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.

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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 constituent 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 differs from state to state.

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Kinetic Molecular View of the Three States

State	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.

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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

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Types of Phase Changes and Their Enthalpies

- Gas to liquid, and vice versa
  - Temperature drops (or pressure rises) $\rightarrow$ molecules in the gas phase come together and form a liquid = **condensation**
  - opposite process (liquid $\rightarrow$ gas) = **vaporization.**
- Liquid to solid, and vice versa
  - Temperature drops further $\rightarrow$ particles move more slowly and become fixed in position = **freezing**
  - opposite change = **melting** or **fusion.**
- Gas to solid, and vice versa
  - Solid to a gas (dry ice or solid CO_2 at room temp) = **sublimation**
  - opposite process (changing from a gas directly into a solid) = **deposition.**

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Two Familiar Phase Changes.

A Deposition

B Vaporization

Figure 12.1

©McGraw-Hill Education   Source: (A) © dlnadesign/Shutterstock.com; (B) © Jill Birschbach PhotoServices

Heats Of Vaporization And Fusion For Several Common Substances
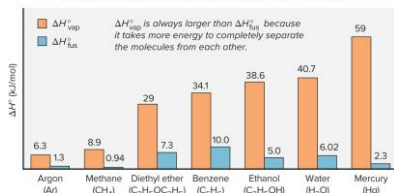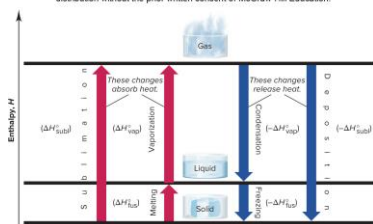
Phase Changes And Their Enthalpy Changes

Figure 12.3

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 = (amount) x (heat capacity) x ΔT**
- **During a phase change**, heat flow occurs at **constant temperature**, as the average distance between particles changes.
  - **q = (amount)(ΔH of phase change)**

A Heating-cooling Curve For The Conversion Of Gaseous Water To Ice

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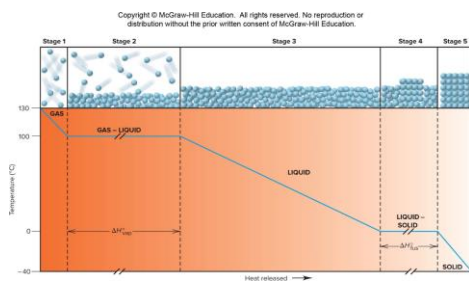
Sample Problem 12.1 – Problem

Finding the Heat of a Phase Change Depicted by Molecular Scenes

- The scenes below represent a phase change of water. Use values for molar heat capacities and heats of phase changes from the text discussion to find the heat (in kJ) released or absorbed when 24.3 g of H_2O undergoes this change.
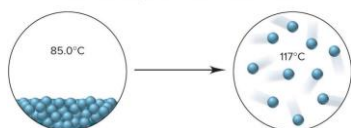
H_2O (mol) = 24.3 g H_2O $* \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 1.35$ mol H_2O

For Stage 1:

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

= (1.35 mol)(75.4 J/mol·°C)(100. − 85.0°C)

= 1527 J = 1.53 kJ

For Stage 2:

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

For Stage 3:

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

= (1.35 mol)(33.1 J/mol·°C)(117 − 100.°C)

= 759.6 J = 0.760 kJ

q_{total} = 1.53 + 54.9 + 0.760 kJ = 57.2 kJ
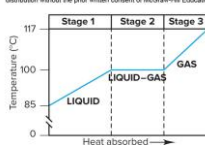
Liquid-gas Equilibrium
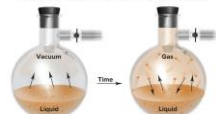
A Molecules in the liquid vaporize.

B Molecules vaporize and condense at the same rate.
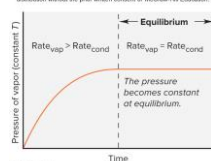
C Plot of pressure vs. time.

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

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

Figure 12.5

The Effect Of Temperature On The Distribution Of Molecular Speeds

higher $T \Longrightarrow$ higher P

These molecules are moving fast enough to vaporize, and more do so at higher T.

Kinetic energy needed to overcome intermolecular forces in liquid

Figure 12.6

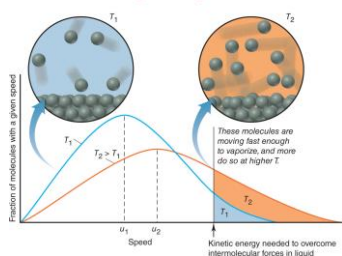## Factors Affecting Vapor Pressure

- As temperature *increases*, the fraction of molecules with enough energy to enter the vapor phase *increases*, and the vapor pressure *increases*.
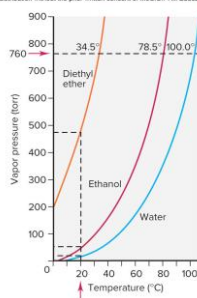
   higher $T \rightarrow$ higher P

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

   weaker forces $\rightarrow$ higher P

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*.

Figure 12.7

The Clausius-Clapeyron Equation

- This equation relates vapor pressure to temperature.

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

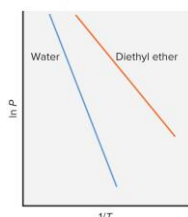- The two-point form is used when the vapor pressures at two different temperatures are known.

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

R = 8.314 J/mol·K

Linear Plots Of The Relationship Between Vapor Pressure And Temperature

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

Figure 12.8

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**.

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Phase Diagram For CO_2

Figure 12.10

©McGraw-Hill Education

Phase Diagram For H_2O

- **Neutral**

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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.

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.

- **Neutral**

## Periodic Trends In Covalent And Van Der Waals Radii
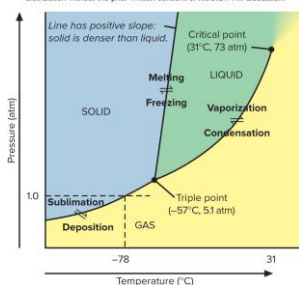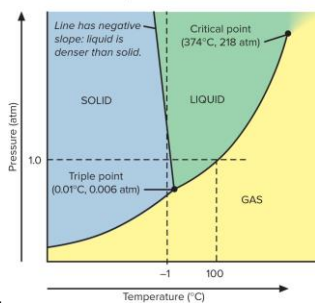
- **Neutral**

Comparison of Bonding Forces

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

Comparison of Non-Bonding Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Ion–dipole		Ion charge–dipole charge	40–600	Na⁺···O(H)(H)
H bond		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	Fe²⁺···O₂
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

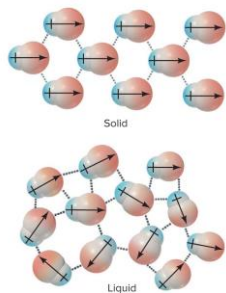## Polar Molecules and Dipole-Dipole Forces

Figure 12.13
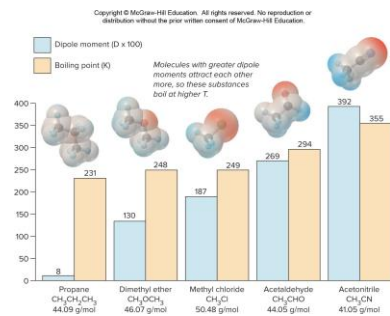
9

Dipole Moment and Boiling Point

Figure 12.14

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.
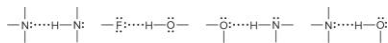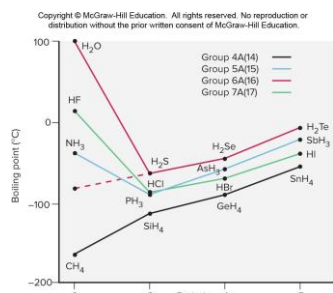

Hydrogen Bonding and Boiling Point

Figure 12.15

Drawing Hydrogen Bonds Between Molecules of a Substance

Which of these substances exhibits H bonding? Draw examples of the H bonds between two molecules of each substance that does. **(a)** C_2H_6 **(b)** CH_3OH **(c)** $CH_3\overset{O}{\overset{\|}{C}}-NH_2$

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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.

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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.

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Dispersion Forces Among Nonpolar Particles
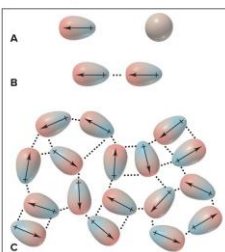
- When atoms are far apart they do not influence one other.
- When atoms are close together, the instantaneous dipole in one atom induces a dipole in the other.
- The process occurs throughout the sample.

Dispersion (London) Forces

- *Dispersion forces* or *London forces* arise 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.

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 12.17

Molecular Shape, Intermolecular Contact, and Boiling Point

n-Pentane
bp = 36.1°C

There are more points at which dispersion forces act.
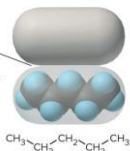
Neopentane
bp = 9.5°C

There are fewer points at which dispersion forces act.
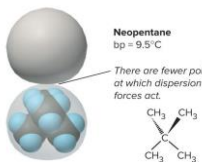
Figure 12.18

Determining the Intermolecular Forces In a Sample
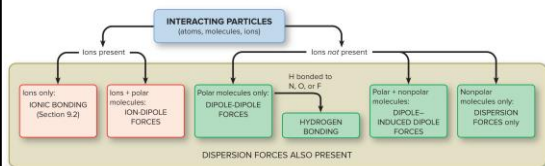
Figure 12.19

Identifying the Types of Intermolecular Forces

For each substance, identify the key bonding and/or intermolecular force(s), and predict which substance 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

SOLUTION:

(a) $MgCl_2$ consists of Mg^{2+} and Cl^- ions held together by ionic bonding forces; PCl_3 ,with a trigonal pyramidal geometry, consists of polar molecules, so intermolecular dipole-dipole forces are present. The forces in $MgCl_2$ are stronger, so it should have a higher boiling point.

(b) CH_3NH_2 and CH_3F both consist of polar molecules of about the same molar mass. CH_3NH_2 has N–H bonds, so it can form H bonds. CH_3F contains a C–F bond but no H–F bond, so dipole-dipole forces occur but not H bonds.
Therefore, CH_3NH_2 should have the higher boiling point.
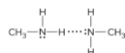
(c) CH_3OH and CH_3CH_2OH molecules both contain an O–H bond, so they can form H bonds. CH_3CH_2OH has an additional $–CH_2–$ group and thus a larger molar mass, which correlates with stronger dispersion forces; therefore, it should have a higher boiling point.
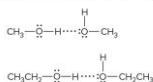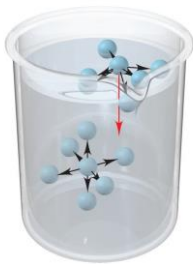
(d) Hexane and 2,2-dimethylbutane are nonpolar molecules of the same molar mass but different molecular shapes. Cylindrical hexane molecules make more intermolecular contact than more compact 2,2-dimethylbutane molecules do, so hexane should have stronger dispersion forces and a higher boiling point.
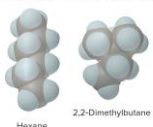
The Molecular Basis Of Surface Tension

- 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.

Surface Tension, Viscosity, and Forces Between Particles

Substance	Formula	Surface Tension (J/m²) at 20°C	Viscosity (N·s/m²) at 20°C	Major Force(s)
Diethyl ether	$CH_3CH_2OCH_2CH_3$	1.7×10^{-2}	0.240×10^{-3}	Dipole-dipole; dispersion
Ethanol	CH_3CH_2OH	2.3×10^{-2}	1.20×10^{-3}	H bonding
Butanol	$CH_3CH_2CH_2CH_2OH$	2.5×10^{-2}	2.95×10^{-3}	H bonding; dispersion
Water	H_2O	7.3×10^{-2}	1.00×10^{-3}	H bonding
Mercury	Hg	48×10^{-2}	1.55×10^{-3}	Metallic bonding

Capillary Action and the Shape Of The Water or Mercury Meniscus In Glass

A. Water displays a concave meniscus.

B. Mercury displays a convex meniscus.
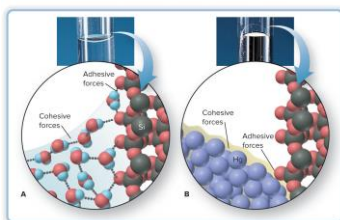
Figure 12.21

Viscosity of Water at Several Temperatures

Temperature (°C)	Viscosity (N·s/m²)
20	1.00×10^{-3}
40	0.65×10^{-3}
60	0.47×10^{-3}
80	0.35×10^{-3}

H-bonding Ability of water

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

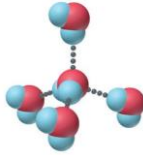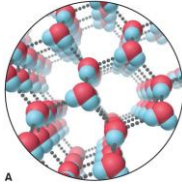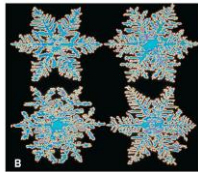**Figure 12.22**

The Hexagonal Structure Of Ice

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

Figure 12.23

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	High Heat Capacity and ΔH_{vap}	Surface Tension and Capillarity	Open Structure of Ice
• 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	• Narrow range of body temperature • Narrow range of Earth's temperatures • Natural water cycle • Winds and storms	• Life on lake surface • Water in soil for plants	• Survival of lake life in winter • Nutrient turnover in lakes • Formation of sand and soil

Figure 12.24

16