CHAPTER

1

STATES OF MATTER AND INTERMOLECULAR FORCES

where does a snowflake's elegant structure come from? Snowflakes may not look exactly alike, but all are made up of ice crystals that have a hexagonal arrangement of molecules. This arrangement is due to the shape of water molecules and the attractive forces between them. Water molecules are very polar and form a special kind of attraction, called a *hydrogen bond*, with other water molecules. Hydrogen bonding is just one of the *intermolecular forces* that you will learn about in this chapter.

START-UPACTIVITY

Heating Curve for Water

PROCEDURE

1. Place several ice cubes in a 250 mL beaker. Fill the beaker halfway with water. Place the beaker on a hot plate. Using a ring stand, clamp a thermometer so that it is immersed in the ice water but not touching the bottom or sides of the beaker. Record the temperature of the ice water after the temperature has stopped changing.

SAFETY PRECAUTIONS

- **2.** Turn on the hot plate and heat the ice water. Using a **stirring rod**, carefully stir the water as the ice melts.
- **3.** Observe the water as it is heated. Continue stirring. Record the temperature of the water every 30 s. Note the time at which the ice is completely melted. Also note when the water begins to boil.
- **4.** Allow the water to boil for several minutes, and continue to record the temperature every 30 s. Turn off the hot plate, and allow the beaker of water to cool.
- **5.** Is your graph a straight line? If not, where does the slope change?

ANALYSIS

- **1.** Make a graph of temperature as a function of time.
- **2.** What happened to the temperature of the ice water as you heated the beaker?
- **3.** What happened to the temperature of the water after the water started boiling?

Pre-Reading Questions

- 1 Name two examples each of solids, liquids, and gases.
 -) What happens when you heat an ice cube?
 - What force is there between oppositely charged objects?



SECTION 1 States and State Changes

SECTION 2 Intermolecular Forces

SECTION 3 Energy of State Changes

<u>SECTION 4</u> Phase Equilibrium



S E C T I O N

States and State Changes

Key Terms

- surface tension
- evaporation
- boiling point
- condensation
- melting
- melting point
- freezing
- freezing point
- sublimation

Topic Link

Refer to the chapter "The Science of Chemistry" for a discussion of states of matter.

OBJECTIVES

- **Relate** the properties of a state to the energy content and particle arrangement of that state of matter.
- **Explain** forces and energy changes involved in changes of state.

States of Matter

Have you ever had candy apples like those shown in **Figure 1**? Or have you had strawberries dipped in chocolate? When you make these treats, you can see a substance in two states. The fruit is dipped into the liquid candy or chocolate to coat it. But the liquid becomes solid when cooled. However, the substance has the same identity—and delicious taste—in both states. Most substances, such as the mercury shown in **Figure 2**, can be in three states: solid, liquid, and gas. The physical properties of each state come from the arrangement of particles.

Solid Particles Have Fixed Positions

The particles in a solid are very close together and have an orderly, fixed arrangement. They are held in place by the attractive forces that are between all particles. Because solid particles can vibrate only in place and do not break away from their fixed positions, solids have fixed volumes and shapes. That is, no matter what container you put a solid in, the solid takes up the same amount of space. Solids usually exist in crystalline form. Solid crystals can be very hard and brittle, like salt, or they can be very soft, like lead. Another example of a solid is ice, the solid state of water.



Figure 1

When you make candy apples, you see a substance in two states. The warm liquid candy becomes a solid when cooled. Solid Hg



Liquid Hg







Liquid Particles Can Move Easily Past One Another

If you add energy as heat to ice, the ice will melt and become liquid water. In other words, the highly ordered crystals of ice will break apart to form the random arrangement of liquid particles. Liquid particles are also held close together by attractive forces. Thus, the density of a liquid substance is similar to that of the solid substance. However, liquid particles have enough energy to be able to move past each other readily, which allows liquids to flow. That is, liquids are fluids. Some liquids can flow very readily, such as water or gasoline. Other liquids, such as molasses, are thicker and very *viscous* and flow very slowly. Like solids, liquids have fixed volumes. However, while solids keep the same shape no matter the container, liquids flow to take the shape of the lower part of a container. Because liquid particles can move past each other, they are noticeably affected by forces between particles, which gives them special properties.

Liquid Forces Lead to Surface Wetting and Capillary Action

Why does water bead up on a freshly waxed car? Liquid particles can have *cohesion*, attraction for each other. They can also have *adhesion*, attraction for particles of solid surfaces. The balance of these forces determines whether a liquid will wet a solid surface. For example, water molecules have a high cohesion for each other and a low adhesion to particles in car wax. Thus, water drops tend to stick together rather than stick to the car wax.

Water has a greater adhesion to glass than to car wax. The forces of adhesion and cohesion will pull water up a narrow glass tube, called a *capillary tube*, shown in **Figure 3**. The adhesion of the water molecules to the molecules that make up the glass tube pulls water molecules up the sides of the tube. The molecules that are pulled up the glass pull other water molecules with them because of cohesion. The water rises up the tube until the weight of the water above the surface level balances the upward force caused by adhesion and cohesion.

Figure 2

Mercury is the only metal that is a liquid at room temperature, but when cooled below -40° C, it freezes to a solid. At 357°C, it boils and becomes a gas.



Refer to the "lons and lonic Compounds" chapter for a discussion of crystal structure.



Figure 3

Capillary action, which moves water up through a narrow glass tube, also allows water to move up the roots and stems of plants.

a Water does not wet the feather, because the water's particles are not attracted to the oily film on the feather's surface.



b A drop of water on a surface has particles that are attracted to each other.

surface tension

the force that acts on the surface of a liquid and that tends to minimize the area of the surface

Liquids Have Surface Tension

Why are water drops rounded? Substances are liquids instead of gases because the cohesive forces between the particles are strong enough to pull the particles together so that they are in contact. Below the surface of the liquid, the particles are pulled equally in all directions by these forces. However, particles at the surface are pulled only sideways and downward by neighboring particles, as shown in the model of a water drop in **Figure 4**.

The particles on the surface have a net force pulling them down into the liquid. It takes energy to oppose this net force and increase the surface area. Energy must be added to increase the number of particles at the surface. Liquids tend to decrease energy by decreasing surface area. The tendency of liquids to decrease their surface area to the smallest size possible is called **surface tension**. Surface tension accounts for many liquid properties. Liquids tend to form spherical shapes, because a sphere has the smallest surface area for a given volume. For example, rain and fog droplets are spherical.

Gas Particles Are Essentially Independent

Gas particles are much farther apart than the particles in solids and liquids. They must go far before colliding with each other or with the walls of a container. Because gas particles are so far apart, the attractive forces between them do not have a great effect. They move almost independently of one another. So, unlike solids and liquids, gases fill whatever container they are in. Thus, the shape, volume, and density of an amount of gas depend on the size and shape of the container.

Because gas particles can move around freely, gases are fluids and can flow easily. When you breathe, you can feel how easily the gases that make up air can flow to fill your lungs. Examples of gases include carbon dioxide, a gas that you exhale, and helium, a gas that is used to fill balloons. You will learn more about gases in the "Gases" chapter.



Wetting a Surface

PROCEDURE

- 1. Wash plastic, steel, and glass plates well by using dilute detergent, and rinse them completely. Do not touch the clean surfaces.
- **2.** Using a **toothpick**, put a small drop of **water** on each

plate. Observe the shape of the drops from the side.

ANALYSIS

- **1.** On which surface does the water spread the most?
- **2.** On which surface does the water spread the least?

SAFETY PRECAUTIONS



- **3.** What can you conclude about the adhesion of water for plastic, steel, and glass?
- **4.** Explain your observations in terms of wetting.

Changing States

The hardening of melted candy on an apple is just one example of how matter changes states. *Freezing* is the change of state in which a liquid becomes a solid. You can observe freezing when you make ice cubes in the freezer. *Melting* is the change of state in which a solid becomes a liquid. For example, a solid wax candle melts when it is lit.

Evaporation—the change of state in which a liquid becomes a gas—takes place when water boils in a pot or evaporates from damp clothing. Gases can become liquids. *Condensation* is the change of state in which a gas becomes a liquid. For example, water vapor in the air can condense onto a cold glass or onto grass as dew in the morning.

But solids can evaporate, too. A thin film of ice on the edges of a windshield can become a gas by *sublimation* as the car moves through the air. Gases become solids by a process sometimes called *deposition*. For example, frost can form on a cold, clear night from water vapor in the air. **Figure 5** shows these six state changes. All state changes are physical changes, because the identity of the substance does not change, while the physical form of the substance does change.

Temperature, Energy, and State

All matter has energy related to the energy of the rapid, random motion of atom-sized particles. This energy of random motion increases as temperature increases. The higher the temperature is, the greater the average kinetic energy of the particles is. As temperature increases, the particles in solids vibrate more rapidly in their fixed positions. Like solid particles, liquid particles vibrate more rapidly as temperature increases, but they can also move past each other more quickly. Increasing the temperature of a gas causes the free-moving particles to move more rapidly and to collide more often with one another.

Generally, adding energy to a substance will increase the substance's temperature. But after a certain point, adding more energy will cause a substance to experience a change of state instead of a temperature increase.







A runner sweats when the body heats as a result of exertion. As sweat evaporates, the body is cooled.

evaporation

the change of a substance from a liquid to a gas

boiling point

the temperature and pressure at which a liquid and a gas are in equilibrium

condensation

the change of state from a gas to a liquid

Figure 7

On a cool night, when humidity is high, water vapor condenses to the liquid state.

Liquid Evaporates to Gas

If you leave an uncovered pan of water standing for a day or two, some of the water disappears. Some of the molecules have left the liquid and gone into the gaseous state. Because even neutral particles are attracted to each other, energy is required to separate them. If the liquid particles gain enough energy of movement, they can escape from the liquid. But where does the energy come from? The liquid particles gain energy when they collide with each other. Sometimes, a particle is struck by several particles at once and gains a large amount of energy. This particle can then leave the liquid's surface through **evaporation**. Because energy must be added to the water, evaporation is an endothermic process. This is why people sweat when they are hot and when they exercise, as shown in **Figure 6**. The evaporation of sweat cools the body.

You may have noticed that a puddle of water on the sidewalk evaporates more quickly on a hot day than on a cooler day. The reason is that the hotter liquid has more high-energy molecules. These high-energy molecules are more likely to gain the extra energy needed to become gas particles more rapidly.

Think about what happens when you place a pan of water on a hot stove. As the liquid is heated, its temperature rises and it evaporates more rapidly. Eventually, it reaches a temperature at which bubbles of vapor rise to the surface, and the temperature of the liquid remains constant. This temperature is the **boiling point**. Why doesn't all of the liquid evaporate at once at the boiling point? The answer is that it takes a large amount of energy to move a molecule from the liquid state to the gaseous state.

Gas Condenses to Liquid

Now, think about what happens if you place a glass lid over a pan of boiling water. You will see liquid form on the underside of the lid. Instead of escaping from the closed pan, the water vapor formed from boiling hits the cooler lid and forms liquid drops through **condensation**. Energy is transferred as heat from the gas particles to the lid. The gas particles no longer have enough energy to overcome the attractive forces between them, so they go into the liquid state. Condensation takes place on a cool night and forms dew on plants, as shown in **Figure 7**. Because energy is released from the water, condensation is an exothermic process.





When the temperature drops below freezing, farmers spray water on the orange trees. Energy is released by water as the water freezes, which warms the oranges and keeps the crop from freezing.

Solid Melts to Liquid

As a solid is heated, the particles vibrate faster and faster in their fixed positions. Their energy of random motion increases. Eventually, a temperature is reached such that some of the molecules have enough energy to break out of their fixed positions and move around. At this point, the solid is **melting.** That is, the solid is becoming a liquid. As long as both the newly formed liquid and the remaining solid are in contact, the temperature will not change. This temperature is the **melting point** of the solid. The energy of random motion is the same for both states. Energy must be absorbed for melting to happen, so melting is endothermic.

Liquid Freezes to Solid

The opposite process takes place when **freezing**, shown in **Figure 8**, takes place. As a liquid is cooled, the movement of particles becomes slower and slower. The particles' energy of random motion decreases. Eventually, a temperature is reached such that the particles are attracted to each other and pulled together into the fixed positions of the solid state, and the liquid crystallizes. This exothermic process releases energy—an amount equal to what is added in melting. As long as both states are present, the temperature will not change. This temperature is the **freezing point** of the liquid. Note that the melting point and freezing point are the same for pure substances.

Solid Sublimes to Gas

The particles in a solid are constantly vibrating. Some particles have higher energy than others. Particles with high enough energy can escape from the solid. This endothermic process is called **sublimation**. Sublimation is similar to evaporation. One difference is that it takes more energy to move a particle from a solid into a gaseous state than to move a particle from a liquid into a gaseous state. A common example of sublimation takes place when mothballs are placed in a chest, as shown on the next page in **Figure 9**. The solid naphthalene crystals in mothballs sublime to form naphthalene gas, which surrounds the clothing and keeps moths away.

melting

the change of state in which a solid becomes a liquid by adding heat or changing pressure

melting point

the temperature and pressure at which a solid becomes a liquid

freezing

the change of state in which a liquid becomes a solid as heat is removed

freezing point

the temperature at which a liquid substance freezes

sublimation

the process in which a solid changes directly into a gas (the term is sometimes also used for the reverse process)

Molecules of naphthalene sublime from the surface of the crystals in the mothball.



Gas Deposits to Solid

The reverse of sublimation is often called *deposition*. Molecules in the gaseous state become part of the surface of a crystal. Energy is released in the exothermic process. The energy released in deposition is equal to the energy required for sublimation. A common example of deposition is the formation of frost on exposed surfaces during a cold night when the temperature is below freezing. In a laboratory, you may see iodine gas deposit as solid crystals onto the surface of a sealed container.

O Section Review

UNDERSTANDING KEY IDEAS

- **1.** Describe what happens to the shape and volume of a solid, a liquid, and a gas when you place each into separate, closed containers.
- **2.** What is surface tension?
- **3.** You heat a piece of iron from 200 to 400 K. What happens to the atoms' energy of random motion?
- **4.** When water boils, bubbles form at the base of the container. What gas has formed?
- **5.** What two terms are used to describe the temperature at which solids and liquids of the same substance exist at the same time?
- **6.** How are sublimation and evaporation similar?
- **7.** Describe an example of deposition.

CRITICAL THINKING

- **8.** The densities of the liquid and solid states of a substance are often similar. Explain.
- **9.** How could you demonstrate evaporation?
- **10.** How could you demonstrate boiling point?
- **11.** You are boiling potatoes on a gas stove, and your friend suggests turning up the heat to cook them faster. Will this idea work?
- **12.** A dehumidifier takes water vapor from the air by passing the moist air over a set of cold coils to perform a state change. How does a dehumidifier work?
- Water at 50°C is cooled to −10°C. Describe what will happen.
- 14. How could you demonstrate melting point?
- **15.** Explain why changes of state are considered physical transitions and not chemical processes.

SECTION



Intermolecular Forces

Key Terms

- intermolecular forces
- dipole-dipole forces
- hydrogen bond
- London dispersion force

OBJECTIVES

- **Contrast** ionic and molecular substances in terms of their physical characteristics and the types of forces that govern their behavior.
- **Describe** dipole-dipole forces.
- **Explain** how a hydrogen bond is different from other dipole-dipole forces and how it is responsible for many of water's properties.
- Describe London dispersion forces, and relate their strength to other types of attractions.

Comparing Ionic and Covalent Compounds

Particles attract each other, so it takes energy to overcome the forces holding them together. If it takes high energy to separate the particles of a substance, then it takes high energy to cause that substance to go from the liquid to the gaseous state. The boiling point of a substance is a good measure of the strength of the forces that hold the particles together. Melting point also relates to attractive forces between particles. Most covalent compounds melt at lower temperatures than ionic compounds do. As shown in **Table 1**, ionic substances with small ions tend to be solids that have high melting points, and covalent substances tend to be gases and liquids or solids that have low melting points.

Table 1 Comparing Ionic and Molecular Substances						
Type of substance	Common use	State at room temperature	Melting point (°C)	Boiling point (°C)		
Ionic substances						
Potassium chloride, KCl	salt substitute	solid	770	sublimes at 1500		
Sodium chloride, NaCl	table salt	solid	801	1413		
Calcium fluoride, CaF ₂	water fluoridation	solid	1423	2500		
Covalent substances						
Methane, CH ₄	natural gas	gas	-182	-164		
Ethyl acetate, CH ₃ COOCH ₂ CH ₃	fingernail polish	liquid	-84	77		
Water, H ₂ O	(many)	liquid	0	100		
Heptadecane, C ₁₇ H ₃₆	wax candles	solid	22	302		

Topic Link

Refer to the "Ions and Ionic Compounds" chapter for a discussion of crystal lattices.

intermolecular forces

the forces of attraction between molecules

dipole-dipole forces

interactions between polar molecules

Topic Link

Refer to the "Covalent Compounds" chapter for a discussion of dipoles.

Oppositely Charged Ions Attract Each Other

Ionic substances generally have much higher forces of attraction than covalent substances. Recall that ionic substances are made up of separate ions. Each ion is attracted to all ions of opposite charge. For small ions, these attractions hold the ions tightly in a crystal lattice that can be disrupted only by heating the crystal to very high temperatures.

The strength of ionic forces depends on the size of the ions and the amount of charge. Ionic compounds with small ions have high melting points. If the ions are larger, then the distances between them are larger and the forces are weaker. This effect helps explain why potassium chloride, KCl, melts at a lower temperature than sodium chloride, NaCl, does. Now compare ions that differ by the amount of charge they have. If the ions have larger charges, then the ionic force is larger than the ionic forces of ions with smaller charges. This effect explains why calcium fluoride, CaF_2 melts at a higher temperature than NaCl does.

Intermolecular Forces Attract Molecules to Each Other

For covalent substances, forces that act between molecules are called **intermolecular forces.** They can be dipole-dipole forces or London dispersion forces. Both forces are short-range and decrease rapidly as molecules get farther apart. Because the forces are effective only when molecules are near each other, they do not have much of an impact on gases. A substance with weak attractive forces will be a gas because there is not enough attractive force to hold molecules together as a liquid or a solid.

The forces that hold the molecules together act only between neighboring molecules. The forces may be weak; some molecular substances boil near absolute zero. For example, hydrogen gas, H₂, boils at -252.8° C. The forces may be strong; some molecular substances have very high boiling points. For example, coronene, C₂₄H₁₂, boils at 525°C.

Dipole-Dipole Forces

In **dipole-dipole forces,** the positive end of one molecule attracts the negative end of a neighboring molecule. Bonds are polar because atoms of differing electronegativity are bonded together. The greater the difference in electronegativity in a diatomic molecule, the greater the polarity is.

Dipole-Dipole Forces Affect Melting and Boiling Points

When polar molecules get close and attract each other, the force is significant if the degree of polarity is fairly high. When molecules are very polar, the dipole-dipole forces are very significant. Remember that the boiling point of a substance tells you something about the forces between the molecules. For example, **Table 2** shows that the polar compound 1-propanol, C_3H_7OH , boils at 97.4°C. The less polar compound of similar size, 1-propanethiol, C_3H_7SH , boils at 67.8°C. However, the nonpolar compound butane, C_4H_{10} , also of similar size, boils at -0.5°C. The more polar the molecules are, the stronger the dipole-dipole forces between them, and thus, the higher the boiling point.

Substance	Boiling point (°C)	Polarity	State at room temperature	Structure
1-propanol, C ₃ H ₇ OH	97.4	polar	liquid	$\begin{array}{ccccc} H & H & H \\ & & \\ H - C - C - C - C - O - H \\ & & \\ H & H & H \end{array}$
1-propanethiol, C ₃ H ₇ SH	67.8	less polar	liquid	H H H H-C-C-C-S-H H H H
Butane, C ₄ H ₁₀	-0.5	nonpolar	gas	$\begin{array}{cccccc} H & H & H & H \\ H & & & & & \\ H - C - C - C - C - C - H \\ H & H & H \\ H & H & H \end{array}$
Water, H ₂ O	100.0	polar	liquid	HH
Hydrogen sulfide, H ₂ S	-60.7	less polar	gas	HH
Ammonia, NH ₃	-33.35	polar	gas	$\overset{H}{\overset{ }_{H-N-H}}$
Phosphine, PH ₃	-87.7	less polar	gas	H H—P—H

Table 2 Comparing Dipole-Dipole Forces

Hydrogen Bonds

Compare the boiling points of H_2O and H_2S , shown in **Table 2.** These molecules have similar sizes and shapes. However, the boiling point of H_2O is much higher than that of H_2S . A similar comparison of NH_3 with PH_3 can be made. The greater the polarity of a molecule, the higher the boiling point is. However, when hydrogen atoms are bonded to very electronegative atoms, the effect is even more noticeable.

Compare the boiling points and electronegativity differences of the hydrogen halides, shown in **Table 3.** As the electronegativity difference increases, the boiling point increases. The boiling points increase somewhat from HCl to HBr to HI but increase a lot more for HF. What accounts for this jump? The answer has to do with a special form of dipole-dipole forces, called a **hydrogen bond.**

Table 3 Boiling Points of the Hydrogen Halides						
Substance	HF	HCI	HBr	HI		
Boiling point (°C)	20	-85	-67	-35		
Electronegativity difference	1.8	1.0	0.8	0.5		

hydrogen bond

the intermolecular force occurring when a hydrogen atom that is bonded to a highly electronegative atom of one molecule is attracted to two unshared electrons of another molecule



Hydrogen Bonds Form with Electronegative Atoms

Strong hydrogen bonds can form with a hydrogen atom that is covalently bonded to very electronegative atoms in the upper-right part of the periodic table: nitrogen, oxygen, and fluorine. When a hydrogen atom bonds to an atom of N, O, or F, the hydrogen atom has a large, partially positive charge. The partially positive hydrogen atom of polar molecules can be attracted to the unshared pairs of electrons of neighboring molecules. For example, the hydrogen bonds shown in Figure 10 result from the attraction of the hydrogen atoms in the H-N and H-O bonds of one DNA strand to the unshared pairs of electrons in the complementary DNA strand. These hydrogen bonds hold together the complementary strands of DNA, which contain the body's genetic information.

Hydrogen Bonds Are Strong Dipole-Dipole Forces

It is not just electronegativity difference that accounts for the strength of hydrogen bonds. One reason that hydrogen bonds are such strong dipoledipole forces is because the hydrogen atom is small and has only one electron. When that electron is pulled away by a highly electronegative atom, there are no more electrons under it. Thus, the single proton of the hydrogen nucleus is partially exposed. As a result, hydrogen's proton is strongly attracted to the unbonded pair of electrons of other molecules. The combination of the large electronegativity difference (high polarity) and hydrogen's small size accounts for the strength of the hydrogen bond.







Hydrogen Bonding Explains Water's Unique Properties

The energy of hydrogen bonds is lower than that of normal chemical bonds but can be stronger than that of other intermolecular forces. Hydrogen bonding can account for many properties. **Figure 11** shows an example of hydrogen bonding that involves oxygen. Water has unique properties. These unique properties are the result of hydrogen bonding.

Water is different from most other covalent compounds because of how much it can participate in strong hydrogen bonding. In water, two hydrogen atoms are bonded to oxygen by polar covalent bonds. Each hydrogen atom can form hydrogen bonds with neighboring molecules. Because of the water molecule's ability to form multiple hydrogen bonds at once, the intermolecular forces in water are strong.

Another different characteristic of water results from hydrogen bonding and the shape of a water molecule. Unlike most solids, which are denser than their liquids, solid water is less dense than liquid water and floats in liquid water. The angle between the two H atoms in water is 104.5°. This angle is very close to the tetrahedral angle of 109.5°. When water forms solid ice, the angle in the molecules causes the special geometry of molecules in the crystal shown in **Figure 11**. Ice crystals have large amounts of open space, which causes ice to have a low density.

The unusual density difference between liquid and solid water explains many important phenomena in the natural world. For example, because ice floats on water, ponds freeze from the top down and not from the bottom up. Thus, fish can survive the winter in water under an insulating layer of ice. Because water expands when it freezes, water seeping into the cracks of rock or concrete can cause considerable damage due to fracturing. You should never freeze water-containing foods in glass containers, which may break when the water freezes and expands.



The nonpolar molecules in gasoline are held together by London dispersion forces, so it is not a gas at room temperature.

London dispersion force

the intermolecular attraction resulting from the uneven distribution of electrons and the creation of temporary dipoles



Temporary dipoles in molecules cause forces of attraction between the molecules.

a Nonpolar molecules can become momentarily polar.

Table 4	Boiling	Points	of the	Noble	Gases
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Substance	Не	Ne	Ar	Kr	Хе	Rn
Boiling point (°C)	-269	-246	-186	-152	-107	-62
Number of electrons	2	10	18	36	54	86

London Dispersion Forces

Some compounds are ionic, and forces of attraction between ions of opposite charge cause the ions to stick together. Some molecules are polar, and dipole-dipole forces hold polar compounds together. But what forces of attraction hold together nonpolar molecules and atoms? For example, gasoline, shown in **Figure 12**, contains nonpolar octane, C_8H_{10} , and is a liquid at room temperature. Why isn't octane a gas? Clearly, some sort of intermolecular force allows gasoline to be a liquid.

In 1930, the German chemist Fritz W. London came up with an explanation. Nonpolar molecules experience a special form of dipole-dipole force called **London dispersion force.** In dipole-dipole forces, the negative part of one molecule attracts the positive region of a neighboring molecule. However, in London dispersion forces, there is no special part of the molecule that is always positive or negative.

London Dispersion Forces Exist Between Nonpolar Molecules

In general, the strength of London dispersion forces between nonpolar particles increases as the molar mass of the particles increases. This is because generally, as molar mass increases, so does the number of electrons in a molecule. Consider the boiling point of the noble gases, as shown in **Table 4.** Generally, as boiling point increases, so does the number of electrons in the atoms. For groups of similar atoms and molecules, such as the noble gases or hydrogen halides, London dispersion forces are roughly proportional to the number of electrons present.



b The instantaneous dipoles that form cause adjacent molecules to polarize.

c These London dispersion forces cause the molecules to attract each other.

London Dispersion Forces Result from Temporary Dipoles

How do electrons play a role in London dispersion forces? The answer lies in the way that electrons move and do not stay still. The electrons in atoms and molecules can move. They not only move about in orbitals but also can move from one side of an atom to the other. When the electrons move toward one side of an atom or molecule, that side becomes momentarily negative and the other side becomes momentarily positive. If the positive side of a momentarily charged molecule moves near another molecule, the positive side can attract the electrons in the other molecule. Or the negative side of the momentarily charged molecule can push the electrons of the other molecule away. The temporary dipoles that form attract each other, as shown in **Figure 13**, and make temporary dipoles form in other molecules. When molecules are near each other, they always exert an attractive force because electrons can move.

Properties Depend on Types of Intermolecular Force

Compare the properties of an ionic substance, NaCl, with those of a nonpolar substance, I_2 , as shown in **Figure 14.** The differences in the properties of the substances are related to the differences in the types of forces that act within each substance. Because ionic, polar covalent, and nonpolar covalent substances are different in electron distribution, they are different in the types of attractive forces that they experience.

While nonpolar molecules can experience only London dispersion forces, polar molecules experience both dipole-dipole forces and London dispersion forces. Determining how much each force adds to the overall force of attraction between polar molecules is not easy. London dispersion forces also exist between ions in ionic compounds, but they are quite small relative to ionic forces and can almost always be overlooked.



Figure 14

Forces between ions are

generally much stronger than the forces between

a The polyatomic ionic compound 1-butylpyridinium nitrate is a liquid solvent at room temperature. The large size of the cations keeps the ionic forces from having a great effect.



b A molecule of coronene, $C_{24}H_{12}$, is very large, yet its flat shape allows it to have relatively strong London dispersion forces.



Particle Size and Shape Also Play a Role

Dipole-dipole forces are generally stronger than London dispersion forces. However, both of these forces between molecules are usually much weaker than ionic forces in crystals. There are exceptions. One major factor is the size of the atoms, ions, or molecules. The larger the particles are, the farther apart they are and the smaller the effects of the attraction are. If an ionic substance has very large ions—especially if the ions are not symmetrical—the ionic substance's melting point can be very low. A few ionic compounds are even liquid at room temperature, such as 1-butylpyridinium nitrate, shown in **Figure 15**.

The shape of the particles can also play a role in determining the strength of attraction. For example, coronene molecules, $C_{24}H_{12}$, are very large. However, they are flat, so they can come close together and the attractive forces have a greater effect. Thus, the boiling point of nonpolar coronene is almost as high as that of some ionic compounds.



UNDERSTANDING KEY IDEAS

- 1. What force holds NaCl units together?
- 2. Describe dipole-dipole forces.
- **3.** What force gives water unique properties?
- **4.** Why does ice have a lower density than liquid water does?
- **5.** Explain why oxygen, nitrogen, and fluorine are elements in molecules that form strong hydrogen bonds.
- **6.** How is the strength of London dispersion forces related to the number of electrons?
- **7.** How do intermolecular forces affect whether a substance is a solid at room temperature?

CRITICAL THINKING

- **8. a.** Which is nonpolar: CF_4 or CH_2F_2 ?
 - **b.** Which substance likely has a higher boiling point? Explain your answer.
- **9.** Are the London dispersion forces between water molecules weaker or stronger than the London dispersion forces between molecules of hydrogen sulfide, H₂S?
- **10.** NH₃ has a much higher boiling point than PH₃ does. Explain.
- **11.** Why does argon boil at a higher temperature than neon does?
- **12.** Which will have the higher melting point, KF or KNO₃? Explain your answer.

S E C T I O N

Energy of State Changes

OBJECTIVES

Define the molar enthalpy of fusion and the molar enthalpy of vaporization, and **identify** them for a substance by using a heating curve.

- **Describe** how enthalpy and entropy of a substance relate to state.
- **Predict** whether a state change will take place by using Gibbs energy.
- **Calculate** melting and boiling points by using enthalpy and entropy.
- **Explain** how pressure affects the entropy of a gas and affects changes between the liquid and vapor states.

Enthalpy, Entropy, and Changes of State

Adding enough energy to boil a pan of water takes a certain amount of time. Removing enough energy to freeze a tray of ice cubes also takes a certain amount of time. At that rate, you could imagine that freezing the water that makes up the iceberg in **Figure 16** would take a *very* long time.

Enthalpy is the total energy of a system. Entropy measures a system's disorder. The energy added during melting or removed during freezing is called the *enthalpy of fusion*. (Fusion means melting.) Particle motion is more random in the liquid state, so as a solid melts, the entropy of its particles increases. This increase is the *entropy of fusion*. As a liquid evaporates, a lot of energy is needed to separate the particles. This energy is the *enthalpy of vaporization*. (Vaporization means evaporation.) Particle motion is much more random in a gas than in a liquid. A substance's *entropy of vaporization* is much larger than its entropy of fusion.



Topic Link 🛌

Refer to the "Causes of Change" chapter for a discussion of enthalpy and entropy.



Figure 16 Melting an i

Melting an iceberg would take a great amount of enthalpy of fusion.



Molar Enthalpy Versus Temperature for Water



Enthalpy and Entropy Changes for Melting and Evaporation

Enthalpy and entropy change as energy in the form of heat is added to a substance, as shown with water in **Figure 17.** The graph starts with 1 mol of solid ice at 250 K (-23° C). The ice warms to 273.15 K. The enthalpy, *H*, increases slightly during this process. At 273.15 K, the ice begins to melt. As long as both ice and liquid water are present, the temperature remains at 273.15 K. The energy added is the *molar enthalpy of fusion* (ΔH_{fus}), which is 6.009 kJ/mol for ice. ΔH_{fus} is the difference in enthalpy between solid and liquid water at 273.15 K as shown in the following equation:

 $\Delta H_{fus} = H_{\text{(liquid at melting point)}} - H_{\text{(solid at melting point)}}$

After the ice melts, the temperature of the liquid water increases as energy is added until the temperature reaches 373.15 K.

At 373.15 K, the water boils. If the pressure remains constant, so does the temperature as long as the two states (liquid and gas) are present. The energy added is the *molar enthalpy of vaporization* (ΔH_{vap}), 40.67 kJ/mol. ΔH_{vap} is the difference in enthalpy between liquid and gaseous water at 373.15 K and is defined in the following equation:

 $\Delta H_{vap} = H_{(vapor at boiling point)} - H_{(liquid at boiling point)}$

After all of the liquid water has evaporated, the energy added increases the temperature of the water vapor.

Like water, almost all substances can be in the three common states of matter. **Table 5** lists the molar enthalpies and entropies of fusion and vaporization for some elements and compounds. Because intermolecular forces are not significant in the gaseous state, most substances have similar values for *molar entropy of vaporization*, ΔS_{vap} .

Table 5Molar Enthalpies and Entropies of Fusion and Vaporization							
Substance	<i>Т_{тр}</i> (К)	∆ <i>H_{fus}</i> (kJ/mol)	∆S _{fus} (J/mol•K)	<i>Т_{ьр}</i> (К)	∆ <i>H_{vap}</i> (kJ/mol)	∆S _{vap} (J/mol•K)	
Nitrogen, N ₂	63	0.71	11.3	77	5.6	72.2	
Hydrogen sulfide, H ₂ S	188	23.8	126.6	214	18.7	87.4	
Bromine, Br ₂	266	10.57	39.8	332	30.0	90.4	
Water, H ₂ O	273	6.01	22.0	373	40.7	108.8	
Benzene, C ₆ H ₆	279	9.95	35.7	353	30.7	87.0	
Lead, Pb	601	4.77	7.9	2022	179.5	88.8	

Gibbs Energy and State Changes

As you have learned, the relative values of H and S determine whether any process, including a state change, will take place. The following equation describes a change in Gibbs energy.

$$\Delta G = \Delta H - T \Delta S$$

You may recall that a process is spontaneous if ΔG is negative. That is, the process can take place with a decrease in Gibbs energy. If ΔG is positive, then a process will not take place unless an outside source of energy drives the process. If ΔG is zero, then the system is said to be in a state of *equilibrium*. At equilibrium, the forward and reverse processes are happening at the same rate. For example, when solid ice and liquid water are at equilibrium, ice melts at the same rate that water freezes. You will learn more about equilibrium in the next section.

Enthalpy and Entropy Determine State

At normal atmospheric pressure, water freezes at 273.15 K (0.00°C). At this pressure, pure water will not freeze at any temperature above 273.15 K. Likewise, pure ice will not melt at any temperature below 273.15 K. This point may be proven by looking at ΔG just above and just below the normal freezing point of water. At the normal freezing point, the enthalpy of fusion of ice is 6.009 kJ/mol, or 6009 J/mol. For changes in state that take place at constant temperature, the entropy change, ΔS , is $\Delta H/T$. Thus, ΔS is (6009 J/mol)/(273.15 K) = 22.00 J/mol•K for the melting of ice.

Now let us calculate the Gibbs energy change for the melting of ice at 273.00 K. For this change, ΔH is positive (energy is absorbed), and ΔS is also positive (greater degree of disorder).

$$\Delta G = \Delta H - T\Delta S = +6009 \text{ J/mol} - (273.00 \text{ K} \times +22.00 \text{ J/mol} \cdot \text{K})$$

= +6009 J/mol - 6006 J/mol = +3 J/mol

Because ΔG is positive, the change will not take place on its own. The ordered state of ice is preferred at this temperature, which is below the normal freezing point.

Similarly, think about the possibility of water freezing at 273.30 K. The ΔH is now negative (energy is released). The ΔS is also negative (greater degree of order in the crystal).

$$\Delta G = \Delta H - T\Delta S = -6009 \text{ J/mol} - (273.30 \text{ K} \times -22.00 \text{ J/mol} \cdot \text{K})$$

= -6009 J/mol - 6013 J/mol = +4 J/mol

 ΔG is positive, so the water will not freeze. The disordered state of liquid water is preferred at 273.30 K, which is above the melting point.

Determining Melting and Boiling Points

For a system at the melting point, a solid and a liquid are in equilibrium, so ΔG is zero. Thus, $\Delta H = T\Delta S$. Rearranging the equation, you get the following relationship, in which *mp* means melting point and *fus* means fusion.

$$T_{mp} = \frac{\Delta H_{fus}}{\Delta S_{fus}}$$

In other words, the melting point of a solid, T_{mp} , is equal to molar enthalpy of fusion, ΔH_{fus} , divided by molar entropy of fusion, ΔS_{fus} . Boiling takes place when the drive toward disorder overcomes the tendency to lose energy. Condensation, shown in **Figure 18**, takes place when the tendency to lose energy overcomes the drive to increase disorder. In other words, when $\Delta H_{vap} > T\Delta S_{vap}$, the liquid state is favored. The gas state is preferred when $\Delta H_{vap} < T\Delta S_{vap}$.

The same situation happens at the boiling point. ΔG is zero when liquid and gas are in equilibrium, so $\Delta H_{vap} = T\Delta S_{vap}$. Thus, given that *bp* stands for boiling point and *vap* stands for vaporization, the following equation is true.

a Water condenses on the wings of the dragonfly when $\Delta H_{vap} > T\Delta S_{vap}$. **b** Water freezes on the flower when $\Delta H_{fus} > T\Delta S_{fus}$.

$$T_{bp} = \frac{\Delta H_{vap}}{\Delta S_{vap}}$$

In other words, the boiling point of a liquid, T_{bp} , is equal to molar enthalpy of vaporization, ΔH_{vap} , divided by molar entropy of vaporization, ΔS_{vap} .





SAMPLE PROBLEM A

Calculating Melting and Boiling Points

The enthalpy of fusion of mercury is 11.42 J/g, and the molar entropy of fusion is 9.79 J/mol•K. The enthalpy of vaporization at the boiling point is 294.7 J/g, and the molar entropy of vaporization is 93.8 J/mol•K. Calculate the melting point and the boiling point.

1 Gather information.

- molar mass of Hg = 200.59 g/mol
- enthalpy of fusion = 11.42 J/g
- molar entropy of fusion = 9.79 J/mol•K
- enthalpy of vaporization = 294.7 J/g
- molar entropy of vaporization = 93.8 J/mol•K
- melting point, $T_{mp} = ?$
- boiling point, $T_{bp} = ?$

2 Plan your work.

First calculate the molar enthalpy of fusion and molar enthalpy of vaporization, which have units of J/mol. Use the molar mass of mercury to convert from J/g to J/mol.

$$\Delta H_{fus} = 11.42 \text{ J/g} \times 200.59 \text{ g/mol} = 2291 \text{ J/mol}$$

 $\Delta H_{vap} = 294.7 \text{ J/g} \times 200.59 \text{ g/mol} = 59 110 \text{ J/mol}$

Set up the equations for determining T_{mp} and T_{bp} .

3 Calculate.

$$T_{mp} = \Delta H_{fus} / \Delta S_{fus} = \frac{2291 \text{ J/mol}}{9.79 \text{ J/mol} \cdot \text{K}} = 234 \text{ K}$$
$$T_{bp} = \Delta H_{vap} / \Delta S_{vap} = \frac{59110 \text{ J/mol}}{93.8 \text{ J/mol} \cdot \text{K}} = 630 \text{ K}$$

4 Verify your result.

Mercury is a liquid at room temperature, so the melting point must be below 298 K (25°C). Mercury boils well above room temperature, so the boiling point must be well above 298 K. These facts fit the calculation.



2 For sulfur dioxide, the molar enthalpy of fusion is 8.62 kJ/mol, and the molar entropy of fusion is 43.1 J/mol•K. ΔH_{vap} is 24.9 kJ/mol, and the molar entropy of vaporization at the boiling point is 94.5 J/mol•K.

3 For ammonia, ΔH_{fus} is 5.66 kJ/mol, and ΔS_{fus} is 29.0 J/mol•K. ΔH_{vap} is 23.33 kJ/mol, and ΔS_{vap} is 97.2 J/mol•K.

PRACTICE HINT

When setting up your equations, use the correct conversion factors so that you get the desired units when canceling. But be careful to keep values for vaporization together and separate from those for fusion. Keep track of your units! You may have to convert from joules to kilojoules or vice versa.



Pressure Can Affect Change-of-State Processes

Boiling points are pressure dependent because pressure has a large effect on the entropy of a gas. When a gas is expanded (pressure is decreased), its entropy increases because the degree of disorder of the molecules increases. At sea level, water boils at 100°C. In Denver, Colorado, where the elevation is 1.6 km, atmospheric pressure is about 0.84 times the pressure at sea level. At that elevation, water boils at about 95°C. On Pike's Peak, where the elevation is 4.3 km, water boils at about 85°C. People often use pressure cookers at that altitude to increase the boiling point of water.

Liquids and solids are almost incompressible. Therefore, changes of atmospheric pressure have little effect on the entropy of substances in liquid or solid states. Ordinary changes in pressure have essentially no effect on melting and freezing. Although the elevation is high and atmospheric pressure is very low, water on Pike's Peak still freezes at 273.15 K. You will learn more about pressure effects on state changes in the next section.

Section Review

UNDERSTANDING KEY IDEAS

- **1.** What is the molar enthalpy of fusion?
- 2. What is the molar enthalpy of vaporization?
- **3.** Compare the sizes of the entropy of fusion and entropy of vaporization of a substance.
- **4.** Explain why liquid water at 273.3 K will not freeze in terms of Gibbs energy.
- **5.** The following process has a ΔG equal to zero at 77 K and standard pressure. In how many states can nitrogen be present at this temperature and pressure?

 $N_2(l) \longrightarrow N_2(g)$

- **6. a.** How does atmospheric pressure affect the boiling point of a liquid?
 - **b.** How does atmospheric pressure affect the melting point of a liquid?

PRACTICE PROBLEMS

7. The enthalpy of fusion of bromine is 10.57 kJ/mol. The entropy of fusion is 39.8 J/mol•K. Calculate the freezing point.

- 8. Calculate the boiling point of bromine given the following information: $Br_2(l) \rightarrow Br_2(g)$ $\Delta H_{vap} = 30.0 \text{ kJ/mol}$ $\Delta S_{vap} = 90.4 \text{ J/mol} \cdot \text{K}$
- 9. The enthalpy of fusion of nitric acid, HNO₃, is 167 J/g. The entropy of fusion is 45.3 J/mol•K. Calculate the melting point.

CRITICAL THINKING

- **10.** In terms of enthalpy and entropy, when does melting take place?
- **11.** Why is the enthalpy of vaporization of a substance always much greater than the enthalpy of fusion?
- **12.** Why is the gas state favored when

$$T > \frac{\Delta H_{vap}}{\Delta S_{vap}} ?$$

13. Determine the change-of-state process described by each of the following:

a.
$$\Delta H_{vap} > T\Delta S_{vap}$$
 c. $\Delta H_{vap} < T\Delta S_{vap}$
b. $\Delta H_{fus} < T\Delta S_{fus}$ **d.** $\Delta H_{fus} > T\Delta S_{fus}$

S E C T I O N



Phase Equilibrium

Key Terms

- phase
- equilibrium
- vapor pressure
- phase diagram
- triple point
- critical point

OBJECTIVES

- **Identify** systems that have multiple phases, and determine whether they are at equilibrium.
- **Understand** the role of vapor pressure in changes of state between a liquid and a gas.
- **Interpret** a phase diagram to identify melting points and boiling points.

Two-Phase Systems

A system is a set of components that are being studied. Within a system, a **phase** is a region that has the same composition and properties throughout. The lava lamp in **Figure 19** is a system that has two phases, each of which is liquid. The two phases in a lava lamp are different from each other because their chemical compositions are different. A glass of water and ice cubes is also a system that has two phases. This system has a solid phase and a liquid phase. However, the two phases have the same chemical composition. What makes the two phases in ice water different from each other is that they are different states of the same substance, water.

Phases do not need to be pure substances. If some salt is dissolved in the glass of water with ice cubes, there are still two phases: a liquid phase (the solution) and a solid phase (the pure ice). In this chapter, we will consider only systems like the ice water, that is, systems that contain one pure substance whose phases are different only by state. phase

a part of matter that is uniform

Figure 19

The lava lamp is a system that has two liquid phases, and the ice water is a system that has a solid phase and a liquid phase.







equilibrium

the state in which a chemical process and the reverse chemical process occur at the same rate such that the concentrations of reactants and products do not change

vapor pressure

the partial pressure exerted by a vapor that is in equilibrium with its liquid state at a given temperature

Figure 21

A few molecules of a liquid have enough energy to overcome intermolecular forces and escape from the surface into the gas phase, which is in equilibrium with the liquid.



Equilibrium Involves Constant Interchange of Particles

If you open a bottle of rubbing alcohol, you can smell the alcohol. Some molecules of alcohol have escaped into the gas phase. When you put the cap back on, an equilibrium is quickly reached. A dynamic **equilibrium** exists when particles are constantly moving between two or more phases yet no net change in the amount of substance in either phase takes place. Molecules are escaping from the liquid phase into a gas at the same rate that other molecules are returning to the liquid from the gas phase. That is, the rate of evaporation equals the rate of condensation.

Similarly, if you keep a glass of ice water outside on a 0° C day, a constant interchange of water molecules between the solid ice and the liquid water will take place. The system is in a state of equilibrium. Figure 20 shows a system that has a solid and a gas at equilibrium.

Vapor Pressure Increases with Temperature

A closed container of water is a two-phase system in which molecules of water are in a gas phase in the space above the liquid phase. Moving randomly above the liquid, some of these molecules strike the walls and some go back into the liquid, as shown in **Figure 21**. An equilibrium, in which the rate of evaporation equals the rate of condensation, is soon created. The molecules in the gas exert pressure when they strike the walls of the container. The pressure exerted by the molecules of a gas, or vapor, phase in equilibrium with a liquid is called the **vapor pressure**. You can define boiling point as the temperature at which the vapor pressure equals the external pressure.

As the temperature of the water increases, the molecules have more kinetic energy, so more of them can escape into the gas phase. Thus, as temperature increases, the vapor pressure increases. This relationship is shown for water in **Table 6.** At 40°C, the vapor pressure of water is 55.3 mm Hg. If you increase the temperature to 80°C, the vapor pressure will be 355.1 mm Hg.

Table	6 Water Press	r-Vapor ure
Temp. (°C)	Pressure (mm Hg)	Pressure (kPa)
0.0	4.6	0.61
10.0	9.2	1.23
20.0	17.5	2.34
30.0	31.8	4.25
40.0	55.3	7.38
50.0	92.5	12.34
60.0	19.9	19.93
70.0	233.7	31.18
80.0	355.1	47.37
90.0	525.8	70.12
100.0	760.0	101.32

Refer to Appendix A to find more values for water-vapor pressure.



At 100°C, the vapor pressure has risen to 760.0 mm Hg, which is standard atmospheric pressure, 1 atm (101.32 kPa). The vapor pressure equals the external pressure, and water boils at 100°C. When you increase the temperature of a system to the point at which the vapor pressure of a substance is equal to standard atmospheric pressure—shown as a dotted line in **Figure 22**—you have reached the substance's *normal boiling point*.

The average kinetic energy of molecules increases about 3% for a 10°C increase in temperature, yet the vapor pressure about doubles or triples. The reason is that the fraction of very energetic molecules that can escape about doubles or triples for a 10°C increase in temperature. You can see this relationship at the high energy part of the curves in Figure 23.



The dotted line shows standard atmospheric pressure. The point at which the red line crosses the dotted line is the normal boiling point for each substance.





Figure 23

For a 10°C rise in temperature, the average random kinetic energy of molecules increases slightly, but the fraction of molecules that have very high energy (> E_a) increases greatly, as shown by the shaded areas to the right.

Phase Diagrams

You know that a substance's state depends on temperature and that pressure affects state changes. To get a complete picture of how temperature, pressure, and states are related for a particular substance, you can look at a **phase diagram.** A phase diagram has three lines. One line is a vapor pressure curve for the liquid-gas equilibrium. A second line is for the liquid-solid equilibrium, and a third line is for the solid-gas equilibrium. All three lines meet at the **triple point.** The triple point is the only temperature and pressure at which three states of a substance can be in equilibrium.

Phase Diagrams Relate State, Temperature, and Pressure

The x-axis of **Figure 24** shows temperature, and the y-axis shows pressure. For any given point (x, y), you can see in what state water will be. For example, at 363 K ($x = 90^{\circ}$ C) and standard pressure (y = 101.3 kPa), you know that water is a liquid. If you look at the point for these coordinates, it in fact falls in the region labeled "Liquid."

Gas-Liquid Equilibrium

Phase Diagram for H₂O

0.61

n

В

0 0.01

Look at point E on the line AD, where gas and liquid are in equilibrium at 101.3 kPa. If you increase the temperature slightly, liquid will evaporate and only vapor will remain. If you decrease the temperature slightly, vapor condenses and only water remains. Liquid exists to the left of line AD, and vapor exists to the right of AD. Along line AD, the vapor pressure is increasing, so the density of the vapor increases. The liquid decreases in density. At a temperature and pressure called the **critical point**, the liquid and vapor phases of a substance are identical. Above this point, the substance is called a *supercritical fluid*. A supercritical fluid is the state that a substance is in when the liquid and vapor phases are indistinguishable.



phase diagram

triple point

a graph of the relationship

between the physical state of a substance and the temperature

and pressure of the substance

the temperature and pressure

conditions at which the solid,

liquid, and gaseous phases of a

substance coexist at equilibrium

the temperature and pressure at which the gas and liquid states of a substance become identical and form one phase

Figure 24

The phase diagram for water shows the physical states of water at different temperatures and pressures. (Note that the diagram is not drawn to scale.)





Triple point

100

Temperature (°C)

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Critical

point

Solid-Liquid Equilibrium

If you move to the left (at constant pressure) along the line EF, you will find a temperature at which the liquid freezes. The line AC shows the temperatures and pressures along which solid and liquid are in equilibrium but no vapor is present. If the temperature is decreased further, all of the liquid freezes. Therefore, only solid is present to the left of AC. Water is an unusual substance: the solid is less dense than the liquid. If the pressure is increased at point F, at constant temperature, water will melt. The line AC has a slightly negative slope, which is very rare in phase diagrams of other substances. If the pressure on this system is increased and you move up the line AC, you can see that pressure has very little effect on the melting point, so the decrease in temperature is very small.

Solid-Gas Equilibrium

Along the line *AB*, solid is in equilibrium with vapor. If the pressure is decreased below the line *AB*, the solid will sublime. This relationship is the basis of freeze-drying foods, such as those shown in **Figure 25**. The food is frozen, and then a vacuum is applied. Water sublimes, which dehydrates the food very quickly. The food breaks down less when water is removed at the low temperature than when water evaporates at normal temperatures.

Phase Diagrams Are Unique to a Particular Substance

Each pure substance has a unique phase diagram, although the general structure is the same. Each phase diagram has three lines and shows the liquid-solid, liquid-gas, and solid-gas equilibria. These three lines will intersect at the triple point. The triple point is characteristic for each substance and serves to distinguish the substance from other substances.





Figure 25

Freeze-drying uses the process of sublimation of ice below the freezing point to dry foods. Many meals prepared for astronauts include freeze-dried foods.

Figure 26

The phase diagram for carbon dioxide shows the physical states of CO_2 at different temperatures and pressures. (Note that the diagram is not drawn to scale.)

The temperature at which the solid and liquid are in equilibrium—the melting point—is affected little by changes in pressure. Therefore, this line is very nearly vertical when pressure is plotted on the *y*-axis and temperature is plotted on the *x*-axis. Again, water is different in that the solid is less dense than the liquid. Therefore, an increase in pressure decreases the melting point. Most substances, such as carbon dioxide, shown in **Figure 26**, experience a slight increase in melting point when the pressure increases. However, the effect of pressure on boiling point is much greater.

SAMPLE PROBLEM B

How to Draw a Phase Diagram

The triple point of carbon dioxide is at -56.7 °C and 518 kPa. The critical point is at 31.1 °C and 7.38×10^3 kPa. Vapor pressure above solid carbon dioxide is 101.3 kPa at -78.5 °C. Solid carbon dioxide is denser than liquid carbon dioxide. Sketch the phase diagram.

Gather information.

- triple point of $CO_2 = -56.7$ °C, 518 kPa
- critical point of $CO_2 = 31.1^{\circ}C$, 7.38×10^3 kPa
- The vapor pressure of the solid is 101.3 kPa (1 atm) at -78.5°C.

2 Plan your work.

- Label the *x*-axis "Temperature" and the *y*-axis "Pressure."
- The vapor pressure curve of the liquid goes from the triple point to the critical point.
- The vapor pressure curve of the solid goes from the triple point through -78.5°C and 101.3 kPa.
- The line for the equilibrium between solid and liquid begins at the triple point, goes upward almost vertically, and has a slightly positive slope.

3 Draw the graph.

The graph that results is shown in Figure 26.

PRACTICE

- a. The triple point of sulfur dioxide is at −73°C and 0.17 kPa. The critical point is at 158°C and 7.87 × 10³ kPa. The normal boiling point of sulfur dioxide is −10°C. Solid sulfur dioxide is denser than liquid sulfur dioxide. Sketch the phase diagram of sulfur dioxide.
 - **b.**What state is sulfur dioxide in at 200 kPa and -100°C?
 - c. What state is sulfur dioxide in at 1 kPa and 80°C?
 - **d.**What happens as you increase the temperature of a sample of sulfur dioxide at 101.3 kPa from -20°C to 20°C?
 - e. What happens as you increase the pressure on a sample of sulfur dioxide at −11°C from 150 kPa to 300 kPa?

PRACTICE HINT

In each phase diagram, the necessary data are triple point, critical point, vapor pressure of the solid or liquid at 1 atm (101.3 kPa), and relative densities of the solid and the liquid. The rough graphs that you draw will be helpful in making predictions but will lack accuracy for most of the data.



The phase diagram for carbon dioxide is similar to that for water, but there are differences. In the phase diagram for carbon dioxide, the horizontal line at 101.3 kPa does not intersect the solid-liquid line. Thus, carbon dioxide is never a liquid at standard pressure. In fact, if you set dry ice, which is solid carbon dioxide, in a room temperature environment, you can see that it sublimes, or changes directly from a solid to a gas.

The horizontal line at 101.3 kPa intersects the vapor pressure curve for the solid at -78.5 °C. Therefore, solid carbon dioxide sublimes at this temperature. This sublimation point is equivalent to the normal boiling point of a liquid such as water. Because dry ice is at equilibrium with carbon dioxide gas at -78.5 °C, it is frequently used to provide this low temperature in the laboratory.

A Section Review

UNDERSTANDING KEY IDEAS

- **1.** A glass of ice water has several ice cubes. Describe the contents of the glass in terms of phase?
- **2.** How is the melting point of a substance defined?
- **3.** What is the connection between vapor pressure and boiling point?
- 4. What is a supercritical fluid?
- **5.** What happens when dry ice is warmed at 1 atm of pressure?

PRACTICE PROBLEMS

- **6.** Describe what happens if you start with water vapor at 0°C and 0.001 kPa and gradually increase the pressure. Assume constant temperature.
- 7. a. The triple point of benzene is at 5.5° C and 4.8 kPa. The critical point is at 289° C and 4.29×10^3 kPa. Vapor pressure above solid benzene is 101.3 kPa at 80.1°C. Solid benzene is denser than liquid benzene. Sketch the phase diagram of benzene.
 - **b.** In what state is benzene at 200 kPa and 80°C?
 - **c.** In what state is benzene at 10 kPa and 100°C?

- **d.** What happens as you increase the temperature of a sample of benzene at 101.3 kPa from 0°C to 20°C?
- **e.** What happens as you decrease the pressure on a sample of benzene at 80°C from 150 kPa to 100 kPa?

CRITICAL THINKING

- **8.** Look at the normal boiling point of diethyl ether in **Figure 22.** What do you think would happen if you warmed a flask of diethyl ether with your hand? (Hint: Normal body temperature is 37°C.)
- **9.** Most rubbing alcohol is isopropyl alcohol, which boils at 82°C. Why does rubbing alcohol have a cooling effect on the skin?
- **10. a.** Atmospheric pressure on Mount Everest is 224 mm Hg. What is the boiling point of water there?
 - **b.** What is the freezing point of water on Mount Everest?
- **11.** Why is the triple point near the normal freezing point of a substance?
- 12. You place an ice cube in a pot of boiling water. The water immediately stops boiling. For a moment, there are three phases of water present: the melting ice cube, the hot liquid water, and the water vapor that formed just before you added the ice. Is this three-phase system in equilibrium? Explain.



SCIENCE AND TECHNOLOGY

C₈H₁₀N₄O₂

CAREER APPLICATION



Food Scientist

Food science is the study of the chemistry, microbiology, and processing of foods. Food technicians are responsible for testing foods for quality and acceptability in carefully controlled taste tests. Microbiologists in the food industry monitor the safety of food products. Food analysts work in laboratories to monitor the composition of foods and the presence of pesticides. Some food scientists create new food products or food ingredients, such as artificial sweeteners. During their course of study, college students in the field of food science can gain valuable experience by working for food manufacturers and government agencies, such as the U.S. Food and Drug Administration. This experience can help students find jobs after graduation.



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Supercritical Fluids New Uses for Carbon Dioxide

If the temperature and pressure of a substance are above the critical point, that substance is a supercritical fluid. Many supercritical fluids are used for their very



Caffeine gives coffee its bitter taste and some people a feeling of restlessness.

effective and selective ability to dissolve other substances. This is very true of carbon dioxide. CO2 can be made into a supercritical fluid at a relatively low temperature and pressure, so little energy is used in preparing it. Supercritical CO₂ is cheap, nontoxic, and nonflammable and is easy to remove.

Getting a Good Night's Sleep

Supercritical CO₂ is used to remove caffeine from coffee beans. First, the green coffee beans are soaked in water. The beans are then placed in the top of a column that is 70 ft high. Supercritical CO₂ fluid at about 93°C and 250 atm enters at the bottom of the column. The caffeine diffuses out of the beans and into the CO₂. The beans near the bottom of the column mix with almost pure CO₂, which dissolves the last caffeine from the beans. It takes about five hours for fresh beans to move out of the column.

The decaffeinated beans are removed from the bottom, dried,



One process used to remove the caffeine from coffee dissolves the caffeine in supercritical CO₂.

and roasted as usual. The caffeine-rich CO_2 is removed at the top and passed upward through another column. Drops of water fall through the supercritical CO₂ and dissolve the caffeine. The water solution of caffeine is removed and sold to make soft-drinks. The pure CO_2 , is recirculated to be used again.

Questions

- **1.** Research advantages of using supercritical CO_2 as a solvent.
- 2. Research and report on other uses of supercritical fluids.

CHAPTER HIGHLIGHTS

KEY TERMS

surface tension evaporation boiling point condensation melting melting point freezing freezing point sublimation

intermolecular forces dipole-dipole forces hydrogen bond London dispersion force KEY IDEAS

SECTION ONE States and State Changes

- Solid particles vibrate in fixed positions. Thus, solids have a definite shape, volume, and density.
- Liquid particles can move past each other. Thus, liquids change shape and have a definite volume and density.
- Gas particles are far apart from each other. Thus, gases can change shape, volume, and density.
- Solids, liquids, and gases convert from one state to another through freezing, melting, evaporation, condensation, sublimation, and deposition.

SECTION TWO Intermolecular Forces

- The strongest force attracting particles together is the ionic force.
- All ions, atoms, and molecules are attracted by London dispersion forces.
- Polar molecules experience the dipole-dipole force. The dipole-dipole force is usually significant only when the molecules are quite polar.
- Hydrogen bonds are stronger dipole-dipole forces.
- Water's unique properties are due to the combination of the shape of a water molecule and the ability of water to form multiple hydrogen bonds.

SECTION THREE Energy of State Changes

- Energy is needed to change solid to liquid, solid to gas, and liquid to gas. Thus, melting, sublimation, and evaporation are endothermic processes.
- For a given substance, the endothermic state change with the greatest increase in energy is sublimation. Evaporation has a slightly smaller increase in energy, and melting has a much smaller increase in energy.
- The molar enthalpy of fusion of a substance is the energy required to melt 1 mol of the substance at the melting point. The molar enthalpy of vaporization of a substance is the energy required to vaporize 1 mol of the substance.

SECTION FOUR Phase Equilibrium

- A phase diagram shows all of the equilibria between the three states of a substance at various temperatures and pressures.
- On a phase diagram, the triple point is where three phases are in equilibrium. Above the critical point, a substance is a supercritical fluid.
- Water is unique in that increased pressure lowers the freezing point.

KEY SKILLS

phase equilibrium

vapor pressure

phase diagram

triple point

critical point

Calculating Melting and Boiling Points Sample Problem A p. 397 **How to Draw a Phase Diagram** Sample Problem B p. 404



USING KEY TERMS

- **1.** Most substances can be in three states. What are they?
- **2.** Explain how solid naphthalene in mothballs is distributed evenly through clothes in a drawer.
- **3.** What is the freezing point of a substance?
- **4.** Carbon tetrachloride, CCl₄, is nonpolar. What forces hold the molecules together?
- **5.** Compare dipole-dipole forces and hydrogen bonds.
- **6.** What is the difference between the terms *state* and *phase*?
- **7.** Define *boiling point* in terms of vapor pressure.
- **8.** What is a triple point?

UNDERSTANDING KEY IDEAS

States and State Changes

- **9.** Compare the arrangement and movement of particles in the solid, liquid, and gas states of matter.
- **10.** What is surface tension?
- A small drop of water assumes an almost spherical form on a Teflon[™] surface. Explain why.
- **12.** What is happening when water is heated from 25°C to 155°C?
- **13.** Give an example of deposition.

Intermolecular Forces

- **14.** Contrast ionic and molecular substances in terms of the types of attractive forces that govern their behavior.
- **15.** Is the melting point of CaCl₂ higher than that of NaCl or lower? Explain your answer.
- **16.** A fellow student says, "All substances experience London dispersion forces of attraction between particles." Is this statement true? Explain your answer.
- **17.** Which has larger London dispersion forces between its molecules, CF₄ or CCl₄?
- **18.** Of the three forces, ionic, dipole-dipole, and London dispersion forces, which is the strongest?
- **19.** Why does ice float in water even though most solids sink in the pure liquid?
- **20.** Why does CBr_4 boil at a higher temperature than CCl_4 does?

Energy of State Changes

- **21.** The molar enthalpy of fusion of water is 6.009 kJ/mol at 0°C. Explain what this statement means.
- **22.** Why is the molar enthalpy of vaporization of a substance much higher than the molar enthalpy of fusion?
- **23.** How do you calculate the entropy change during a change of state at equilibrium?
- **24.** Why is the entropy of a substance higher in the liquid state than in the solid state?
- **25.** At 100°C, the enthalpy change for condensation of water vapor to liquid is negative. Is the entropy change positive, or is it negative?

- **26.** ΔH for a process is positive, and ΔS is negative. What can you conclude about the process?
- **27.** Explain why liquid water at 273.0 K will not melt in terms of Gibbs energy.
- **28** What thermodynamic values do you need to know to calculate a substance's melting point?
- **29.** How does pressure affect the entropy of a gas?
- **30.** How does pressure affect changes between the liquid and vapor states?

Phase Equilibrium

- **31.** You have sweetened iced tea with sugar, and ice cubes are present. How many phases are present?
- **32.** The term *vapor pressure* almost always means the equilibrium vapor pressure. What physical arrangement is needed to measure vapor pressure?
- **33.** What is meant by the statement that a liquid and its vapor in a closed container are in a state of equilibrium?
- **34.** As the temperature of a liquid increases, what happens to the vapor pressure?



- **35.** Use the above graph of the vapor pressure of water versus temperature to answer the following questions.
 - **a.** At what point(s) does water boil at standard atmospheric pressure?
 - **b.** At what point(s) is water only in the liquid phase?
 - **c.** At what point(s) is water only in the vapor phase?
 - **d.** At what point(s) is liquid water in equilibrium with water vapor?
- **36.** What two fixed points are on all phase diagrams?

PRACTICE PROBLEMS



Sample Problem A Calculating Melting and Boiling Points

Calculate the temperatures for the following phase changes. (Liquids are at the normal boiling point.)

- 37. The enthalpy of fusion of chlorine, Cl₂, is 6.40 kJ/mol, and the entropy of fusion is 37.2 J/mol•K.
- 38. The enthalpy of fusion of sulfur trioxide is 8.60 kJ/mol, and the entropy of fusion is 29.7 J/mol•K.
- 39. The enthalpy of vaporization of butane, C₄H₁₀, is 22.44 kJ/mol, and the entropy of vaporization is 82.2 J/mol•K.
- **40.** ΔH_{vap} for silicon tetrachloride is 28.7 kJ/mol, and ΔS_{vap} is 86.7 J/mol•K.

Sample Problem B How to Draw a Phase Diagram

41. The critical point for krypton is at -64°C and a pressure of 5.5 × 10³ kPa. The triple point is at -157.4°C and a pressure of 73.2 kPa. At -172°C, the vapor pressure is 13 kPa. The normal boiling point is -152°C. Sketch the phase diagram.

42. The critical point for carbon tetrachloride is at 283° C and 4.5×10^{3} kPa. The triple point is at -87.0° C and 28.9 kPa. The normal boiling point is 76.7° C. Sketch the phase diagram.

MIXED REVIEW

- **43.** Calculate the melting point of acetic acid at standard pressure. The enthalpy of fusion of acetic acid is 11.54 kJ/mol, and the entropy of fusion is 39.8 J/mol•K.
- **44.** ΔH_{vap} for gold is 324 kJ/mol, and ΔS_{vap} is 103.5 J/mol•K. Calculate the boiling point of gold.
- **45.** The critical point for HBr is at 90°C and 8.56×10^3 kPa. The triple point is at -87.0°C and 29 kPa. The normal boiling point is -66.5°C. Sketch the phase diagram.

CRITICAL THINKING

- **46.** How can water be made to evaporate rapidly at room temperature?
- **47.** How does a pressure cooker work?
- **48.** Which would have the higher boiling point: chloroform, CHCl₃, or bromoform, CHBr₃?
- **49.** You know that the enthalpy change for vaporizing water is $\Delta H_{vap} = H_{gas} H_{liq}$. What is the Gibbs energy change for this process?
- **50.** Explain why steam produces much more severe burns than the same amount of boiling water does.
- **51.** Chloroethane $(T_{bp} = -13^{\circ}\text{C})$ has been used as a local anesthetic. When the liquid is sprayed onto the skin, it cools the skin enough to freeze and numb the skin. Explain the cooling effect of this liquid.
- **52.** Is it possible to have *only* liquid water present in a container at 0.00°C? Explain.

- 53. Consider a system composed of water vapor and liquid at equilibrium at 100°C. Do the molecules of H₂O in the vapor have more kinetic energy than molecules in the liquid do? Explain.
- **54.** Look at the phase diagram for carbon dioxide. How can CO₂ be made to boil?

ALTERNATIVE ASSESSMENT

- 55. Liquid crystals are substances that have properties of both liquids and crystals. Write a report on these substances and their various uses.
- **56.** Some liquids lose all viscosity when cooled to extremely low temperatures—a phenomenon called *superfluidity*. Find out more about the properties of superfluid substances.
- **57.** Many scientists think that more than 99% of the known matter in the universe is made of a fourth state of matter called plasma. Research plasmas, and report your findings to the class.
- **58.** Prepare a report about the adjustments that must be made when cooking and baking at high elevations. Collect instructions for high-elevation adjustments from packages of prepared food mixes. Explain why changes must be made in recipes that will be prepared at high elevations. Check your library for cookbooks that contain information about food preparation at high elevations.

CONCEPT MAPPING



59. Use the following terms to create a concept map: *boiling point, liquids, vapor pressure, gases, melting point, states,* and *equilibrium.*



Study the graph below, and answer the questions that follow. For help in interpreting graphs, see Appendix B, "Study Skills for Chemistry."

- **60.** What is the normal boiling point of water?
- **61.** Give the coordinates for a point at which only liquid water is present.
- **62.** Give the coordinates for a point at which liquid water is in equilibrium with vapor.
- **63.** Give the coordinates for a point at which only vapor is present.
- **64.** What is the vapor pressure of water at point E?
- **65.** What will happen if the vapor at point D is cooled at constant pressure?



Phase Diagram for H₂O

TECHNOLOGY AND LEARNING

66. Graphing Calculator

Calculating Vapor Pressure by Using a Table

The graphing calculator can run a program that calculates a table for the vapor pressure in atmospheres at different temperatures (K) given the number of moles of a gas and the volume of the gas (V). Given a 0.50 mol gas sample with a volume of 10 L, you can calculate the pressure at 290 K by using a table. Use this program to make the table. Next, use the table to perform the calculations.

Go to Appendix C. If you are using a TI-83 Plus, you can download the program VAPOR and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. After you have run the program, answer the questions.

- **a.** What is the pressure for 1.3 mol of a gas with a volume of 8.0 L and a temperature of 320 K?
- **b.** What is the pressure for 1.5 mol of a gas with a volume of 10.0 L and a temperature of 340 K?
- **c.** Two gases are measured at 300 K. One has an amount of 1.3 mol and a volume of 7.5 L, and the other has an amount of 0.5 mol and a volume of 10.0 L. Which gas has the lesser pressure?

STANDARDIZED TEST PREP



UNDERSTANDING CONCEPTS

Directions (1-3): For each question, write on a separate sheet of paper the letter of the correct answer.

1 Which of the following has the greatest force between particles?

A .	Cl ₂	С.	HOCl
В.	HCl	D.	NaCl

- Water boils at 100°C. Ethyl alcohol boils at 78.5°C. Which of these statements is **true**?
- **F.** Vapor pressure is not related to boiling point.
- **G.** Water has a higher vapor pressure at a temperature of 78.5°C.
- **H.** Ethyl alcohol has a higher vapor pressure at a temperature of 78.5°C.
- **I.** Water and ethyl alcohol have the same vapor pressure at a temperature of 78.5°C.

Which of the following forms the strongest hydrogen bonds?

A.	CH_4	С.	H_2O
B.	C_2H_6	D.	H ₂ Se

Directions (4-6): For each question, write a short response.



4 As a covalent compound melts, heat energy is added and enthalpy increases, but the temperature does not change. What is the effect on the molecules of the added energy?



5 In what way can all forces between particles be considered polar in nature?

6 How does the process of sublimation demonstrate that solids as well as liquids have a vapor pressure?

READING SKILLS

Directions (7–9): Read the passage below. Then answer the questions.

If the temperature in a citrus orchard drops below –2°C for several hours, the fruit will freeze and be destroyed. Citrus growers spray tiny droplets of heated water to protect the crop if a freeze is predicted. Part of the protection comes from the heat released as the heated water cools. However, much of the heat that protects trees from freezing is released as the water freezes. The phase change from liquid to solid releases 6.01 kilojoules of energy for each mole of water. Creating a layer of ice on the tree actually prevents it from freezing.

- 7 How is the enthalpy of fusion of water involved in protecing citrus crops from freezing?
 - **F.** Heat is released as water changes from gas to liquid.
 - **G.** Heat is released as water changes from liquid to gas.
 - **H.** Heat is released as water changes from liquid to solid.
 - I. Heat is released as water changes from solid to liquid.

8 How much heat energy is provided to a tree branch by the formation of 36 grams of ice?

A.	−12.02 kJ	С.	6.01 kJ
B.	-6.01 kJ	D.	12.02 kJ



below freezing?

INTERPRETING GRAPHICS

Directions (10–14): For *each* question below, record the correct answer on a separate sheet of paper.

10 A phase diagram for a substance one intersection of temperature and pressure known as a triple point. What condition only exists at the triple point?

The illustration below represents a closed system containing a substance in both liquid and gas states. Use the illustration below to answer questions 11 through 14.

Substance in a Closed System

11 Which phrase below **best** describes the system shown above?

- **F.** a system that is not in equilibrium
- **G.** a system in which the rate of condensation is equal to the rate of evaporation
- **H.** a system in which the rate of condensation is greater than the rate of evaporation
- I. a system in which the concentration of the gas equals the concentration of the liquid

12 What would be the effect on this system if temperature were increased? **A.** more of the particles will be in the gas phase

B. more of the particles will be in the liquid phase

C. the ratio of particles in the gas and liquid phases does not change

D. depending on intermolecular forces, the ratio of particles in the two phases can increase or decrease



13 In which phase is the entropy higher?

14 If the flask contains water at one atmosphere pressure, what is the maximum temperature in kelvins of the flask?



Pay close attention to words such as not, only, rather, and some that appear in questions.



CHAPTER

