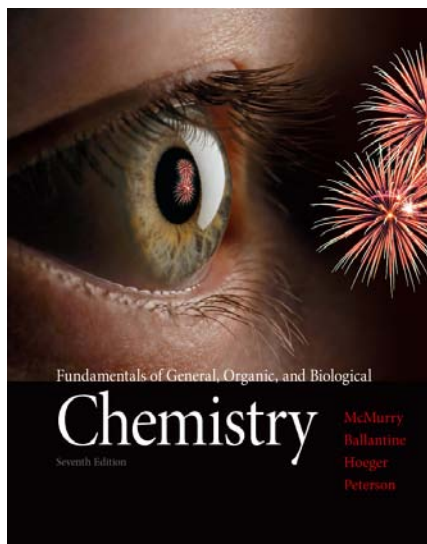


Chapter 8 Lecture



Fundamentals of General, Organic, and Biological Chemistry

7th Edition

McMurry, Ballantine, Hoeger, Peterson

Chapter Eight

Gases, Liquids, and Solids

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ALWAYS LEARNING

PEARSON

Outline

- 8.1 States of Matter and Their Changes
- 8.2 Intermolecular Forces
- 8.3 Gases and the Kinetic–Molecular Theory
- 8.4 Pressure
- 8.5 Boyle’s Law: The Relation between Volume and Pressure
- 8.6 Charles’ Law: The Relation between Volume and Temperature
- 8.7 Gay-Lussac’s Law: The Relation between Pressure and Temperature
- 8.8 The Combined Gas Law
- 8.9 Avogadro’s Law: The Relation between Volume and Molar Amount
- 8.10 The Ideal Gas Law
- 8.11 Partial Pressure and Dalton’s Law
- 8.12 Liquids
- 8.13 Water: A Unique Liquid
- 8.14 Solids
- 8.15 Changes of State

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Goals

1. What are the major intermolecular forces, and how do they affect the states of matter?

Be able to explain dipole–dipole forces, London dispersion forces, and hydrogen bonding, recognize which of these forces affect a given molecule, and how these forces are related to the physical properties of a substance.

2. How do scientists explain the behavior of gases?

Be able to state the assumptions of the kinetic–molecular theory and use these assumptions to explain the behavior of gases.

3. How do gases respond to changes in temperature, pressure, and volume?

Be able to use Boyle's law, Charles's law, Gay-Lussac's law, and Avogadro's law to explain the effect on gases of a change in pressure, volume, or temperature.

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Goals

4. What is the ideal gas law?

Be able to use the ideal gas law to find the pressure, volume, temperature, or molar amount of a gas sample.

5. What is partial pressure?

Be able to define partial pressure and use Dalton's law of partial pressures.

6. What are the various kinds of solids, and how do they differ?

Be able to recognize the different kinds of solids and describe their characteristics.

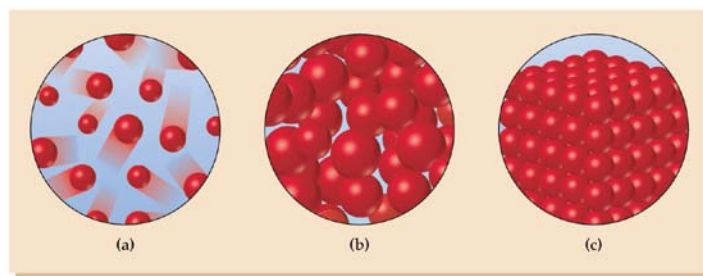
7. What factors affect a change of state?

Be able to apply the concepts of heat change, equilibrium, vapor pressure, and intermolecular forces to changes of state.

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8.1 States of Matter and Their Changes

- Matter exists in any of three phases, or *states*—solid, liquid, and gas.
- The state depends on the relative strength of the attractive forces between particles compared to the kinetic energy of the particles.



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8.1 States of Matter and Their Changes

- The transformation of a substance from one state to another is called a *phase change*, or a **change of state**.
- Every change of state is reversible and characterized by a free-energy change.

Free-energy change

Enthalpy change	Temperature (in kelvins)	Entropy change
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$$\Delta G = \Delta H - T\Delta S$$

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- ΔH is a measure of the heat absorbed or released.
- ΔS is a measure of the change in molecular disorder.

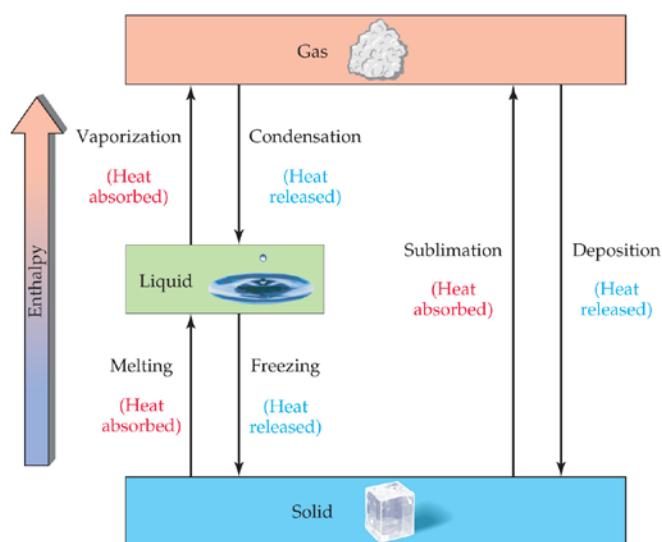
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8.1 States of Matter and Their Changes

- The sign of ΔG is temperature-dependent.
- The temperature at which the liquid phase is in equilibrium with the solid phase is called the **melting point**.
- The temperature at which the gas phase is in equilibrium with the liquid phase is called the **boiling point**.
- A solid can change directly to a gas without going through the liquid state in a process called *sublimation*. Dry ice (solid CO_2) changes directly to a gas without melting.

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8.1 States of Matter and Their Changes



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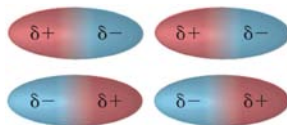
8.2 Intermolecular Forces

- **Intermolecular force** is a force that acts between molecules and holds molecules close to one another.
- In gases, intermolecular forces are negligible.
- In liquids and solids, the stronger the intermolecular forces, the higher the melting and boiling points.
- There are three major types of intermolecular forces: *dipole–dipole*, *London dispersion*, and *hydrogen bonding*.

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8.2 Intermolecular Forces

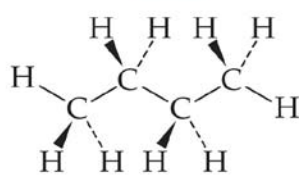
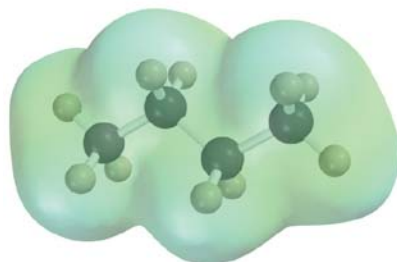
- **Dipole-Dipole Forces:**
 - Molecules that contain polar covalent bonds may have a net molecular polarity.
 - The positive and negative ends of different molecules are attracted to one another.



- Dipole–dipole forces are weak, but the effects of dipole–dipole forces are important, as can be seen by looking at the difference in boiling points between polar and nonpolar molecules.

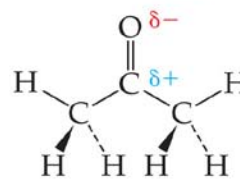
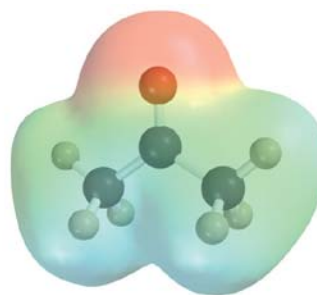
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8.2 Intermolecular Forces



Butane (C_4H_{10})

Mol wt = 58 amu
bp = $-0.5^\circ C$



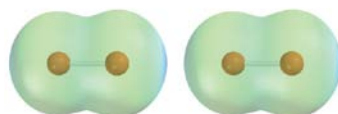
Acetone (C_3H_6O)

Mol wt = 58 amu
bp = $56.2^\circ C$

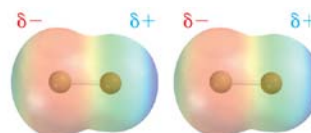
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8.2 Intermolecular Forces

- **London Dispersion Forces:**
 - All molecules experience these forces.
 - At any given *instant* there may be more electrons at one end of a molecule than at the other, giving a short-lived polarity.
 - The larger the molecular weight and surface area, the greater the temporary polarization of a molecule.



(a)

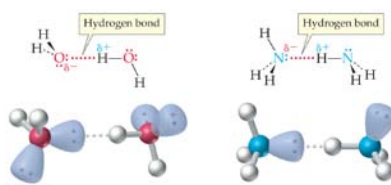


(b)

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8.2 Intermolecular Forces

- **Hydrogen Bonding:**
 - The attraction between a hydrogen atom bonded to an O, N, or F atom and another nearby O, N, or F atom.
 - An unusually strong dipole–dipole interaction.
 - In water, each oxygen atom has two lone pairs and two hydrogen atoms, allowing the formation of four hydrogen bonds.



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8.2 Intermolecular Forces

TABLE 8.2 A Comparison of Intermolecular Forces

Force	Strength	Characteristics
Dipole–dipole	Weak (1 kcal/mol, 4 kJ/mol))	Occurs between polar molecules
London dispersion	Weak (0.5–2.5 kcal/mol, 2–10 kJ/mol)	Occurs between all molecules; strength depends on size
Hydrogen bond	Moderate (2–10 kcal/mol, 8–40 kJ/mol)	Occurs between molecules with O–H, N–H, and F–H bonds

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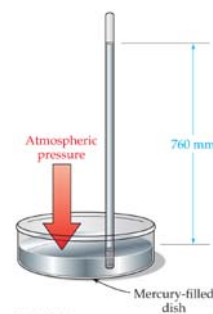
8.3 Gases and the Kinetic Molecular Theory

- The **kinetic–molecular theory of gases** is a group of assumptions that explain the behavior of gases.
 1. A gas consists of particles moving at random with no attractive forces between them.
 2. The amount of space occupied by the gas particles themselves is much smaller than the amount of space between particles.
 3. The average kinetic energy of gas particles is proportional to the Kelvin temperature
 4. Collisions of gas particles, either with other particles or with the wall of their container, are elastic; that is, the total kinetic energy of the particles is constant.
 5. A gas that obeys all the assumptions of the kinetic–molecular theory is called an ideal gas.

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8.4 Pressure

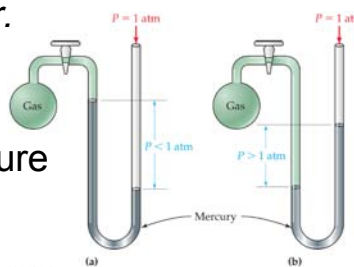
- **Pressure (P)** is the force per unit area pushing against a surface.
- **Atmospheric pressure:** A column of air weighing 14.7 lb presses down on each square inch of the earth's surface at sea level.
- Millimeters of mercury (mmHg) or *torr* are a common unit of pressure, after the height of a column of mercury in a barometer.



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8.4 Pressure

- Gas pressure in a container is measured using a *manometer*.
- The difference between the mercury levels indicates the difference between gas pressure and atmospheric pressure.
- Pressure is given in the SI system by the *pascal* (Pa).



$$1 \text{ atm} = 760 \text{ mmHg} = 14.7 \text{ psi} = 101,325 \text{ Pa}$$

$$1 \text{ mmHg} = 1 \text{ torr} = 133.32 \text{ Pa}$$

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8.4 Pressure

Greenhouse Gases and Global Warming

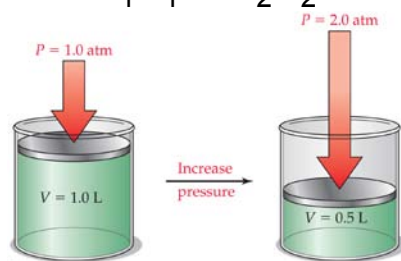
- The mantle of gases surrounding the earth is not uniform, consisting of layers. The differing ability of the gases in these layers to absorb radiation is responsible for life on earth as we know it.
- The *stratosphere*—the layer extending from about 12 km up to 50 km altitude—contains the ozone layer that is responsible for absorbing harmful UV radiation.
- The *troposphere* is the layer extending from the surface up to about 12 km altitude.
- Much of the radiant energy reaching the earth's surface from the sun is reflected back into space, but some is absorbed by atmospheric gases, particularly water vapor, carbon dioxide, and methane.
- This absorbed radiation acts to maintain a relatively stable temperature of 15 °C (59 °F) at the earth's surface.
- The concentration of atmospheric CO₂ has risen from an estimated 290 parts per million (ppm) in 1850 to current levels approaching 400 ppm.
- The increase in CO₂ levels correlates with a concurrent increase in average global temperatures.

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8.5 Boyle's Law: The Relation between Volume and Pressure

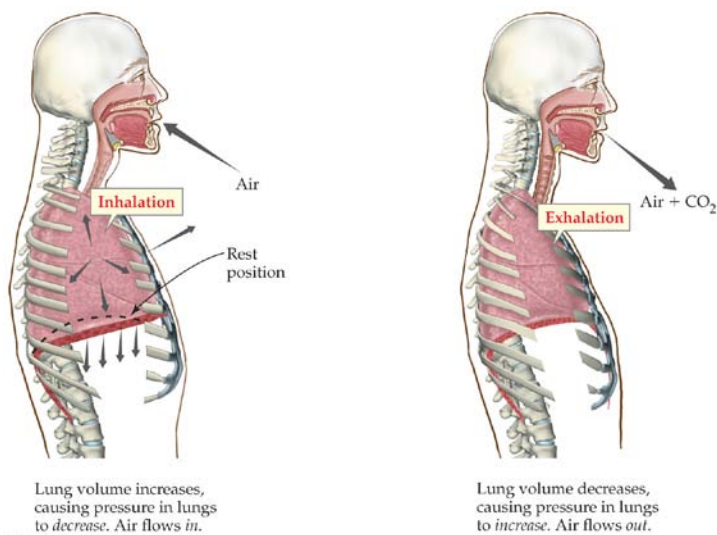
- **Boyle's law:** The volume of a fixed amount of gas at a constant temperature decreases proportionately as its pressure increases. If the pressure of a gas sample is doubled, the volume is halved.

$$P_1V_1 = P_2V_2$$



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8.5 Boyle's Law: The Relation between Volume and Pressure



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8.5 Boyle's Law: The Relation between Volume and Pressure

Blood Pressure

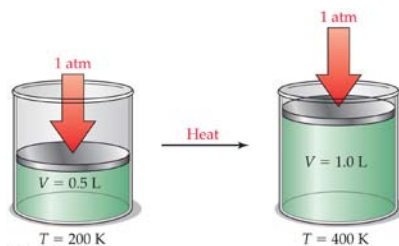
- A normal adult male has a reading near 120/80 mmHg, and a normal adult female has a reading near 110/70 mmHg. Abnormally high values signal an increased risk of heart attack and stroke.
- *Systolic pressure* is the maximum pressure developed in the artery just after contraction, as the heart forces the maximum amount of blood into the artery.
- *Diastolic pressure* is the minimum pressure that occurs at the end of the heart cycle.
- Blood pressure is most often measured by a *sphygmomanometer*, a device consisting of a squeeze bulb, a flexible cuff, and a mercury manometer.
- The cuff is placed around the upper arm over the brachial artery and inflated by the squeeze bulb to about 200 mmHg pressure, an amount great enough to squeeze the artery shut and prevent blood flow. Air is then slowly released from the cuff, and pressure drops. As cuff pressure reaches the systolic pressure, blood spurts through the artery, creating a turbulent tapping sound that can be heard through a stethoscope. The pressure registered at the moment the first sounds are heard is the systolic blood pressure.
- When the pressure in the cuff becomes low, blood flow becomes smooth, and a diastolic blood pressure reading is recorded on the manometer.

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8.6 Charles's Law: The Relation between Volume and Temperature

- **Charles's law:** The volume of a fixed amount of gas at constant pressure is directly proportional to its Kelvin temperature. If the Kelvin temperature of the gas is doubled, its volume doubles

$$V_1/T_1 = V_2/T_2$$



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8.7 Gay-Lussac's Law: The Relation between Pressure and Temperature

- **Gay-Lussac's law:** The pressure of a fixed amount of gas at constant volume is directly proportional to its Kelvin temperature. As temperature goes up or down, pressure also goes up or down.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

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8.8 The Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- If any five of the six quantities in this equation are known, the sixth can be calculated.
- If any of the three variables T , P , or V is constant, that variable drops out of the equation.
- *For a fixed amount of gas, the combined gas law is the only equation you need to remember.*

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8.9 Avogadro's Law: The Relation between Volume and Molar Amount

- **Avogadro's law** states that the volume of a gas is directly proportional to its molar amount at a constant pressure and temperature. A sample that contains twice the molar amount has twice the volume.
- **Standard temperature and pressure (STP)** is 0 °C (273 K) and 1 atm (760 mmHg).
- **Standard molar volume of any ideal gas at STP** is 22.4 L/mol.

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8.10 The Ideal Gas Law

- The relationships among the four variables P , V , T , and n for gases can be combined into a single expression called the **ideal gas law**.

$$\frac{PV}{nT} = R$$

- The constant R is called the **gas constant**. Its value depends on the units chosen for pressure.

$$R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} \text{ or } 62.4 \text{ L}\cdot\text{mmHg}/\text{mol}\cdot\text{K}$$

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8.10 The Ideal Gas Law

TABLE 8.3 A Summary of the Gas Laws

	Gas Law	Variables	Constant
Boyle's law	$P_1V_1 = P_2V_2$	P, V	n, T
Charles's law	$V_1/T_1 = V_2/T_2$	V, T	n, P
Gay-Lussac's law	$P_1/T_1 = P_2/T_2$	P, T	n, V
Combined gas law	$P_1V_1/T_1 = P_2V_2/T_2$	P, V, T	n
Avogadro's law	$V_1/n_1 = V_2/n_2$	V, n	P, T
Ideal gas law	$PV = nRT$	P, V, T, n	R

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8.11 Partial Pressure and Dalton's Law

- Each particle in a gas acts independently, so the chemical identity of its neighbors is irrelevant.
- *Mixtures* of gases behave the same as pure gases and obey the same laws.
- Dry air is a mixture of 21% oxygen, 78% nitrogen, and 1% argon by volume.
- 21% of atmospheric pressure is caused by O₂, 78% by N₂, and 1% by Ar.
- The contribution of each gas in a mixture to the total pressure of the mixture is called the **partial pressure** of that gas.

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8.11 Partial Pressure and Dalton's Law

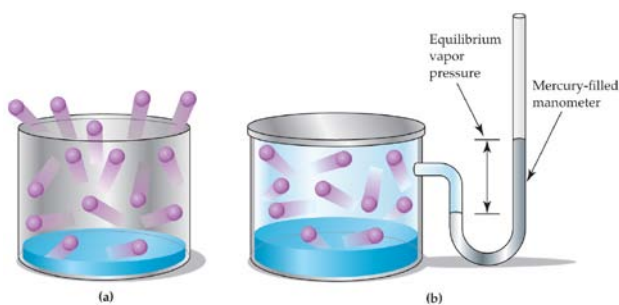
$$P_{\text{total}} = P_{\text{gas 1}} + P_{\text{gas 2}} + \dots$$

- *The partial pressure exerted by each gas in a mixture is the same pressure that the gas would exert if it were alone.*
- The pressure exerted by each gas depends on the frequency of collisions of its molecules with the walls of the container. This frequency does not change when other gases are present.
- Pressure decreases rapidly with altitude. The partial pressure of oxygen in air, therefore decreases with increasing altitude, which leads to difficulty in breathing at high elevations.

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8.12 Liquids

- Molecules are in constant motion in the liquid state. If a molecule has enough energy, it can break free of the liquid and escape into the gas state, called **vapor**.



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8.12 Liquids

- If a liquid is in a closed container, the random motion of the molecules occasionally brings them back into the liquid.
- Evaporation and condensation take place at the same rate, and the concentration of vapor in the container is constant.
- **Vapor pressure** is the partial pressure of vapor molecules in equilibrium with a liquid.

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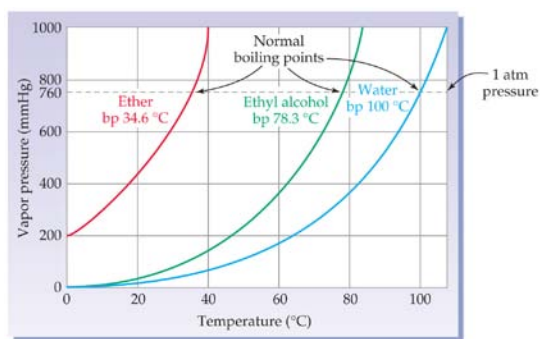
8.12 Liquids

- Vapor pressure depends on both temperature and identity of a liquid.
- Vapor pressure rises with increasing temperature.
- When the vapor pressure is equal to the atmospheric pressure, the liquid boils.
- **Normal boiling point** is the boiling point at a pressure of exactly 1 atmosphere.

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8.12 Liquids

- The vapor pressure and boiling point of a liquid depend on the intermolecular forces at work between liquid molecules.
- When atmospheric pressure is lower than normal, as at high altitudes, boiling points are lower as well.



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8.12 Liquids

- The measure of a liquid's resistance to flow is called its *viscosity*.
- Viscosity increases with increasing intermolecular forces.
- *Surface tension* is caused by the difference between the intermolecular forces experienced by molecules at the surface of the liquid and those experienced by molecules in the interior.

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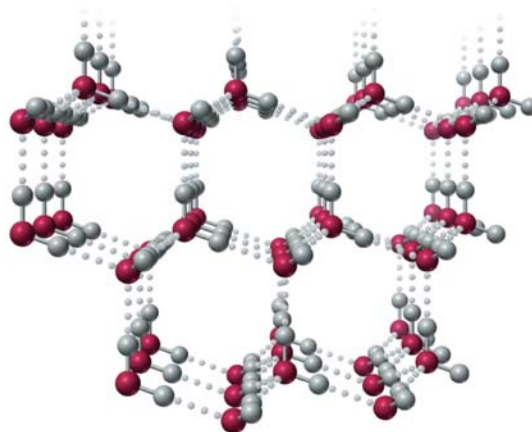
8.13 Water: A Unique Liquid

- Water covers nearly 71% of the earth's surface, it accounts for 66% of the mass of an adult human body, and it is needed by all living things.
- Because of strong hydrogen bonding, water has many unique properties.
- Water has the highest specific heat of any liquid.
- Water has an unusually high *heat of vaporization*.

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8.13 Water: A Unique Liquid

- Liquid water is denser than solid water (ice).



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8.14 Solids

- A **crystalline solid** is one whose atoms, molecules, or ions are rigidly held in an ordered arrangement.
 - *Ionic solids* are those whose constituent particles are ions. A crystal is composed of alternating + and –ions in a regular three-dimensional arrangement held together by ionic bonds.
 - *Molecular solids* constituent particles are molecules held together by intermolecular forces.
 - *Covalent network solids* atoms are linked together by covalent bonds into a giant three-dimensional array. In effect, a covalent network solid is one *very* large molecule.

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8.14 Solids

- **Metallic solids** can be viewed as vast three-dimensional arrays of metal cations immersed in a sea of electrons.
 - The electron sea acts as a glue to hold the cations together and as a mobile carrier of charge to conduct electricity.
 - Bonding attractions extend uniformly in all directions, so metals are malleable rather than brittle. When a metal crystal receives a sharp blow, the electron sea adjusts to the new distribution of cations.

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8.14 Solids

- An **amorphous solid** is one whose constituent particles are randomly arranged and have no ordered long-range structure.
 - Amorphous solids often result when liquids cool before they can achieve internal order, or when their molecules are large and tangled together.
 - Glass, tar, opal, and some hard candies are amorphous solids.
 - Amorphous solids soften over a wide temperature range and shatter to give pieces with curved rather than planar faces.

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8.14 Solids

TABLE 8.4 Types of Solids

Substance	Smallest Unit	Interparticle Forces	Properties	Examples
Ionic solid	Ions	Attraction between positive and negative ions	Brittle and hard; high mp; crystalline	NaCl, KI, $\text{Ca}_3(\text{PO}_4)_2$
Molecular solid	Molecules	Intermolecular forces	Soft; low to moderate mp; crystalline	Ice, wax, frozen CO_2 , all solid organic compounds
Covalent network	Atoms	Covalent bonds	Very hard; very high mp; crystalline	Diamond, quartz (SiO_2), tungsten carbide (WC)
Metal or alloy	Metal atoms	Metallic bonding (attraction between metal ions and surrounding mobile electrons)	Lustrous; soft (Na) to hard (Ti); high melting; crystalline	Elements (Fe, Cu, Sn, . . .), bronze (CuSn alloy), amalgams (Hg + other metals)
Amorphous solid	Atoms, ions, or molecules (including polymer molecules)	Any of the above	Noncrystalline; no sharp mp; able to flow (may be very slow); curved edges when shattered	Glasses, tar, some plastics

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8.15 Changes of State

- When a solid is heated, molecules begin to stretch, bend, and vibrate more vigorously, and atoms or ions wiggle about with more energy.
- If enough energy is added and the motions become vigorous enough, particles start to break free from one another and the substance starts to melt.
- The quantity of heat required to completely melt one gram of a substance once it has reached its melting point is called its **heat of fusion**.

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8.15 Changes of State

- When a liquid is heated, all the added heat goes into raising the temperature.
- Once the boiling point is reached, heat goes into freeing molecules from their neighbors as they escape into the gas state.
- The quantity of heat needed to completely vaporize a liquid at its boiling point is the **heat of vaporization**.
- A liquid with a low heat of vaporization is *volatile*.

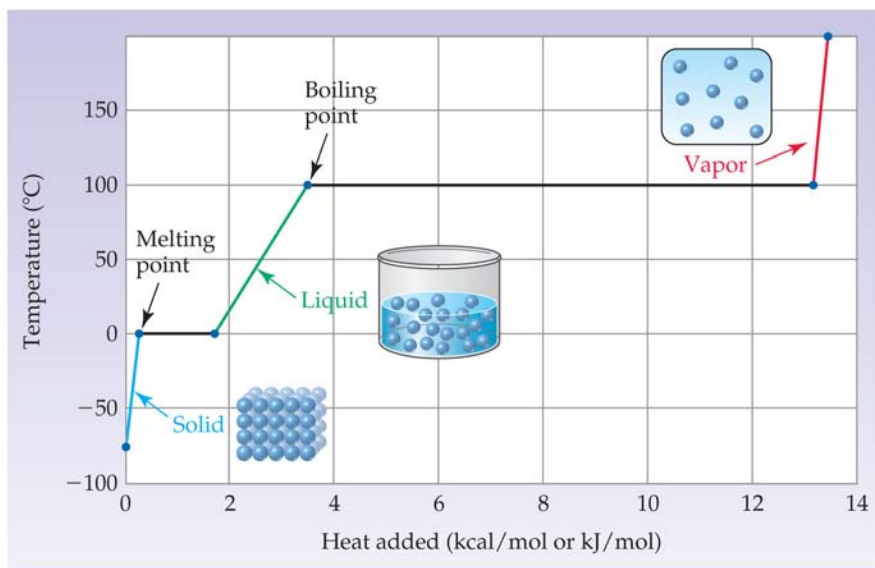
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8.15 Changes of State

- When a substance is above or below its phase change temperature, adding or removing heat will change the temperature of the substance.
- When a substance is at its phase change temperature, heat is used to overcome the intermolecular forces holding particles in that phase.
- The temperature remains constant until *all* particles have been converted.

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8.15 Changes of State



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8.15 Changes of State

- If intermolecular forces are strong then large amounts of heat must be added to overcome them, and the heats of fusion and vaporization will be large.

TABLE 8.5 Melting Points, Boiling Points, Heats of Fusion, and Heats of Vaporization of Some Common Substances

Substance	Melting Point (°C)	Boiling Point (°C)	Heat of Fusion (cal/g; J/g)	Heat of Vaporization (cal/g; J/g)
Ammonia	-77.7	-33.4	84.0; 351	327; 1370
Butane	-138.4	-0.5	19.2; 80.3	92.5; 387
Ether	-116	34.6	23.5; 98.3	85.6; 358
Ethyl alcohol	-117.3	78.5	26.1; 109	200; 837
Isopropyl alcohol	-89.5	82.4	21.4; 89.5	159; 665
Sodium	97.8	883	14.3; 59.8	492; 2060
Water	0.0	100.0	79.7; 333	540; 2260

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8.15 Changes of State

CO₂ as an Environmentally Friendly Solvent

- When it enters an unusual and rarely seen state of matter called the *supercritical state*, CO₂ becomes a remarkable solvent.
- The supercritical state represents a situation that is intermediate between liquid and gas. There is *some* space between molecules, but not much.
- Supercritical CO₂ exists above the *critical point*, when the pressure is above 72.8 atm and the temperature is above 31.2 °C.
- Because open spaces already exist between CO₂ molecules, it is energetically easy for molecules to slip in.
- Supercritical CO₂ is used to decaffeinate coffee beans and to obtain spice extracts and fragrant oils. Perhaps the most important future application is the use of carbon dioxide for dry-cleaning clothes, replacing environmentally harmful chlorinated solvents.
- Supercritical CO₂ is nontoxic and nonflammable.
- Industrial processes using CO₂ are designed as closed systems so that CO₂ is recaptured after use and continually recycled. No organic solvent vapors are released into the atmosphere and no toxic liquids seep into groundwater supplies. The future looks bright for this new technology.

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Chapter Summary

1. What are the major intermolecular forces, and how do they affect the states of matter?

- There are three major types of *intermolecular forces*, which act to hold molecules near one another in solids and liquids.
 - *Dipole–dipole forces* are the electrical attractions that occur between polar molecules.
 - *London dispersion forces* occur between all molecules as a result of temporary molecular polarities due to unsymmetrical electron distribution. These forces increase in strength with molecular weight and with the surface area of molecules.
 - *Hydrogen bonding*, the strongest of the three intermolecular forces, occurs between a hydrogen atom bonded to O, N, or F and a nearby O, N, or F atom.

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Chapter Summary, Continued

2. How do scientists explain the behavior of gases?

- According to the *kinetic-molecular theory of gases*, the physical behavior of gases can be explained by assuming that they consist of particles moving rapidly at random, separated from other particles by great distances, and colliding without loss of energy.
- Gas pressure is the result of molecular collisions with a surface.

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Chapter Summary, Continued

3. How do gases respond to changes in temperature, pressure, and volume?

- *Boyle's law* says that the volume of a fixed amount of gas at constant temperature is inversely proportional to its pressure.
- *Charles's law* says that the volume of a fixed amount of gas at constant pressure is directly proportional to its Kelvin temperature.
- *Gay-Lussac's law* says that the pressure of a fixed amount of gas at constant volume is directly proportional to its Kelvin temperature.
- Boyle's law, Charles's law, and Gay-Lussac's law together give the *combined gas law*, which applies to changing conditions for a fixed quantity of gas.
- *Avogadro's law* says that equal volumes of gases at the same temperature and pressure contain the same number of moles.

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Chapter Summary, Continued

4. What is the ideal gas law?

- The four gas laws together give the *ideal gas law*, which relates the effects of temperature, pressure, volume, and molar amount.
- At 0 °C and 1 atm pressure, called *standard temperature and pressure* (STP), 1 mol of any gas occupies a volume of 22.4 L.

5. What is partial pressure?

- The amount of pressure exerted by an individual gas in a mixture is called the *partial pressure* of the gas.
- According to *Dalton's law*, the total pressure exerted by the mixture is equal to the sum of the partial pressures of the individual gases.

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Chapter Summary, Continued

6. What are the various kinds of solids, and how do they differ?

- Solids are either crystalline or amorphous.
- *Crystalline solids* are those whose constituent particles have an ordered arrangement; *amorphous solids* lack internal order and do not have sharp melting points. There are several kinds of crystalline solids: *ionic solids* are those like sodium chloride, whose constituent particles are ions.
- *Molecular solids* are those like ice, whose constituent particles are molecules held together by intermolecular forces.
- *Covalent network solids* are those like diamonds, whose atoms are linked together by covalent bonds into a giant three-dimensional array.
- *Metallic solids*, such as silver or iron, also consist of large arrays of atoms, but their crystals have metallic properties, such as electrical conductivity.

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Chapter Summary, Continued

7. What factors affect a change of state?

- When a solid is heated, particles begin to move around freely at the *melting point*, and the substance becomes liquid.
- The amount of heat necessary to melt a given amount of solid at its melting point is its *heat of fusion*.
- As a liquid is heated, molecules escape from the surface of a liquid until an equilibrium is reached between liquid and gas, resulting in a *vapor pressure* of the liquid.
- At a liquid's *boiling point*, its vapor pressure equals atmospheric pressure, and the entire liquid is converted into gas.
- The amount of heat necessary to vaporize a given amount of liquid at its boiling point is called its *heat of vaporization*.

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