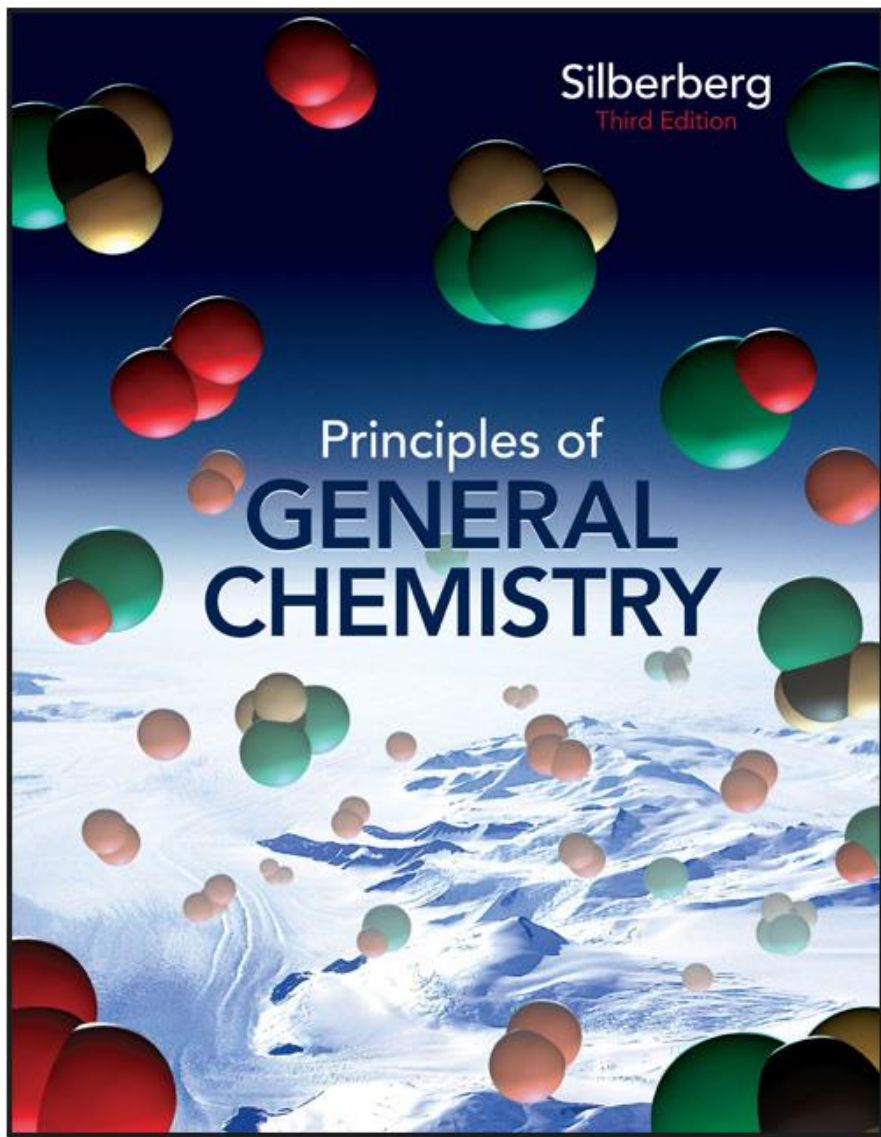




Chapter 12

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

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~~



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.

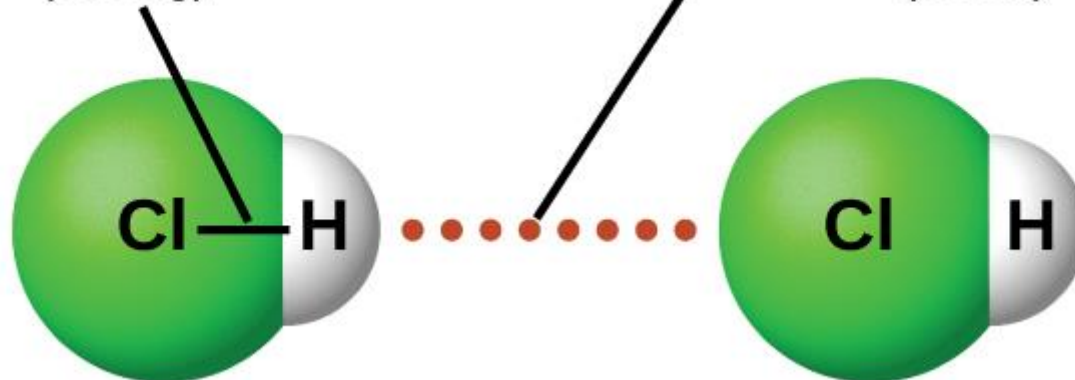
H₂O molecules are present whether the substance is in the solid, liquid, or gas phase.

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



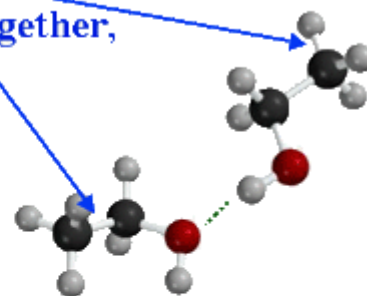
Intramolecular force
(strong)

Intermolecular force
(weak)



Intramolecular Forces -

Force which keeps molecule together,
i.e., bonds.



Intermolecular Forces -

Attractive force between molecules.
Responsible for keeping matter in
solid or liquid phase.

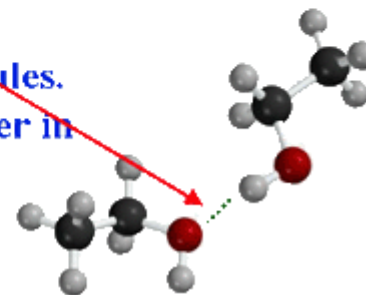


Table 12.1 A Macroscopic Comparison of Gases, Liquids, and Solids

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

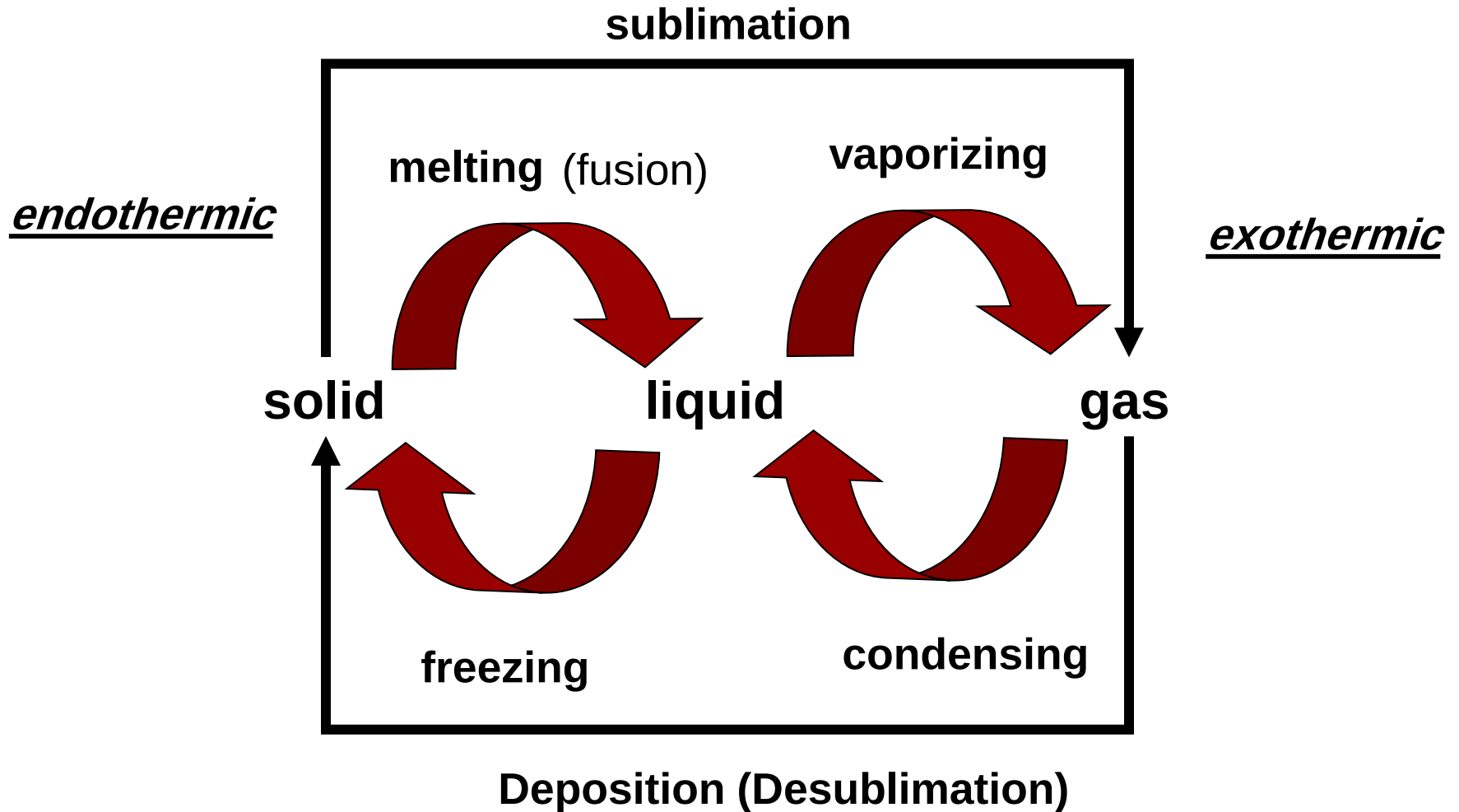


Figure 12.1 Heats of vaporization and fusion for several common substances.

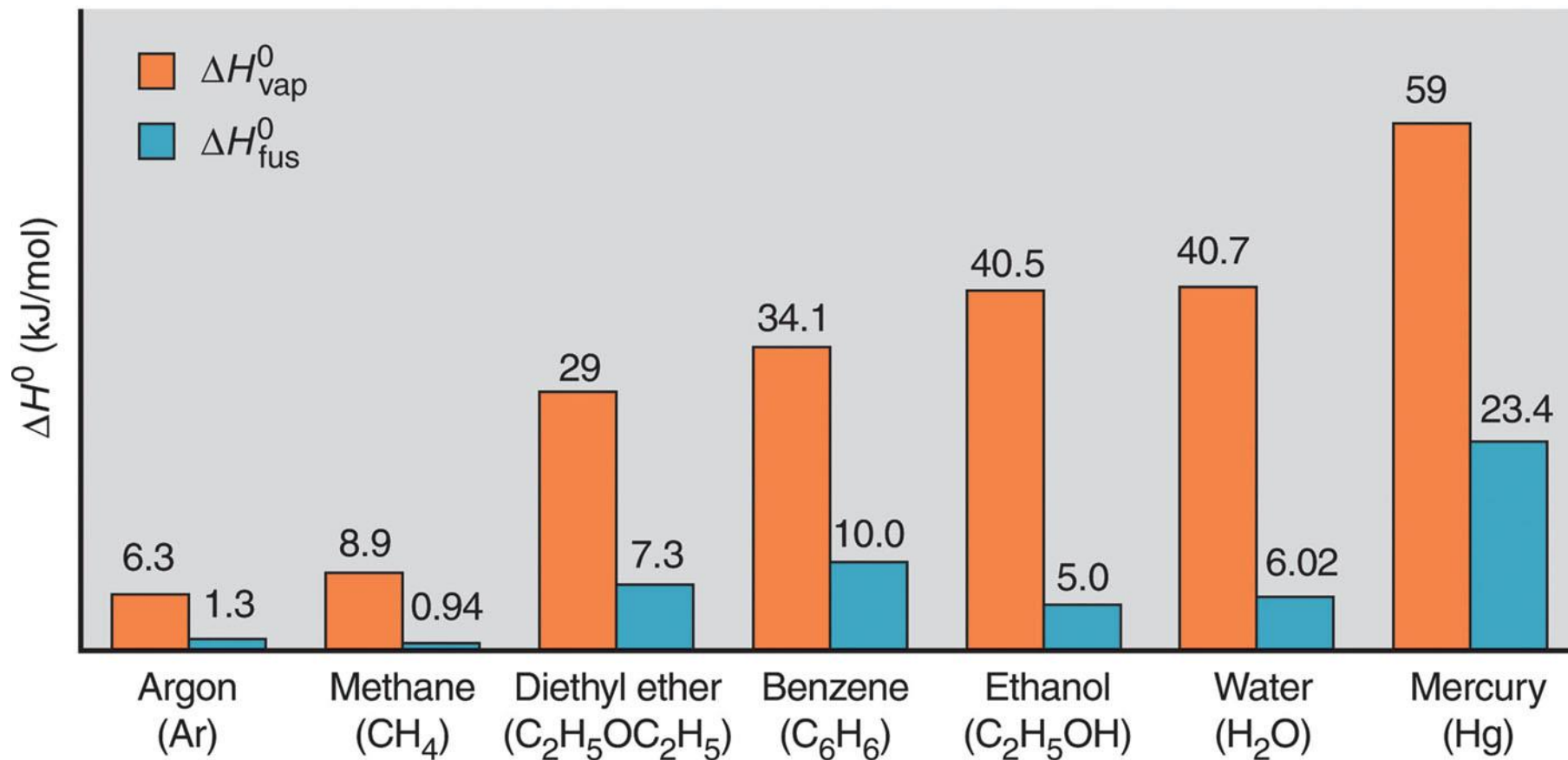
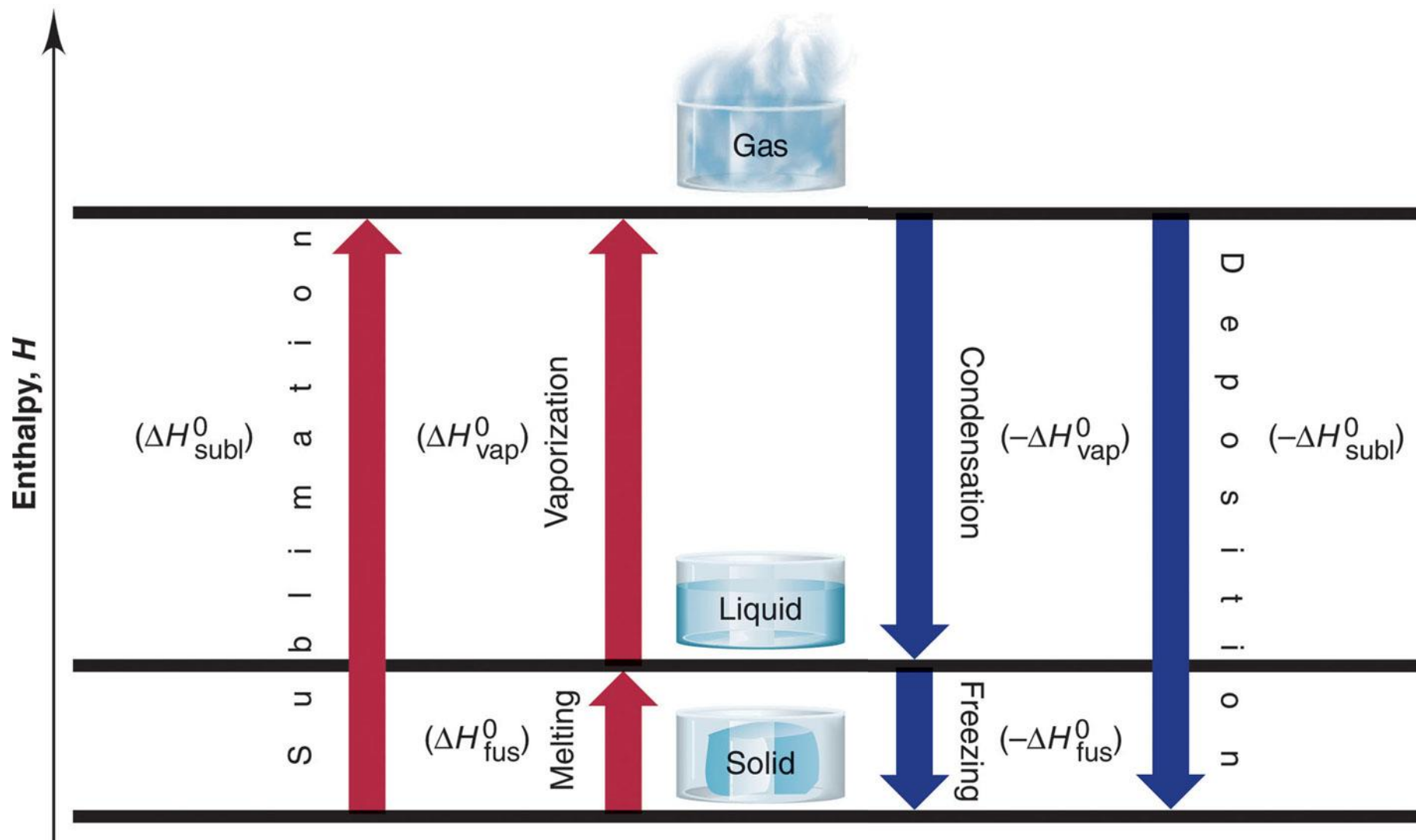


Figure 12.2 Phase changes and their enthalpy changes.



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.

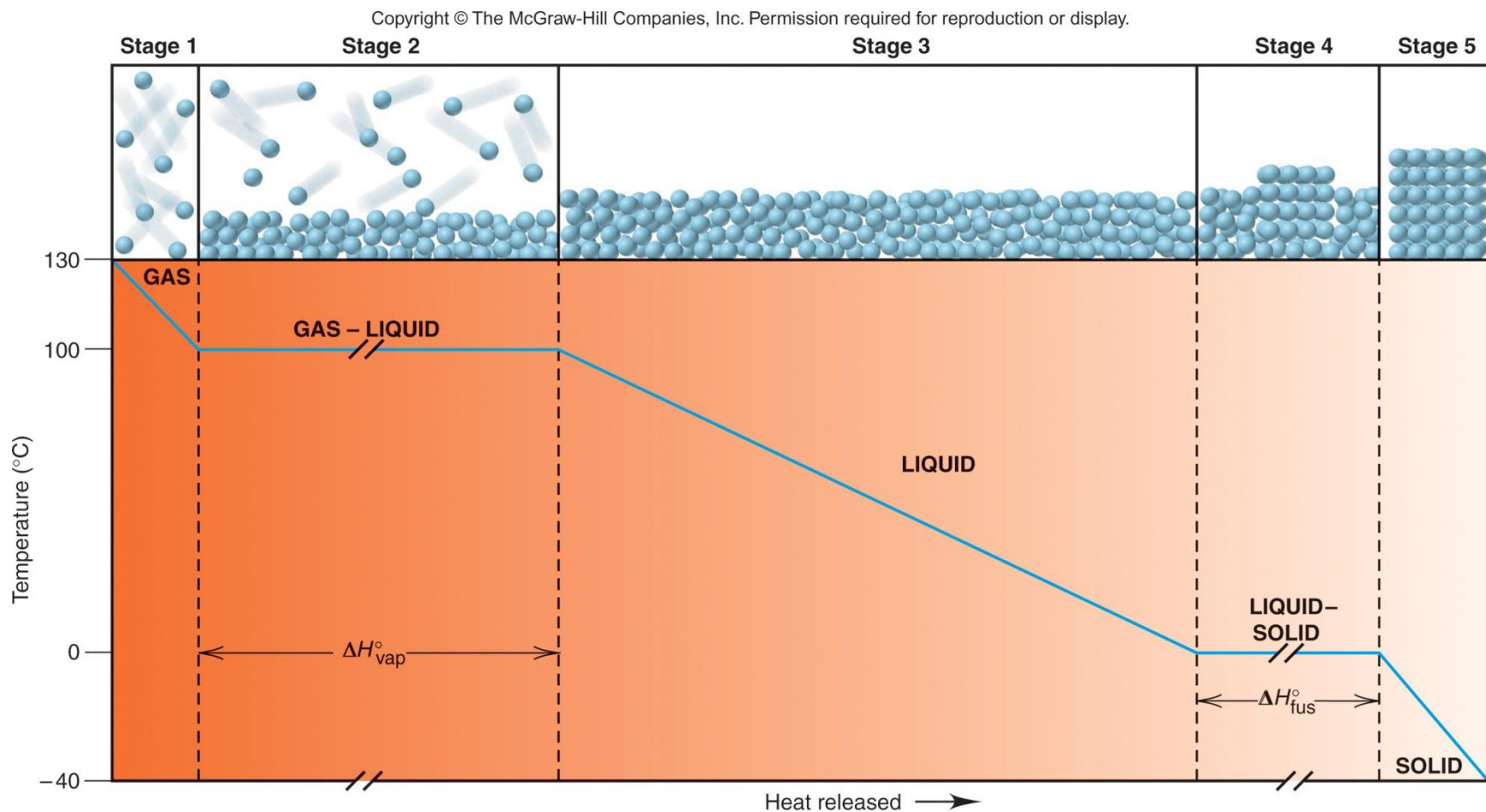
$$q = (\text{amount}) \times (\text{heat capacity}) \times \Delta T$$

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

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



Figure 12.3 A cooling curve for the conversion of gaseous water to ice.

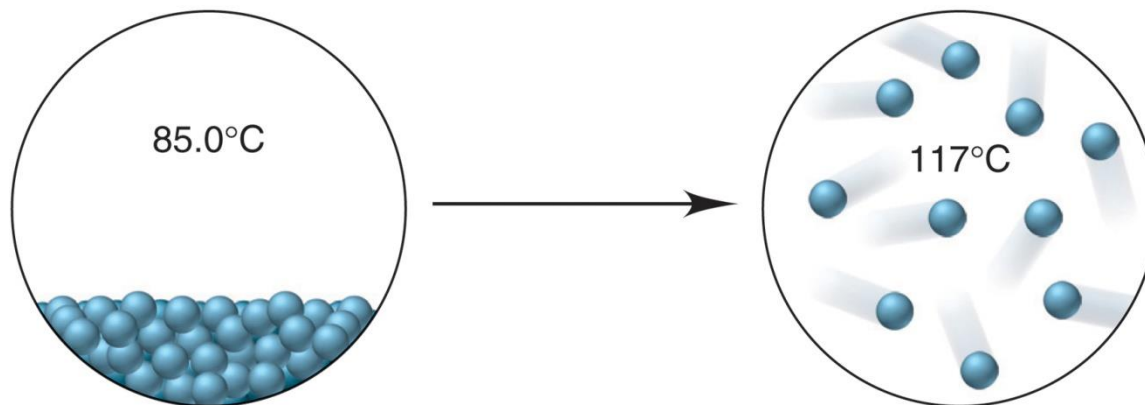


Sample Problem 12.1

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.

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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.



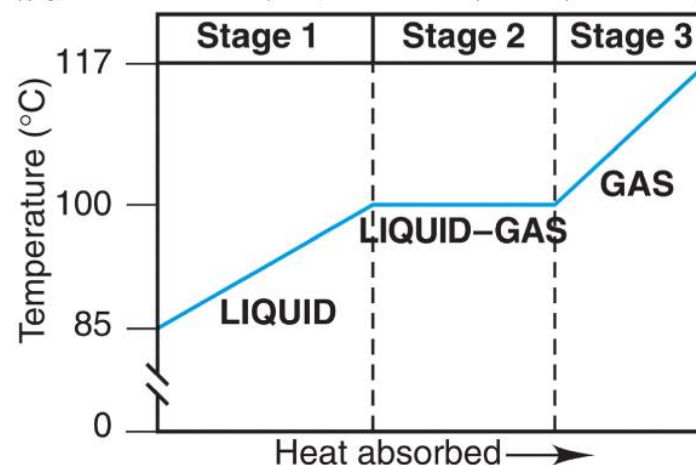
Sample Problem 12.1

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

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$$\text{mol H}_2\text{O} = 24.3 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 1.35 \text{ mol H}_2\text{O}$$

For Stage 1:

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

$$\text{Molar heat capacity } (C) = q / \text{moles} \times \Delta T \quad (\text{J/mol} \cdot ^\circ\text{C})$$

$$C \text{ of H}_2\text{O}(l) = 4.184 \text{ J/g} \cdot \text{K} \times 18.02 \text{ g/mol} = 75.40 \text{ J/mol} \cdot \text{K}$$

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

$$= (1.35 \text{ mol})(75.4 \text{ J/mol} \cdot ^\circ\text{C})(100. - 85.0^\circ\text{C})$$

$$= 1527 \text{ J} = 1.53 \text{ kJ}$$



Sample Problem 12.1

For Stage 2:

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

For Stage 3:

$$\begin{aligned} q &= n \times C_{\text{water}(g)} \times \Delta T \\ &= (1.35 \text{ mol})(33.1 \text{ J/mol}\cdot^\circ\text{C})(117 - 100.^\circ\text{C}) \\ &= 759.6 \text{ J} = 0.760 \text{ kJ} \end{aligned}$$

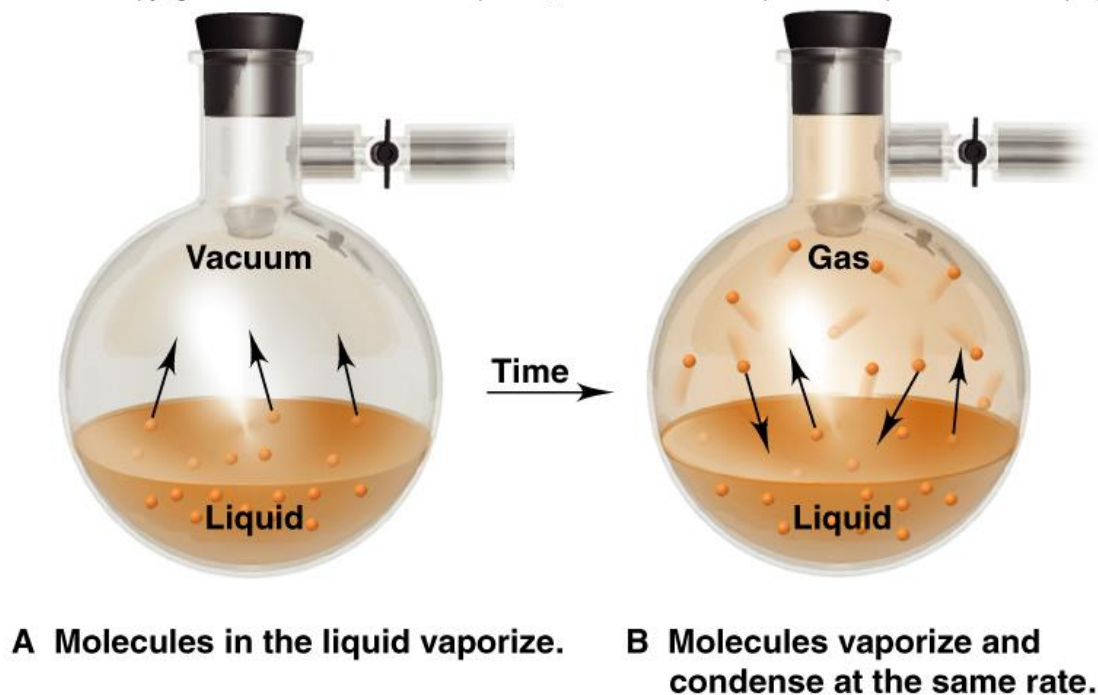
$$C \text{ of H}_2\text{O}(g) = 1.843 \text{ J/g}\cdot\text{K}$$

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



Figure 12.4 Liquid-gas equilibrium.

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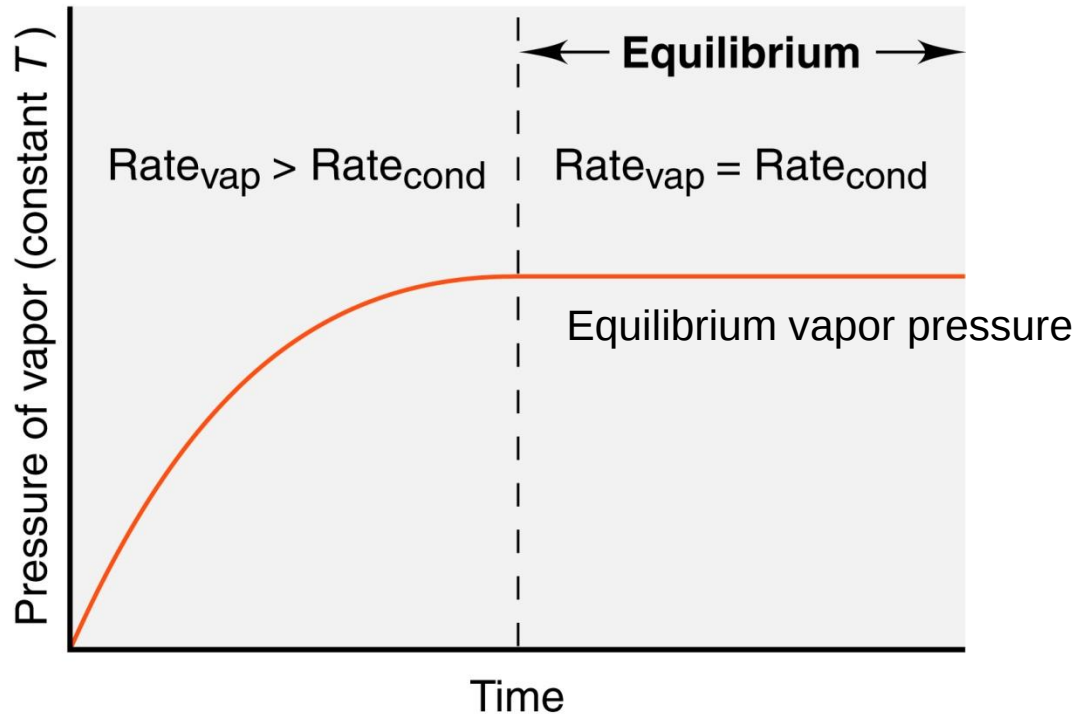


In a closed flask, the system reaches a state of ***dynamic equilibrium***, where molecules are leaving and entering the liquid at the ***same rate***.



Figure 12.4 continued

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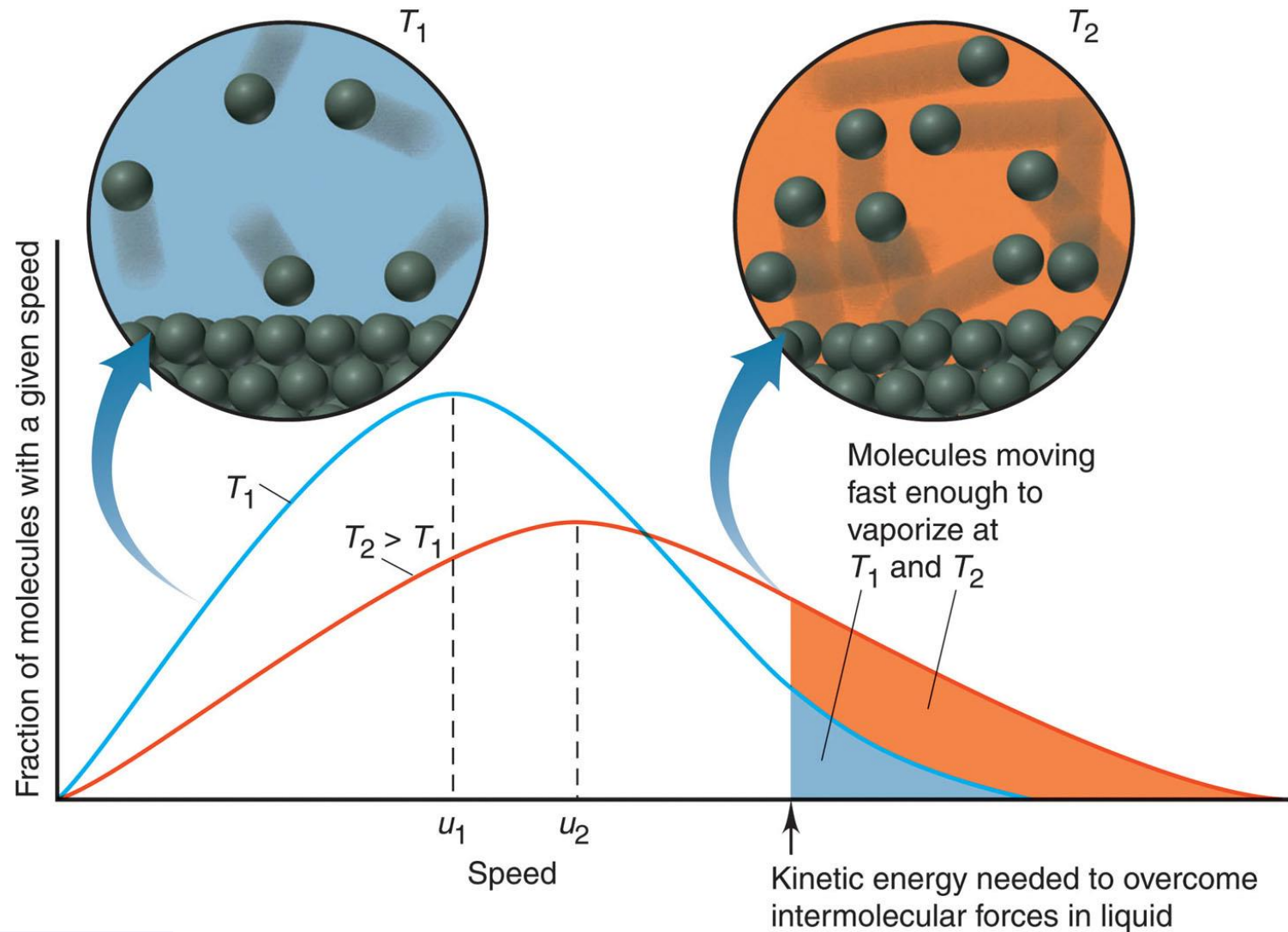


C Plot of pressure vs. time.

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 12.5 **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*.

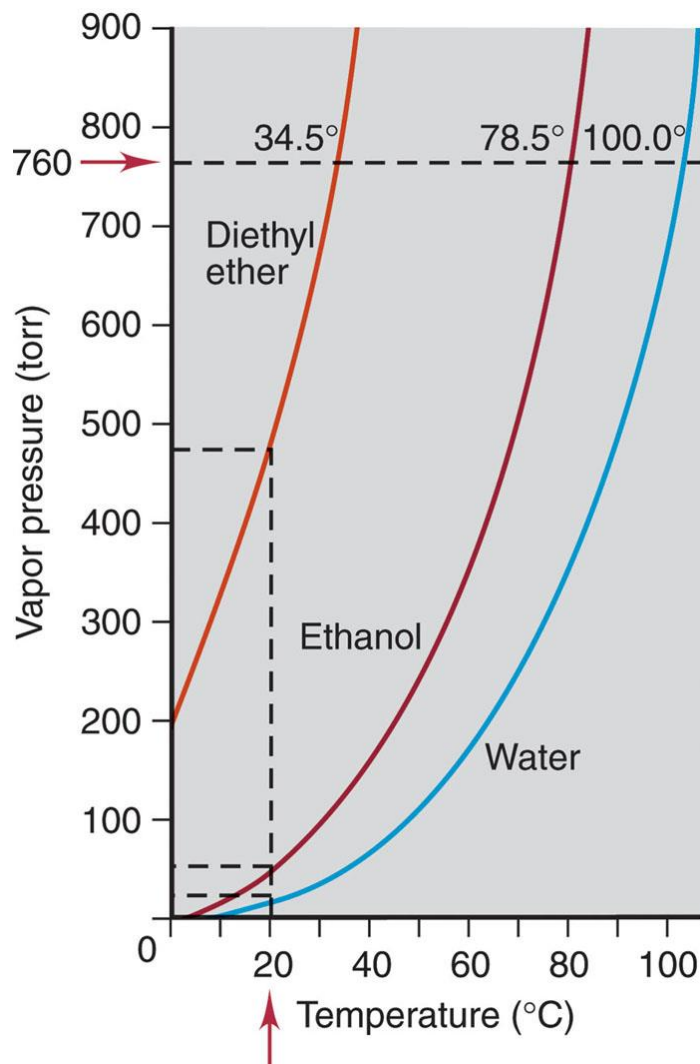
higher $T \longrightarrow$ higher P

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

weaker forces $\longrightarrow$ higher P



Figure 12.6 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.

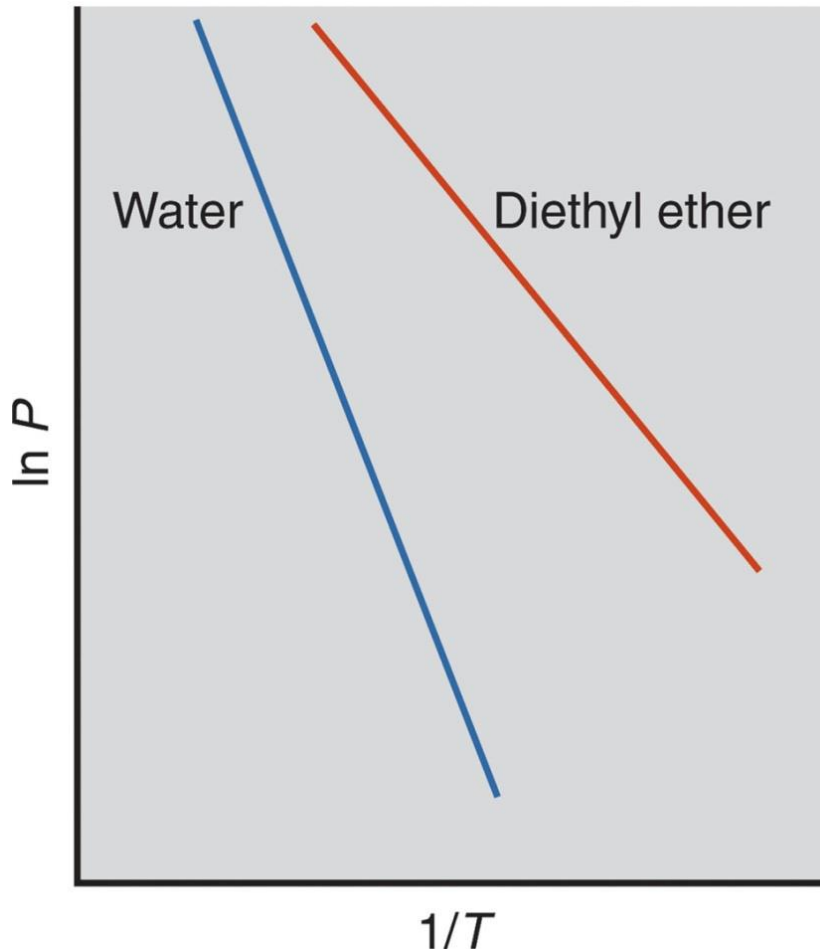
$$\ln P = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C$$

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 12.7 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:

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad T_1 = 34.9^\circ\text{C} + 273.15 = 308.0 \text{ K}$$

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

$$T_2 = 350. \text{ K} - 273.15 = 77^\circ\text{C}$$



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 12.8

Phase diagram for CO_2 .

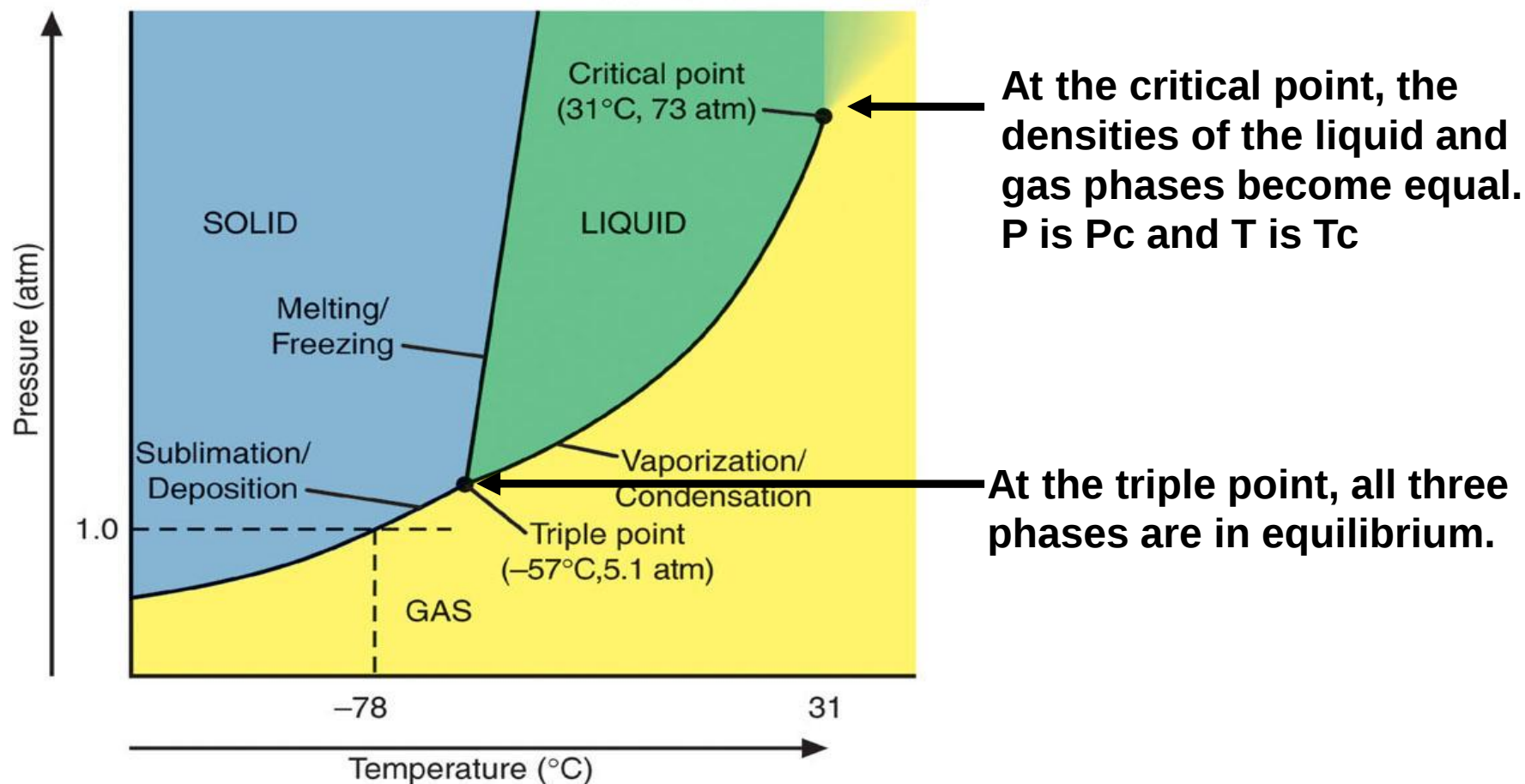
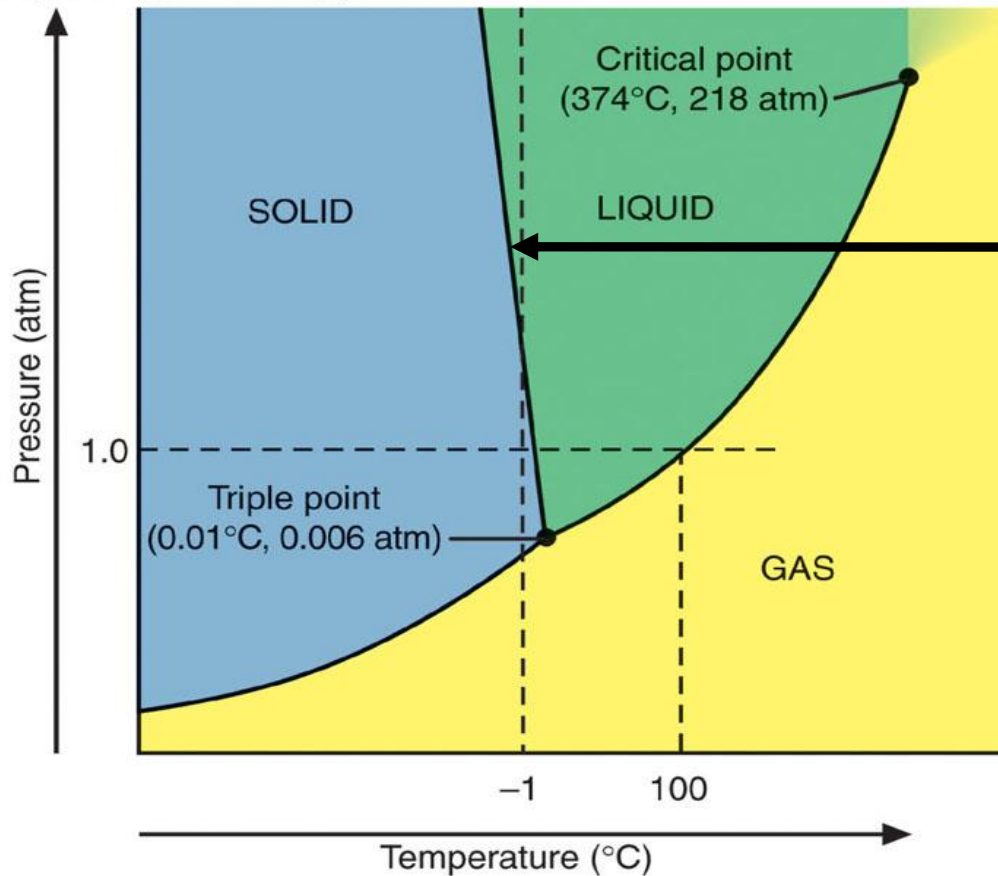


Figure 12.8

Phase diagram for H₂O.



The solid-liquid line slants to the *left* for H₂O, 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.

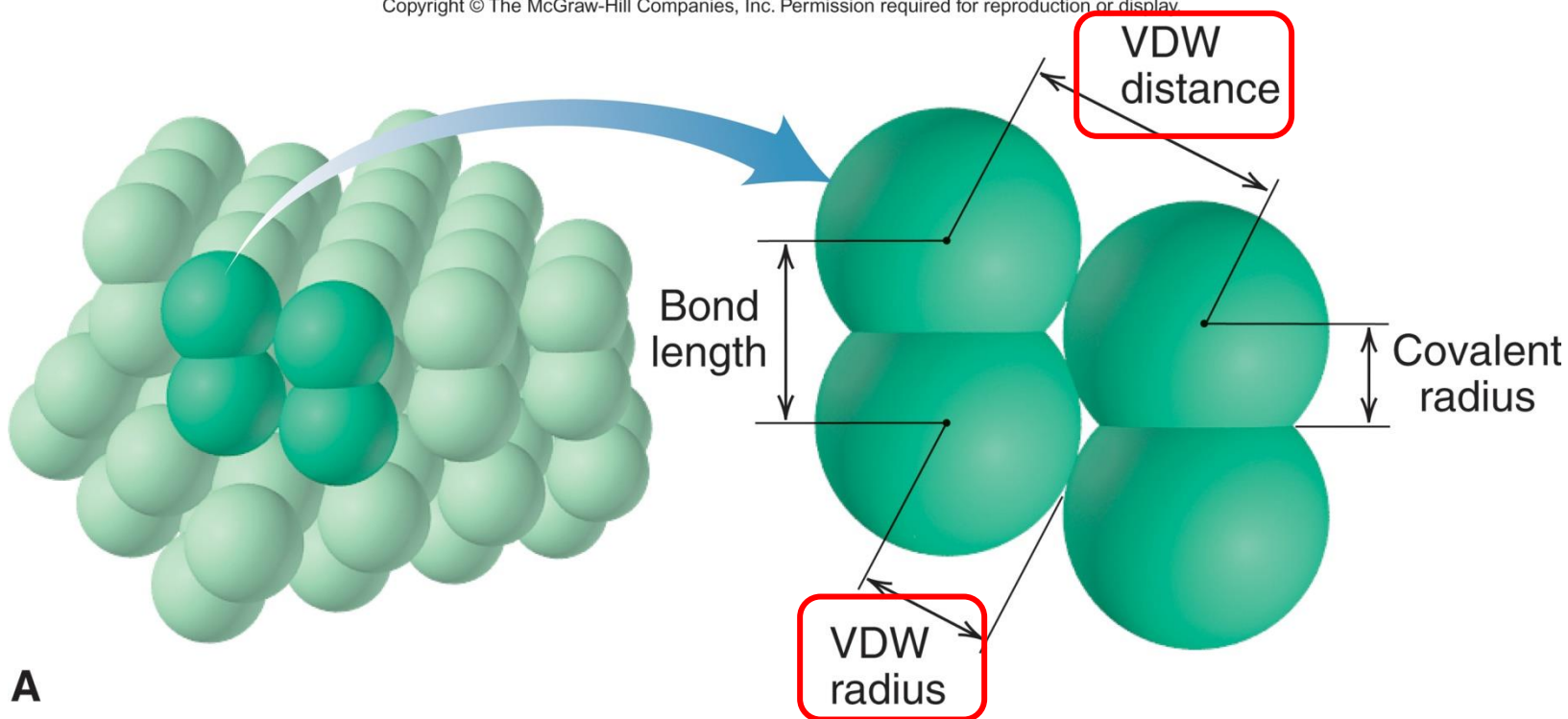
Intermolecular forces are relatively ***weak*** compared to bonding forces because they involve smaller charges that are farther apart.



Figure 12.9A Covalent and van der Waals radii.

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

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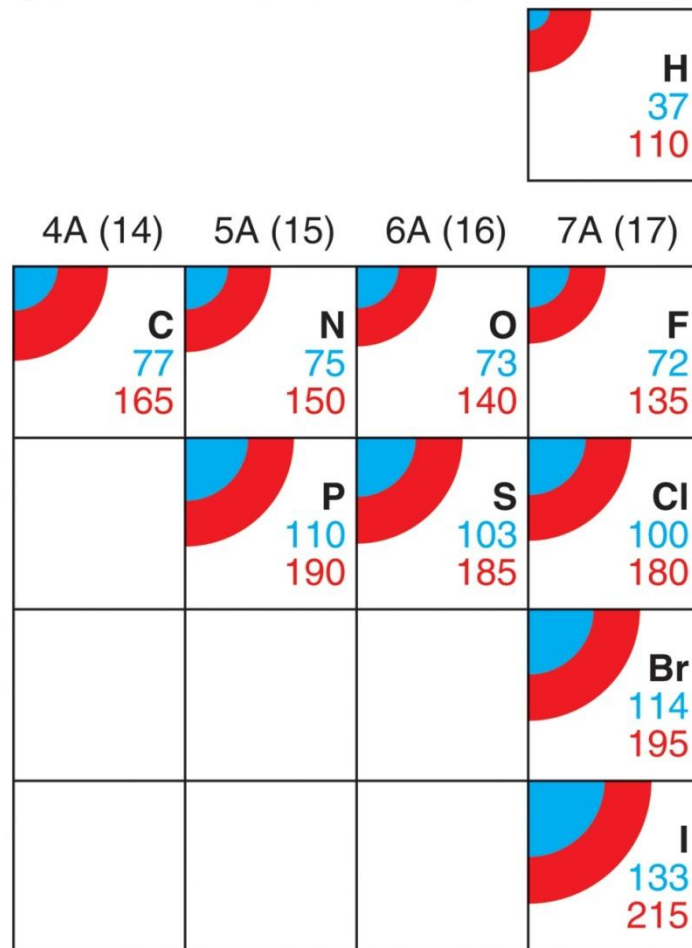


The van der Waals ***radius*** is one-half the closest distance between the nuclei of two ***nonbonded*** atoms. The VDW radius is ***always larger*** than the covalent radius.



Figure 12.9B Periodic trends in covalent and van der Waals radii.

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B



Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

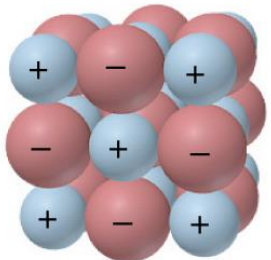
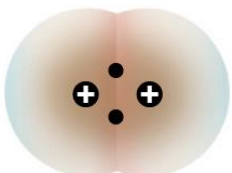
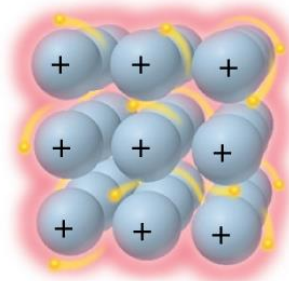
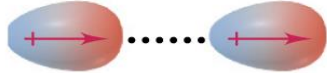
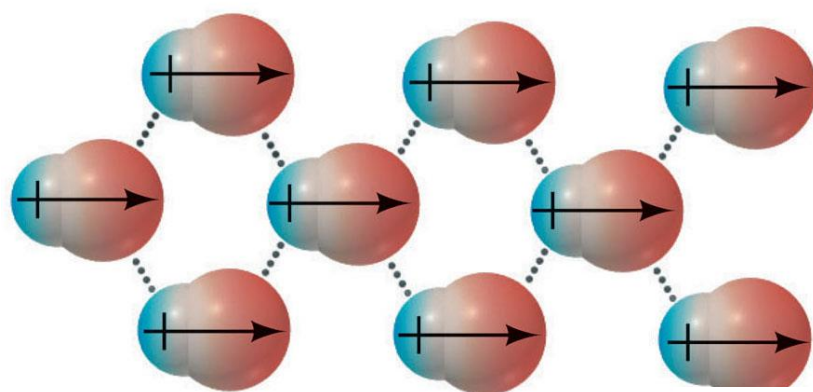
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

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

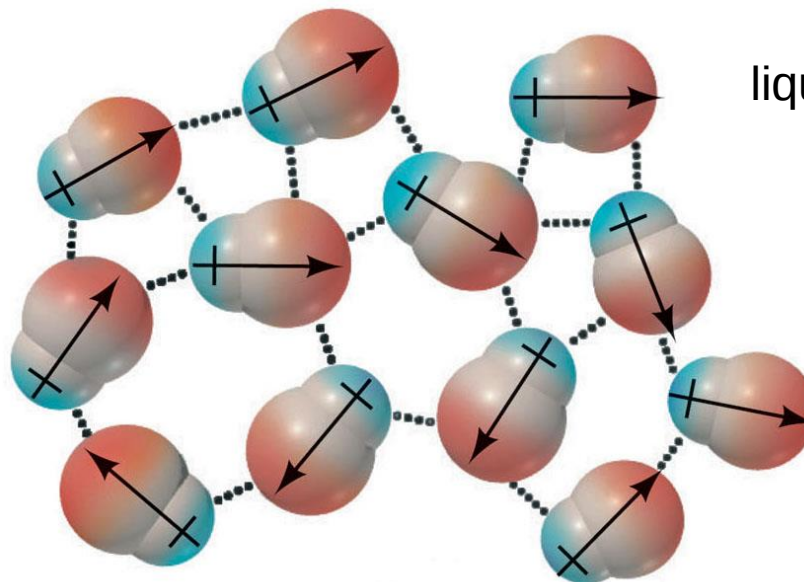
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge— dipole charge	40–600	$\text{Na}^+ \cdots \text{O} \begin{array}{l} \text{H} \\ \text{H} \end{array}$
H bond		Polar bond to H— dipole charge (high EN of N, O, F)	10–40	$\begin{array}{c} \text{:}\ddot{\text{O}}\text{—H} \\ \\ \text{H} \end{array} \cdots \begin{array}{c} \text{:}\ddot{\text{O}}\text{—H} \\ \\ \text{H} \end{array}$
Dipole-dipole		Dipole charges	5–25	$\text{I—Cl} \cdots \text{I—Cl}$
Ion–induced dipole		Ion charge— polarizable e^- cloud	3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole–induced dipole		Dipole charge— polarizable e^- cloud	2–10	$\text{H—Cl} \cdots \text{Cl—Cl}$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$\text{F—F} \cdots \text{F—F}$

dipole-dipole forces.



solid

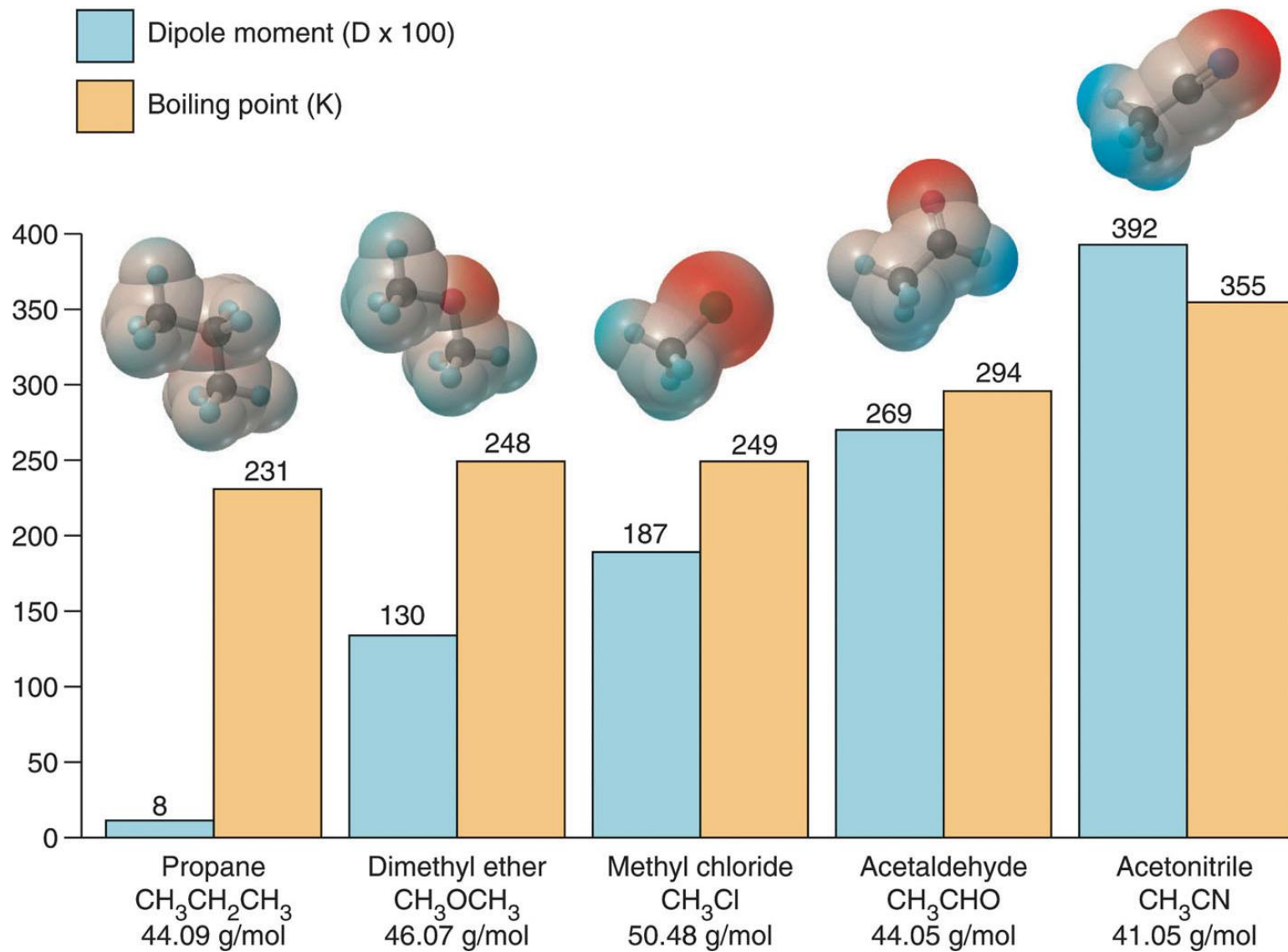
The positive pole of one polar molecule attracts the negative pole of another.



liquid



Figure 12.11 **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.

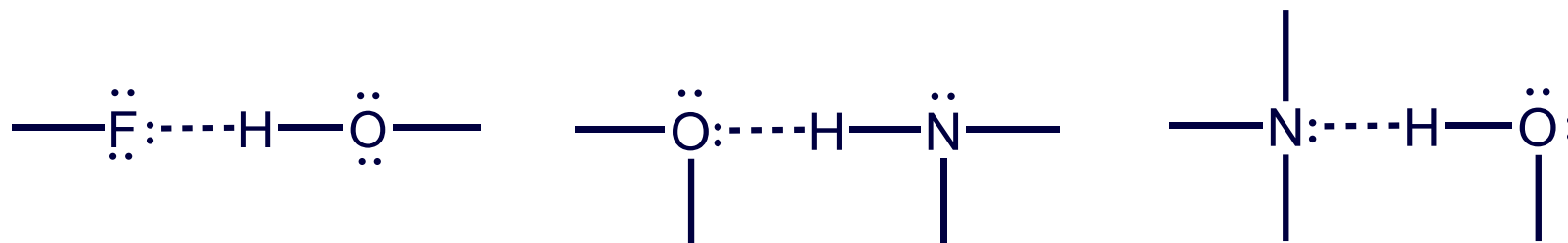
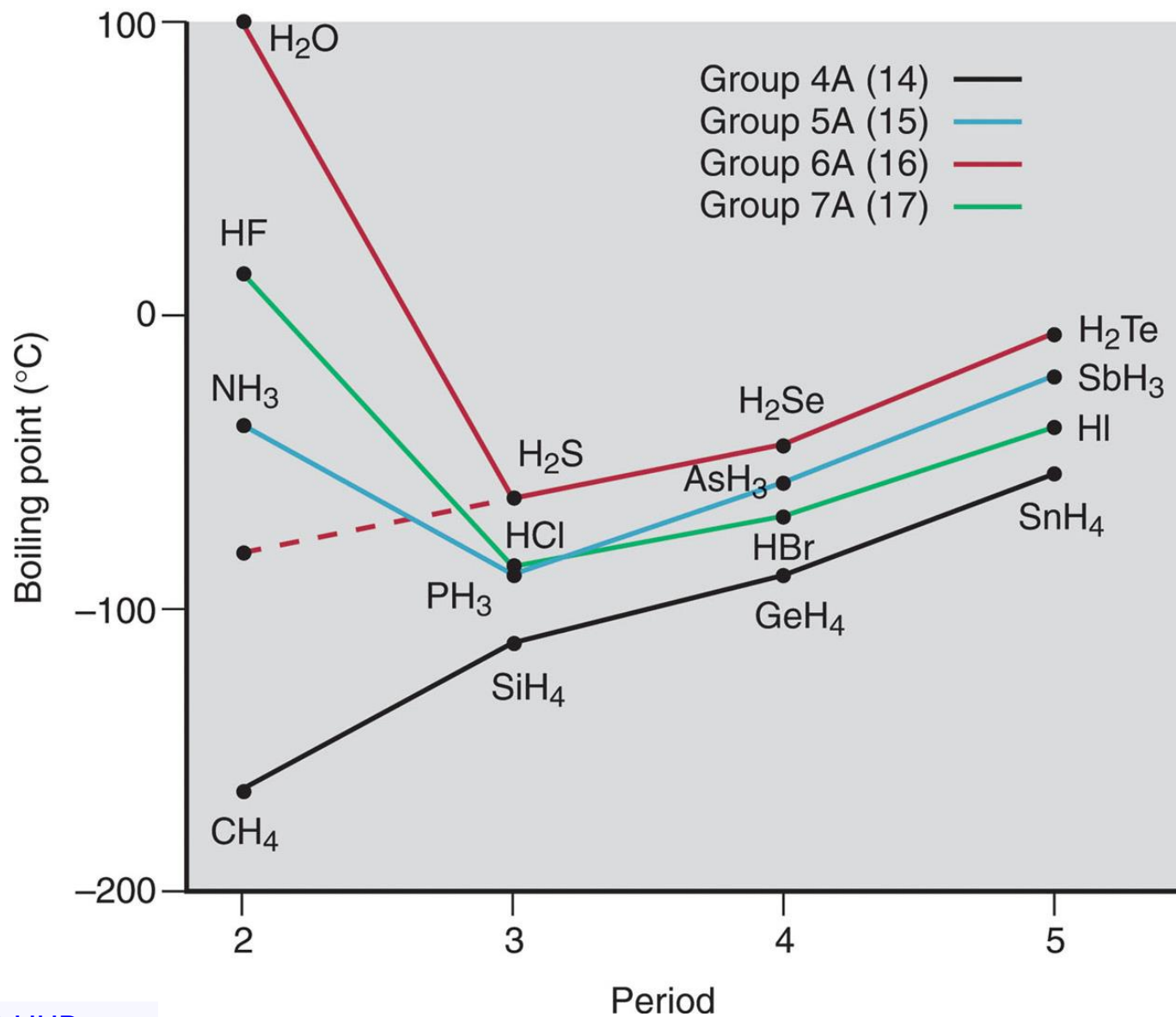


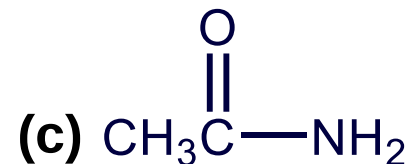
Figure 12.12 Hydrogen bonding and boiling point.



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.



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 $\text{---B:} \cdots \text{H---A}$.

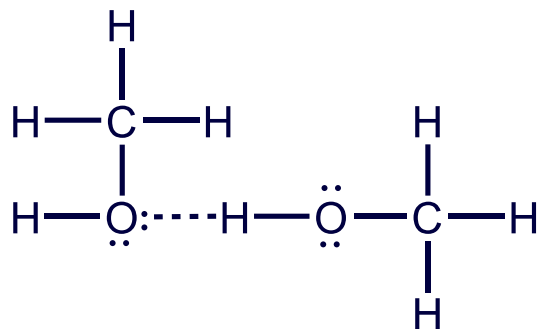
SOLUTION:

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

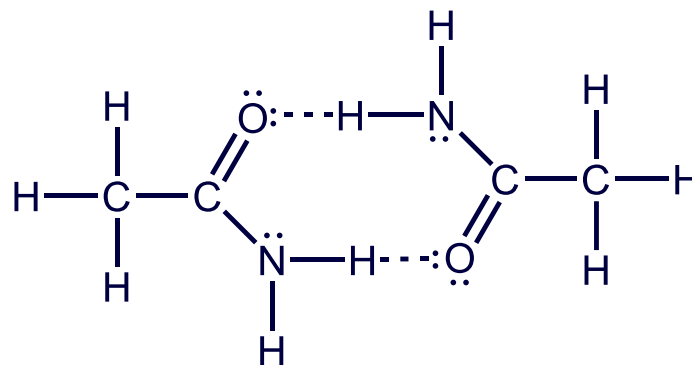
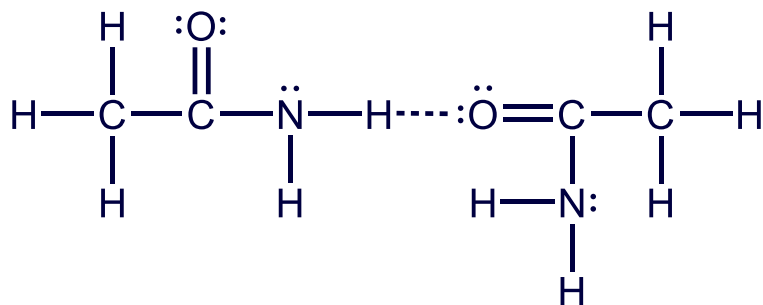


Sample Problem 12.3

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



(c) $\text{CH}_3\text{C}(=\text{O})\text{NH}_2$ 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.

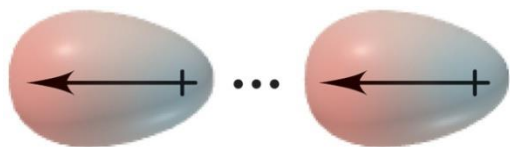
Polarizability ***decreases across a period*** because of increasing Z_{eff} .

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

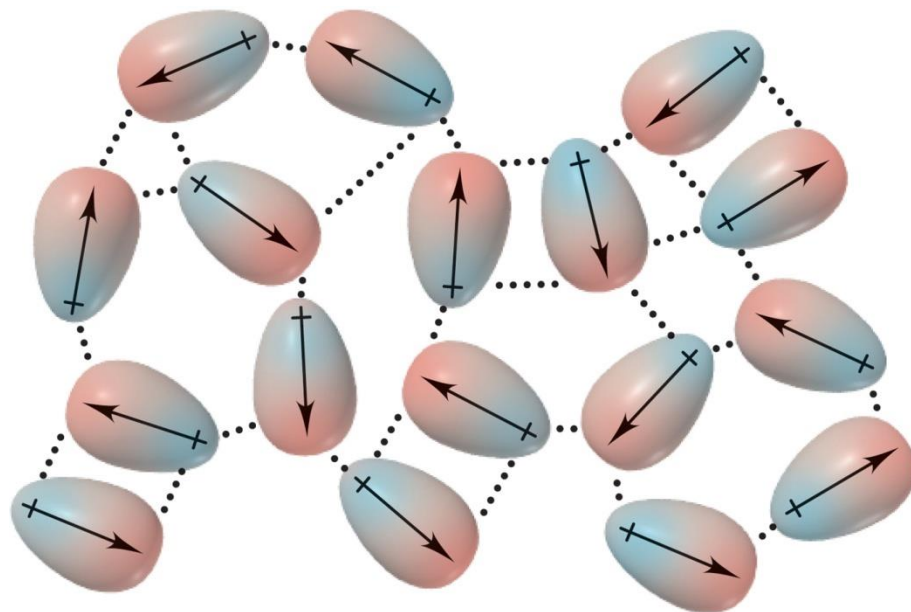
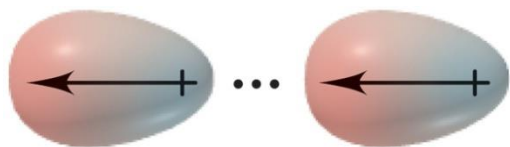


Figure 12.13 **Dispersion forces among nonpolar particles.**

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 12.14 Molar mass and trends in boiling point.

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7A (17)	8A (18)
Formula Model <i>Molar mass</i> <i>Boiling point (K)</i>	He 4.003 4.22
F₂ 38.00 85.0	Ne 20.18 27.1
Cl₂ 70.91 239	Ar 39.95 87.3
Br₂ 159.8 333	Kr 83.80 120
I₂ 253.8 458	Xe 131.3 165

Increasing strength of dispersion forces

Dispersion forces are stronger for larger, more polarizable particles.

Polarizability correlates closely with molar mass for similar particles.



Figure 12.15 **Molecular shape, intermolecular contact, and boiling point.**

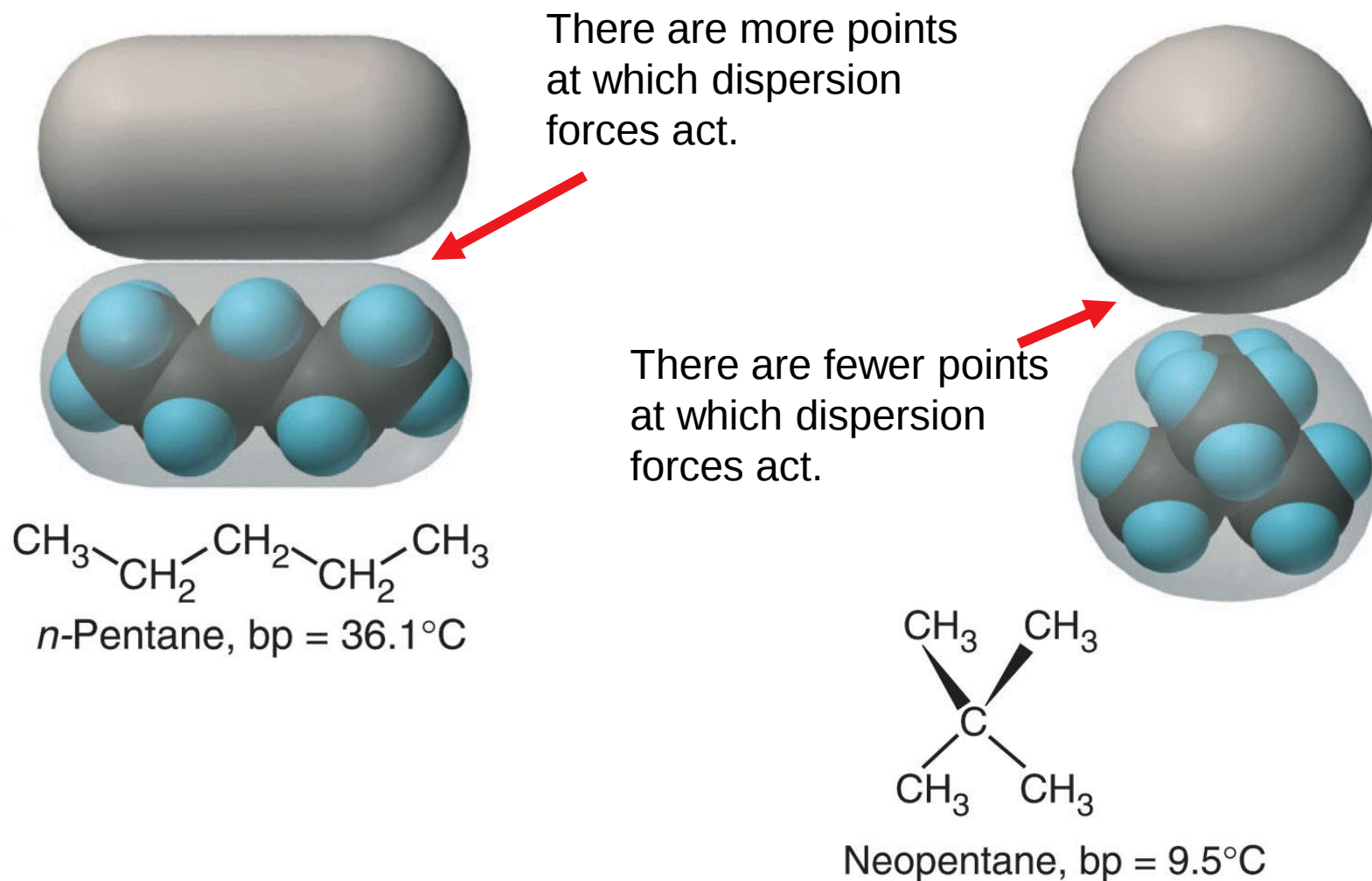
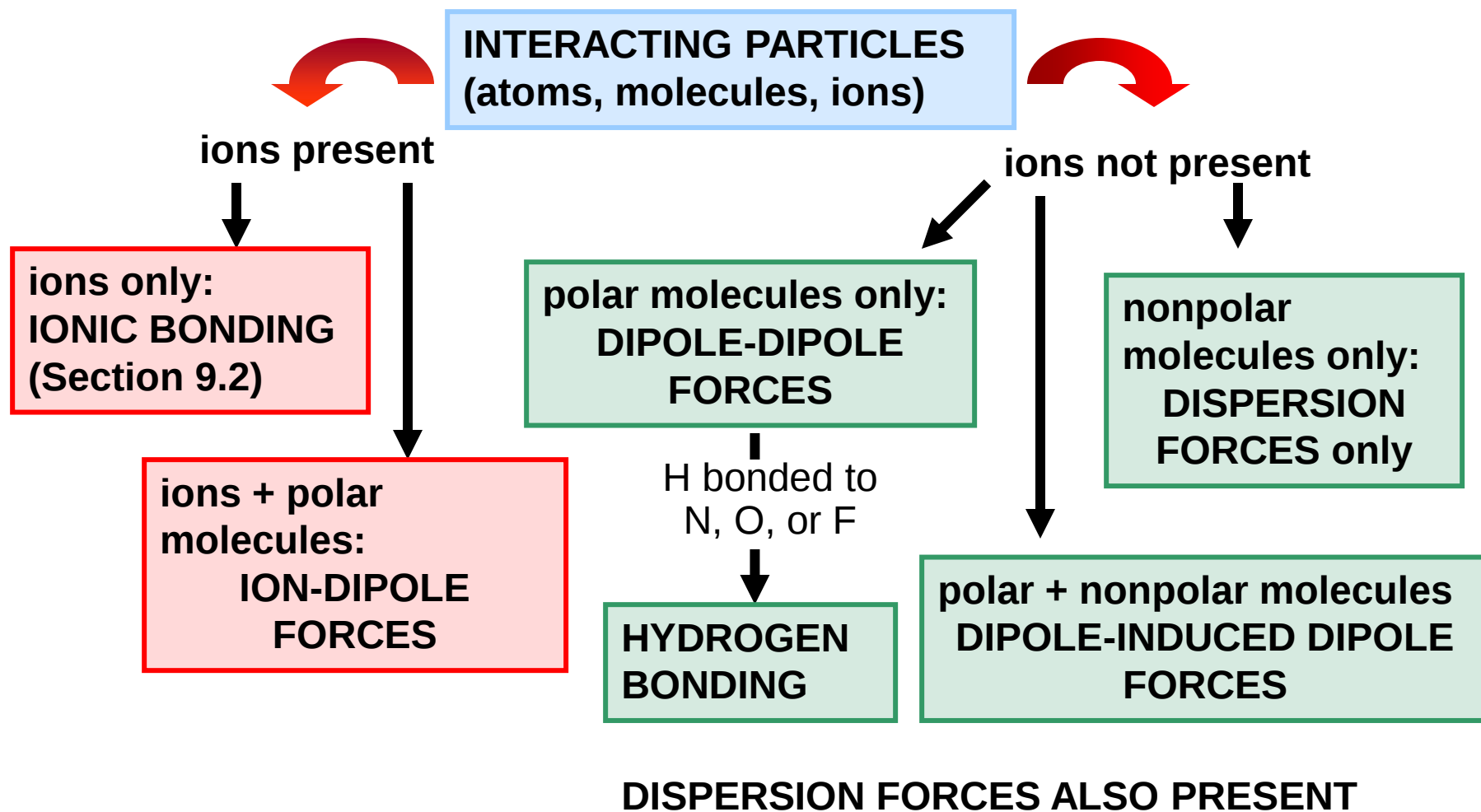


Figure 12.16 Determining the intermolecular forces in a sample.



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 $\text{CH}_3\text{CH}_2\text{OH}$

(d) Hexane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) or 2,2-dimethylbutane

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

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:

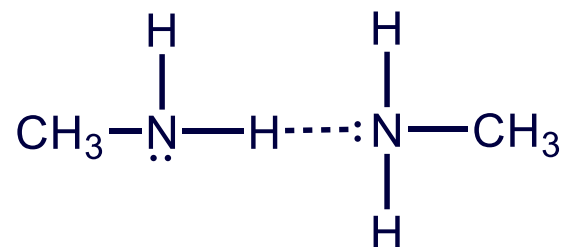
- (a) MgCl_2 consists of Mg^{2+} and Cl^- ions held together by **ionic bonding forces**; PCl_3 consists of polar molecules, so intermolecular **dipole-dipole** forces are present. The ionic bonding forces in MgCl_2 are stronger than the dipole-dipole forces in PCl_3 .

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.

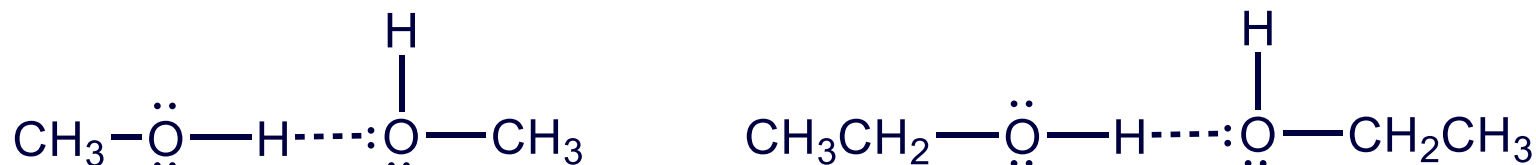


CH_3NH_2 has a higher boiling point than CH_3F .



Sample Problem 12.4

- (c) CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$ are both **polar molecules** and both contain a covalent O-H bond. Both can therefore form **H bonds**.



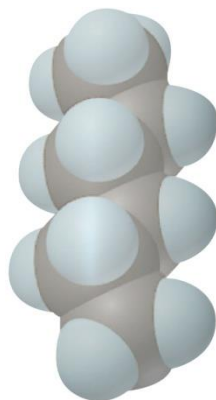
$\text{CH}_3\text{CH}_2\text{OH}$ has a larger molar mass than CH_3OH and its **dispersion forces** are therefore stronger.

$\text{CH}_3\text{CH}_2\text{OH}$ has a higher boiling point than CH_3OH .

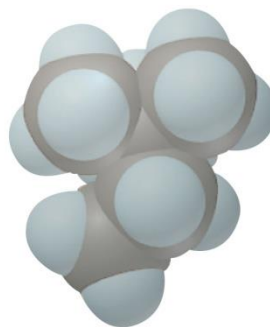


Sample Problem 12.4

- (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.



Hexane



2,2-Dimethylbutane

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 $\text{CH}_3\text{CH}_2\text{OH}$ (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.

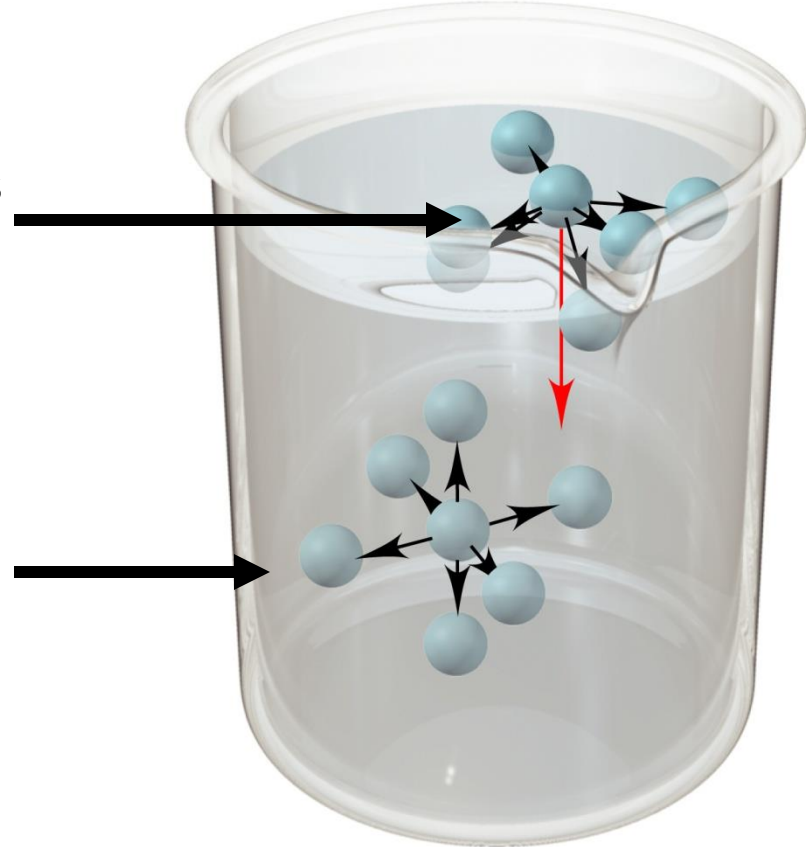


Figure 12.17 The molecular basis of surface tension.

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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.



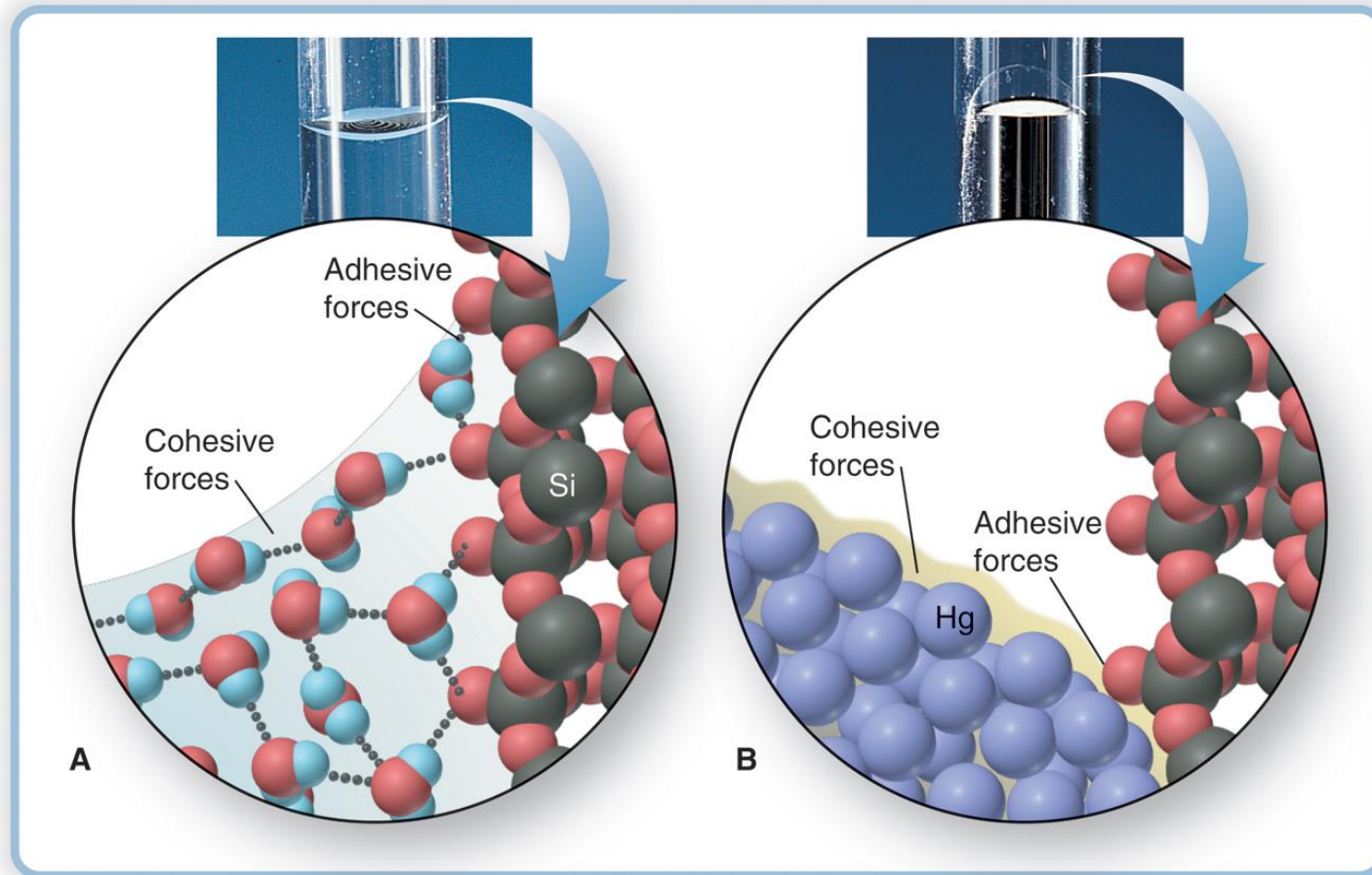
Table 12.3 Surface Tension and Forces Between Particles

Substance	Formula	Surface Tension (J/m ²) at 20°C	Major Force(s)
Diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃	1.7x10 ⁻²	Dipole-dipole; dispersion
Ethanol	CH ₃ CH ₂ OH	2.3x10 ⁻²	H bonding
Butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	2.5x10 ⁻²	H bonding; dispersion
Water	H ₂ O	7.3x10 ⁻²	H bonding
Mercury	Hg	48x10 ⁻²	Metallic bonding



Figure 12.18 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.

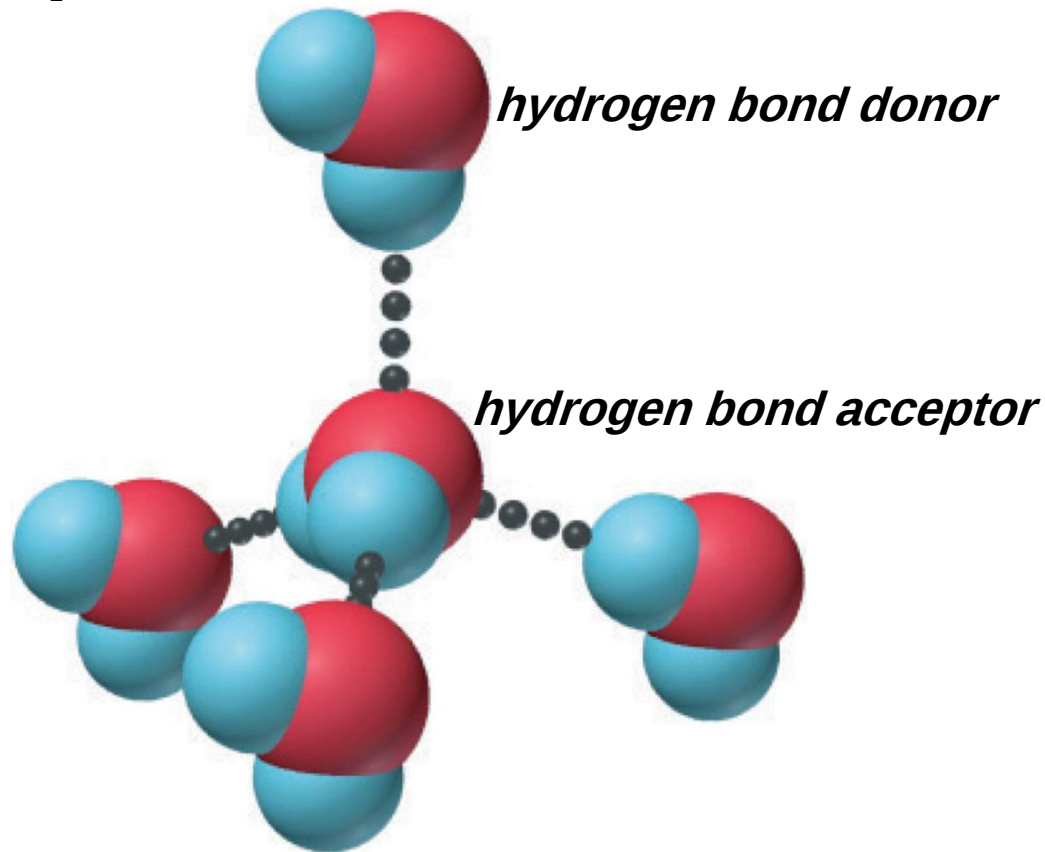
Temperature (°C)	Viscosity (N·s/m ²)*
20	1.00×10^{-3}
40	0.65×10^{-3}
60	0.47×10^{-3}
80	0.35×10^{-3}

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



The uniqueness of water

H-bonding ability of water.



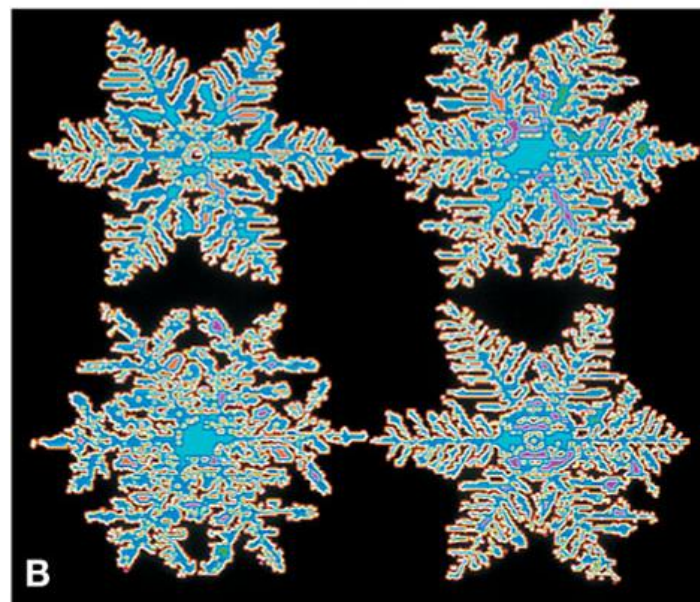
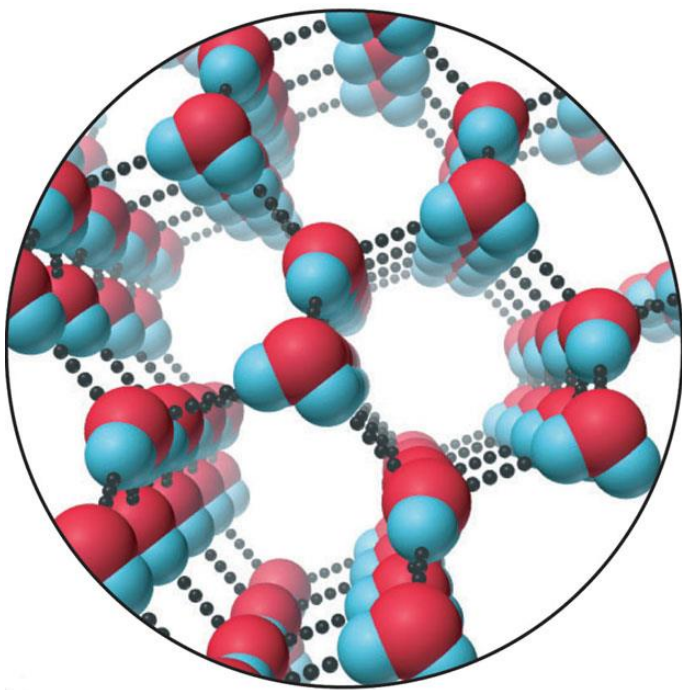
Each H_2O molecule can form ***four*** H bonds to other molecules, resulting in a tetrahedral arrangement.



- 1- Solvent properties : its results of its polarity and hydrogen bond ability.
dissolve ionic compounds through ion-dipole forces
- 2- Thermal properties : water has high specific heat capacity (water has so many strong hydrogen bonding).
- 3- surface properties of water : water has high surface tension and high capillary
- 4- Density of solid and liquid water : ice has hexagonal structure, this organization explain the negative slope of solid liquid line in phase diagram. The large space within ice give the Solid state lower density than the liquid.



Figure 12.20 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.

