Chapter 12

Intermolecular Forces:

Liquids, Solids, and Phase Changes

Intermolecular Forces: Liquids, Solids, and Phase Changes

12.1 An Overview of Physical States and Phase Changes

12.2 Quantitative Aspects of Phase Changes

12.3 Types of Intermolecular Forces

12.4 Properties of the Liquid State

12.5 The Uniqueness of Water

12.6 The Solid State: Structure, Properties, and Bonding

12.7 Advanced Materials

Phases of Matter

Each physical state of matter is a ***phase***, a physically distinct, homogeneous part of a system.

The properties of each phase are determined by the balance between the ***potential*** and ***kinetic*** energy of the particles.

The ***potential*** energy, in the form of ***attractive forces***, tends to draw particles together.

The ***kinetic*** energy associated with movement tends to disperse particles.

Attractive Forces

Intramolecular or ***bonding*** forces are found ***within*** a molecule. The ***chemical*** behavior of each phase of matter is the same because the same basic particle is present in each case.

H_2O molecules are present whether the substance is in the solid, liquid, or gas phase.

Intermolecular or ***nonbonding*** forces are found ***between*** molecules. The ***physical*** behavior of each phase of matter is different because the ***strength*** of these forces differ from state to state.

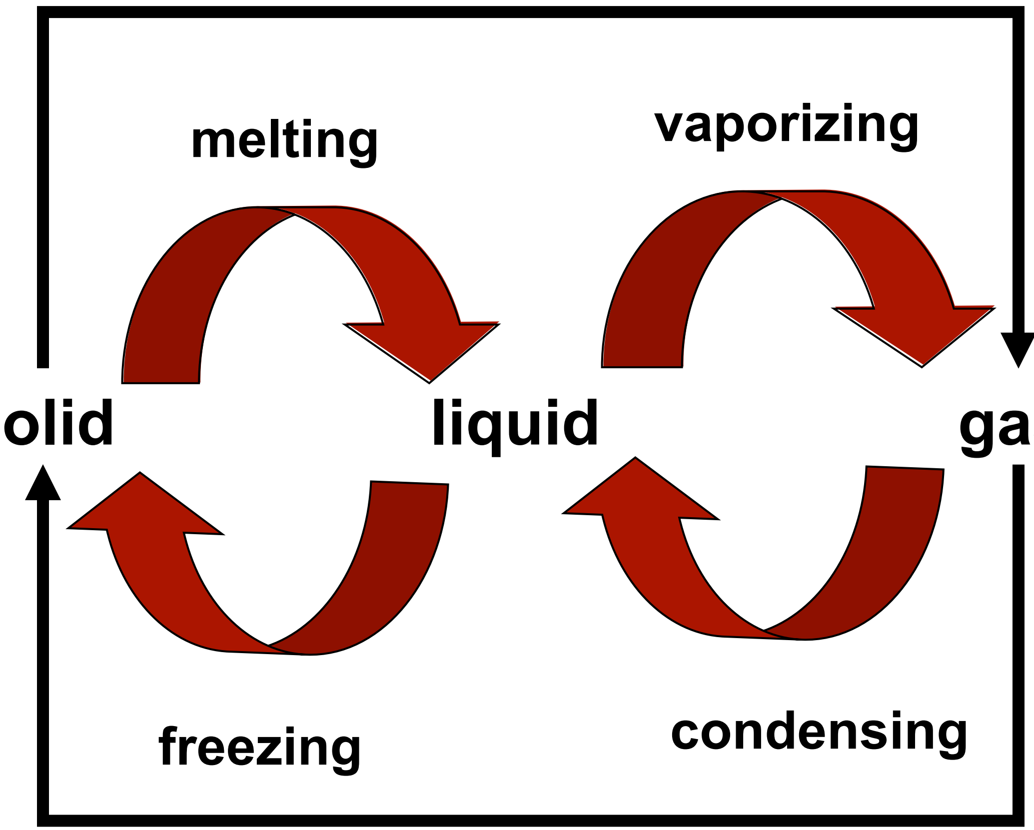
Table 12.1 A Macroscopic Comparison of Gases, Liquids, and Solids

State	Shape and Volume	Compressibility	Ability to Flow
Gas	Conforms to shape and volume of container	High	High
Liquid	Conforms to shape of container; volume limited by surface	Very low	Moderate
Solid	Maintains its own shape and volume	Almost none	Almost none

Kinetic Molecular View of the Three States

	Attractive Forces vs. Kinetic Energy	Properties
Gas	Attractive forces are weak relative to kinetic energy.	Particles are far apart. A gas has no fixed shape or volume.
Liquid	Attractive forces are stronger because particles have less kinetic energy.	A liquid can flow and change shape, but has a fixed volume.
Solid	Attractions dominate motion. Particles are fixed in place relative to each other.	A solid has a fixed shape and volume.

Phase Changes



sublimation

exothermic

melting

vaporizing

solid

liquid

gas

endothermic

freezing

condensing

deposition

Figure 12.1 Two familiar phase changes.

A **Deposition**

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B **Vaporization**

Figure 12.2 Heats of vaporization and fusion for several common substances.

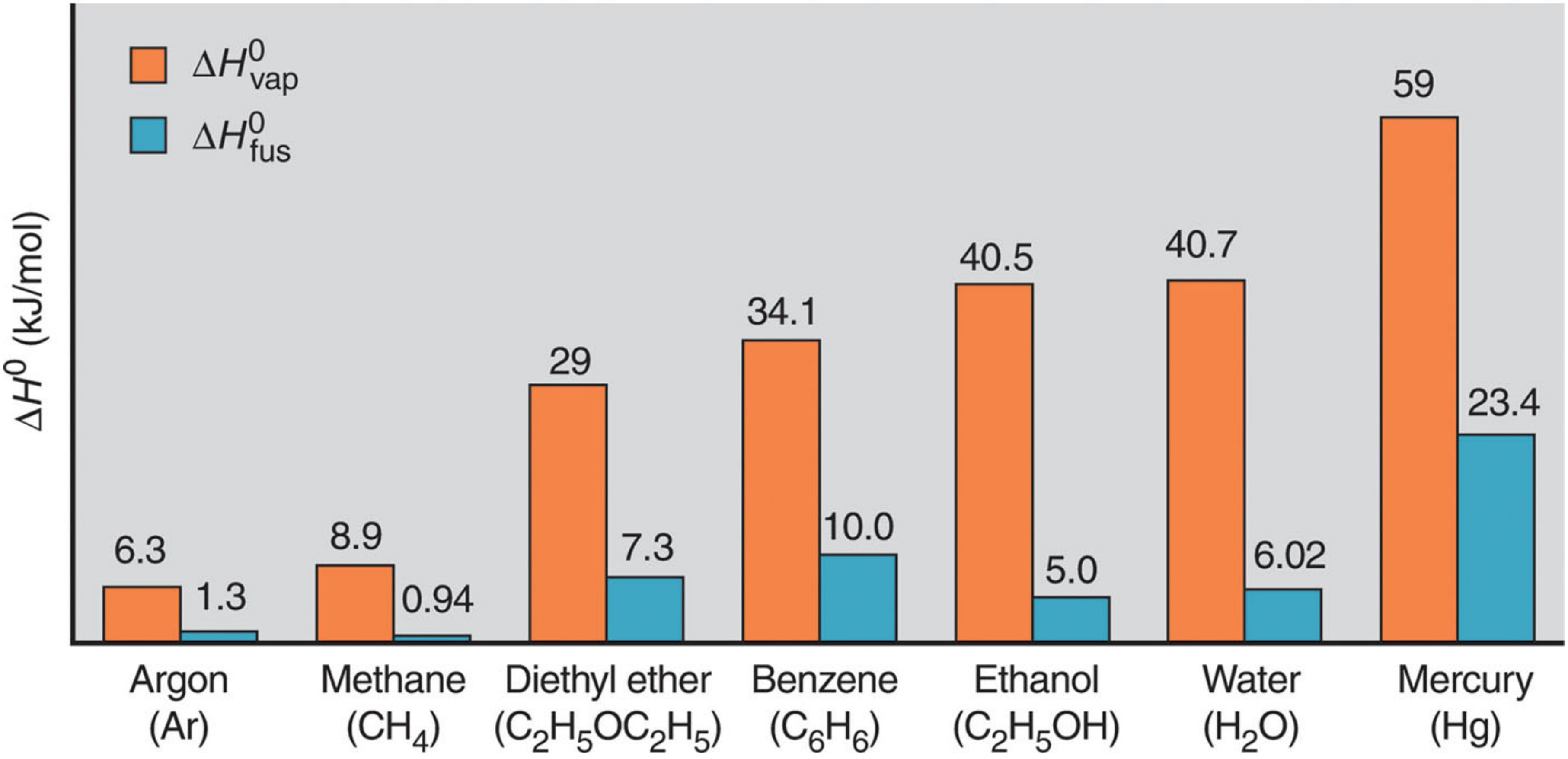
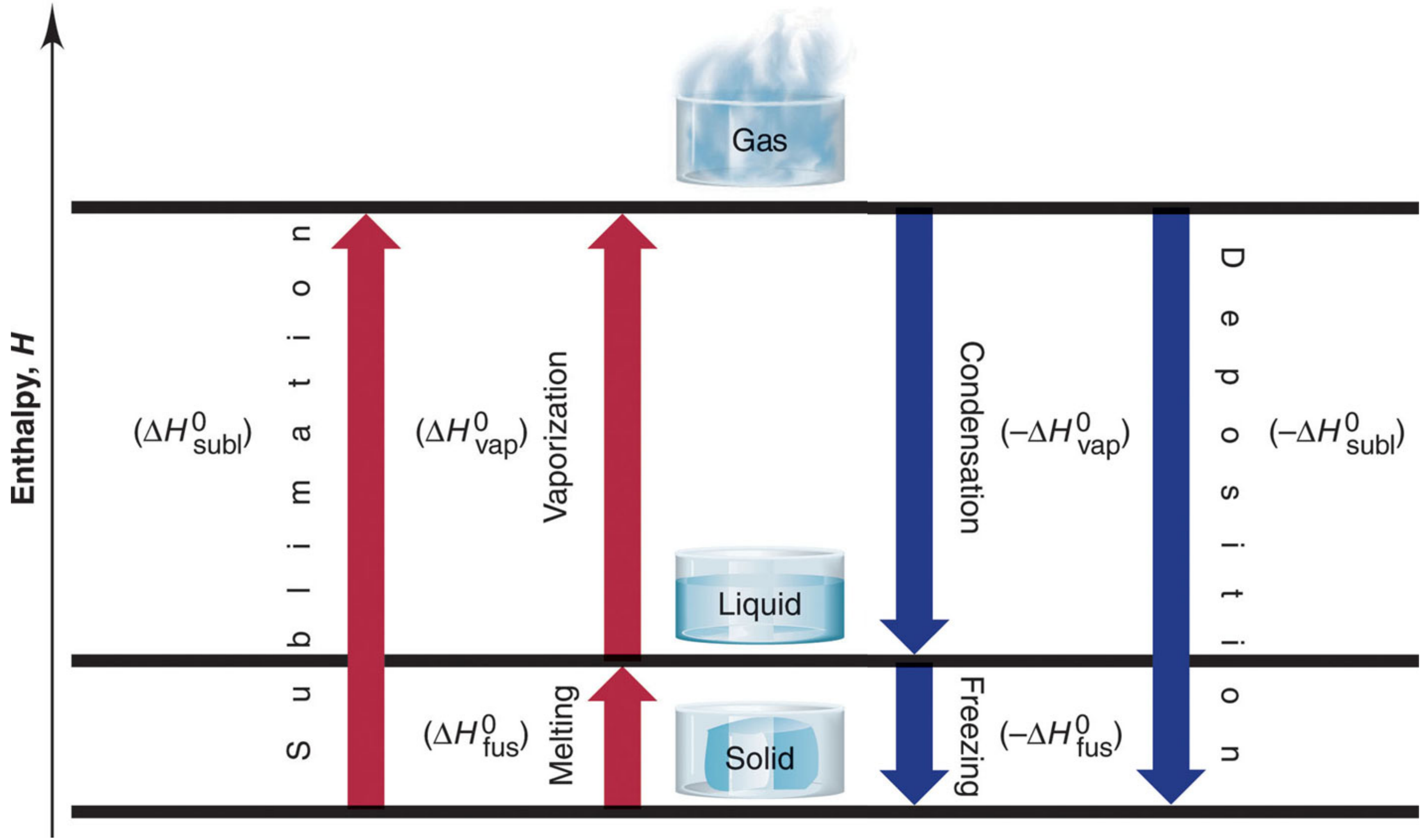


Figure 12.3 Phase changes and their enthalpy changes.



Quantitative Aspects of Phase Changes

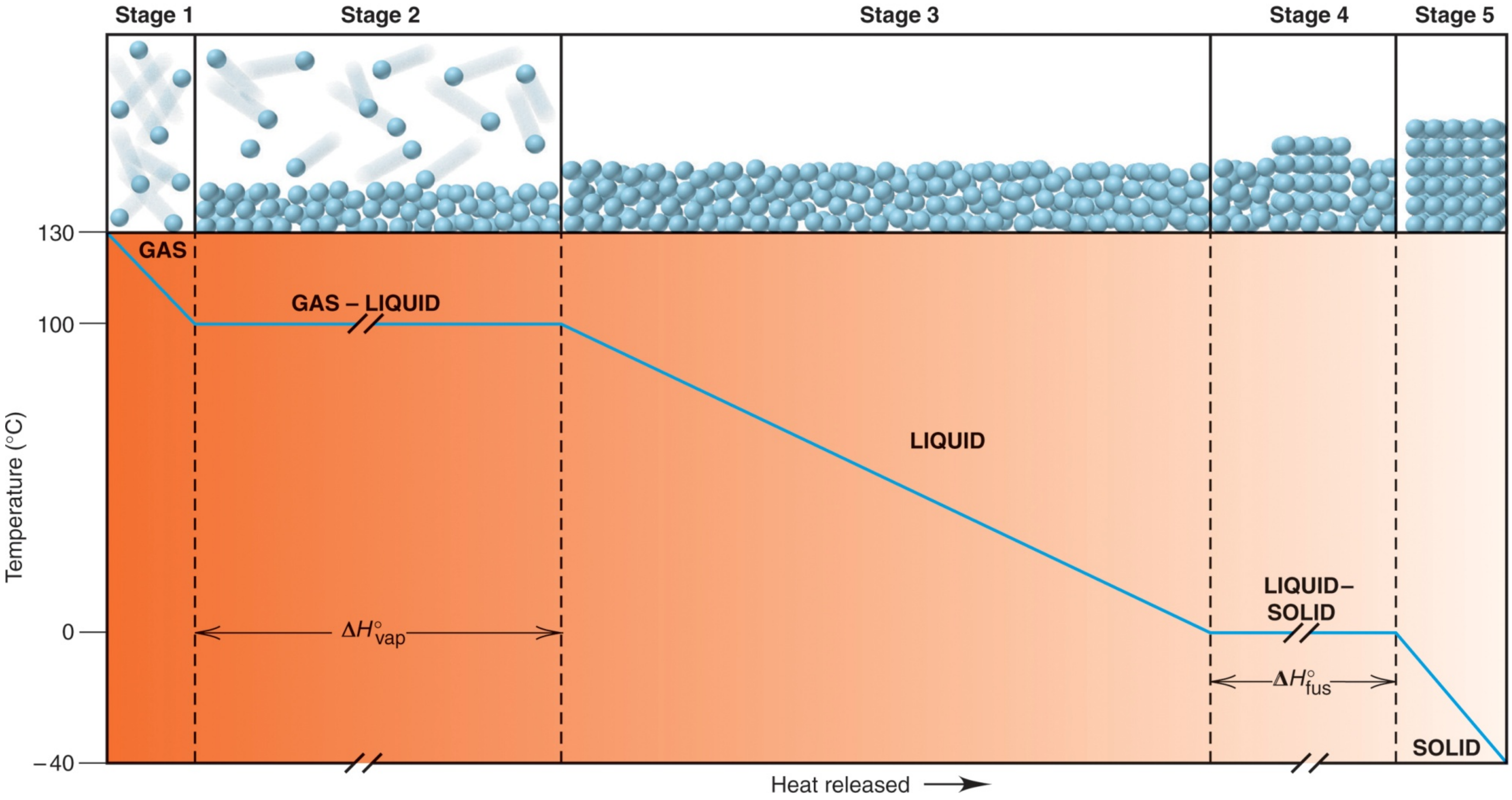
Within a phase, heat flow is accompanied by a ***change in temperature***, since the average E_k of the particles changes.

$$\boxed{q = (\text{amount}) \text{ x } (\text{heat capacity}) \text{ x } \Delta T}$$

During a phase change, heat flow occurs at ***constant temperature***, as the average distance between particles changes.

$$\boxed{q = (\text{amount})(\Delta H \text{ of phase change})}$$

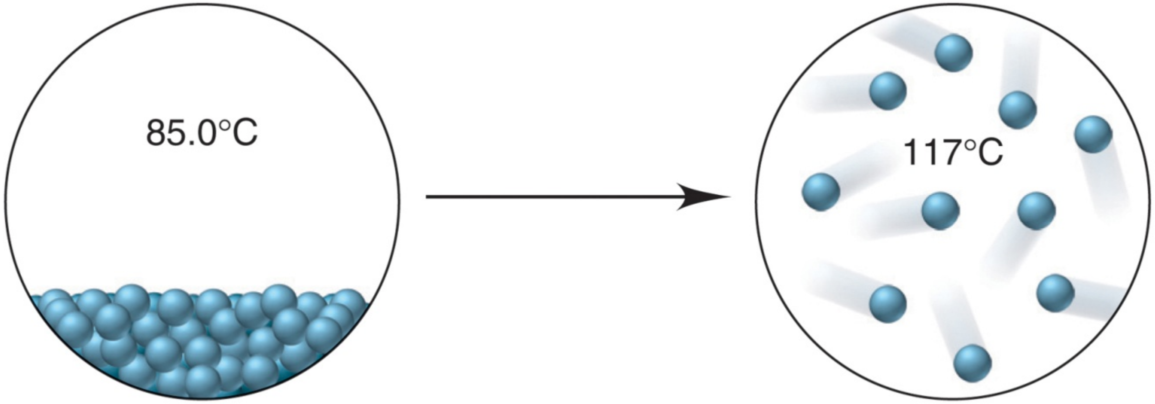
Figure 12.4 A cooling curve for the conversion of gaseous water to ice.



Sample Problem 12.1

Finding the Heat of a Phase Change Depicted by Molecular Scenes

PROBLEM: The scenes below represent a phase change of water. Select data from the previous text discussion to find the heat (in kJ) released or absorbed when 24.3 g of H_2O undergoes this change.



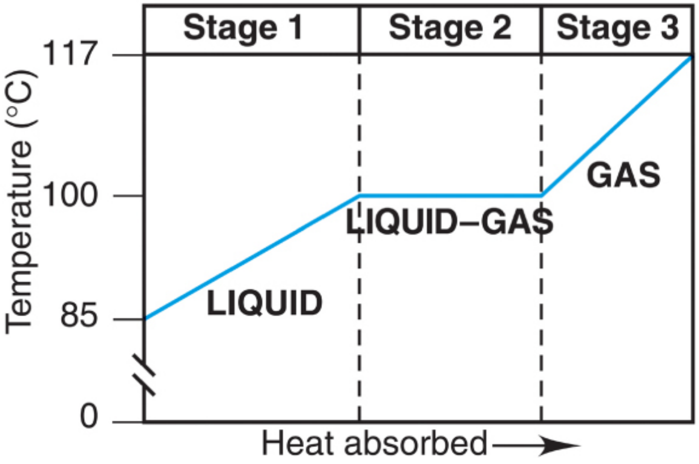
PLAN: The scenes show a disorderly, condensed phase at 85.0°C changing to separate particles at 117°C. A liquid is becoming a gas, so the scene shows vaporization. We must identify the number of stages in the process and calculate the heat absorbed in each.

Sample Problem 12.1

SOLUTION:

There are 3 stages involved in this process:

1) heating of the liquid to its boiling point
2) the phase change from liquid to gas
3) heating the gas to the final temperature



$$\text{mol } H_2O = 24.3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 1.35 \text{ mol } H_2O$$

For Stage 1:

$$q = n \times C_{\text{water}(l)} \times \Delta T$$
$$= (1.35 \text{ mol})(75.4 \text{ J/mol·°C})(100. - 85.0\text{°C})$$
$$= 1527 \text{ J} = 1.53 \text{ kJ}$$

Sample Problem 12.1

For Stage 2:

$q = n(\Delta H°_{vap}) = (1.35\ \text{mol})(40.7\ \text{kJ/mol}) = 54.9\ \text{kJ}$

For Stage 3:

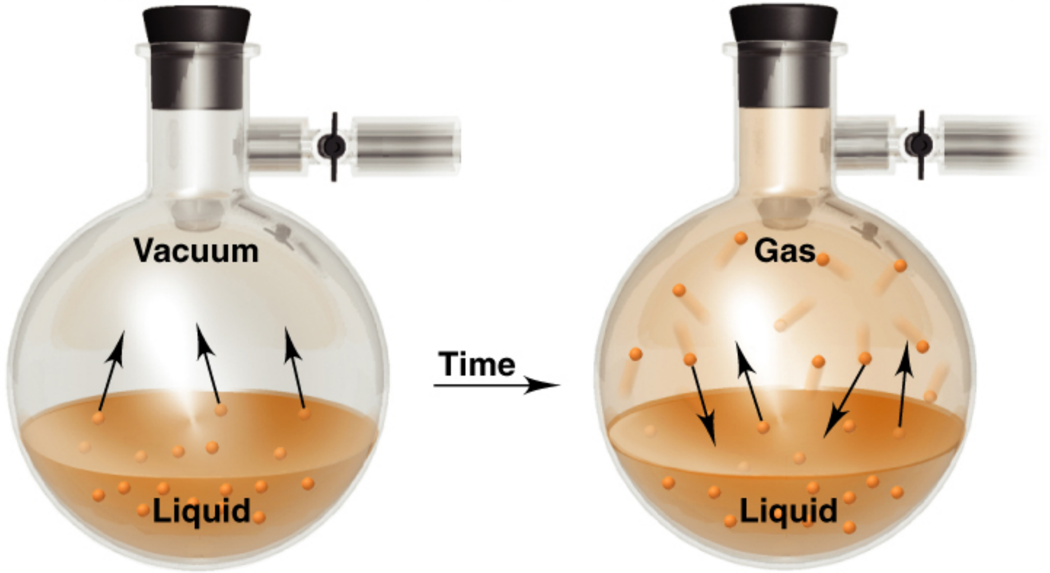
$q = n \times C_{\text{water}(g)} \times \Delta T$

$= (1.35\ \text{mol})(33.1\ \text{J/mol}\cdot°\text{C})(117 - 100.°\text{C})$

$= 759.6\ \text{J} = 0.760\ \text{kJ}$

$$\boxed{q_{\text{total}} = 1.53 + 54.9 + 0.760\ \text{kJ} = 57.2\ \text{kJ}}$$

Figure 12.5 Liquid-gas equilibrium.

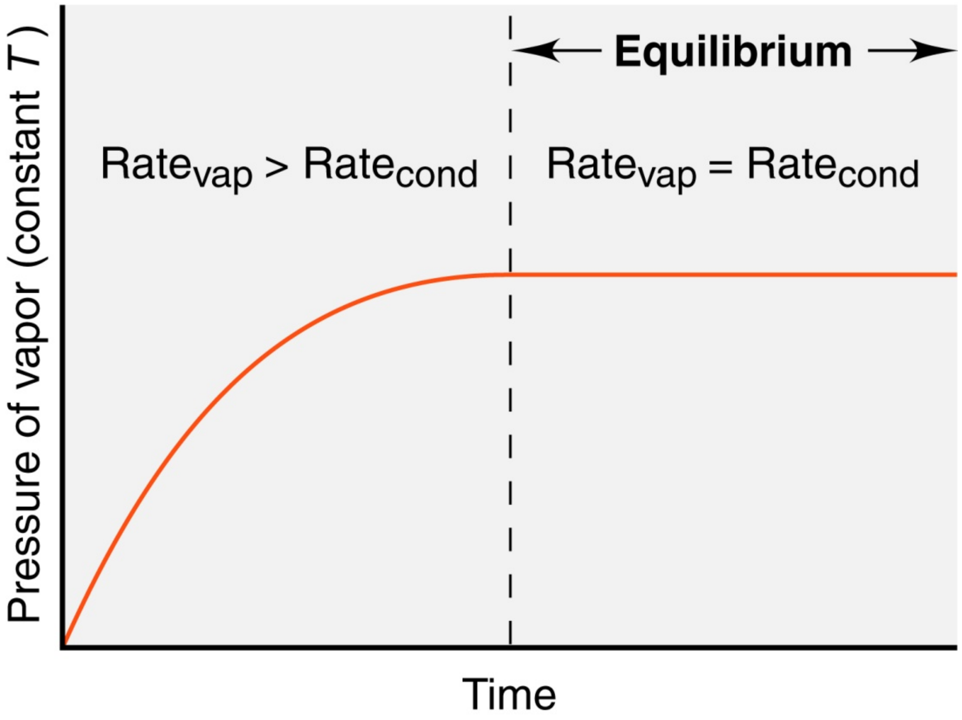


A Molecules in the liquid vaporize.

B Molecules vaporize and condense at the same rate.

In a closed flask, the system reaches a state of ***dynamic equilibrium***, where molecules are leaving and entering the liquid at the ***same rate***.

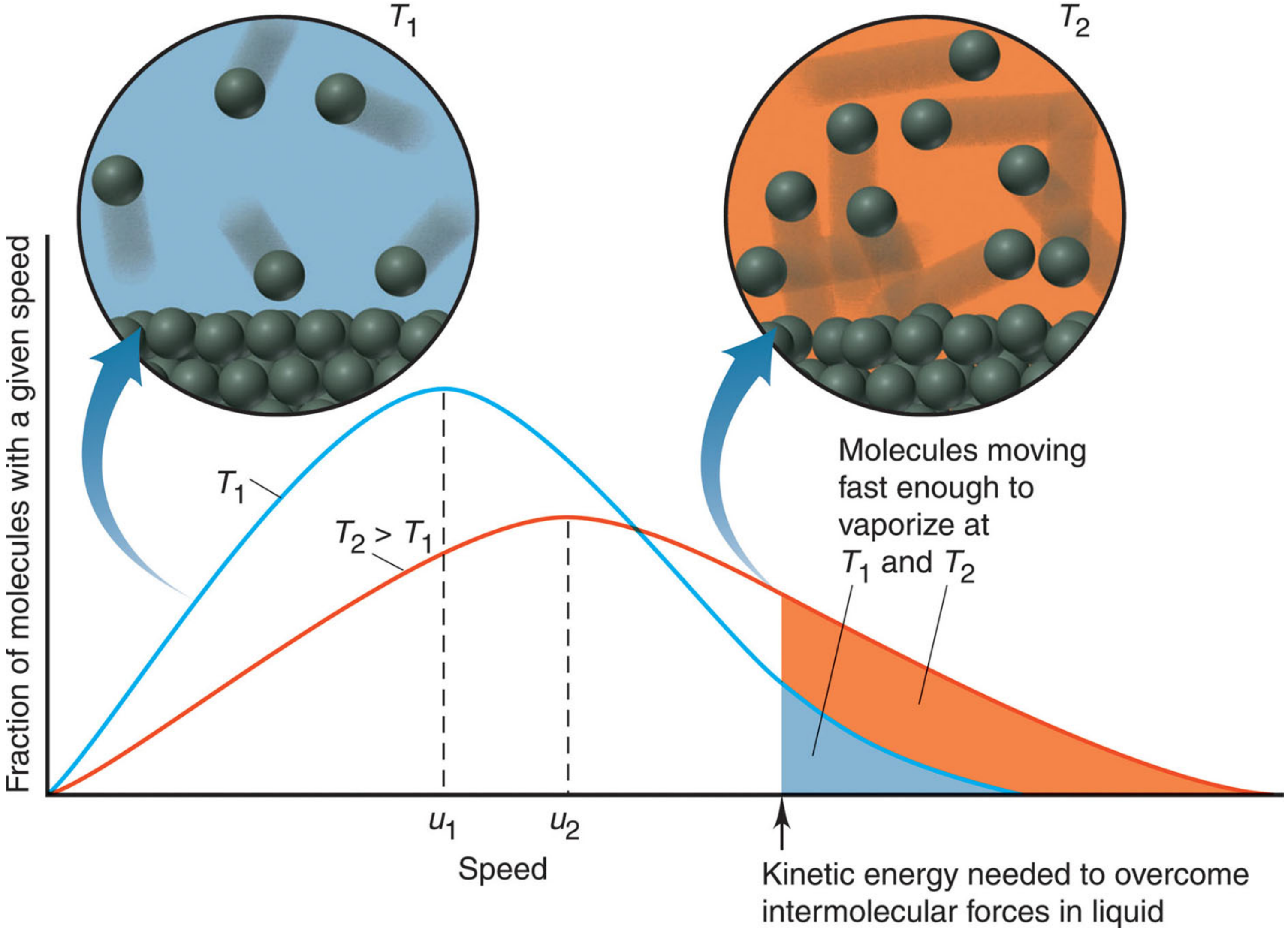
Figure 12.5 continued



C Plot of pressure vs. time.

The ***vapor pressure*** is the pressure exerted by the vapor on the liquid. The pressure increases until equilibrium is reached; **at equilibrium the pressure is constant**.

Figure 12.6 The effect of temperature on the distribution of molecular speeds.



Factors affecting Vapor Pressure

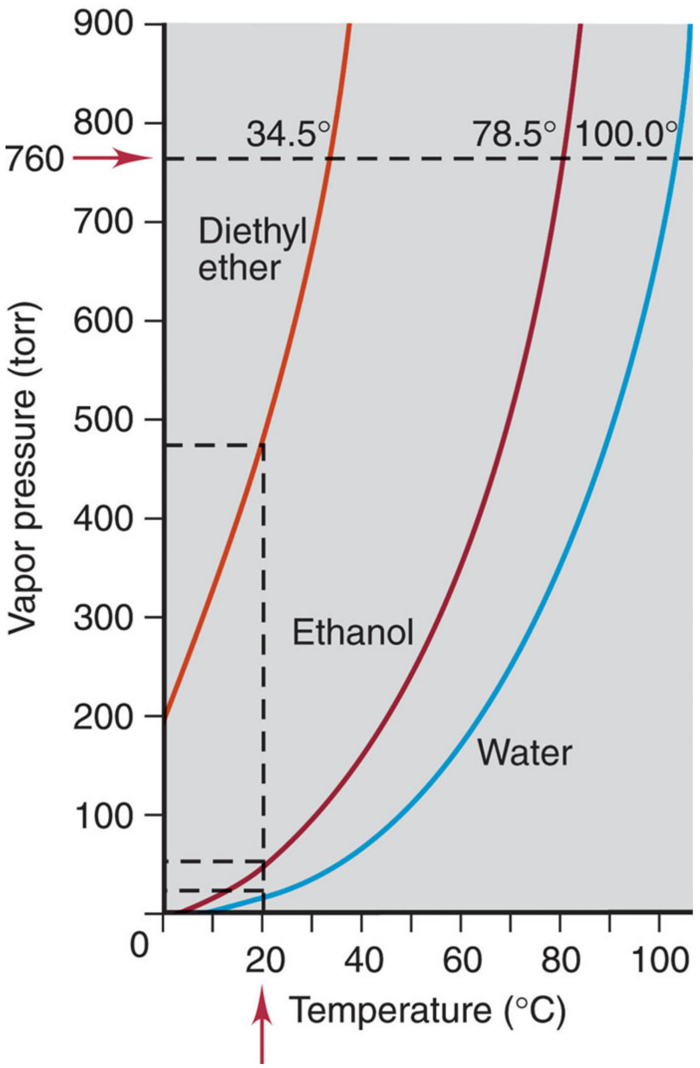
As temperature ***increases***, the fraction of molecules with enough energy to enter the vapor phase ***increases***, and the vapor pressure ***increases***.

higher *T* ➡ **higher *P***

The ***weaker*** the intermolecular forces, the ***more*** easily particles enter the vapor phase, and the ***higher*** the vapor pressure.

weaker forces ➡ **higher *P***

Figure 12.7 Vapor pressure as a function of temperature and intermolecular forces.



Vapor pressure ***increases*** as temperature ***increases***.

Vapor pressure ***decreases*** as the strength of the intermolecular forces ***increases***.

The Clausius-Clapeyron Equation

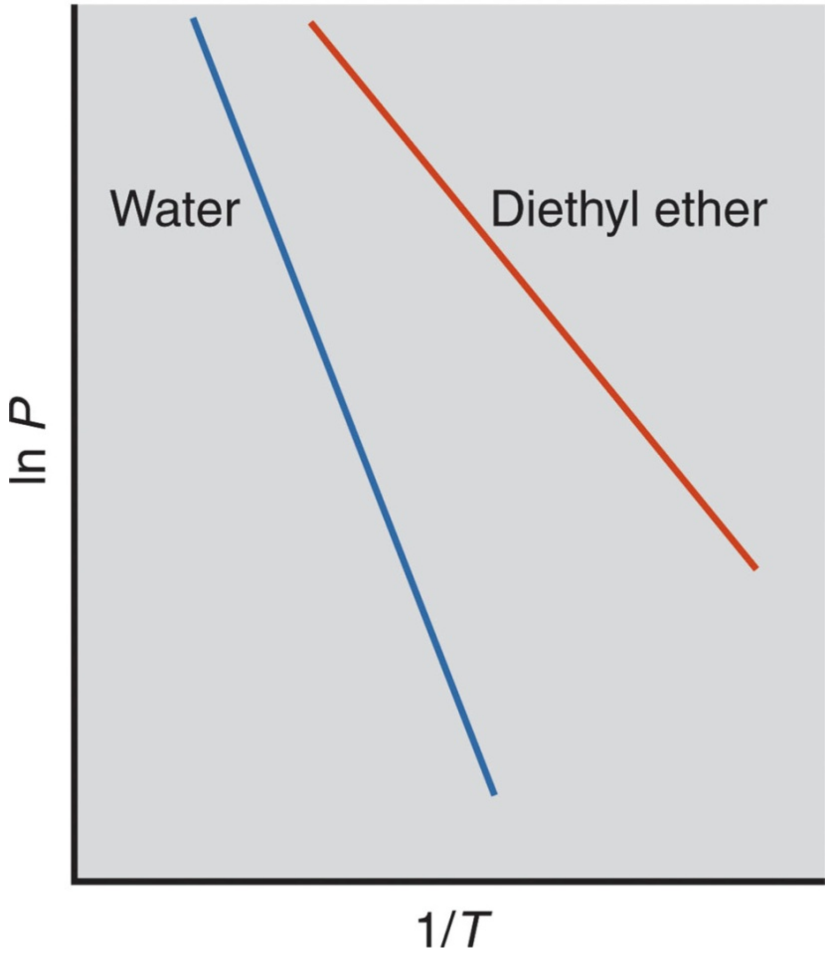
This equation relates vapor pressure to temperature.

$$\ln P = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}\right) + C$$

The two-point form is used when the vapor pressures at two different temperatures are known.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Figure 12.8 **Linear plots of the relationship between vapor pressure and temperature.**



$$\ln P = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}\right) + C$$

$$\text{slope} = \frac{-\Delta H_{\text{vap}}}{R}$$

Sample Problem 12.2 Applying the Clausius-Clapeyron Equation

PROBLEM: The vapor pressure of ethanol is 115 torr at 34.9°C. If ΔH_{vap} of ethanol is 40.5 kJ/mol, calculate the temperature (in °C) when the vapor pressure is 760 torr.

PLAN: We are given 4 of the 5 variables in the Clausius-Clapeyron equation, so we substitute these into the equation and solve for T_2. T values must be converted to K.

SOLUTION:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$T_1 = 34.9°\text{C} + 273.15 = 308.0 \text{ K}$$

$$\ln \frac{760 \text{ torr}}{115 \text{ torr}} = -\frac{40.5 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}}\left(\frac{1}{T_2} - \frac{1}{308.0 \text{ K}}\right)$$

$$\boxed{T_2 = 350.\text{ K} - 273.15 = 77°\text{C}}$$

Vapor Pressure and Boiling Point

The ***boiling point*** of a liquid is the temperature at which the vapor pressure equals the external pressure.

The ***normal boiling point*** of a substance is observed at standard atmospheric pressure or 760 torr.

As the external pressure on a liquid ***increases***, the boiling point ***increases***.

Figure 12.9 **Iodine subliming.**

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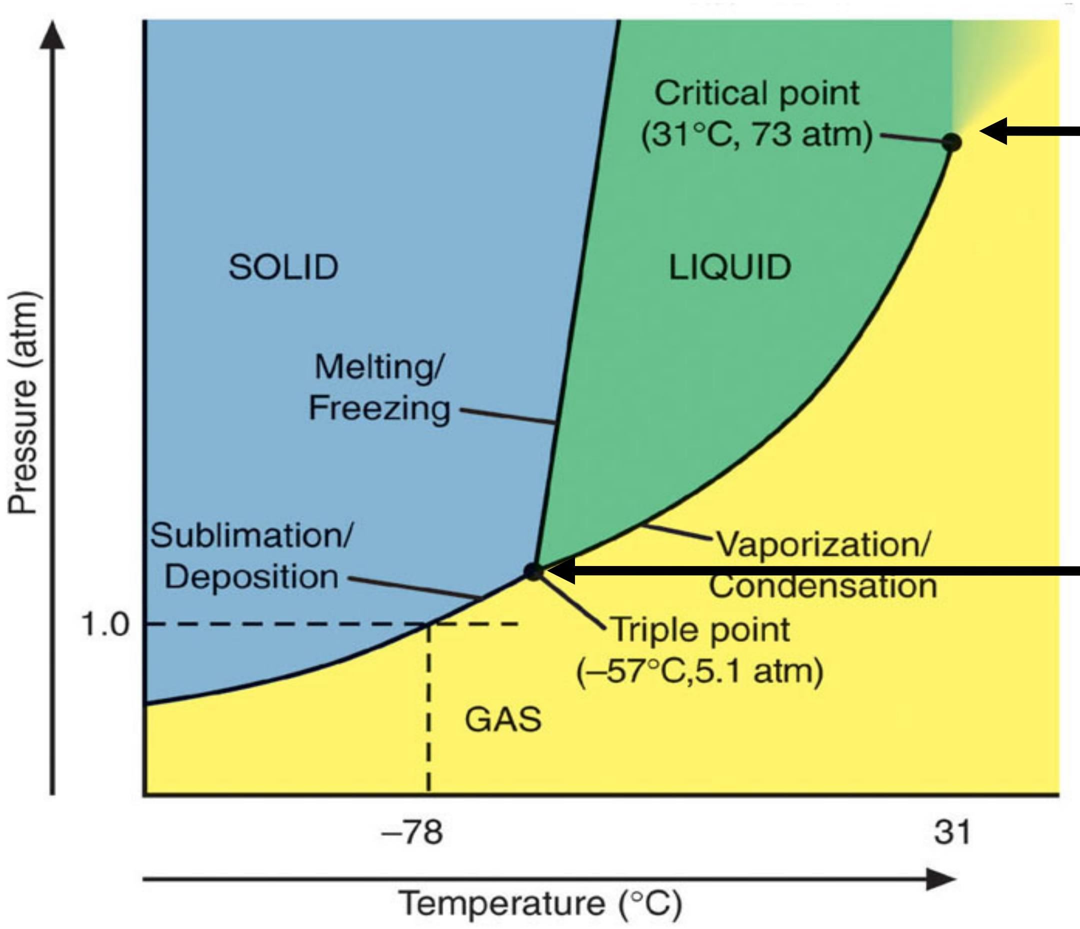
After the solid sublimes, vapor deposits on a cold surface.

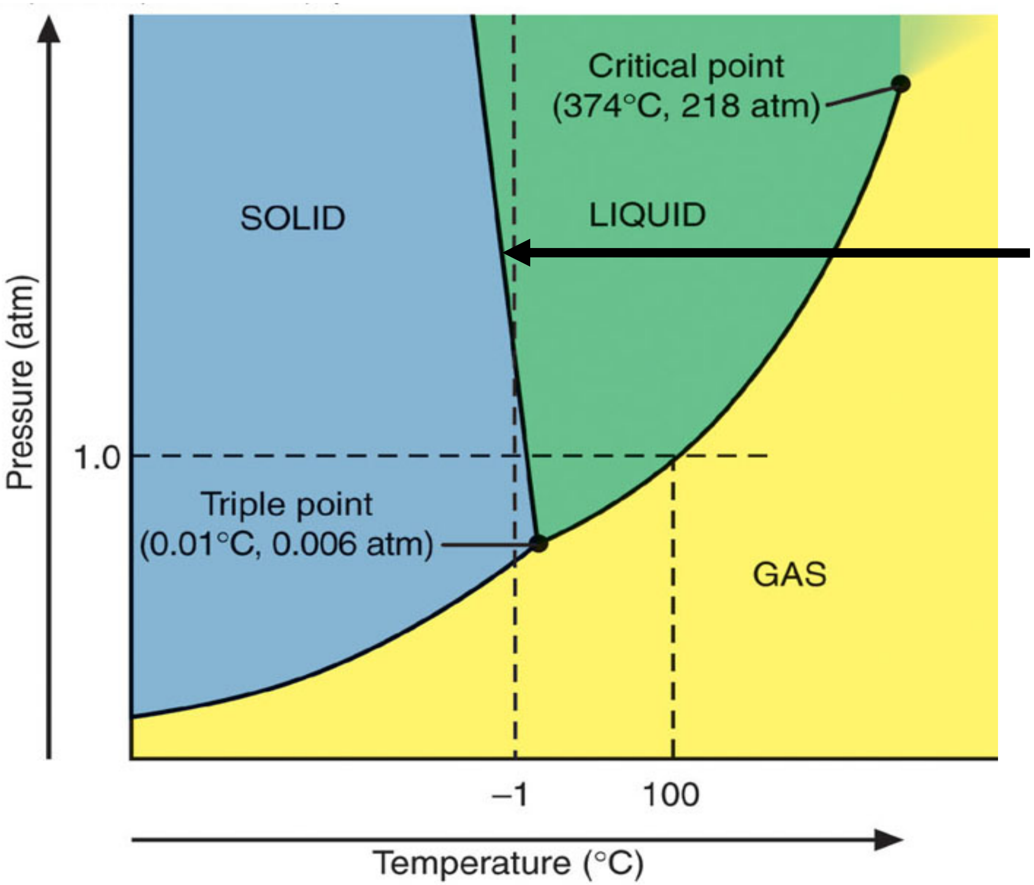
Figure 12.10 Phase diagram for CO_2.



At the critical point, the densities of the liquid and gas phases become equal.

At the triple point, all three phases are in equilibrium.

Figure 12.11 **Phase diagram for H_2O.**



The solid-liquid line slants to the *left* for H_2O, because the solid is *less* dense than the liquid. Water expands on freezing.

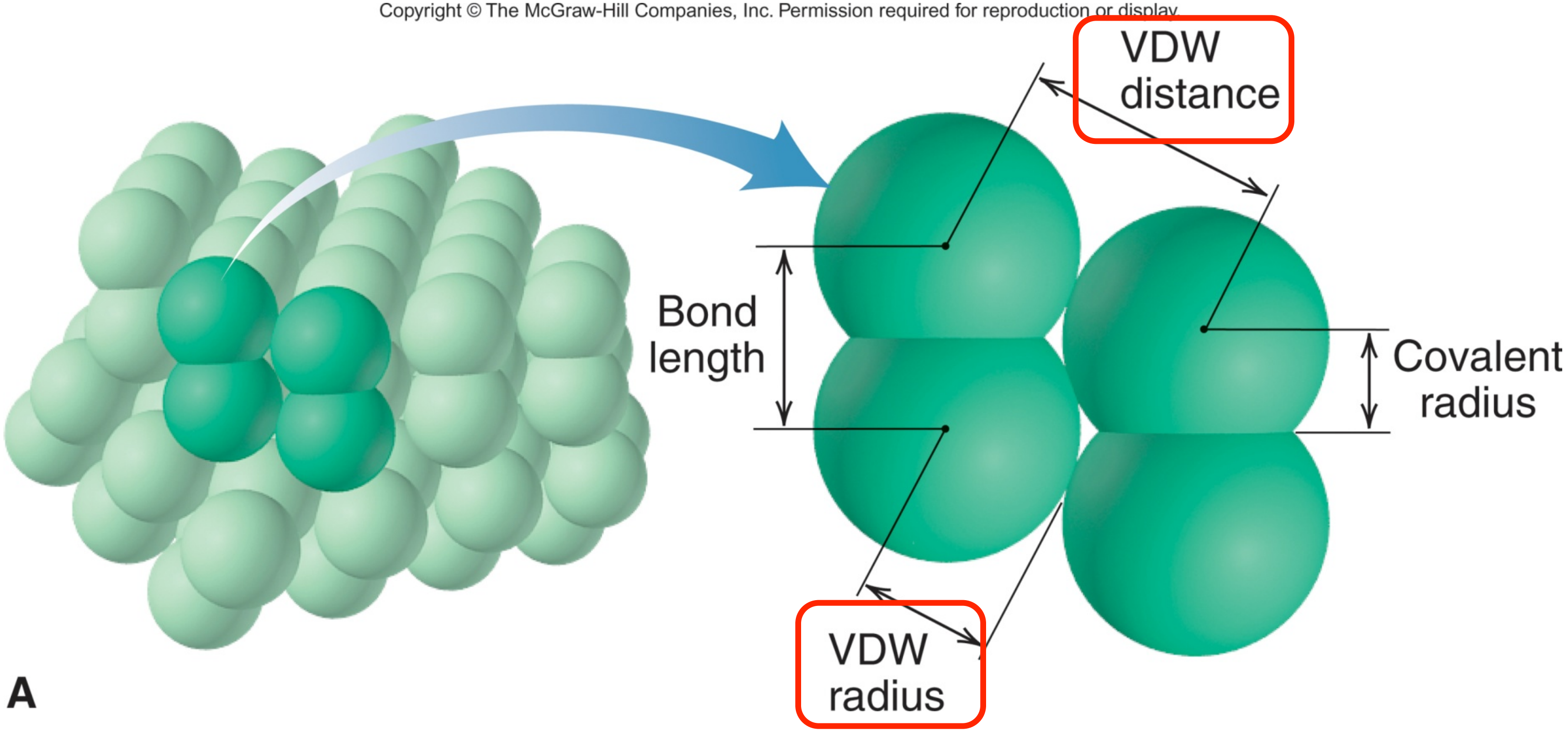
The Nature of Intermolecular Forces

Intermolecular forces arise from the attraction between molecules with partial charges, or between ions and molecules.

Intermolecular forces are relatively ***weak*** compared to bonding forces because they involve smaller charges that are farther apart.

Figure 12.12A Covalent and van der Waals radii.

The van der Waals ***distance*** is the distance between two ***nonbonded*** atoms in ***adjacent*** molecules.



The van der Waals ***radius*** is one-half the closest distance between the nuclei of two ***nonbonded*** atoms. The VDW radius is ***always larger*** than the covalent radius.

Figure 12.12B Periodic trends in covalent and van der Waals radii.

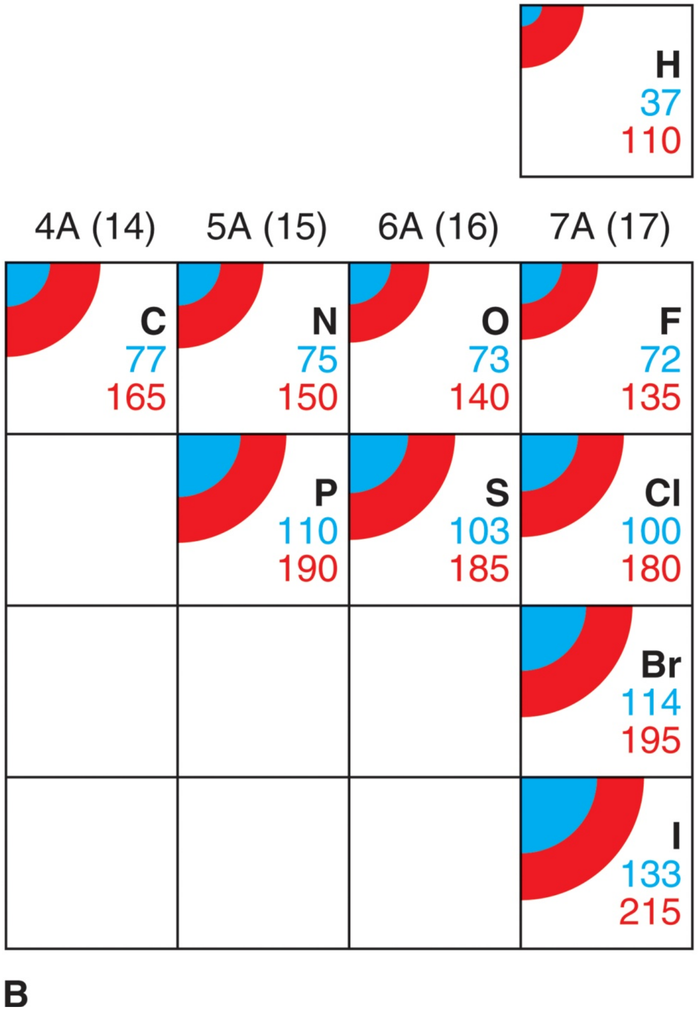


Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

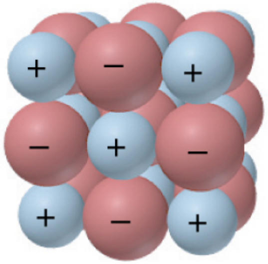
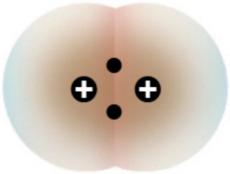
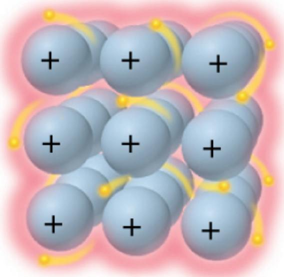
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces (continued)

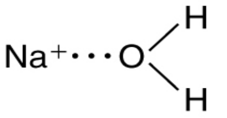
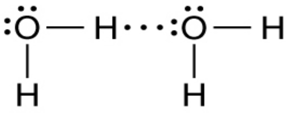
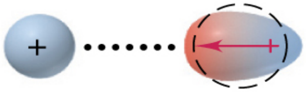
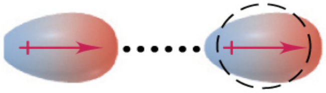
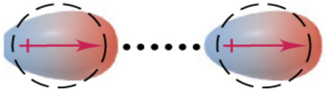
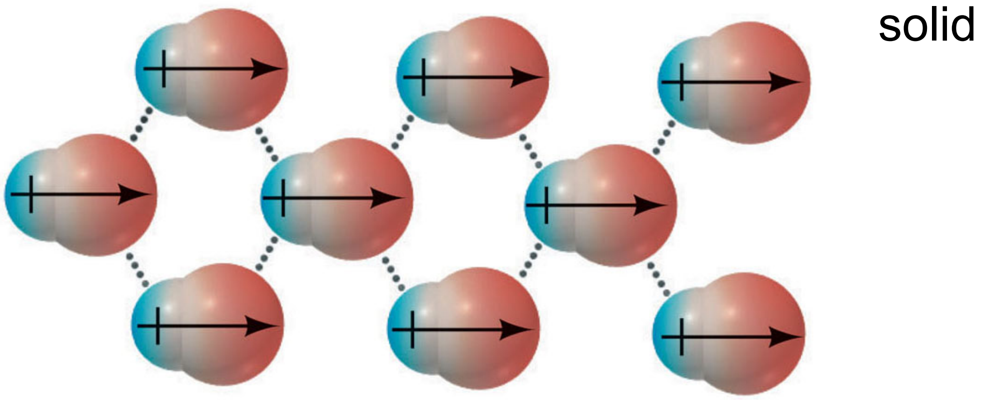
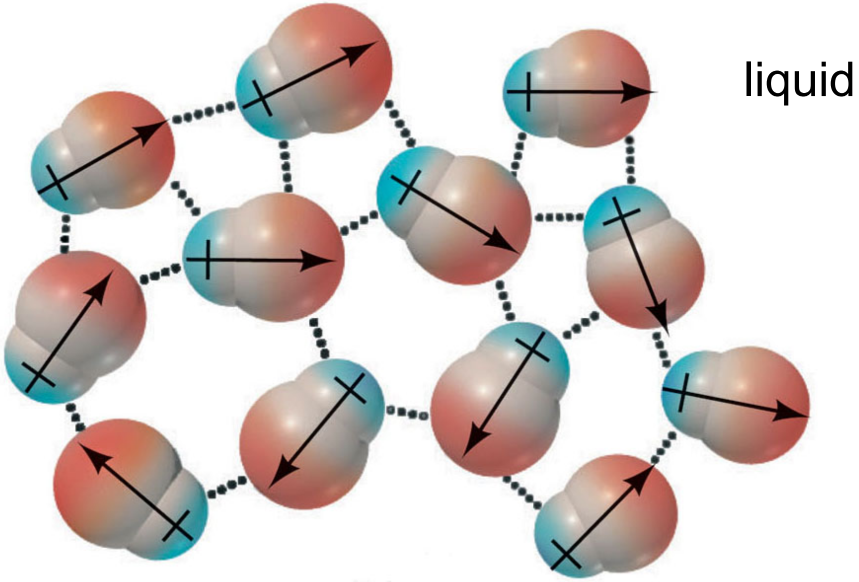
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	
H bond	$\overset{\delta-}{-A}-\overset{\delta+}{H}\cdots\cdots\cdots:\overset{\delta-}{B}-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	
Dipole-dipole		Dipole charges	5–25	I—Cl···I—Cl
Ion–induced dipole		Ion charge–polarizable e$^-$ cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e$^-$ cloud	2–10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e$^-$ clouds	0.05–40	F—F···F—F

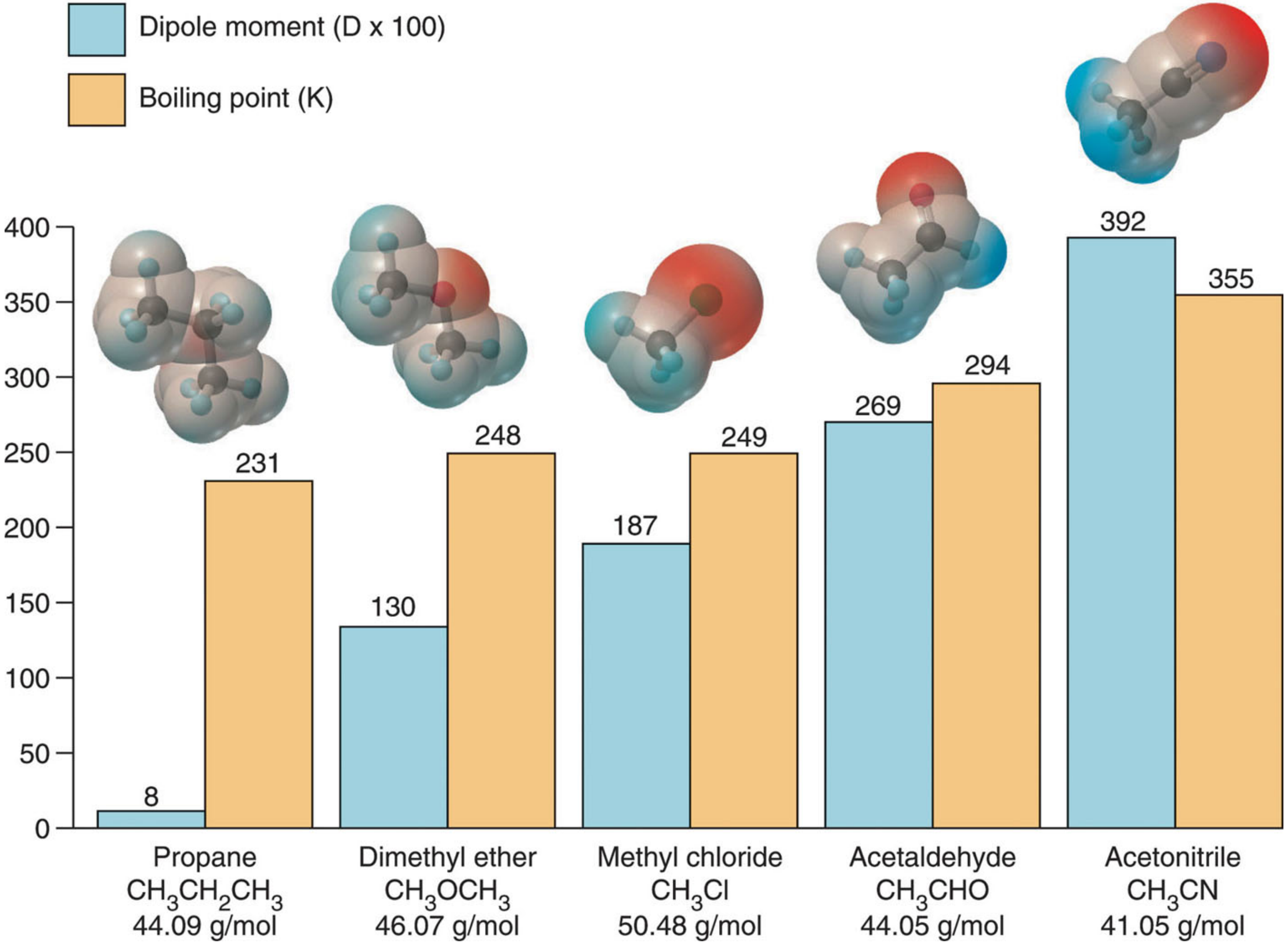
Figure 12.13 Polar molecules and dipole-dipole forces.





The positive pole of one polar molecule attracts the negative pole of another.

Figure 12.14 Dipole moment and boiling point.



The Hydrogen Bond

Hydrogen bonding is possible for molecules that have a ***hydrogen atom*** covalently bonded to a small, highly electronegative atom with ***lone electron pairs***, specifically ***N, O, or F***.

An intermolecular ***hydrogen bond*** is the attraction between the ***H atom*** of one molecule and a ***lone pair of the N, O, or F atom*** of another molecule.

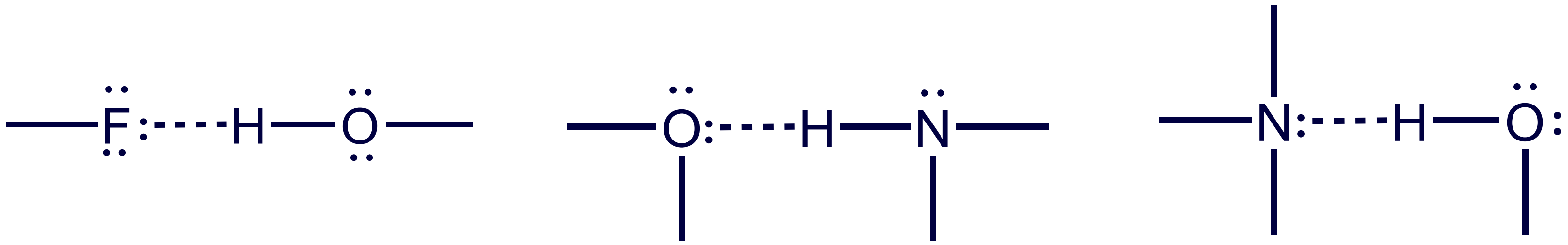
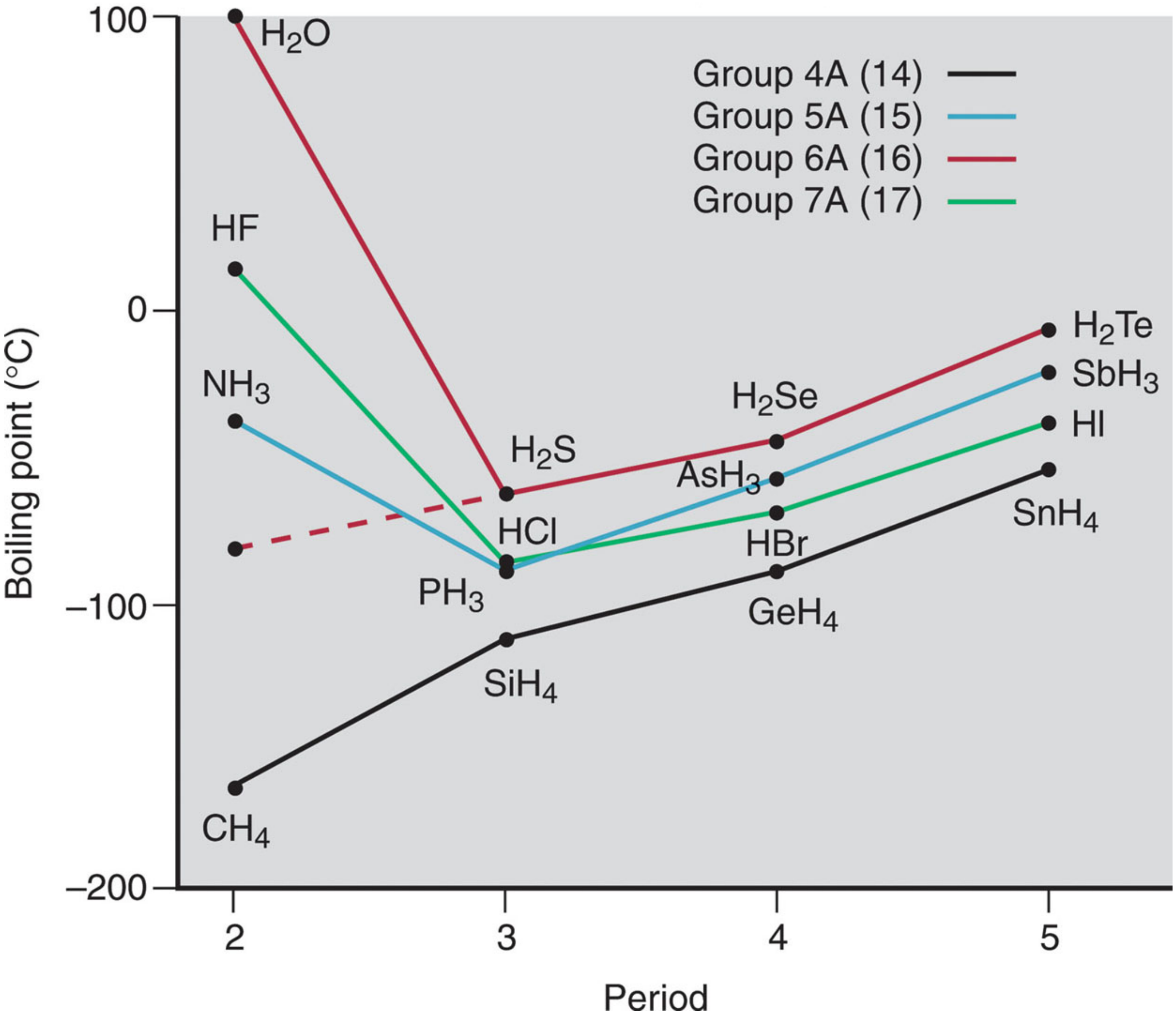


Figure 12.15 Hydrogen bonding and boiling point.

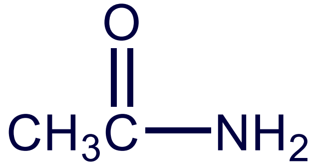


Sample Problem 12.3

Drawing Hydrogen Bonds Between Molecules of a Substance

PROBLEM: Which of the following substances exhibits H bonding? For any that do, draw the H bonds between two of its molecules.

(a) C_2H_6 **(b)** CH_3OH **(c)**



$CH_3C(=O)-NH_2$

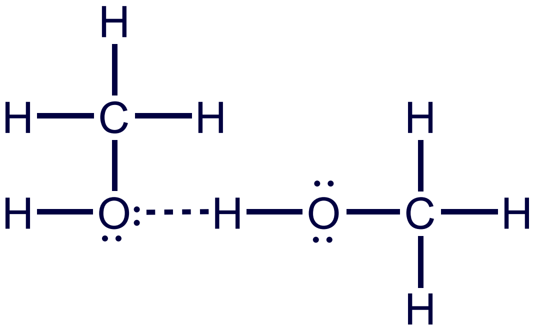
PLAN: If the molecule does not contain N, O, or F it cannot form H bonds. If it contains any of these atoms covalently bonded to H, we draw two molecules in the pattern –B:----H–A.

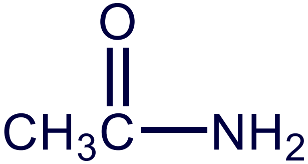
SOLUTION:

(a) C_2H_6 has no N, O, or F, so **no H-bonds can form**.

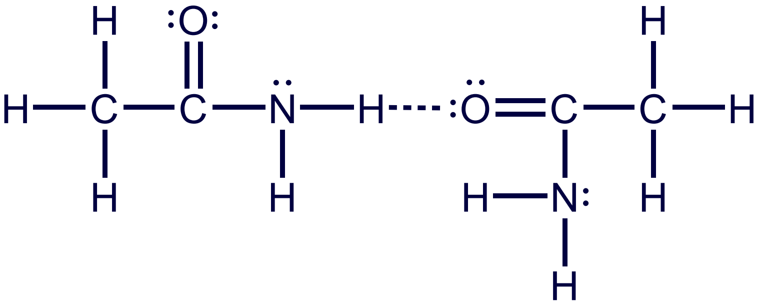
Sample Problem 12.3

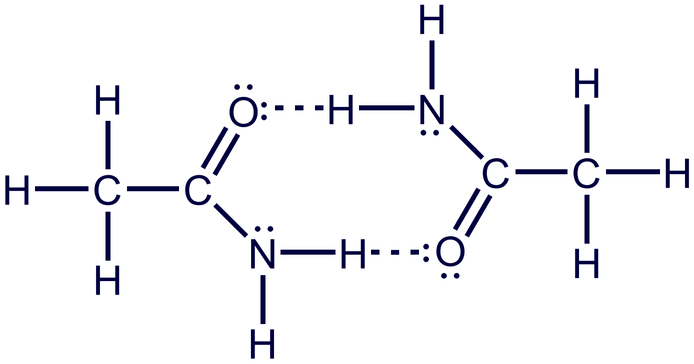
(b) CH_3OH contains a covalent bond between O and H. It can form H bonds between its molecules:



(c) 

$CH_3C(=O)-NH_2$ can form H bonds at two sites:





Polarizability and Induced Dipoles

A nearby electric field can ***induce*** a distortion in the electron cloud of an atom, ion, or molecule.

- For a ***nonpolar*** molecule, this induces a ***temporary dipole moment***.
- For a ***polar*** molecule, the field ***enhances*** the existing dipole moment.

The ***polarizability*** of a particle is the ease with which its electron cloud is distorted.

Trends in Polarizability

Smaller particles are ***less polarizable*** than larger ones because their electrons are held more tightly.

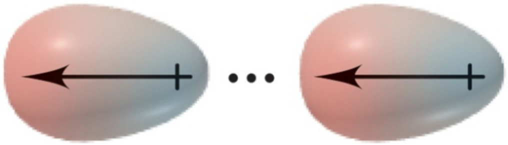
Polarizability ***increases down a group*** because atomic size increases and larger electron clouds distort more easily.

Polarizability ***decreases across a period*** because of increasing Z_{eff}.

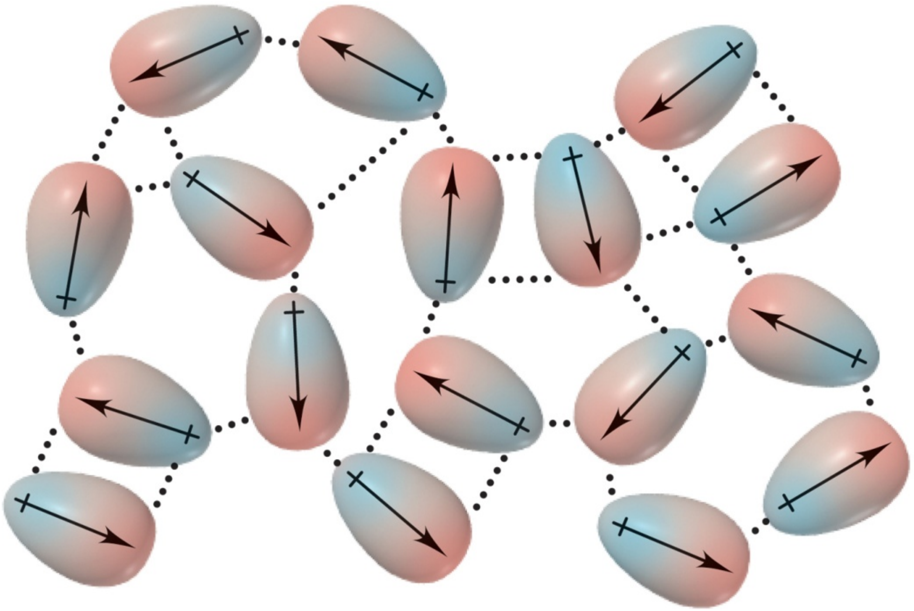
Cations are smaller than their parent atoms and less polarizable; anions show the opposite trend.

Figure 12.16 Dispersion forces among nonpolar particles.

A. When atoms are far apart they do not influence one other.



B. When atoms are close together, the instantaneous dipole in one atom induces a dipole in the other.



C. The process occurs throughout the sample.

Dispersion (London) Forces

Dispersion forces or ***London forces*** arises when an ***instantaneous dipole*** in one particle ***induces*** a dipole in another, resulting in an attraction between them.

Dispersion forces exist between ***all particles***, increasing the energy of attraction in all matter.

Dispersion forces are ***stronger*** for ***more polarizable*** particles.

In general, larger particles experience stronger dispersion forces than smaller ones.

Figure 12.17 Molar mass and trends in boiling point.

Dispersion forces are stronger for larger, more polarizable particles.

Polarizability correlates closely with molar mass for similar particles.

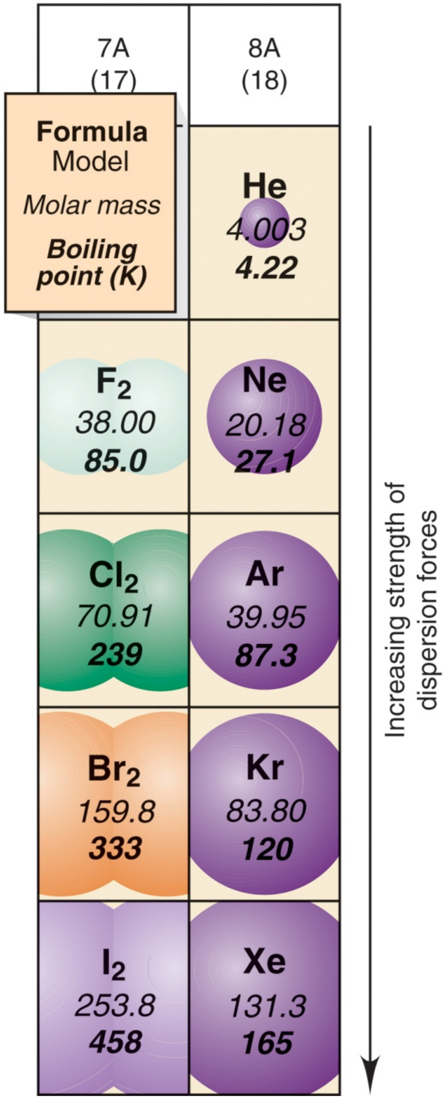
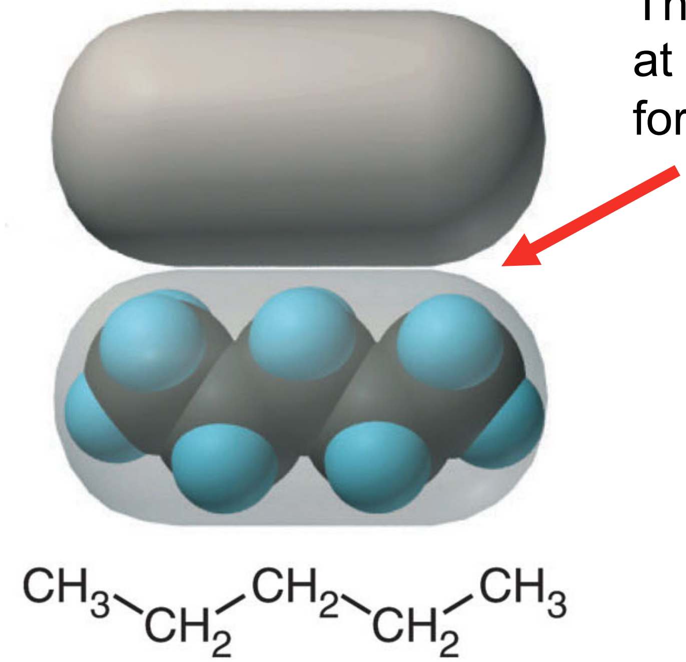


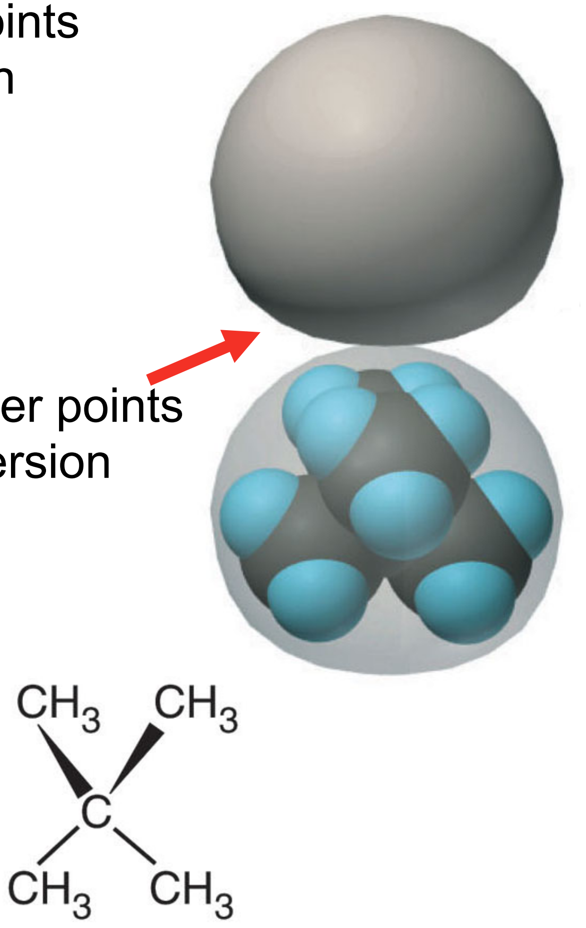
Figure 12.18 Molecular shape, intermolecular contact, and boiling point.



There are more points at which dispersion forces act.

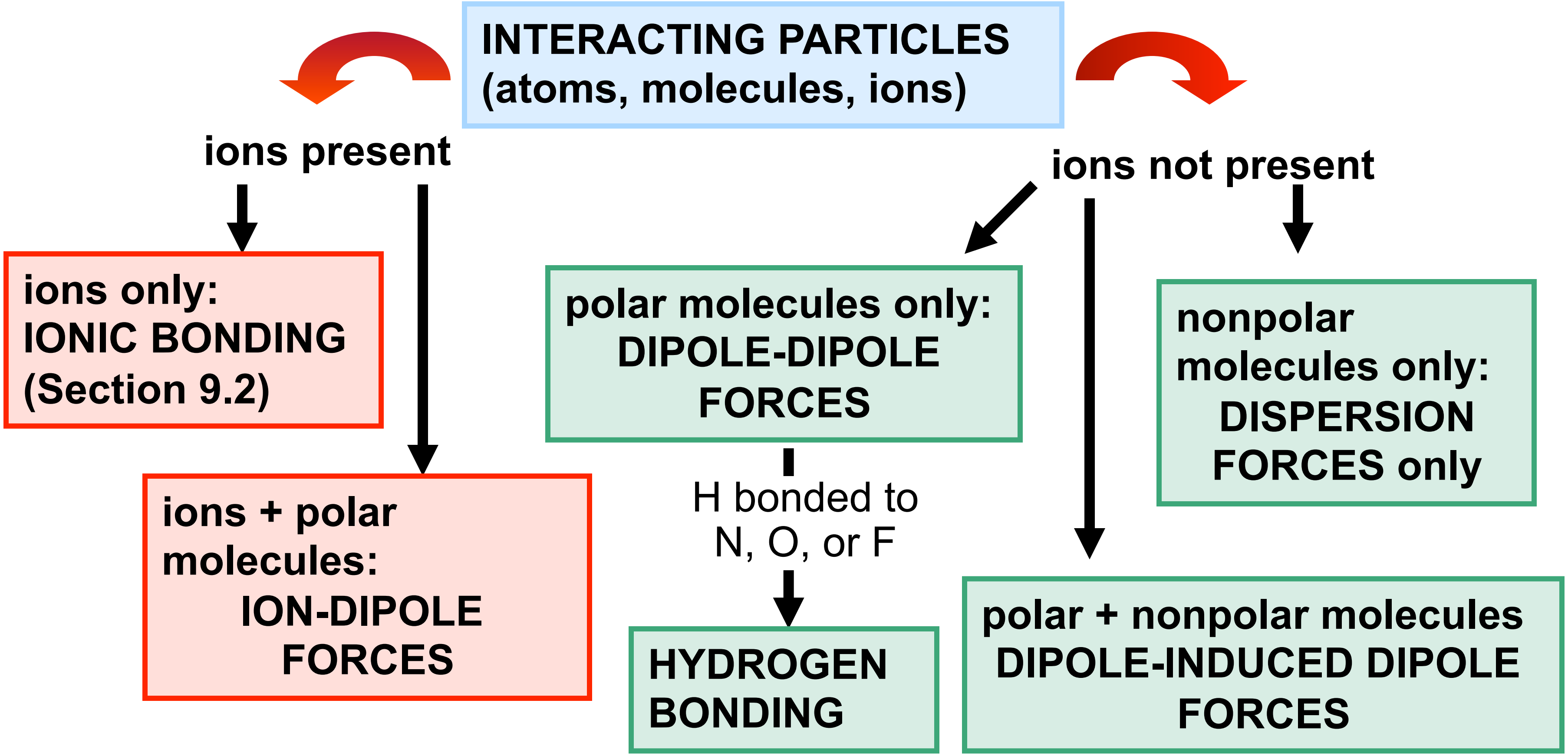
n-Pentane, bp = 36.1°C

There are fewer points at which dispersion forces act.



Neopentane, bp = 9.5°C

Figure 12.19 Determining the intermolecular forces in a sample.



INTERACTING PARTICLES (atoms, molecules, ions)

ions present

ions only: **IONIC BONDING** **(Section 9.2)**

ions + polar molecules: **ION-DIPOLE FORCES**

ions not present

polar molecules only: **DIPOLE-DIPOLE FORCES**

H bonded to N, O, or F

HYDROGEN BONDING

polar + nonpolar molecules **DIPOLE-INDUCED DIPOLE FORCES**

nonpolar molecules only: **DISPERSION FORCES only**

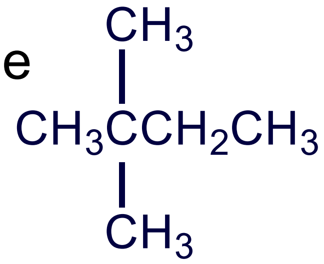
DISPERSION FORCES ALSO PRESENT

Sample Problem 12.4 Predicting the Types of Intermolecular Forces

PROBLEM: For each pair of substances, identify the key bonding and/or intermolecular force(s), and predict which one of the pair has the higher boiling point:

(a) $MgCl_2$ or PCl_3 **(b)** CH_3NH_2 or CH_3F **(c)** CH_3OH or CH_3CH_2OH

(d) Hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) or 2,2-dimethylbutane



$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_2CH_3$$

PLAN: We examine the formulas and structures for key differences between the members of each pair: Are ions present? Are molecules polar or nonpolar? Is N, O, or F bonded to H? Do molecular compounds have different masses or shapes?

Sample Problem 12.4

Remember that:

- Bonding forces are stronger than nonbonding (intermolecular) forces.
- Hydrogen bonding is a strong type of dipole-dipole force.
- Dispersion forces are decisive when the difference is molar mass or molecular shape.

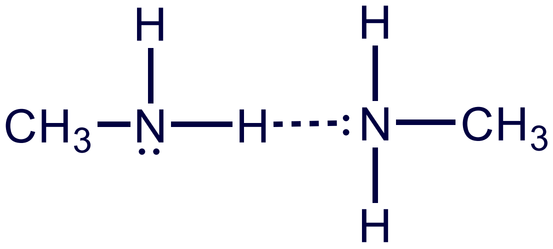
SOLUTION:

(a) $MgCl_2$ consists of Mg^{2+} and Cl^- ions held together by **ionic bonding forces**; PCl_3 consists of polar molecules, so intermolecular **dipole-dipole** forces are present. The ionic bonding forces in $MgCl_2$ are stronger than the dipole-dipole forces in PCl_3.

$MgCl_2$ has a higher boiling point than PCl_3.

Sample Problem 12.4

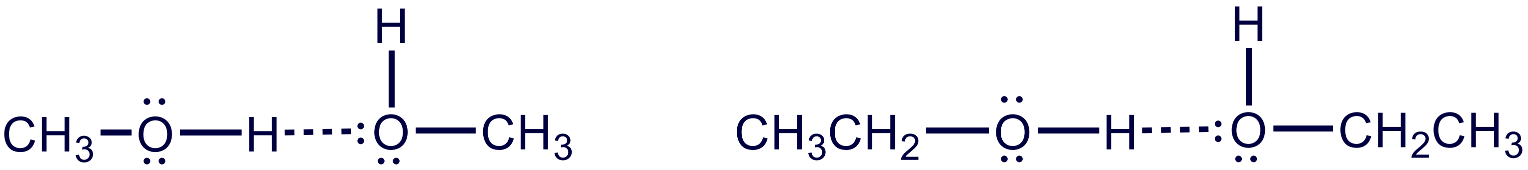
(b) CH_3NH_2 and CH_3F both consist of **polar molecules** of about the same molar mass. CH_3NH_2 has covalent N-H bonds, so it can form **H bonds** between its molecules. CH_3F contains a C-F bond but no H-F bond, so **dipole-dipole** forces occur but not H bonds.



CH_3NH_2 has a higher boiling point than CH_3F.

Sample Problem 12.4

(c) CH_3OH and CH_3CH_2OH are both **polar molecules** and both contain a covalent O-H bond. Both can therefore form **H bonds**.



$CH_3-\ddot{\underset{..}{O}}-H\cdots:\overset{\overset{H}{|}}{\underset{..}{O}}-CH_3$

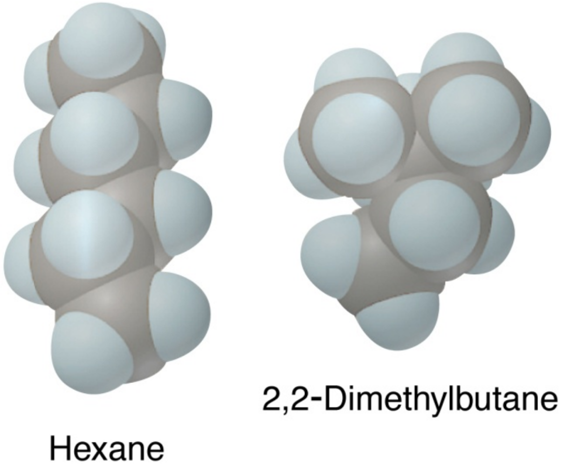
$CH_3CH_2-\ddot{\underset{..}{O}}-H\cdots:\overset{\overset{H}{|}}{\underset{..}{O}}-CH_2CH_3$

CH_3CH_2OH has a larger molar mass than CH_3OH and its **dispersion forces** are therefore stronger.

CH_3CH_2OH has a higher boiling point than CH_3OH.

Sample Problem 12.4

(d) Hexane and 2,2-dimethylbutane are both **nonpolar molecules** and therefore experience **dispersion forces** as their only intermolecular force. They have equal molar masses but different molecular shapes.



Cylindrical hexane molecules make more intermolecular contact than the more compact 2,2-dimethylbutane molecules.

Hexane has a higher boiling point than 2,2-dimethylbutane.

Sample Problem 12.4

CHECK:

The actual boiling points show our predictions are correct:

(a) $MgCl_2$ (1412°C) and PCl_3 (76°C)

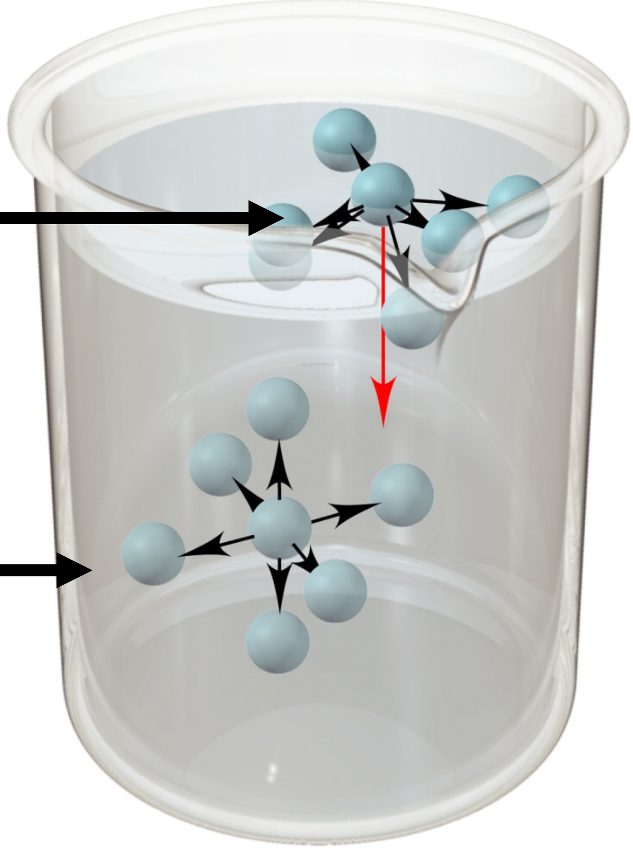
(b) CH_3NH_2 (-6.3°C) and CH_3F (-78.4°C)

(c) CH_3OH (64,7°C) and CH_3CH_2OH (78.5°C)

(d) Hexane (69°C) and 2,2-dimethylbutane (49.7°C)

Remember that ***dispersion forces are always present***, but in (a) and (b) they are much less significant than the other forces that occur.

Figure 12.20 **The molecular basis of surface tension.**



A surface molecule experiences a *net attraction downward*. This causes a liquid surface to have the smallest area possible.

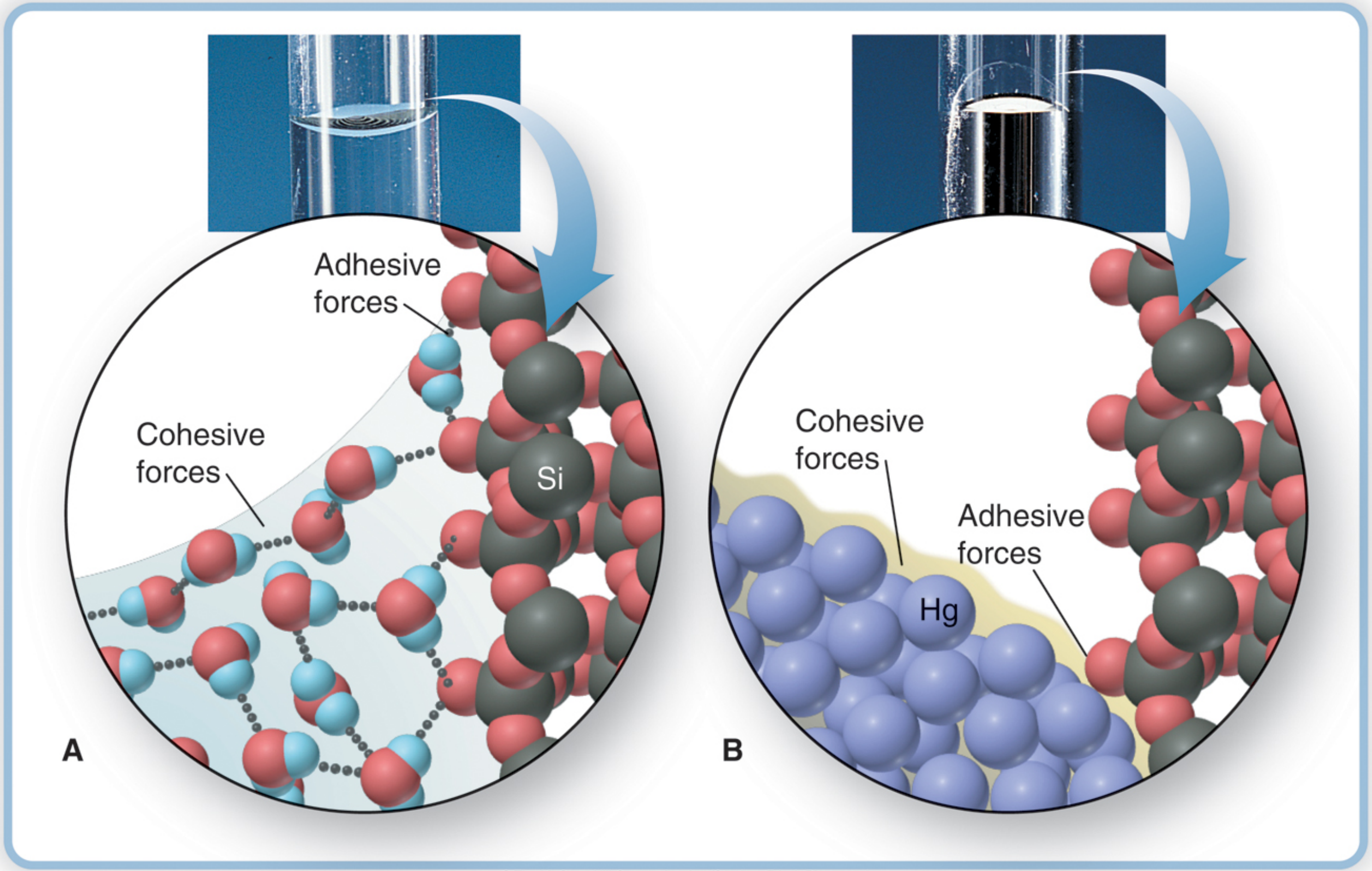
An interior molecule is attracted by others on all sides.

Surface tension is the energy required to increase the surface area of a liquid. The ***stronger*** the forces between the particles the ***higher*** the surface tension.

Table 12.3 Surface Tension and Forces Between Particles

Substance	Formula	Surface Tension (J/m^2) at 20^0C	Major Force(s)
Diethyl ether	$CH_3CH_2OCH_2CH_3$	$1.7x10^{-2}$	Dipole-dipole; dispersion
Ethanol	CH_3CH_2OH	$2.3x10^{-2}$	H bonding
Butanol	$CH_3CH_2CH_2CH_2OH$	$2.5x10^{-2}$	H bonding; dispersion
Water	H_2O	$7.3x10^{-2}$	H bonding
Mercury	Hg	$48x10^{-2}$	Metallic bonding

Figure 12.21 **Capillary action and the shape of the water or mercury meniscus in glass.**



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A. Water displays a concave meniscus.

B. Mercury displays a convex meniscus.

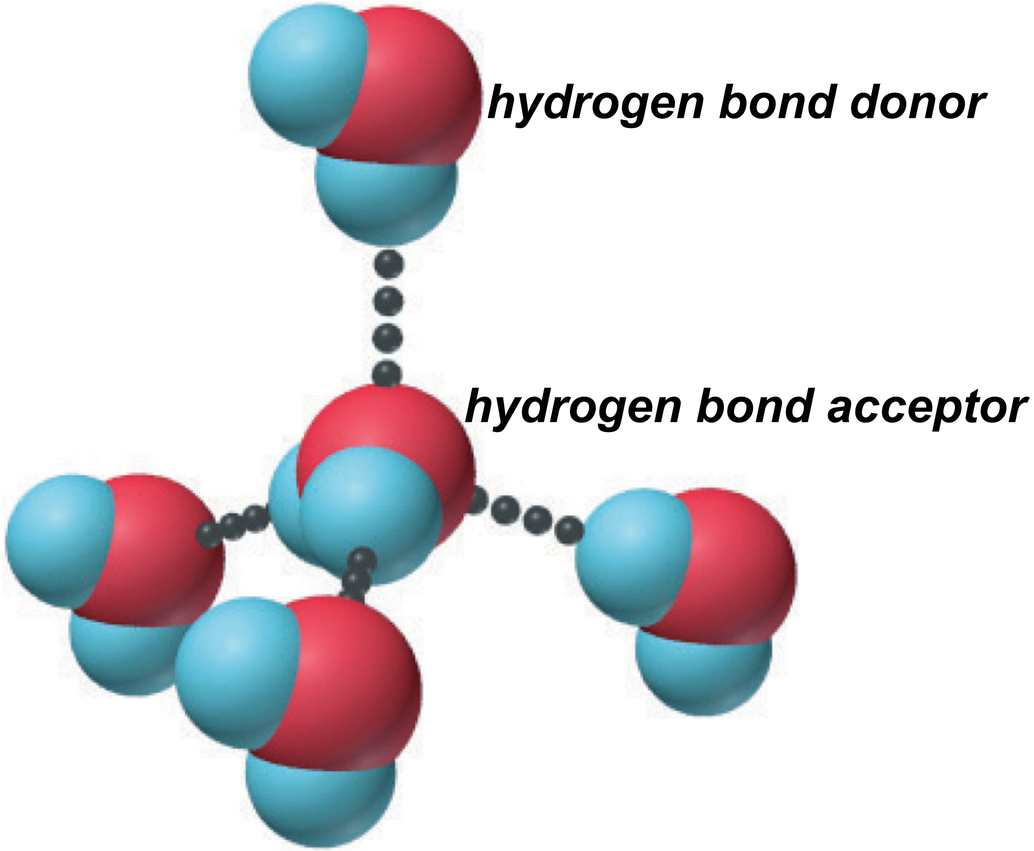
Table 12.4 Viscosity of Water at Several Temperatures

Viscosity is resistance of a fluid to flow.

Temperature (°C)	Viscosity (N·s/m^2)*
20	1.00×10^{-3}
40	0.65×10^{-3}
60	0.47×10^{-3}
80	0.35×10^{-3}

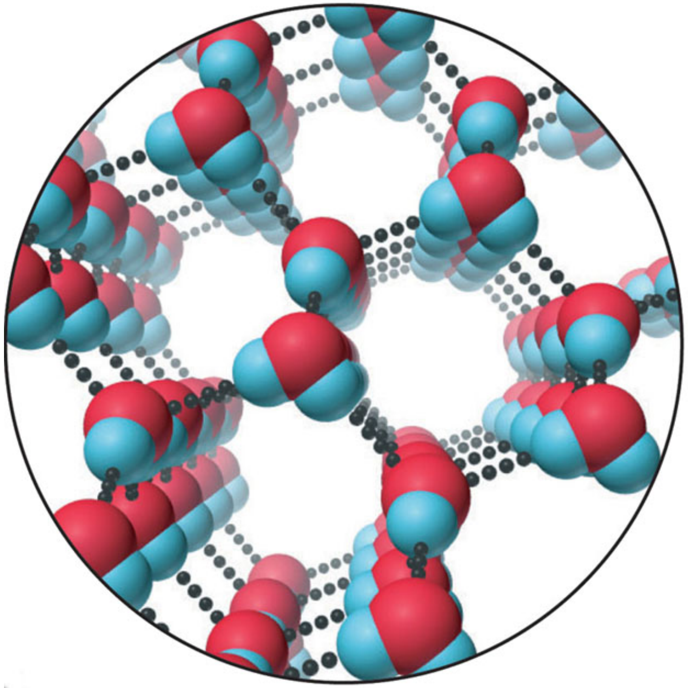
*The units of viscosity are Newton-seconds per square meter.

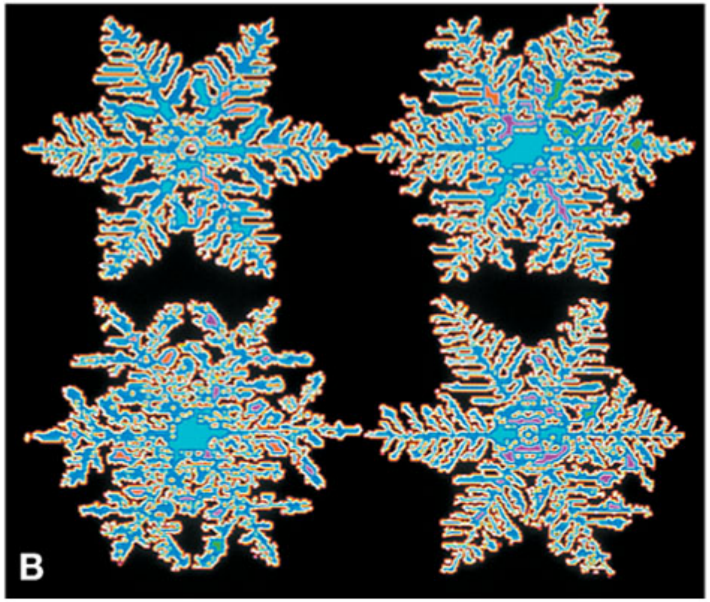
Figure 12.22 H-bonding ability of water.



Each H_2O molecule can form ***four*** H bonds to other molecules, resulting in a tetrahedral arrangement.

Figure 12.23 The hexagonal structure of ice.





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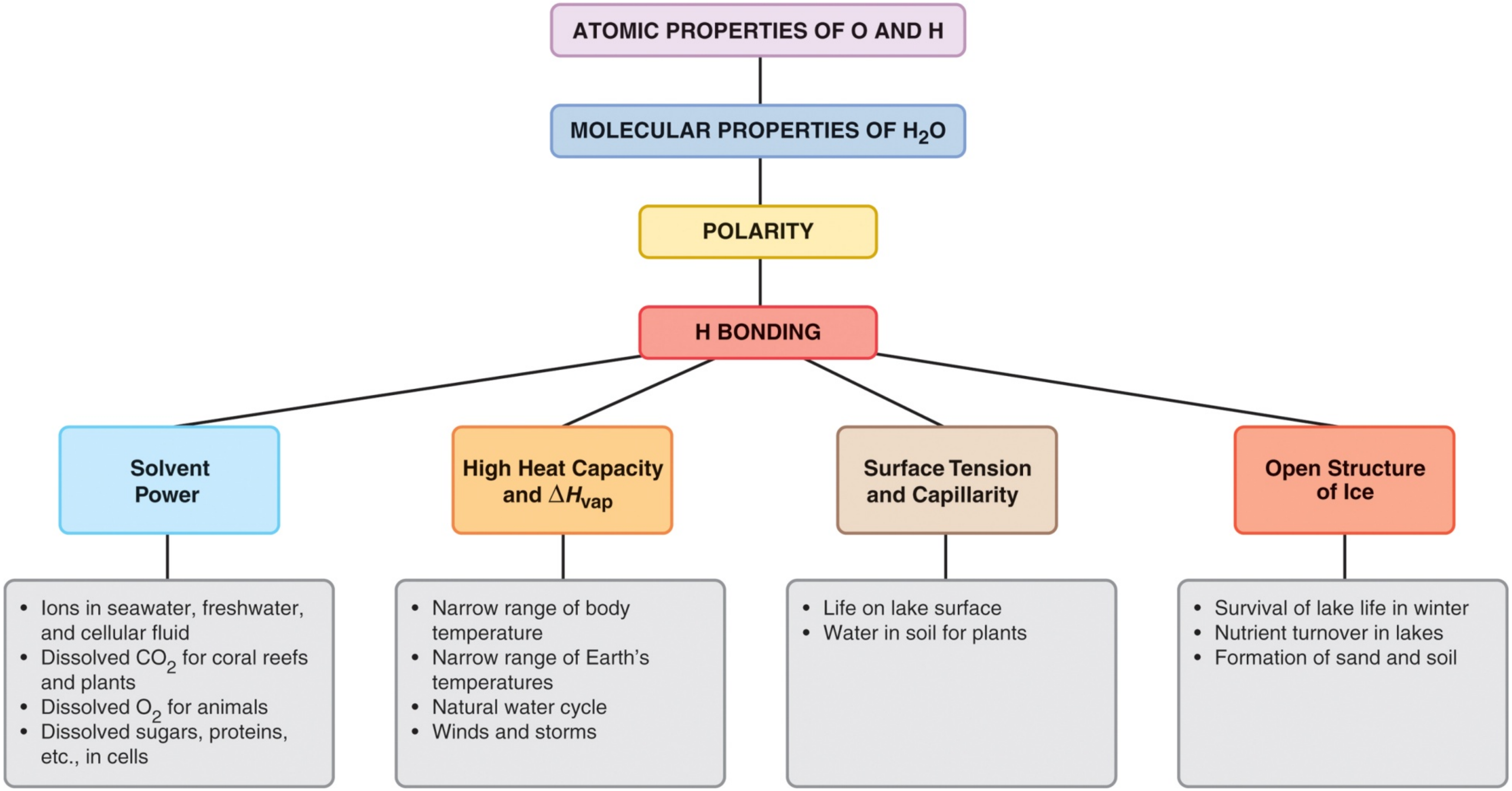
Ice has an open structure due to H bonding. Ice is therefore ***less dense*** than liquid water.

Figure 12.24 The unique macroscopic behavior of water that emerges from its atomic and molecular properties.



ATOMIC PROPERTIES OF O AND H

MOLECULAR PROPERTIES OF H_2O

POLARITY

H BONDING

Solvent Power

- Ions in seawater, freshwater, and cellular fluid
- Dissolved CO_2 for coral reefs and plants
- Dissolved O_2 for animals
- Dissolved sugars, proteins, etc., in cells

High Heat Capacity and ΔH_{vap}

- Narrow range of body temperature
- Narrow range of Earth's temperatures
- Natural water cycle
- Winds and storms

Surface Tension and Capillarity

- Life on lake surface
- Water in soil for plants

Open Structure of Ice

- Survival of lake life in winter
- Nutrient turnover in lakes
- Formation of sand and soil

The Solid State

Solids are divided into two categories:

Crystalline solids have well defined shapes due to the orderly arrangement of their particles.

Amorphous solids lack orderly arrangement and have poorly defined shapes.

A ***crystal*** is composed of particles packed in an orderly three-dimensional array called the ***crystal lattice***.

Figure 12.25 The beauty of crystalline solids.

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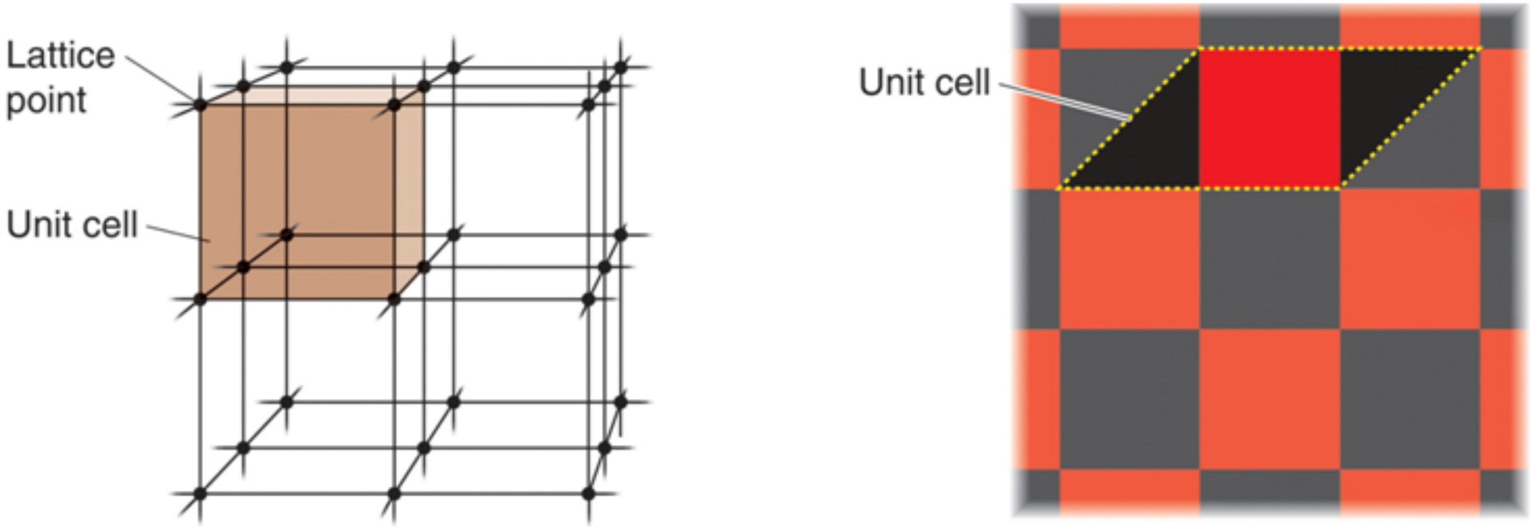
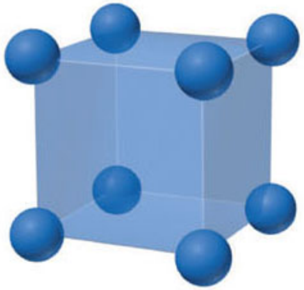
Figure 12.26 The crystal lattice and the unit cell.



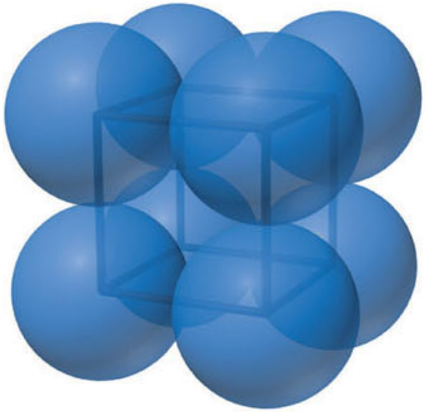
A Portion of 3-D lattice

B 2-D analogy for unit cell and lattice

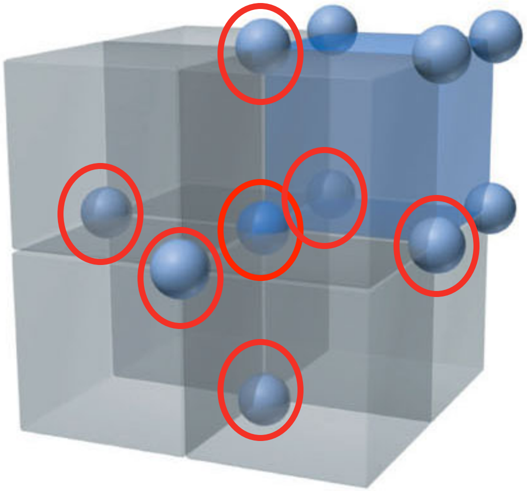
Figure 12.27A Simple cubic unit cell.



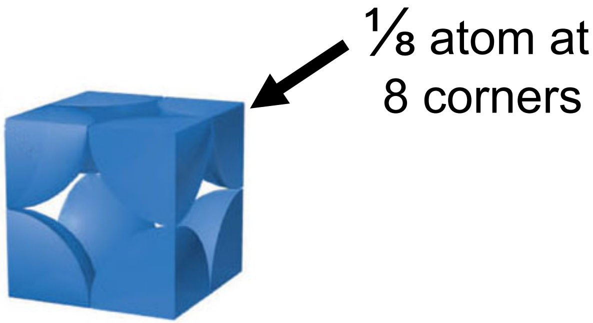
Expanded view.



Space-filling view.

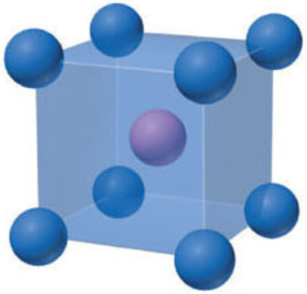


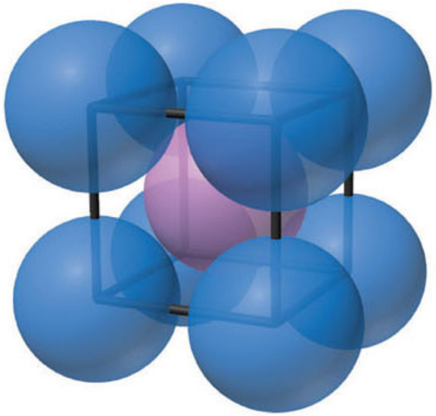
Coordination number = 6

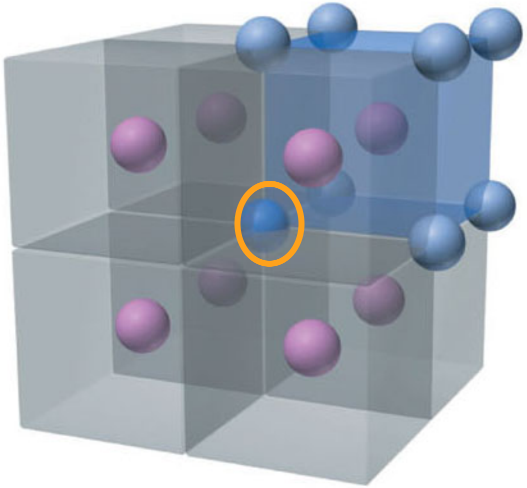


Atoms/unit cell = (⅛ x 8) = 1

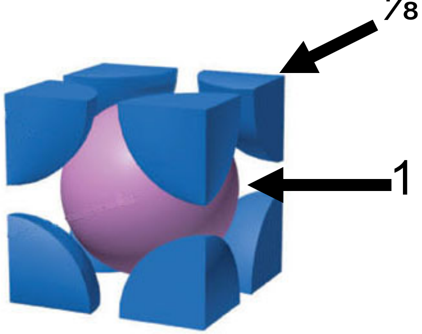
Figure 12.27B Body-centered cubic unit cell.







Coordination number = 8

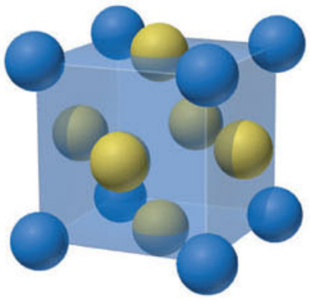


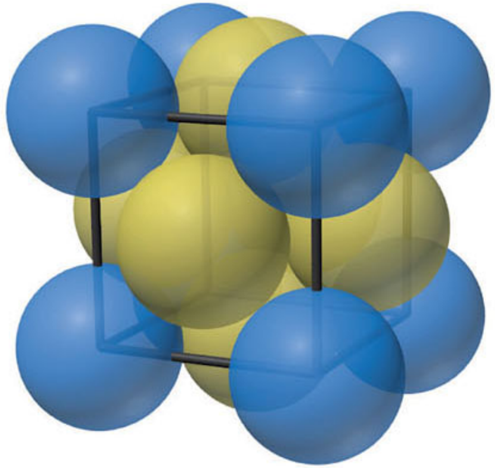
⅛ atom at 8 corners

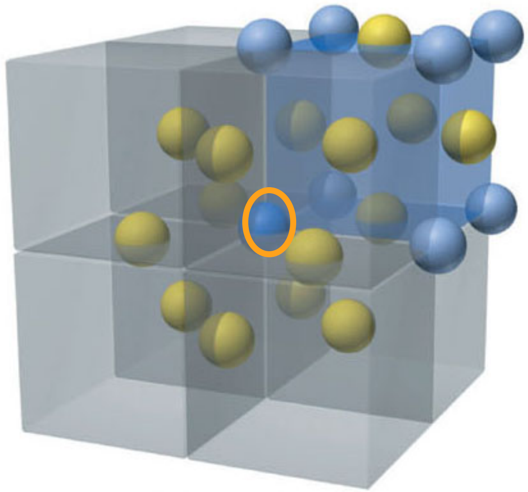
1 atom at center

Atoms/unit cell = (⅛ x 8) + 1 = 2

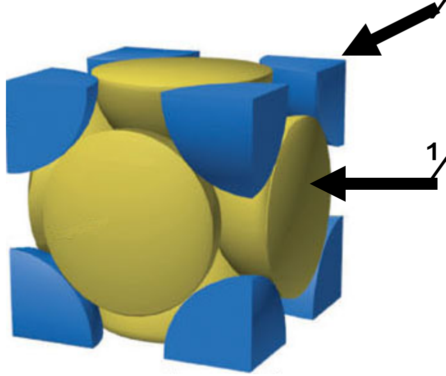
Figure 12.27C **The face-centered cubic cell.**







Coordination number = 12

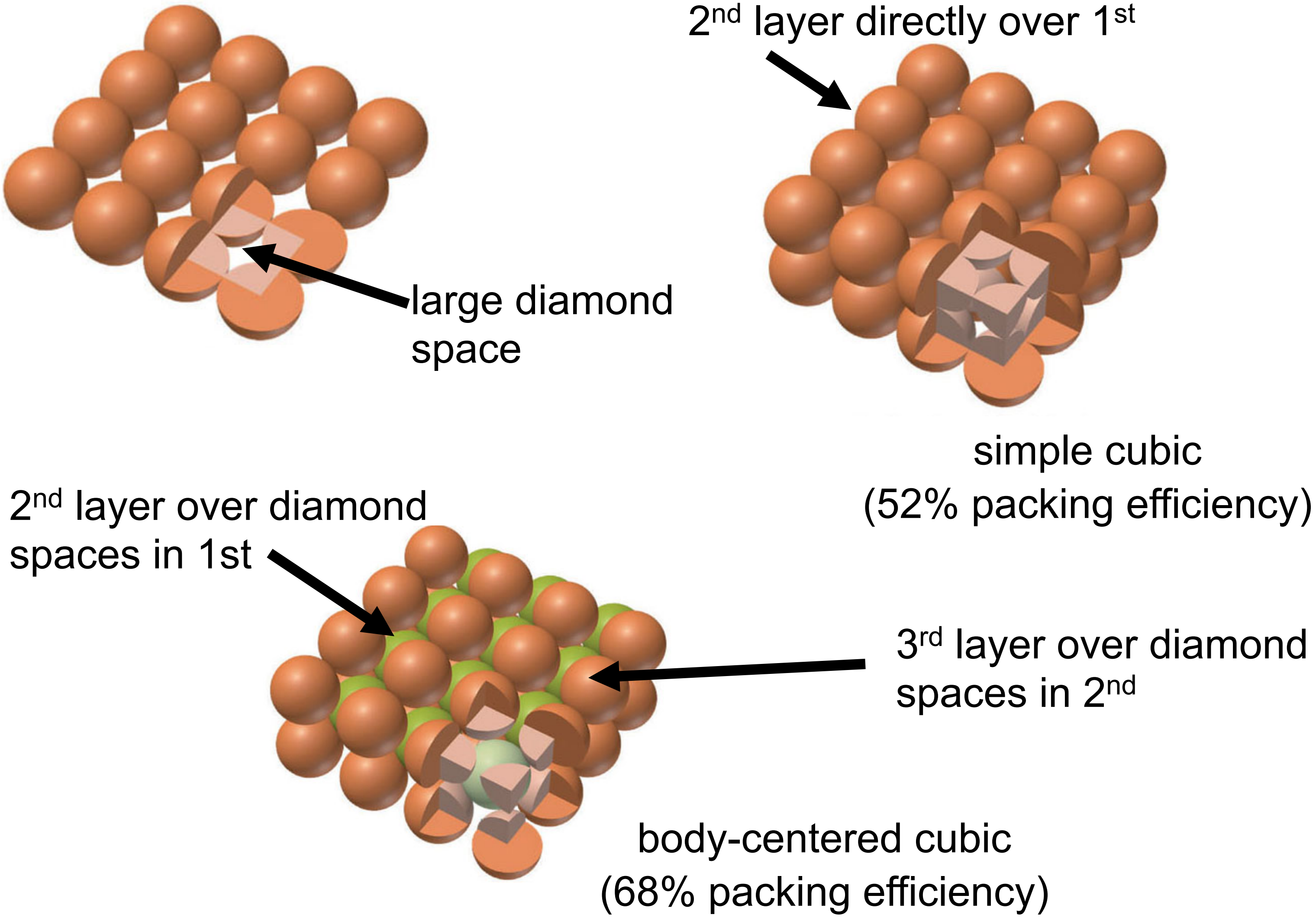


⅛ atom at 8 corners

½ atom at 6 faces

Atoms/unit cell = (⅛ x 8) + (½ x 6) = 4

Figure 12.28 **Packing spheres to obtain three cubic and hexagonal cells.**



2nd layer directly over 1st

large diamond space

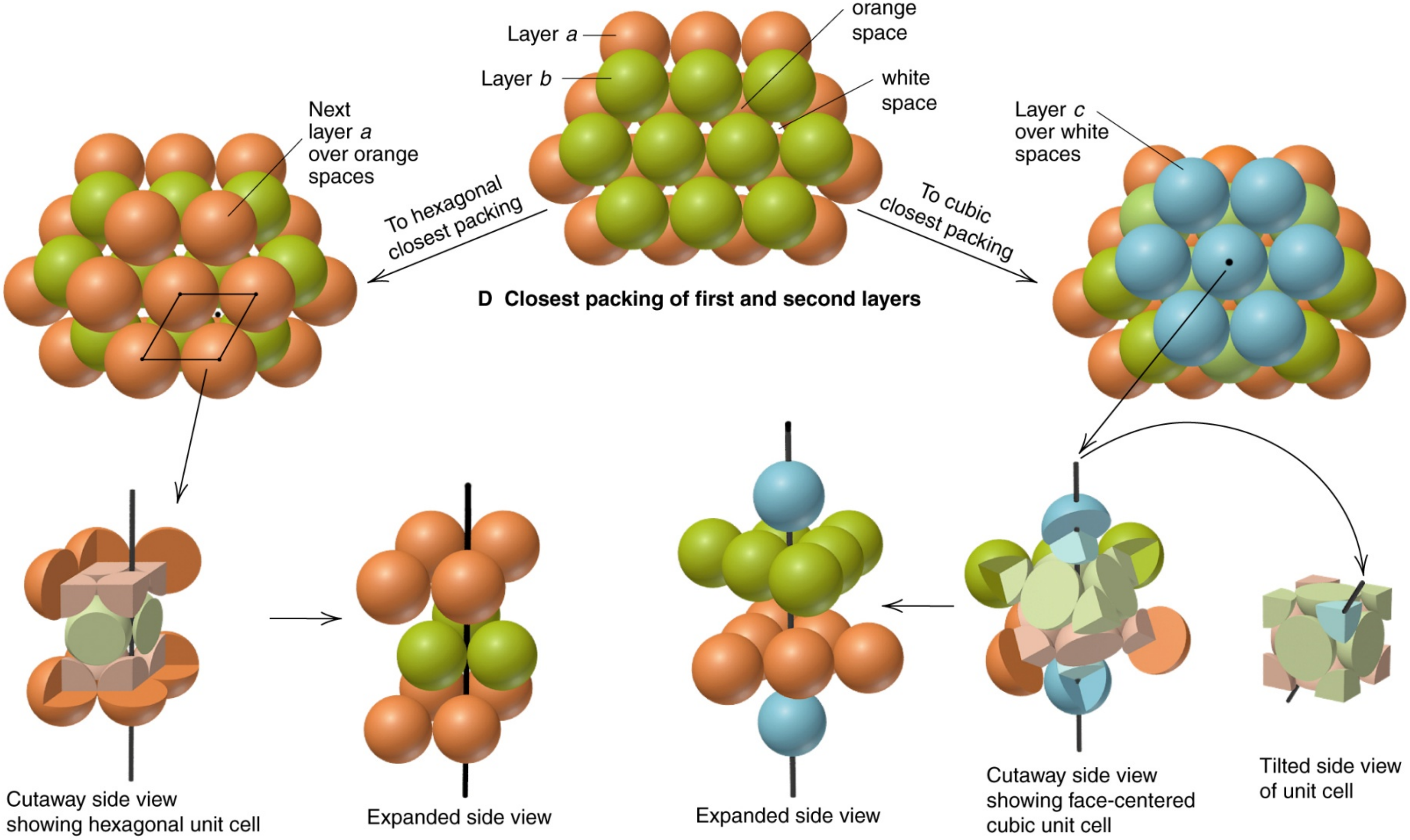
simple cubic
(52% packing efficiency)

2nd layer over diamond spaces in 1st

3rd layer over diamond spaces in 2nd

body-centered cubic
(68% packing efficiency)

Figure 12.28 continued



D Closest packing of first and second layers

E Hexagonal closest packing (*abab*...) (74%)

F Cubic closest packing (*abcabc*...) (74%)

Sample Problem 12.5 **Determining Atomic Radius**

PROBLEM: Barium is the largest nonradioactive alkaline earth metal. It has a body-centered cubic unit cell and a density of 3.62 g/cm^3. What is the atomic radius of barium?

(Volume of a sphere = $\frac{4}{3}\pi r^3$.)

PLAN: An atom is spherical, so we can find its radius from its volume. If we multiply the reciprocal of density (volume/mass) by the molar mass (mass/mol), we find the volume/mole of Ba metal. The metal crystallizes in a body-centered cubic structure, so 68% of this volume is occupied by 1 mol of the Ba atoms themselves (see Figure 12.28C). Dividing by Avogadro's number gives the volume of one Ba atom, from which we find the radius.

Sample Problem 3.6

PLAN:

density (g/cm^3) of Ba metal

find reciprocal and
multiply by $\mathcal{M}$(g/mol)

volume (cm^3) per mole of Ba metal

multiply by packing efficiency

volume (cm^3) per mole of Ba atoms

divide by Avogadro's number

volume (cm^3) of Ba atom

$$V = \frac{4}{3}\pi r^3$$

radius (cm) of Ba atom

Sample Problem 12.5

SOLUTION:

$$\text{Volume/mole of Ba metal} = \frac{1}{\text{density}} \times \mathcal{M} = \frac{1\ \text{cm}^3}{3.62\ \text{g Ba}} \times \frac{137.3\ \text{g Ba}}{1\ \text{mol Ba}}$$

$$= 37.9\ \text{cm}^3\text{/mol Ba}$$

$$\text{Volume/mole of Ba atoms} = \text{cm}^3\text{/mol Ba} \times \text{packing efficiency}$$

$$= 37.9\ \text{cm}^3\text{/mol Ba} \times 0.68$$

$$= 26\ \text{cm}^3\text{/mol Ba atoms}$$

$$\text{Volume of Ba atom} = \frac{26\ \text{cm}^3}{1\ \text{mol Ba atoms}} \times \frac{1\ \text{mol Ba atoms}}{6.022\text{x}10^{23}\ \text{Ba atoms}}$$

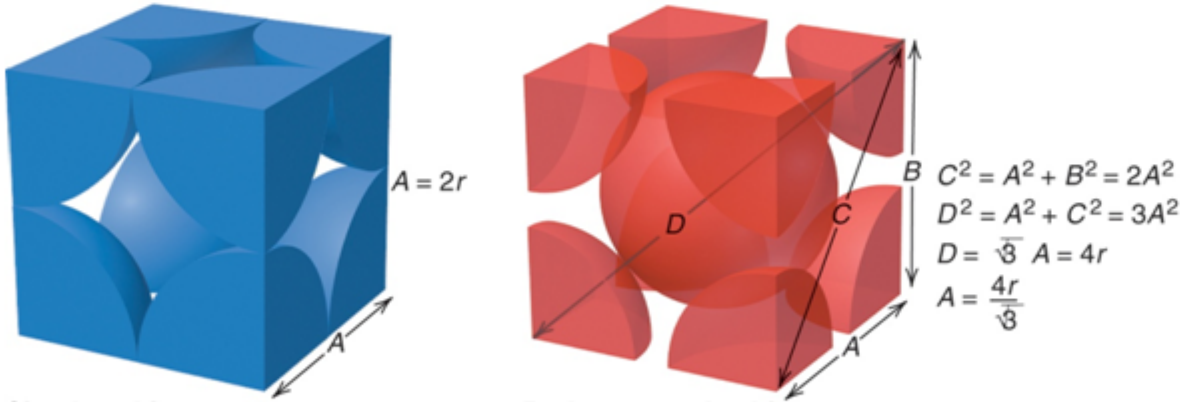
$$= 4.3 \times 10^{-23}\ \text{cm}^3\text{/Ba atom}$$

Sample Problem 12.5

$$V \text{ of Ba atom} = \frac{4}{3}\pi r^3$$

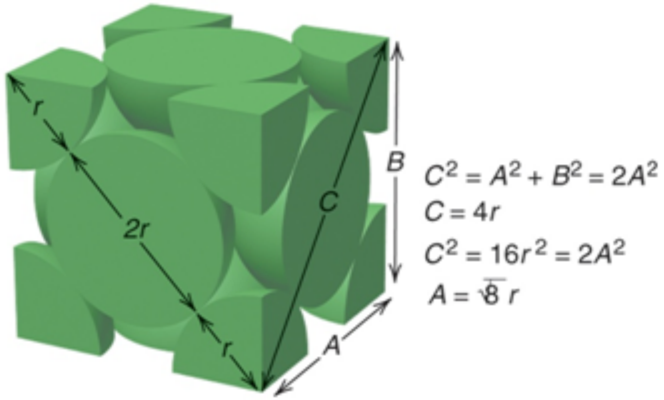
$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3(4.3\text{x}10^{-23}\text{cm}^3)}{4 \text{ x } 3.14}} \quad \boxed{= 2.2 \text{ x } 10^{-8} \text{ cm}}$$

Figure 12.29 Edge length and atomic (ionic) radius in the three cubic unit cells.



Simple cubic

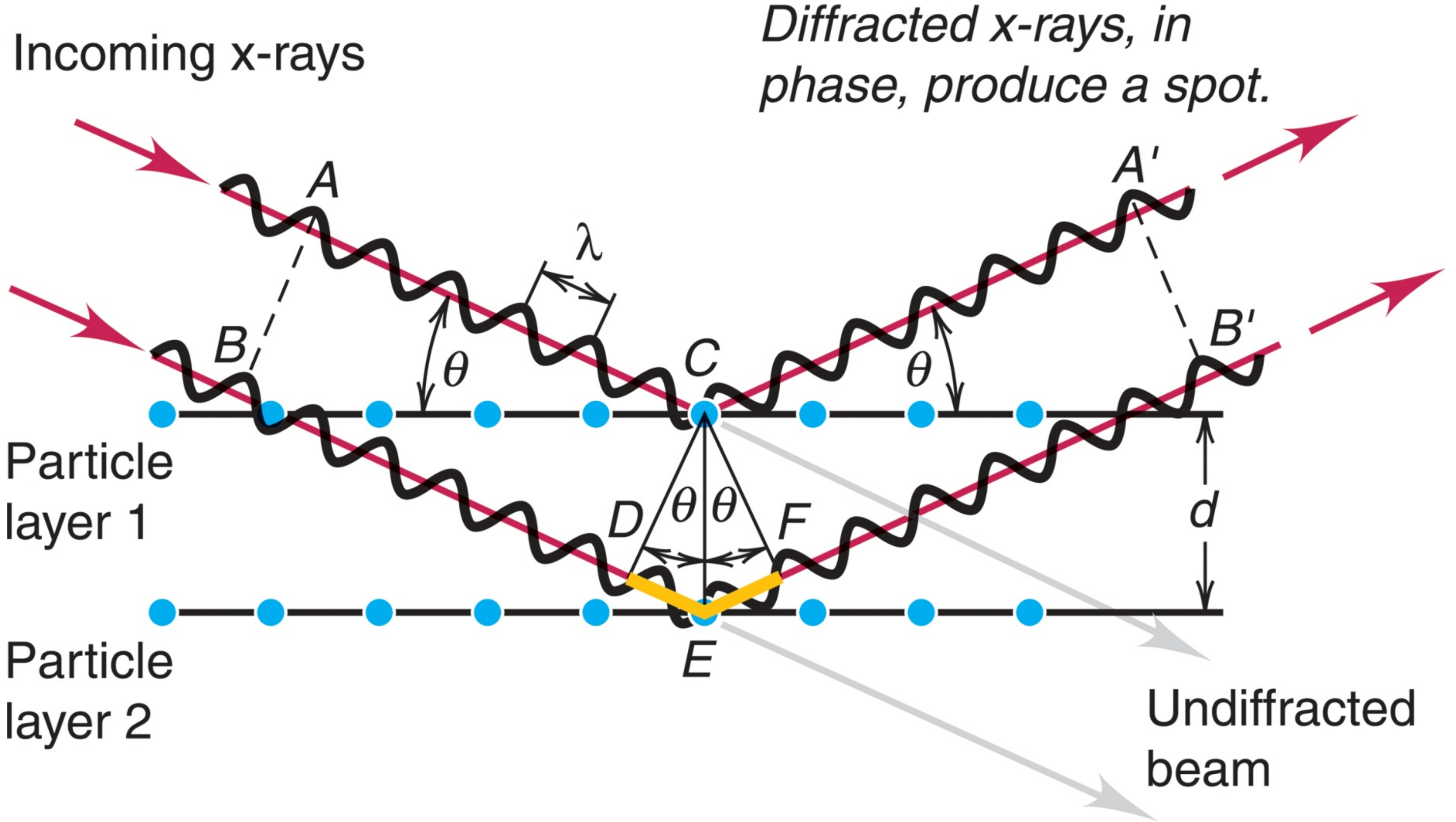
Body-centered cubic



Face-centered cubic

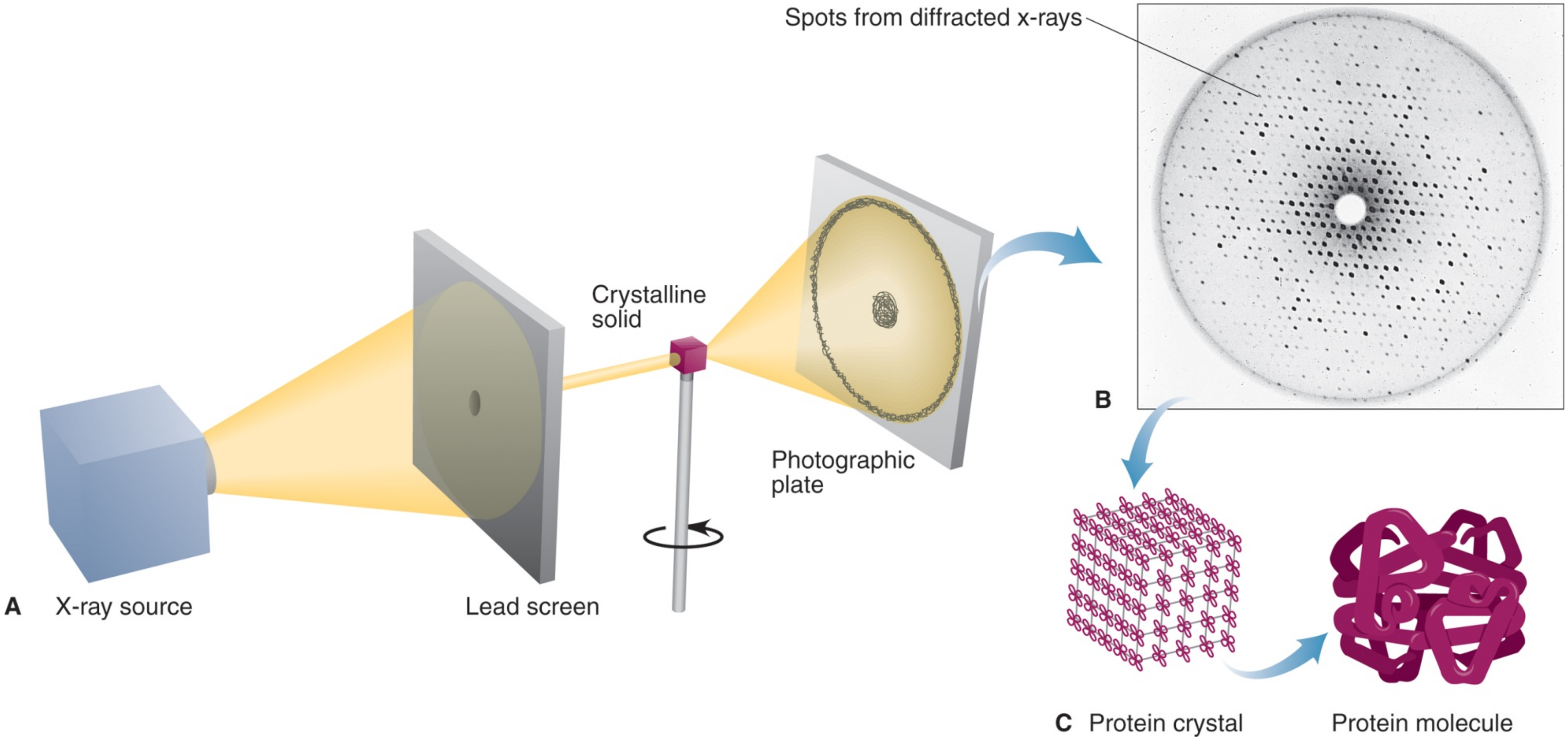
Tools of the Laboratory

Figure B12.1 **Diffraction of x-rays by crystal planes.**



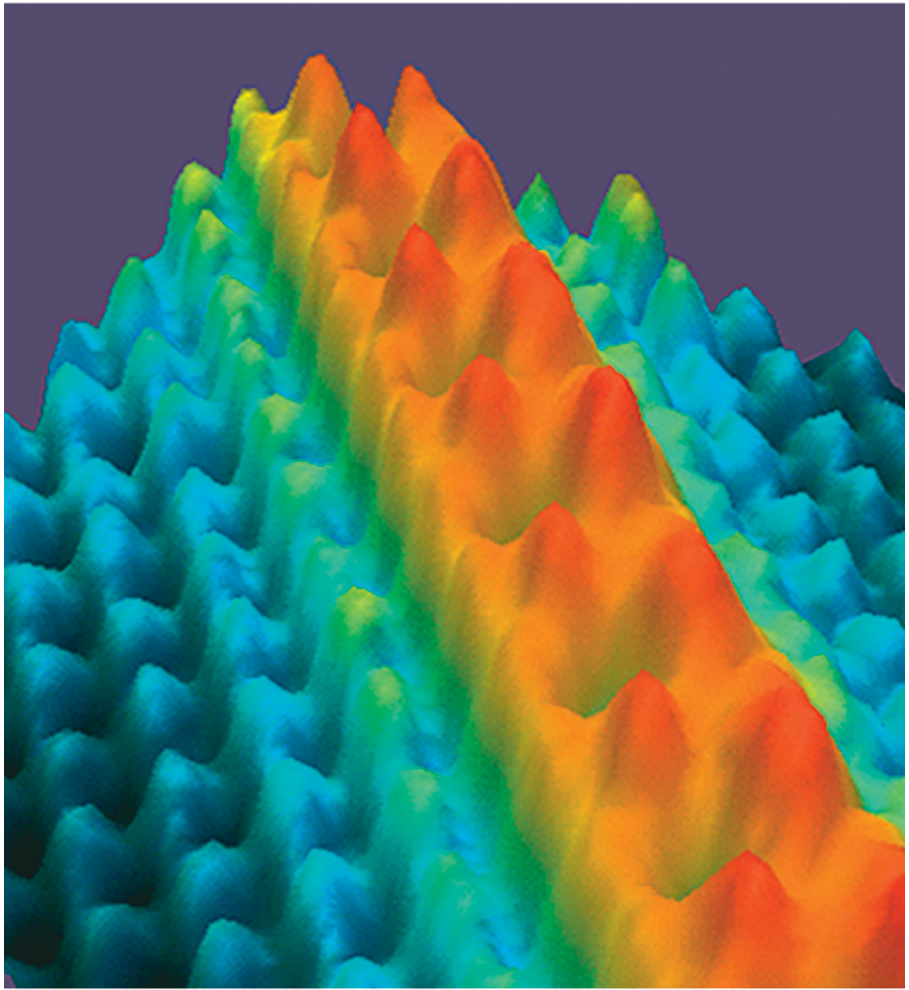
Tools of the Laboratory

Figure B12.2 Formation of an x-ray diffraction pattern of the protein hemoglobin.



Tools of the Laboratory

Figure B12.3 **A scanning tunneling micrograph of cesium atoms (*red*) on gallium arsenide.**



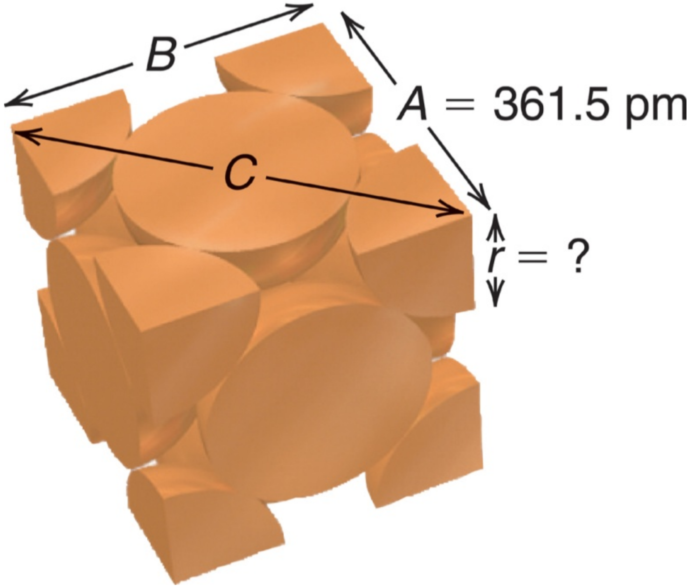
Courtesy National Institute of Standards and Technology

Cesium atoms on gallium arsenide surface

Sample Problem 12.6 Determining Atomic Radius from the Unit Cell

PROBLEM: Copper adopts cubic closest packing, and the edge length of the unit cell is 361.5 pm. What is the atomic radius of copper?

PLAN: Cubic closest packing has a face-centered cubic unit cell, and we know the edge length. With Figure 12.29 and *A* = 361.5 pm, we solve for *r*.



Sample Problem 12.6

SOLUTION:

Using the Pythagorean theorem to find C, the diagonal of the cell's face:

$$C = \sqrt{A^2 + B^2}$$

The unit cell is a cube, so $A = B$, Therefore

$$C = \sqrt{2A^2} = \sqrt{2(361.5\ \text{pm})^2} = 511.2\ \text{pm}$$

$$C = 4r\text{, so } r = \frac{511.2\ \text{pm}}{4}\ \boxed{\mathbf{= 127.8\ pm}}$$

Types of Crystalline Solids

Atomic solids consist of individual atoms held together only by dispersion forces.

Molecular solids consist of individual molecules held together by various combinations of intermolecular forces.

Ionic solids consist of a regular array of cations and anions.

Metallic solids have exhibit an organized crystal structure.

Network Covalent solids consist of atoms covalently bonded together in a three-dimensional network.

Figure 12.30

Cubic closest packing of frozen argon (face-centered cubic cell).

Figure 12.31

Cubic closest packing (face-centered unit cell) of frozen CH_4.

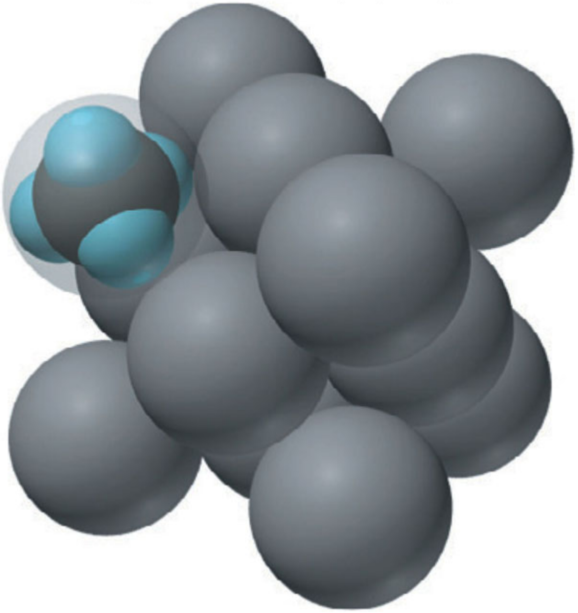


Table 12.5 Characteristics of the Major Types of Crystalline Solids

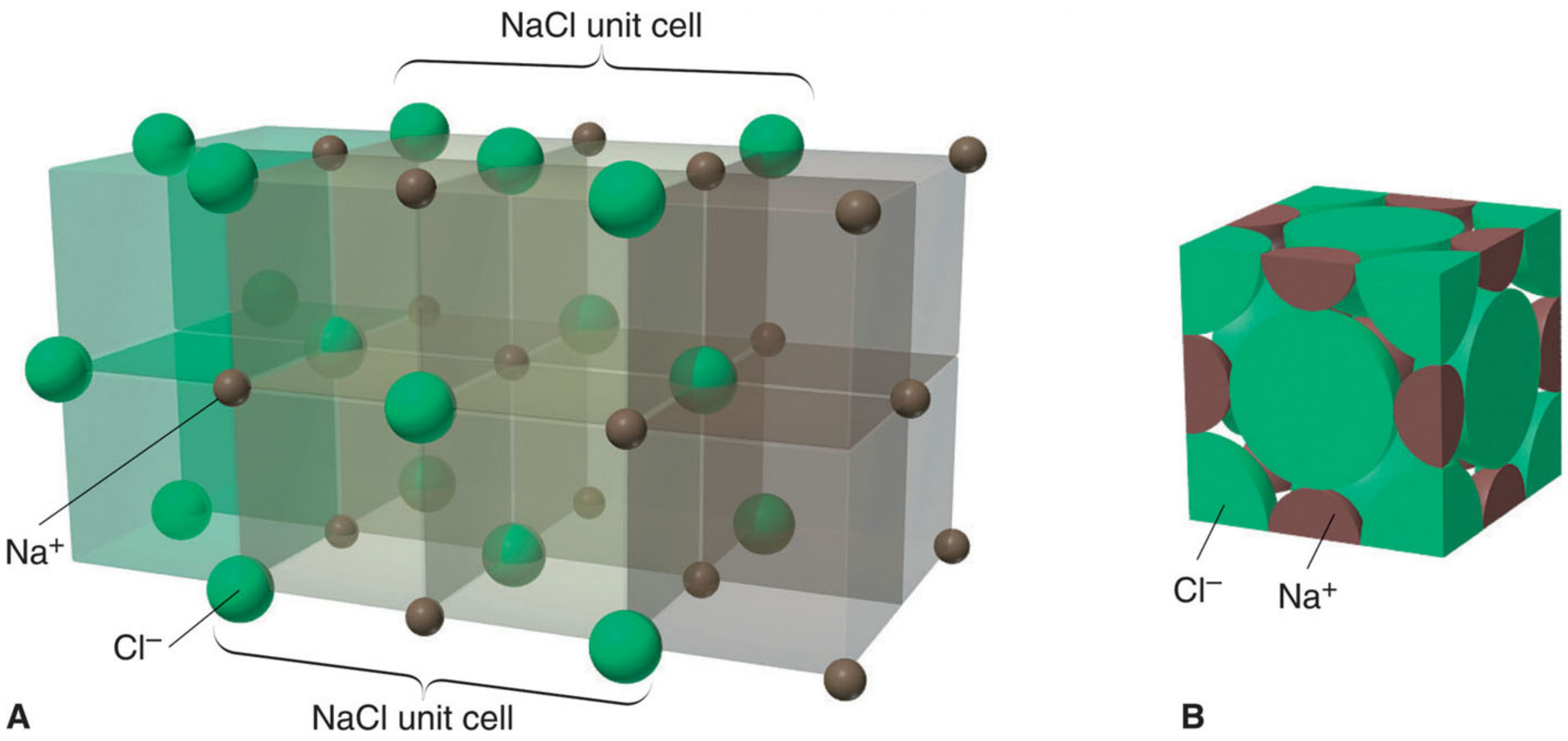
Type	Particle(s)	Interparticle Forces	Physical Properties	Examples [mp, °C]
Atomic	Atoms	Dispersion	Soft, very low mp, poor thermal and electrical conductors	Group 8A(18) (Ne [-249) to Rn [-71])
Molecular	Molecules	Dispersion, dipole-dipole, H bonds	Fairly soft, low to moderate mp, poor thermal and electrical conductors	*Nonpolar*[*] O_2 [-219], C_4H_{10} [-138] Cl_2 [-101], C_6H_{14} [-95] P_4 [44.1] *Polar* SO_2 [-73], $CHCl_3$ [-64] HNO_3 [-42], H_2O [0.0] CH_3COOH [17]

[*] Nonpolar molecular solids are arranged in order of increasing molar mass. Note the correlation with increasing melting point (mp).

Table 12.5 Characteristics of the Major Types of Crystalline Solids

Type	Particle(s)	Interparticle Forces	Physical Properties	Examples [mp, °C]
Ionic	Positive and negative ions	Ion-ion attraction	Hard and brittle, high mp, good thermal and electrical conductors when molten	NaCl [801] CaF_2 [1423] MgO [2852]
Metallic	Atoms	Metallic bond	Soft to hard, low to very high mp, excellent thermal and electrical conductors, malleable and ductile	Na [97.8] Zn [420] Fe [1535]
Network covalent	Atoms	Covalent bond	Very hard, very high mp, usually poor thermal and electrical conductors	SiO_2 (quartz) [1610] C (diamond) [~4000]

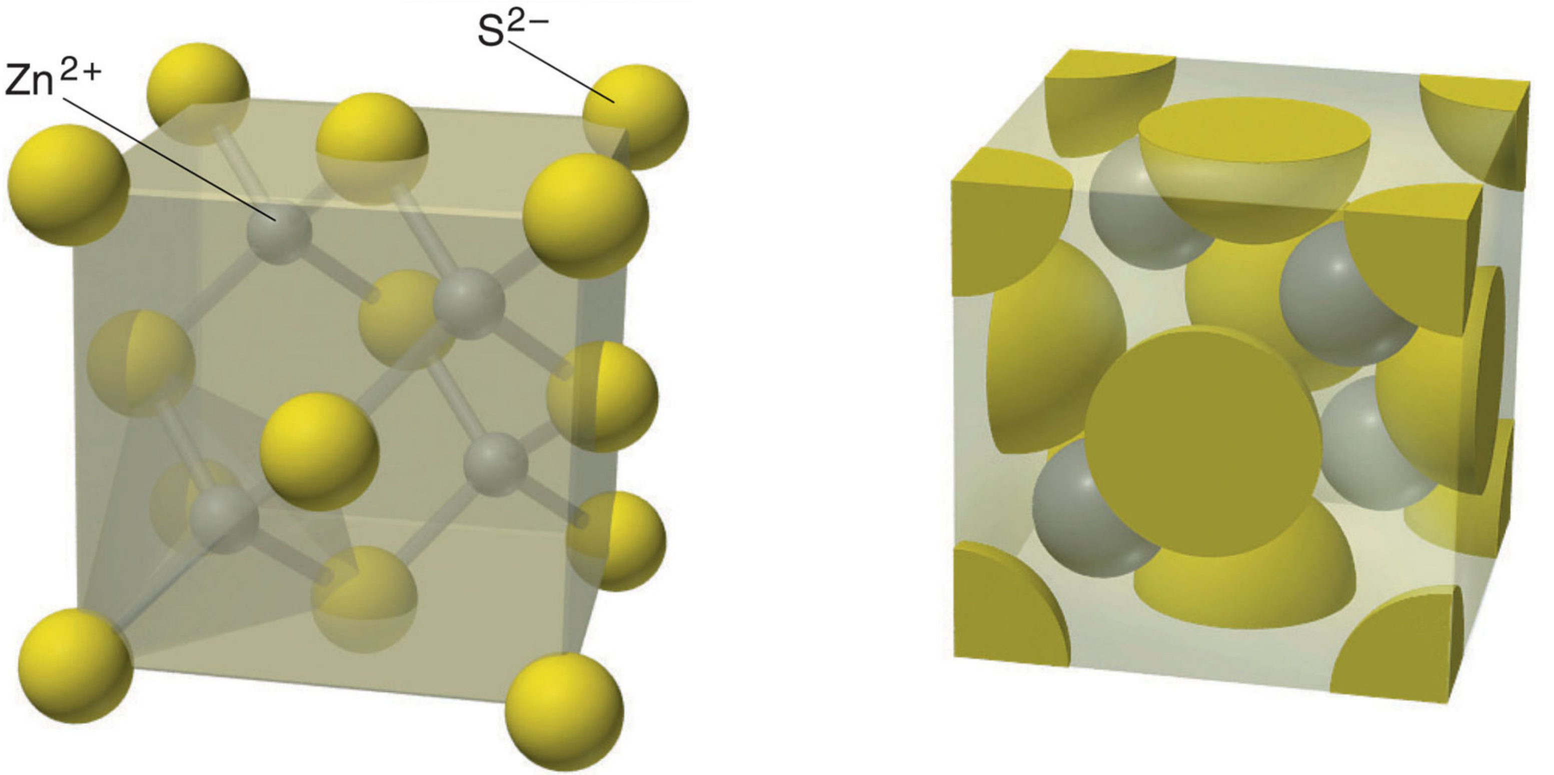
Figure 12.32 The sodium chloride structure.



Expanded view.

Space-filling model.

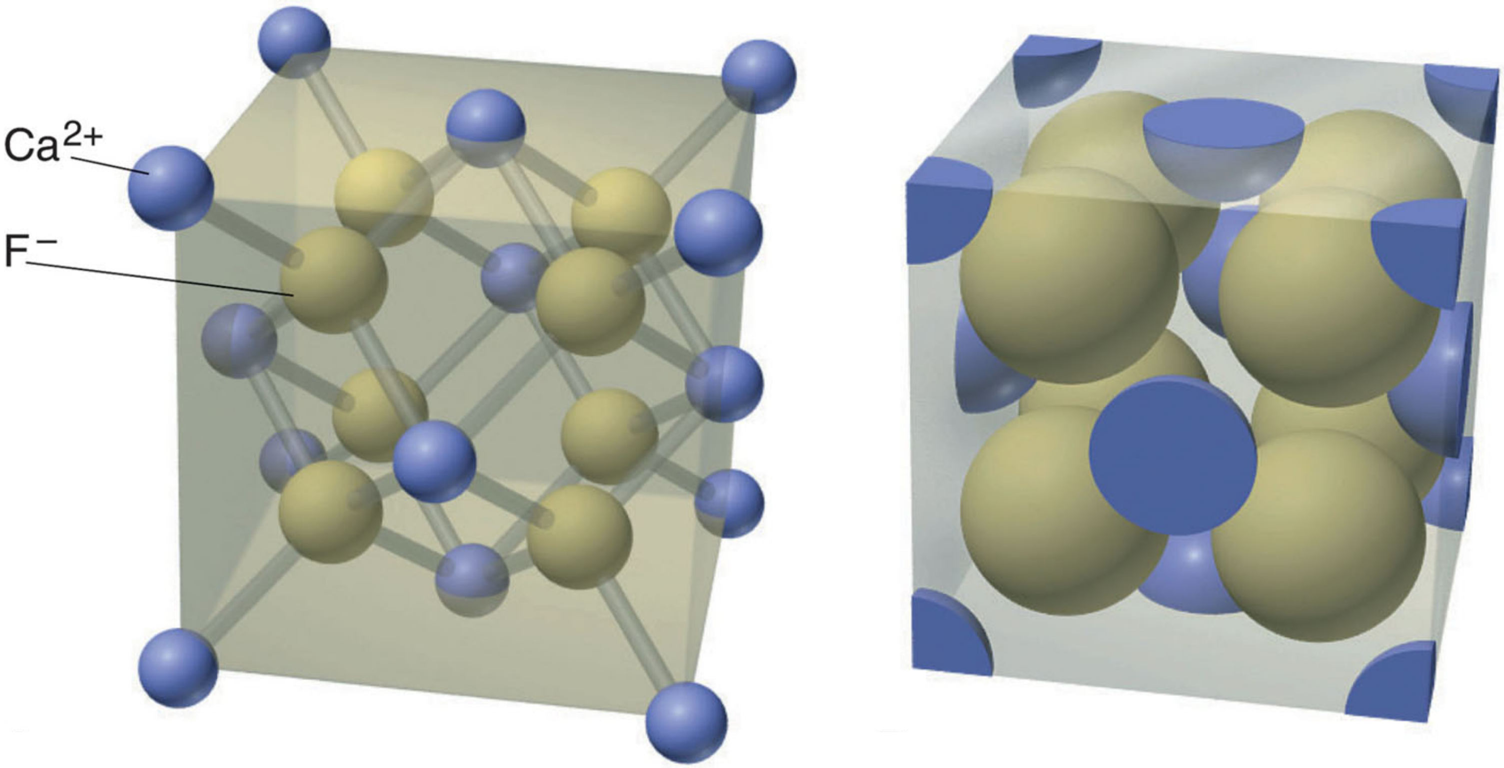
Figure 12.33 The zinc blende structure.



A. Expanded view (with bonds shown for clarity).

B. The unit cell is expanded a bit to show interior ions.

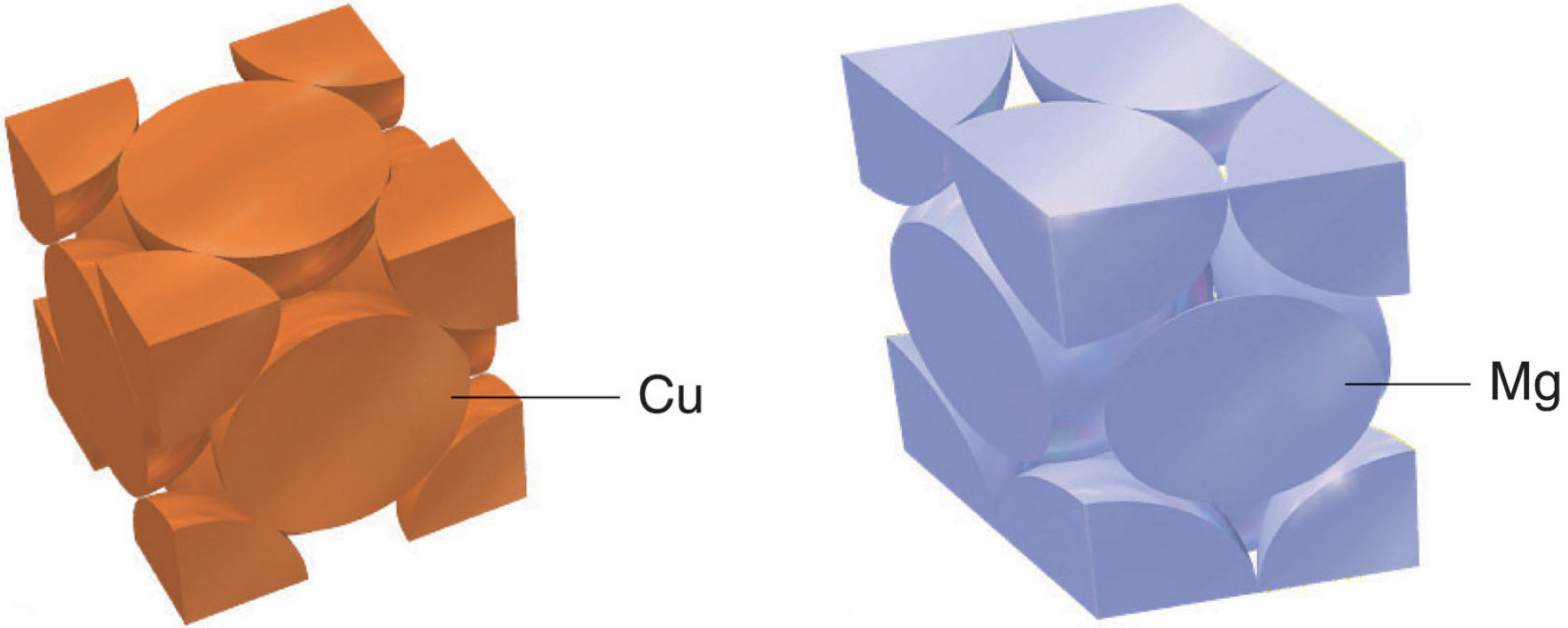
Figure 12.34 The fluorite structure.



A. Expanded view (with bonds shown for clarity).

B. The unit cell is expanded a bit to show interior ions.

Figure 12.35 **Crystal structures of metals.**

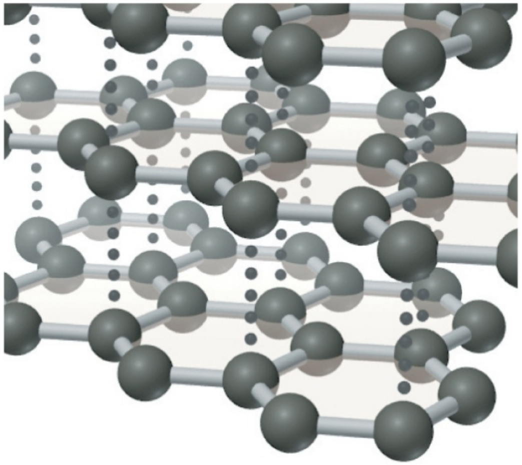


A. Copper adopts cubic closest packing.

B. Magnesium adopts hexagonal closest packing.

Table 12.6 Comparison of the Properties of Diamond and Graphite.

Property	Graphite	Diamond
Density (g/cm^3)	2.27	3.51
Hardness	< 1 (very soft)	10 (hardest)
Melting point (K)	4100	4100
Color	Shiny black	Colorless transparent
Electrical Conductivity	High (along sheet)	None
ΔH_{rxn} for combustion (kJ/mol)	-393.5	-395.4
ΔH°_f (kJ/mol)	0 (standard state)	1.90



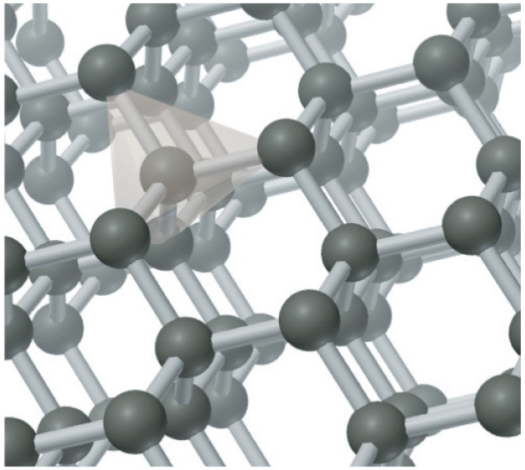
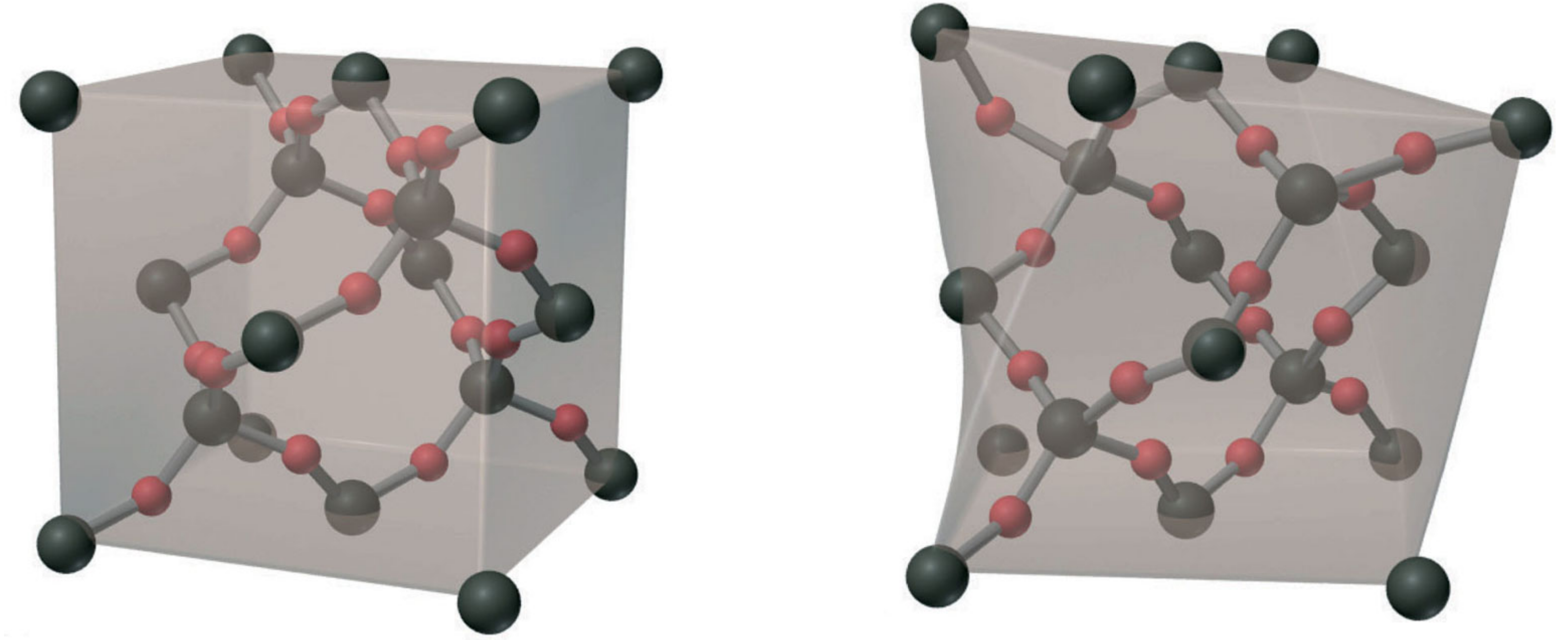


Figure 12.36 Crystalline and amorphous silicon dioxide.



A. Cristobalite, a crystalline form of silica (SiO_2) shows cubic closest packing.

B. Quartz glass is amorphous with a generally disordered structure.

Figure 12.37 The band of molecular orbitals in lithium metal.

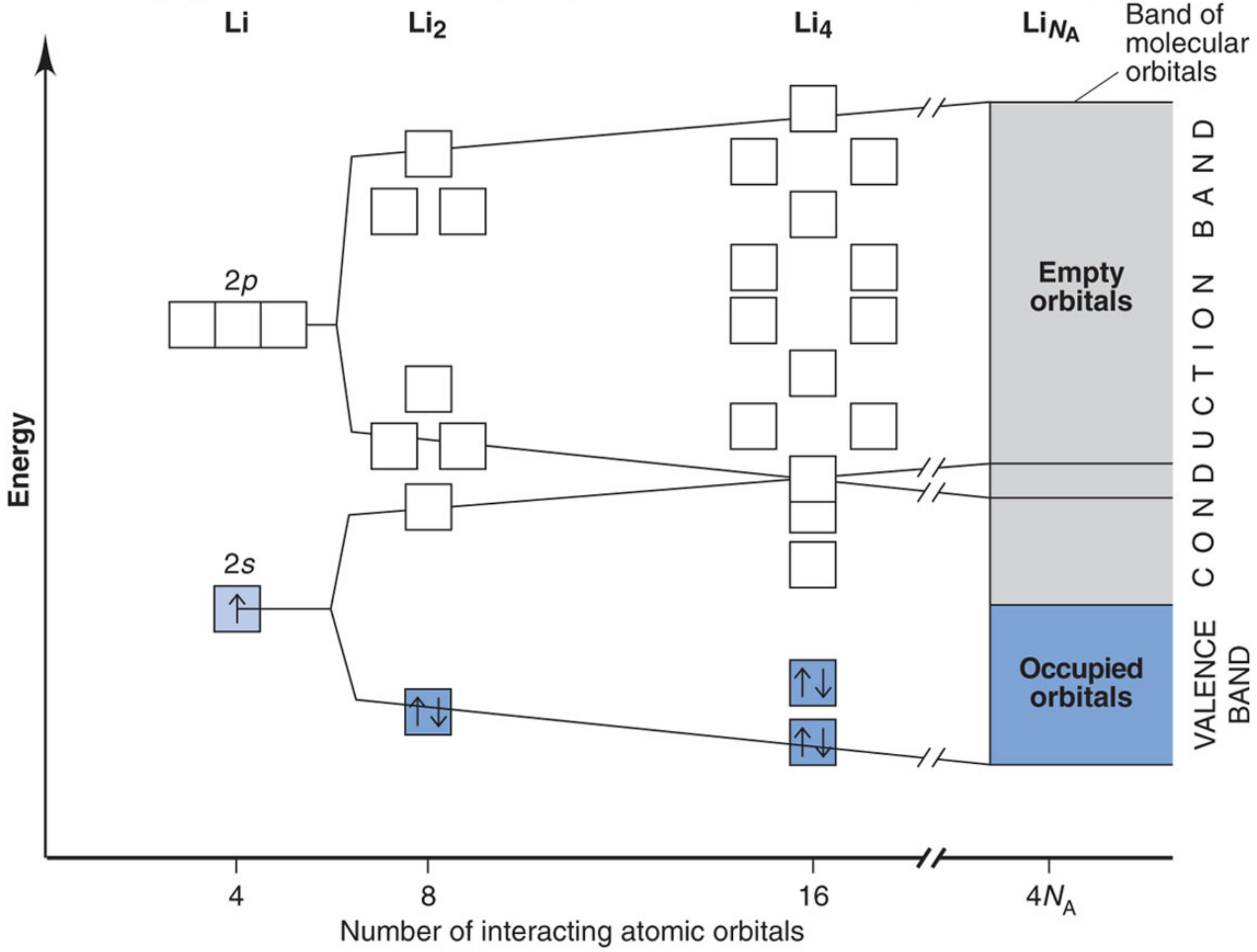
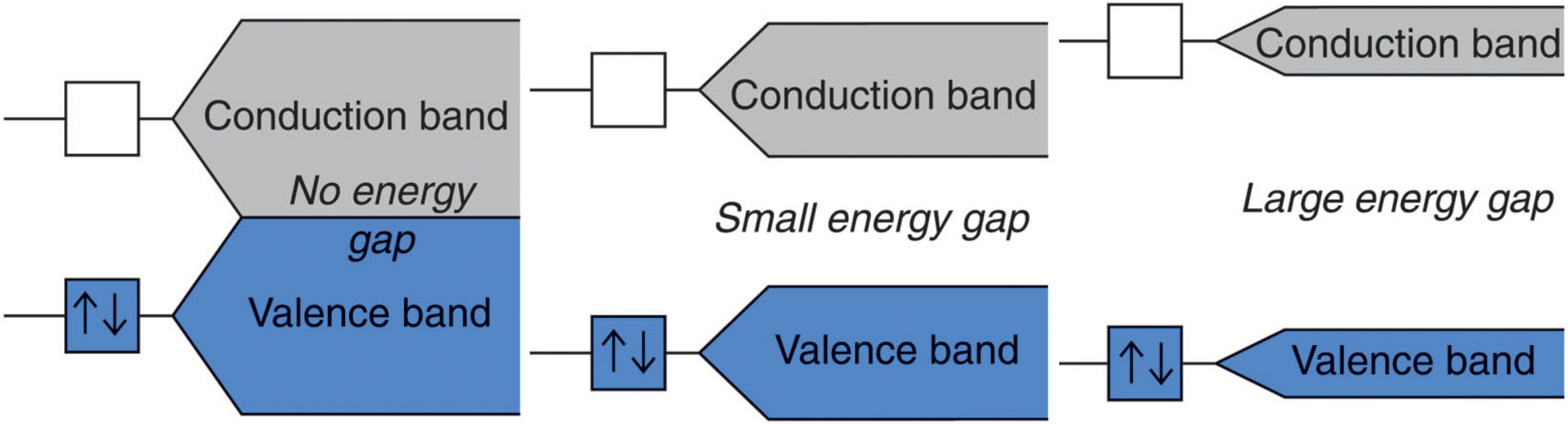


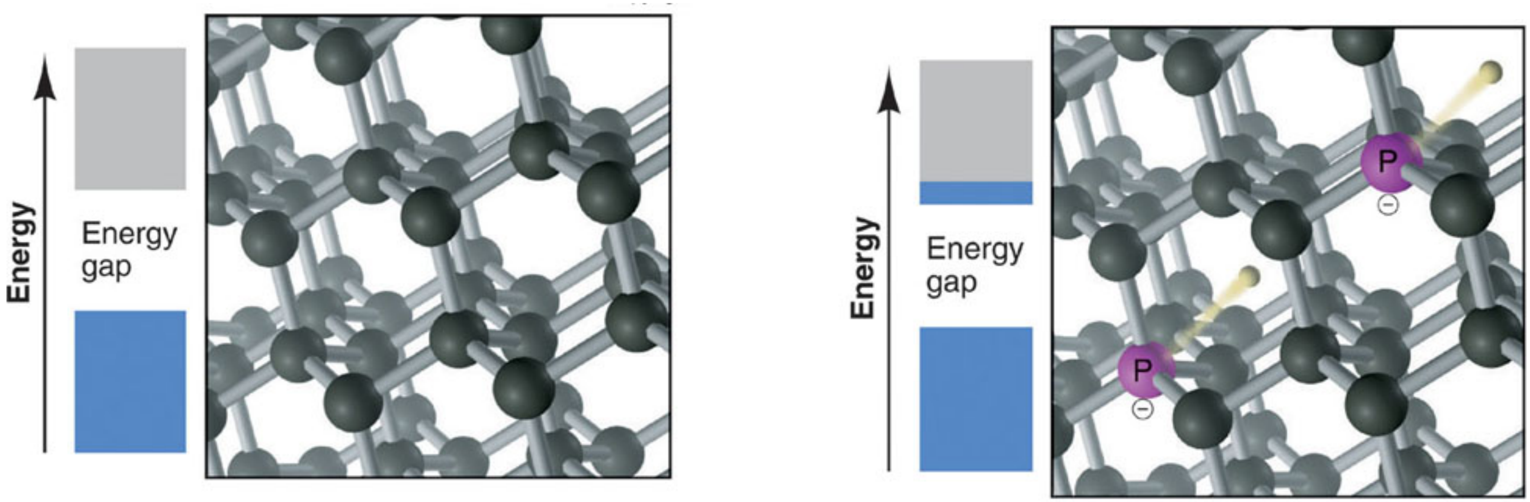
Figure 12.38 Electrical conductivity in a conductor, semiconductor, and insulator.



conductor semiconductor insulator

The conducting properties of a substance are determined by the energy gap between the valence and conduction bands of MOs.

Figure 12.39 Crystal structures and band representations of doped semiconductors.



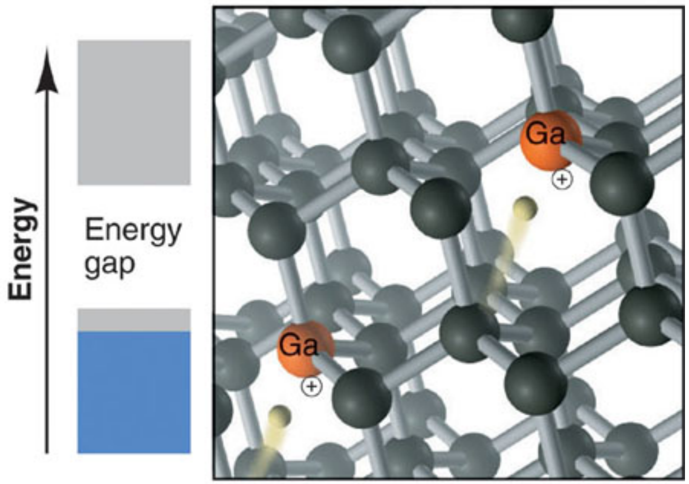
A Pure silicon crystal

B n-Type doping with phosphorus

Pure silicon has an energy gap between its valence and conduction bands. Its conductivity is low at room temperature.

Doping silicon with phosphorus adds additional valence e^-. These enter the conductance band, bridging the energy gap and increasing conductivity.

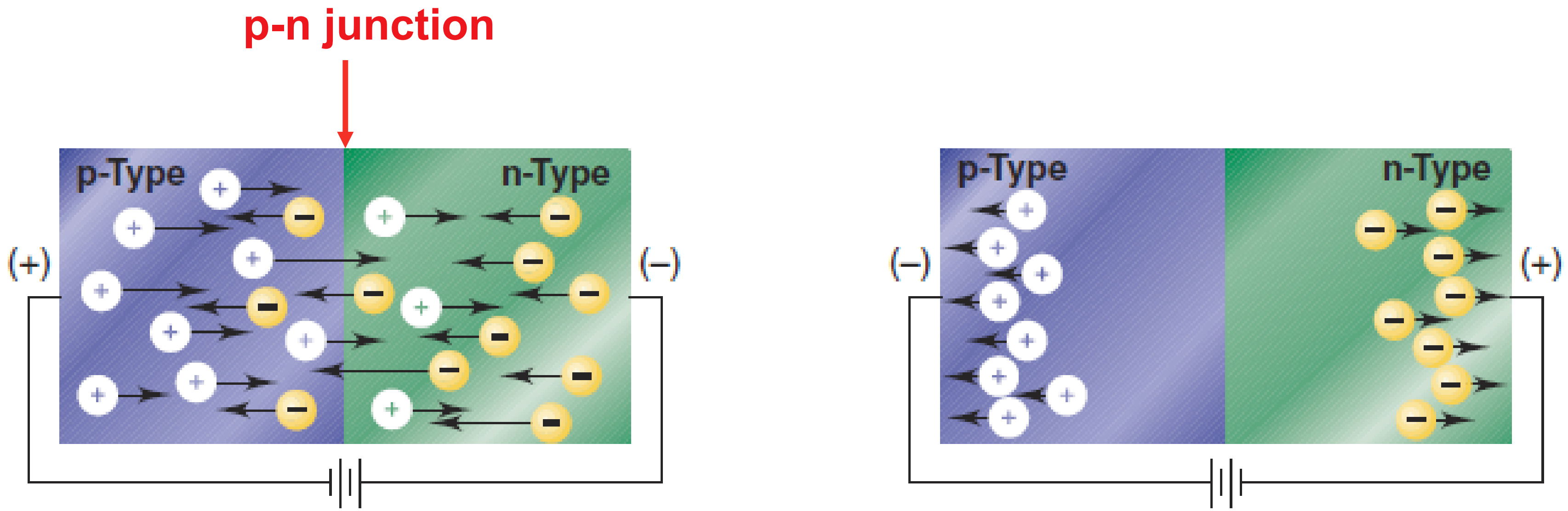
Figure 12.39 continued



C p-Type doping with gallium

Doping silicon with gallium removes electrons from the valence band and introduces positive ions. Si electrons can migrate to the empty orbitals, increasing conductivity.

Figure 12.40 The p-n junction.

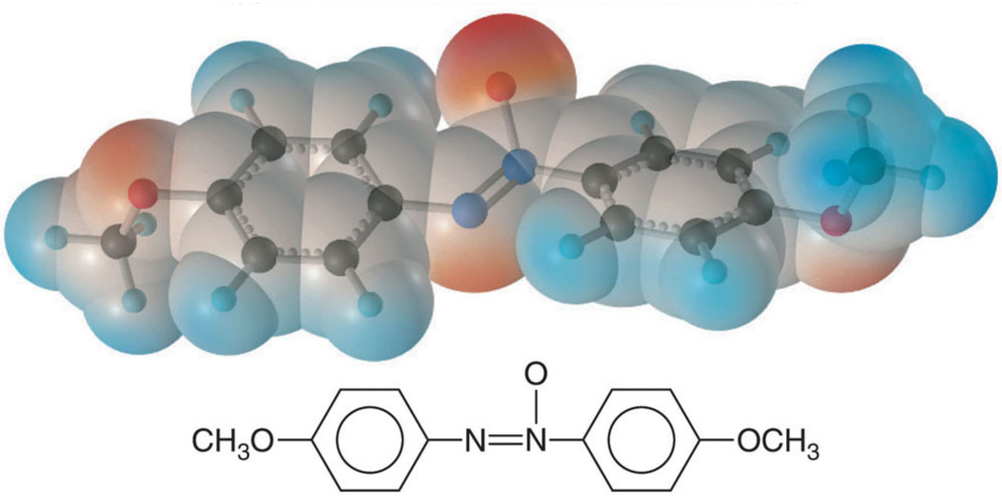


A Flow of electrons and holes creates a current.

B No current.

Placing a p-type semiconductor adjacent to an n-type creates a p-n junction. Electrons flow freely in the n-to-p direction.

Figure 12.41 Structures of two typical molecules that form liquid crystal phases.



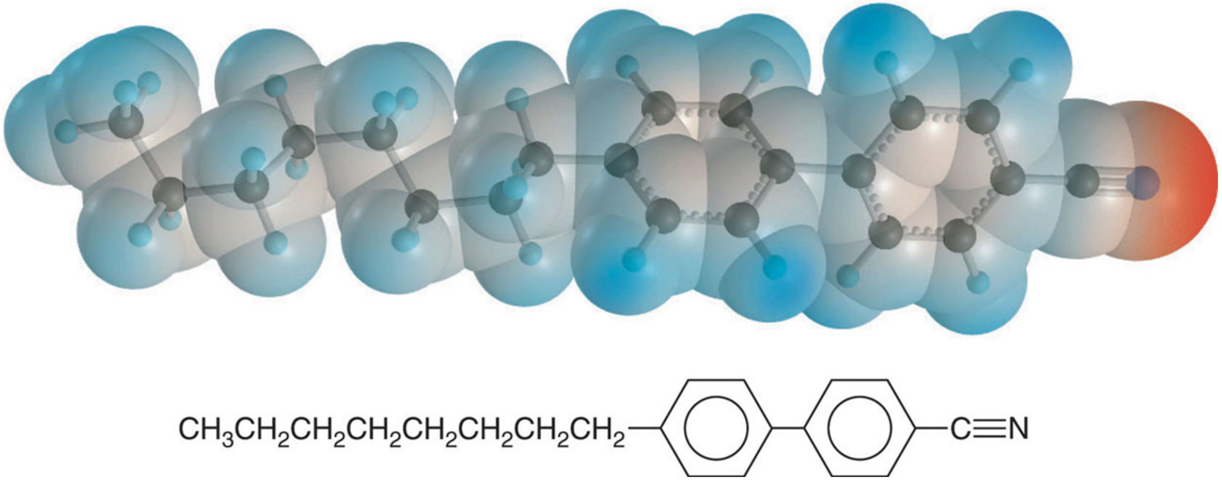
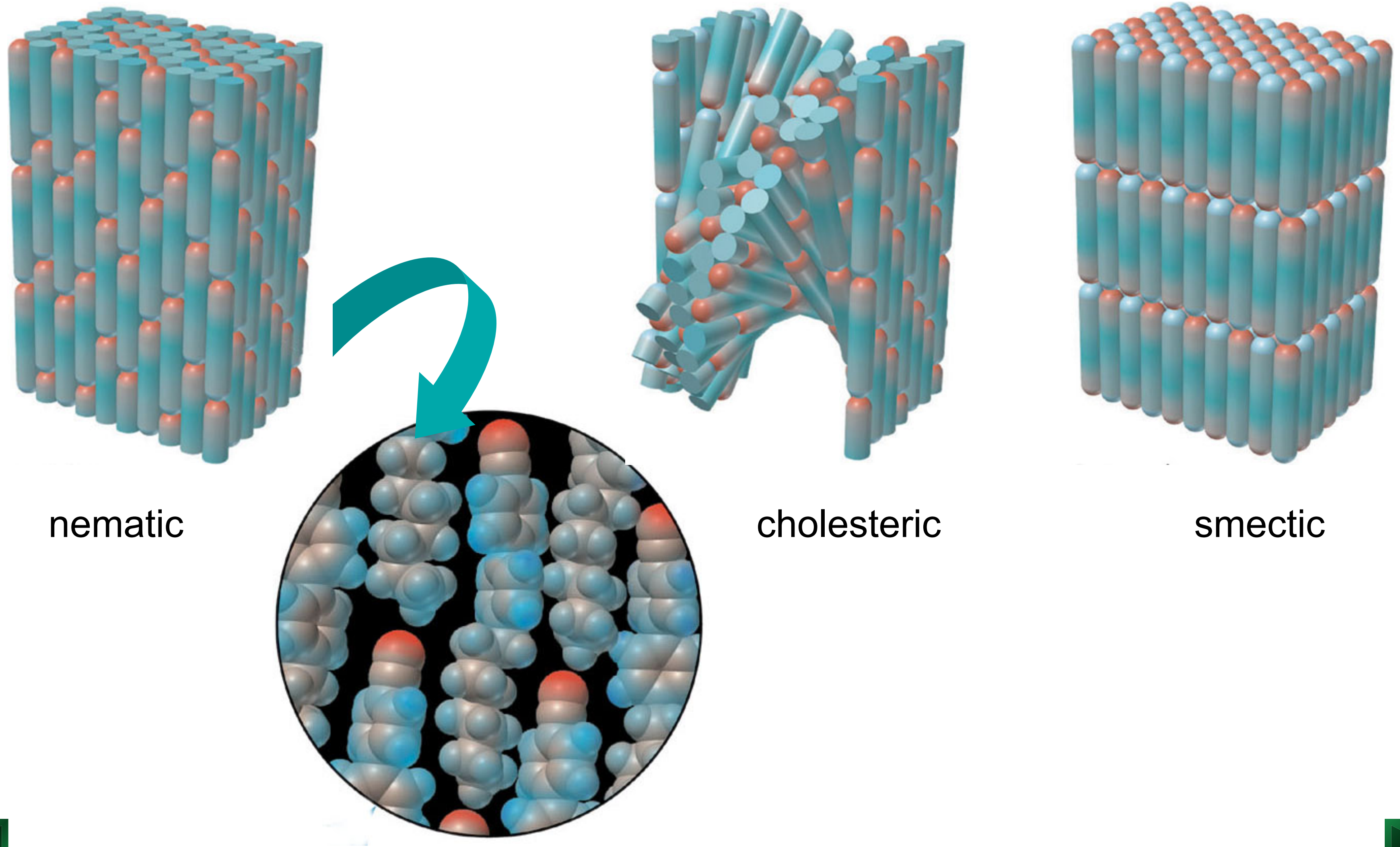


Figure 12.42 The three common types of ordering in liquid crystal phases.

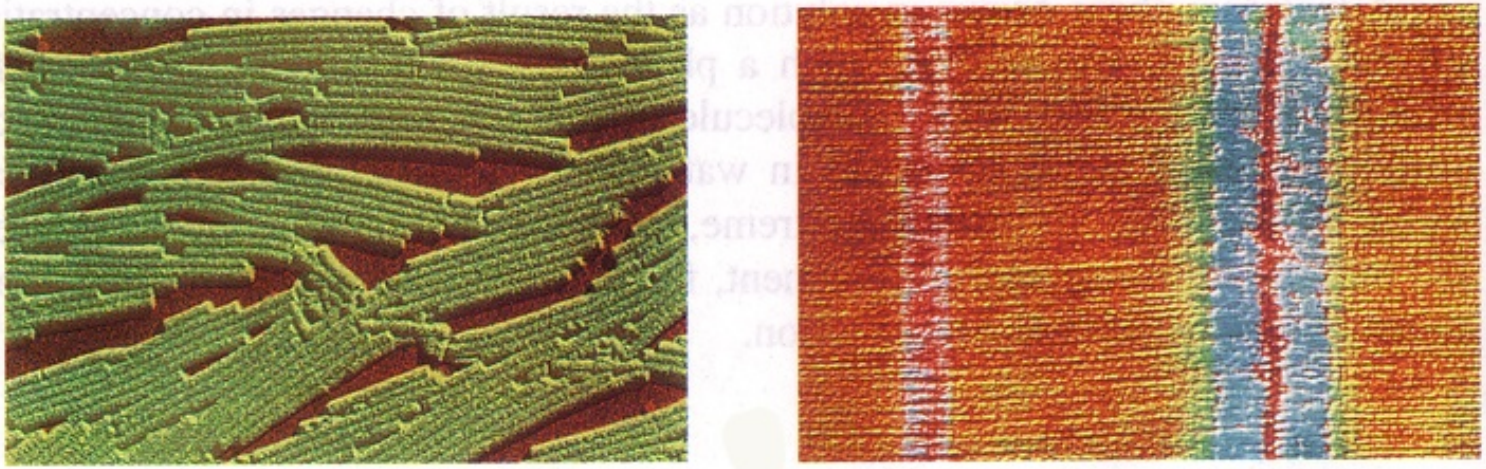


nematic

cholesteric

smectic

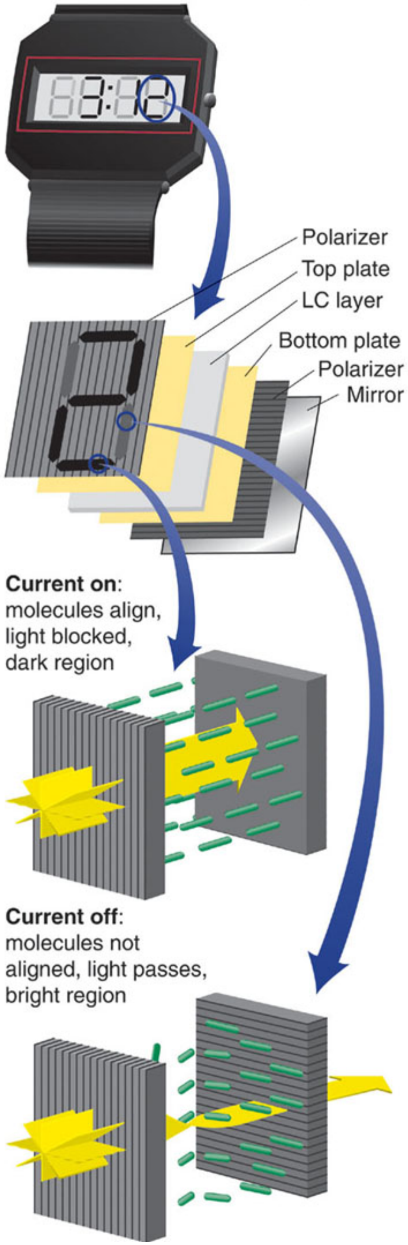
Figure 12.43 Liquid crystal-type phases in biological systems.



A. Nematic arrays of tobacco mosaic virus particles within the fluid of a tobacco leaf.

B. The smectic-like arrangement of actin and myosin protein filaments in voluntary muscle cells.

Figure 12.44

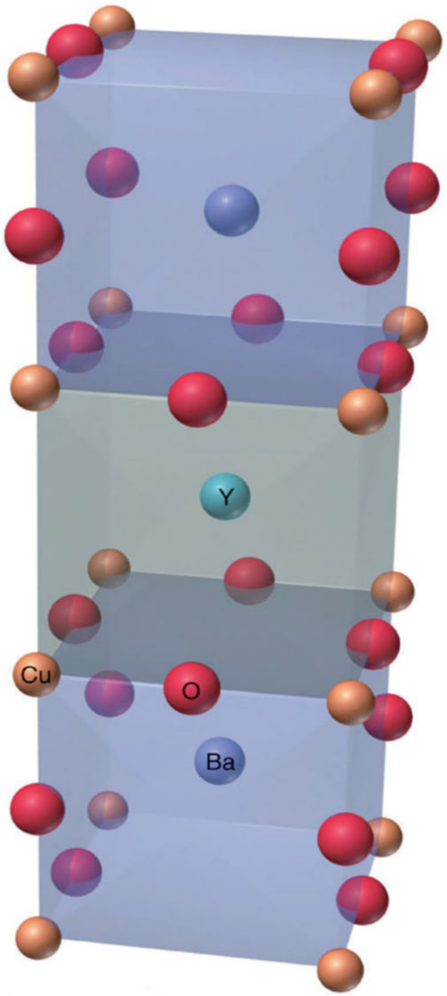


A liquid crystal display (LCD).

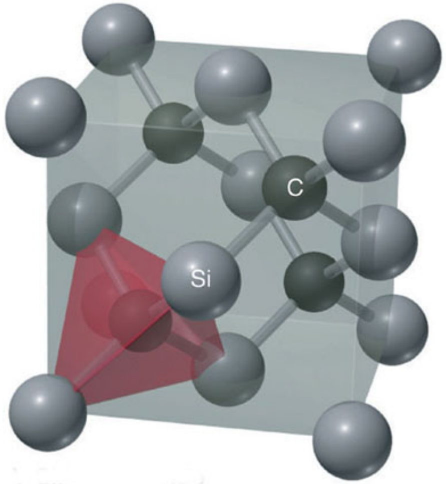
Table 12.7 Some Uses of Modern Ceramics and Ceramic Mixtures

Ceramic	Applications
SiC, Si_3N_4, TiB_2, Al_2O_3	Whiskers (fibers) to strengthen Al and other ceramics
Si_3N_4	Car engine parts; turbine rotors for “turbo” cars; electronic sensor units
Si_3N_4, BN, Al_2O_3	Supports or layering materials (as insulators) in electronic microchips
SiC, Si_3N_4, TiB_2, ZrO_2, Al_2O_3, BN	Cutting tools, edge sharpeners (as coatings and whole devices), scissors, surgical tools, industrial “diamond”
BN, SiC	Armor-plating reinforcement fibers (as in Kevlar composites)
ZrO_2, Al_2O_3	Surgical implants (hip and knee joints)

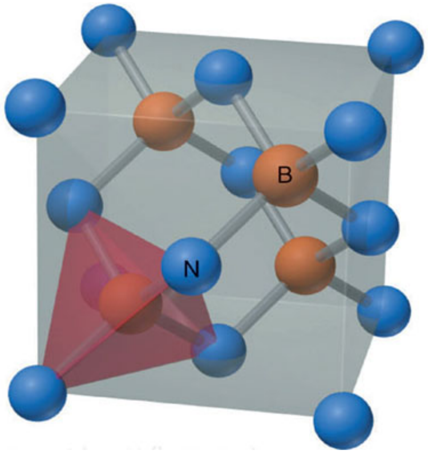
Figure 12.45 Expanded view of the atom arrangements in some modern ceramic materials.



$YBa_2Cu_3O_7$



SiC
silicon carbide



BN
cubic boron nitride (borazon)

Table 12.8 Molar Masses of Some Common Polymers

Name	$\mathcal{M}_{polymer}$ (g/mol)	*n*	Uses
Acrylates	2×10^5	2×10^3	Rugs, carpets
Polyamide (nylons)	1.5×10^4	1.2×10^2	Tires, fishing line
Polycarbonate	1×10^5	4×10^2	Compact discs
Polyethylene	3×10^5	1×10^4	Grocery bags
Polyethylene (ultra-high molecular weight)	5×10^6	2×10^5	Hip joints
Poly(ethylene terephthalate)	2×10^4	1×10^2	Soda bottles
Polystyrene	3×10^5	3×10^3	Packing; coffee cups
Poly(vinyl chloride)	1×10^5	1.5×10^3	Plumbing

Figure 12.46 The random-coil shape of a polymer chain.

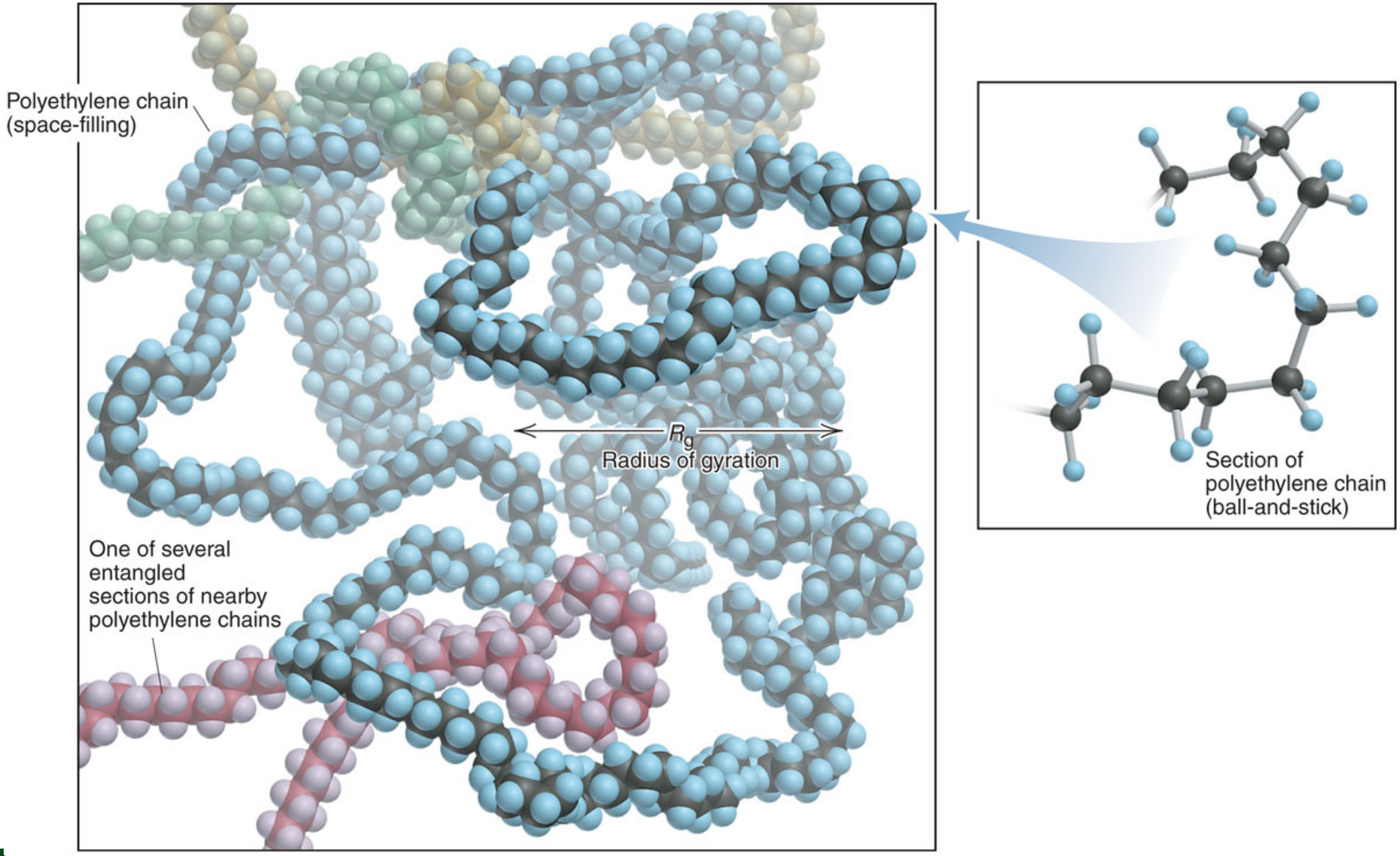


Figure 12.47 The semicrystallinity of a polymer chain.

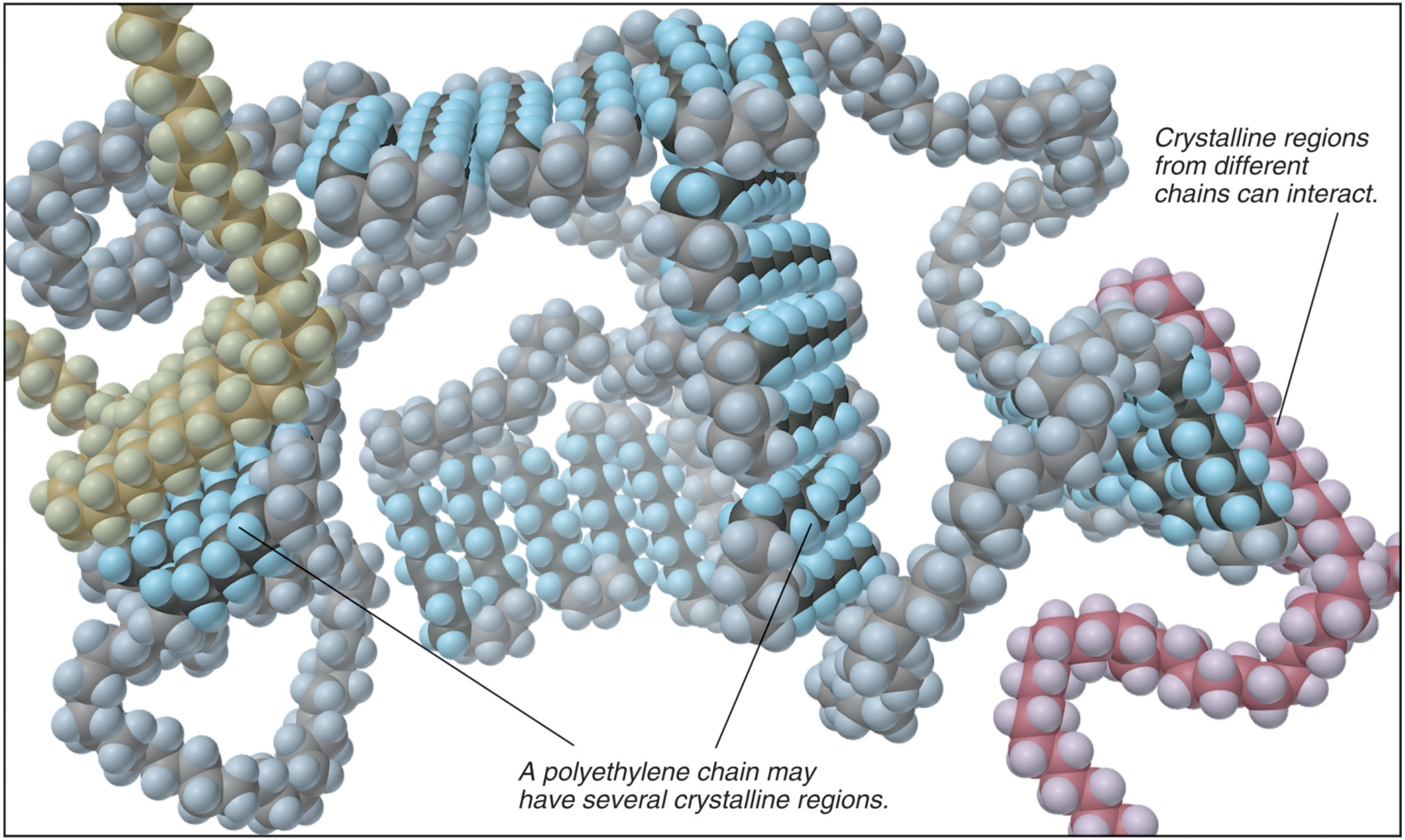


Figure 12.48 The viscosity of a polymer in aqueous solution.

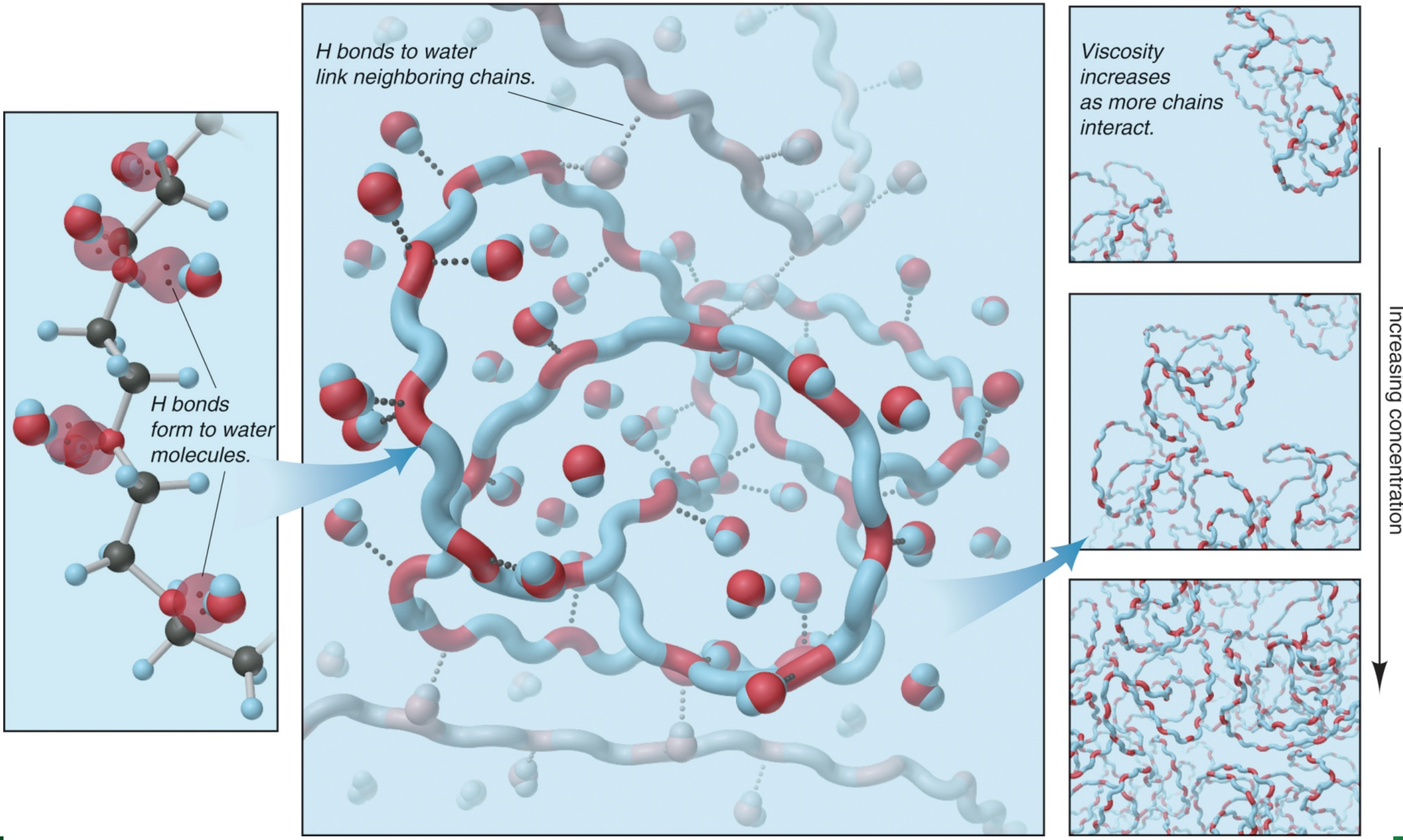
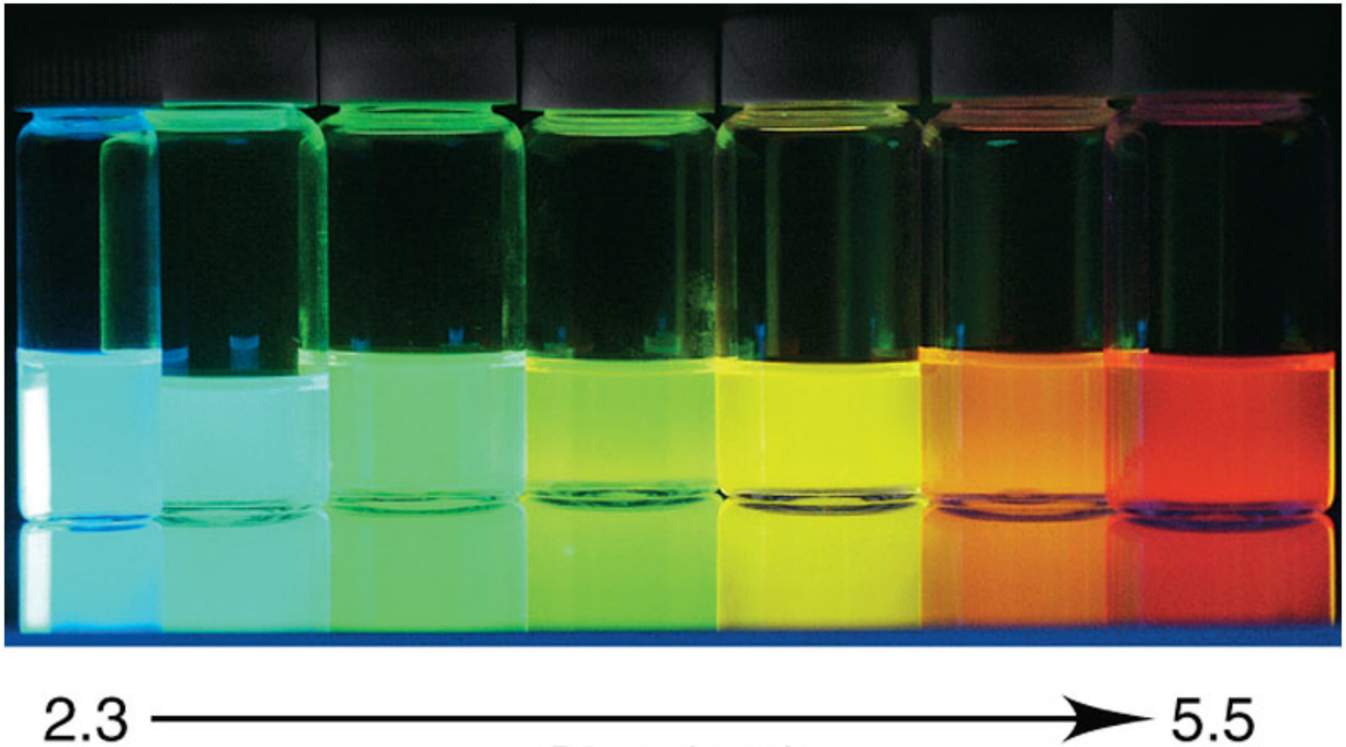


Table 12.9 Some Common Elastomers

Name	T_g(°C)*	Uses
Poly (dimethyl siloxane)	-123	Breast implants
Polybutadiene	-106	Rubber bands
Polyisoprene	-65	Surgical gloves
Polychloroprene (neoprene)	-43	Footwear, medical tubing

*Glass transition temperature

Figure 12.49 The colors of quantum dots.



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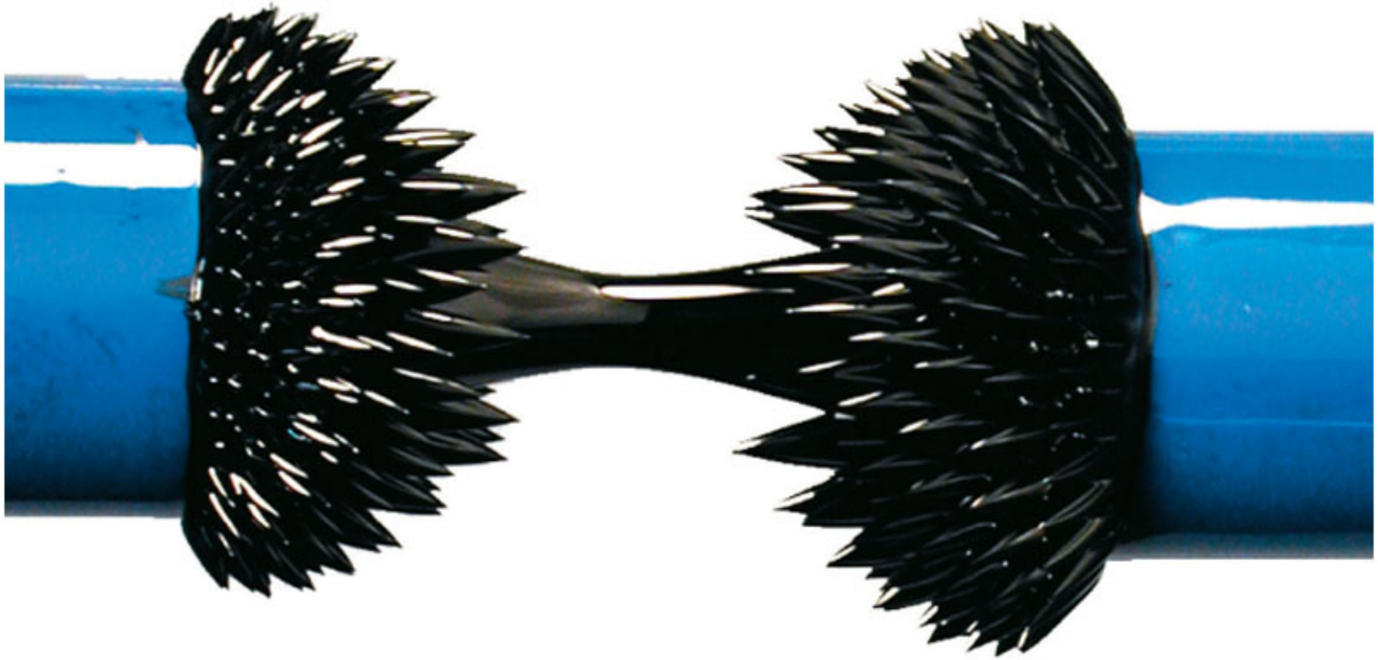
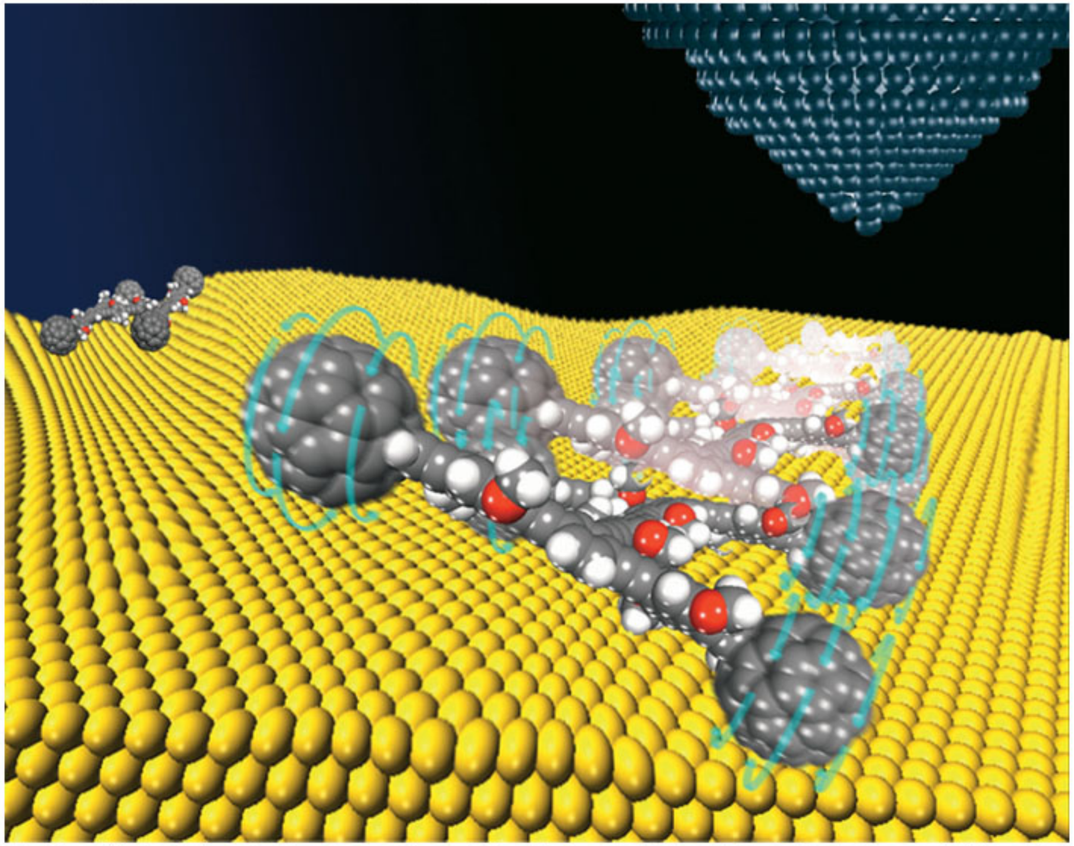
Quantum dots are nanoparticles of semiconducting materials (e.g., GaAs or GaSe) that are smaller than 10 nm.

Figure 12.50 The magnetic behavior of a ferrofluid.



Nanoparticles of magnetite (Fe_3O_4) dispersed in a viscous fluid are suspended between the poles of a magnet.

Figure 12.51 Driving a nanocar.



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The nanocar, with buckyball wheels, is only 4 nm wide and is “driven” on a gold surface under the direction of an atomic force microscope.