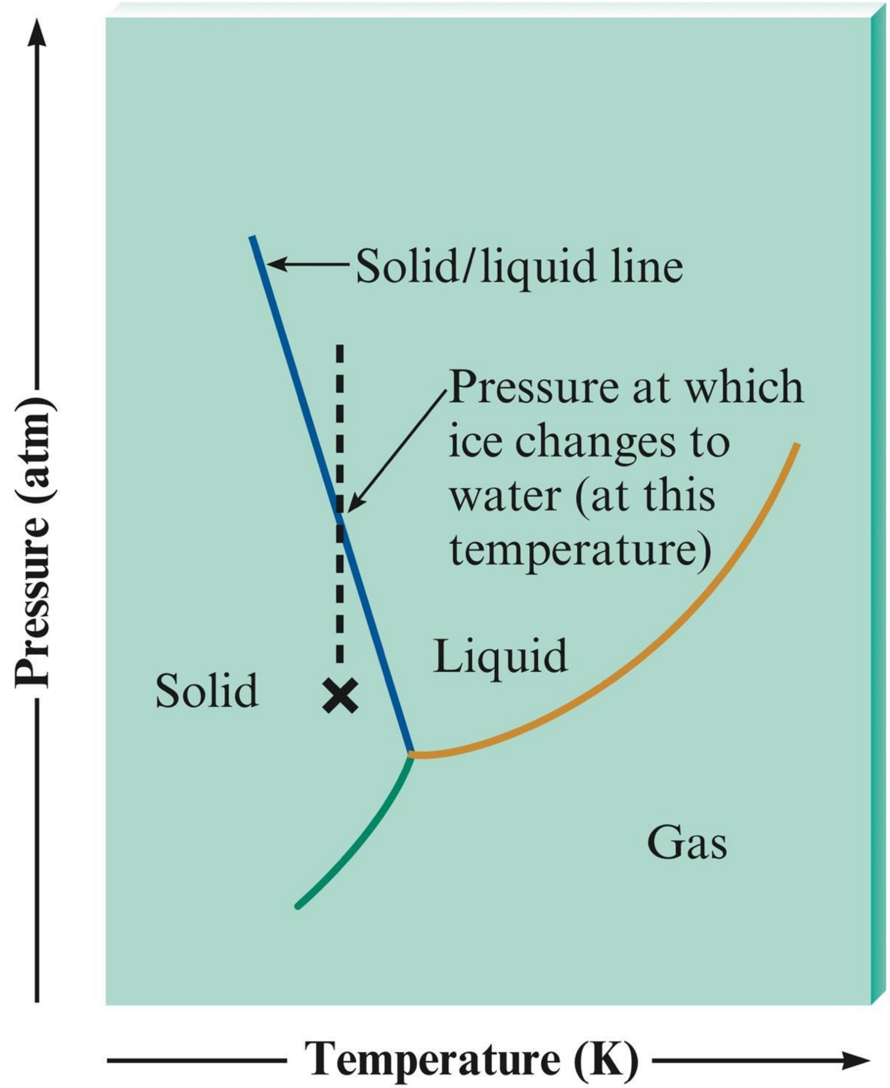
Explain why.

- A convenient way of representing the phases of a substance as a function of temperature and pressure:
  - Triple point
  - Critical point
  - Phase equilibrium lines

Phase Diagram for Carbon Dioxide



Phase Diagram for Water



CONCEPT CHECK!

As intermolecular forces increase, what happens to each of the following? Why?

- Boiling point
- Viscosity
- Surface tension
- Enthalpy of fusion
- Freezing point
- Vapor pressure
- Heat of vaporization