

CHAPTER 14

LIQUIDS: CONDENSATION, EVAPORATION, AND DYNAMIC EQUILIBRIUM

Over the past weeks, you have seen numerous examples of how chemistry can deepen your understanding of everyday phenomena. In this chapter, we revisit the topic of liquids and the changes they undergo, in order to explain some of the things you might experience on an unusually warm spring morning.

7:47 A.M. You get out of bed and take a quick shower. As you step out of the shower, you shiver with cold, even though the day is already warm.

7:51 A.M. You turn toward the bathroom mirror to comb your hair, but it's so steamed up you can hardly see yourself. What causes water to collect on the mirror's surface?

7:54 A.M. The water that dripped onto the floor has almost dried up now, but the water that collects in the bottom of your toothbrush cup never seems to disappear. Why?

8:01 A.M. Drops of cologne land on the counter. Why do they evaporate so much more quickly than water, and even more quickly in the heat from your blow dryer?

8:03 A.M. You notice a can of hair spray sitting on the window ledge in the hot sun. You've heard that if its temperature gets high enough, the can will explode. What causes that to happen?

8:04 A.M. Heating the water for your morning tea, you wonder what causes bubbles to form when the water boils—and why they don't form until the water becomes extremely hot. That reminds you—why did it take so long to boil the potatoes during your backpacking trip to the high Sierras last week?

8:12 A.M. Whew! That's a lot of wondering for the first few minutes of your day. Why not relax, drink your tea, and settle down to read this chapter? All of your questions are about to be answered.

Review Skills

The presentation of information in this chapter assumes that you can already perform the tasks listed below. You can test your readiness to proceed by answering the Review Questions at the end of the chapter. This might also be a good time to read the Chapter Objectives, which precede the Review Questions.

- Describe the relationship between the temperature of a substance and the motion of its component particles. (Section 2.1.)
- Compare the freedom of motion and the attractions between the component particles in solids, liquids, and gases. (Section 2.1.)
- Given a formula for a compound, classify it as either a molecular compound or an ionic compound. (Section 3.2.)
- Given the names or formulas for two elements, decide whether the bond that would form between them would be covalent or ionic. (Section 3.2.)
- Given a name or chemical formula, tell whether it represents a binary ionic compound, an ionic compound with polyatomic ion(s), a binary covalent compound, a binary acid, or an oxyacid. (Section 5.3.)
- Convert between names and chemical formulas for binary ionic compounds, ionic compounds with polyatomic ion(s), binary covalent compounds, binary acids, and oxyacids. (Section 5.3.)
- Given the formula for a molecule or polyatomic ion, draw a reasonable Lewis structure for it. (Section 12.2.)
- Given the Lewis structure or enough information to produce it, draw the geometric sketch of a molecule, including bond angles. (Section 12.4.)

14.1 Changing from Gas to Liquid and from Liquid to Gas—An Introduction to Dynamic Equilibrium

14.2 Boiling Liquids

14.3 Particle-Particle Attractions



Why does water vapor condense on a bathroom mirror?

14.1 Changing from Gas to Liquid and from Liquid to Gas—An Introduction to Dynamic Equilibrium

Our discussion of liquids focuses on two opposing processes: **condensation**, in which liquids are formed from gases, and **evaporation**, in which liquids return to gases. An understanding of these processes will help us understand the dynamics of all reversible physical and chemical changes.

The Process of Condensation

You have probably noticed that the steam from a hot shower deposits liquid droplets on all the surfaces of your bathroom, but have you ever thought about what's happening on the submicroscopic level of atoms and molecules when this happens? How does water vapor differ from liquid water, and why does water change from one state to the other? (Note that we use the term **vapor** to describe the gaseous form of a substance that is liquid at normal temperatures and pressures. We also use it to describe gas that has recently come from a liquid.)

OBJECTIVE 2

Picture yourself riding on a water molecule in a system in which water vapor is present at a relatively high temperature. The first image in Figure 14.1 shows how you might visualize this gas. The spheres in this figure represent the particles of any substance; they could be atoms or molecules. For our discussion, each of the spheres represents a water molecule. Initially, your molecule moves in a straight line, with no significant interactions with other particles. Then, all of a sudden, it collides violently with a slower-moving water molecule. Because of the collision, your particle changes direction and slows down, the other molecule speeds up, and both molecules move off along new, straight-line paths. The contact between the two particles was so brief that at no time did you detect any attraction or repulsion between them. They simply collided, bounced off each other, and moved apart.

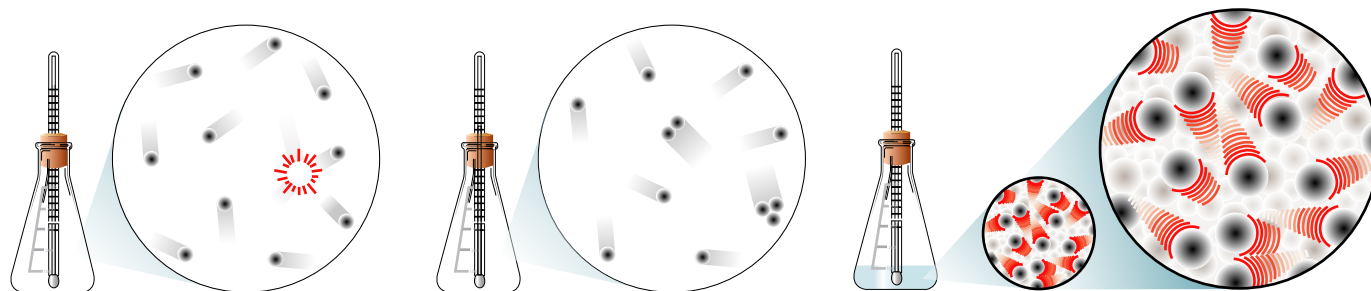
OBJECTIVE 2

Now picture the same system as we slowly decrease the vapor's temperature, reducing the average velocity of the molecules. The collisions between your molecule and others decrease in violence, so much so that sometimes two colliding molecules stick together for awhile, held by a mutual attraction. (One of the goals of this chapter is to describe this attraction and other types of attractions between particles.) Initially, these attractions do not last very long. A faster-moving water molecule slams into your pair, knocking them apart, and all three particles continue on alone. As the temperature decreases further, however, pairs of molecules are less likely to be knocked apart. Instead, they begin to form trios and even larger clusters (Figure 14.1, middle image).

OBJECTIVE 2

The slower the particles move, the harder it becomes for them to escape their mutual attractions. The molecule clusters grow so large that they fall to the bottom of the container (or cling to its sides), where they combine to form liquid water (Figure 14.1, image on the right). This is the process of condensation.

In short, as the gaseous water molecules in the steam from a hot shower cool, they cluster—or condense—into droplets of liquid water, forming a fog that fills the room. These droplets then combine with other droplets and collect on every surface in the bathroom, including your bathroom mirror.



At a high temperature, there are no significant attractions between the particles.

As the temperature is lowered, attractions between particles lead to the formation of very small clusters that remain in the gas phase.

As the temperature is lowered further, the particles move slowly enough to form clusters so large that they drop to the bottom of the container and combine to form a liquid.

OBJECTIVE 2

Figure 14.1
The Change from Gas to Liquid

The Process of Evaporation

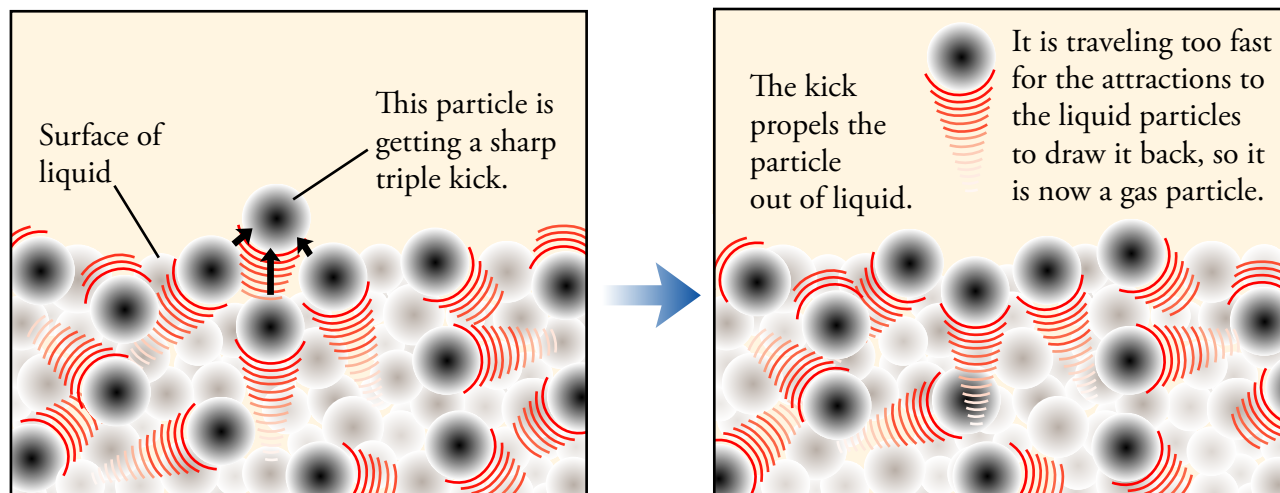
Why does rainwater on a flat street evaporate so much faster than the same amount of water in a deep puddle? Why does nail polish remover evaporate so much more quickly than water, and why do all liquids evaporate more quickly when they are hot? Many factors affect the **rate of evaporation**, the amount of liquid changing to gas per second. We begin our exploration of them by reviewing some information first presented in Section 2.1.

To get an idea of the changes taking place when a liquid evaporates, picture yourself riding on a molecule in a liquid held inside a closed container (Figure 14.2). In a typical liquid, about 70% of the volume is occupied by particles, so there is not much empty space for you and your molecule to move into. Your movement is further hindered by the attractions between your molecule and the other molecules around it. Nevertheless, you bump and jostle to all parts of the container, colliding with other particles, changing velocity and direction, breaking old attractions, and making new ones.

Now picture your particle moving toward the surface of the liquid. If it continues along the same trajectory when it gets to the surface, its momentum (mass times

OBJECTIVE 3

Figure 14.2
Evaporation



velocity) will take you out of the liquid, into the space above—until the attractions that hold the particles together in the liquid pull you back. If your particle is moving fast enough, though, its momentum can take it so far beyond the surface that the attractions will be broken. In that case, the particle escapes the liquid and joins the vapor above the liquid (Figure 14.2 on the previous page).

OBJECTIVE 4

For a particle to escape from the surface of a liquid, it must meet the following criteria:

- The particle must be at the liquid's surface.
- Its direction of motion must take it beyond the liquid's surface.
- Its momentum must be great enough to overcome the backward pull of the other particles at the surface.



The fastest water molecules are escaping from the water on his skin. The average velocity, and thus the temperature, of the remaining water molecules is lower.

How Evaporation Causes Cooling

OBJECTIVE 5

Particles must have a relatively high velocity in order to break the attractions holding them in the liquid. Particles with relatively low velocity do not have enough momentum to escape. Thus fast moving particles escape, and slow moving particles do not. After the more rapidly moving particles have escaped, the particles left in the liquid have a lower average velocity, and lower average velocity means lower temperature. In other words, evaporation lowers a liquid's temperature. We experience this change in temperature when we step out of a shower or a swimming pool.

Rate of Evaporation

OBJECTIVE 6

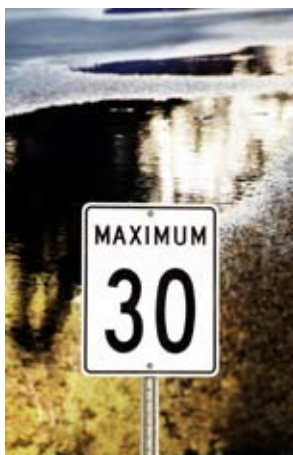
The rate of evaporation—the number of particles moving from liquid to gas per second—depends on three factors:

- Surface area of the liquid
- Strength of attractions between the particles in the liquid
- Temperature of the liquid

OBJECTIVES 7 & 8

Greater surface area means more particles at the surface of a liquid, which leads to a greater rate of evaporation. Picture two identical glasses of water. One glass is left on a table, and the second glass is emptied onto the floor. At the same temperature, the percentage of particles with the momentum needed to escape from the surface is the same for both samples of water, but the only particles that get an opportunity to escape are particles at or near the surface. Because there are a lot more particles at the surface of the water on the floor, the number of particles that escape from that water into the gas phase is much greater than for the water in the glass. This explains why rain evaporates so much faster from a flat street than from a deep puddle.

Weaker attractions between particles also lead to a higher rate of evaporation. Consider the differences between liquid acetone and liquid water. Acetone, CH_3COCH_3 , is a common laboratory solvent and the main ingredient in many nail polish removers. If you have ever used it, you probably noticed that it evaporates much more rapidly than water. The attractions between acetone molecules are weaker than those between water molecules, so it is easier for particles to escape from the surface of liquid acetone than from liquid water. At the same temperature, more molecules will escape per second from the acetone than from the water (Figure 14.3).



Water evaporates much more quickly from a flat street than from a deep pothole.

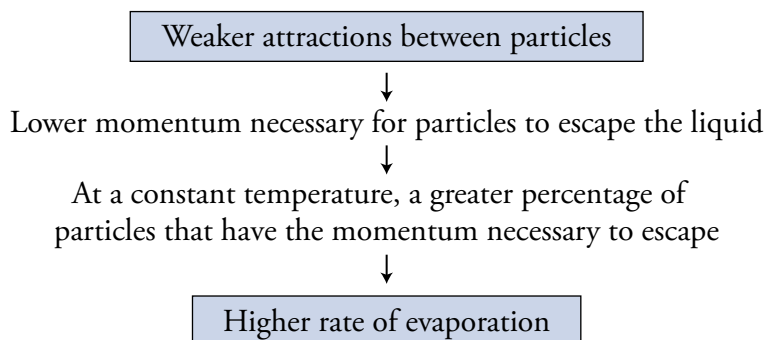
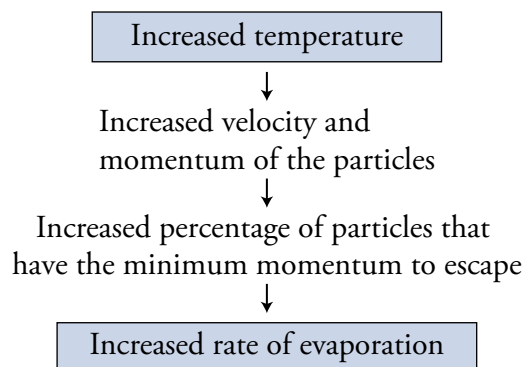


Figure 14.3
Attractions Influence Rate of Evaporation

OBJECTIVE 8

The rate of evaporation is also dependent on the liquid's temperature. Increased temperature increases the average velocity and momentum of the particles. As a result, a greater percentage of particles will have the minimum momentum necessary to escape, so the liquid will evaporate more quickly (Figure 14.4). This explains why rainwater on a city street evaporates much more rapidly when the sun comes out.



OBJECTIVE 9

Figure 14.4
Temperature Influences Rate of Evaporation

Dynamic Equilibrium Between Liquid and Vapor

In a closed container, evaporation and condensation can take place at the same time. Our model helps us visualize this situation.

Picture a container that is partly filled with liquid and then closed tightly so that nothing can escape. As soon as the liquid is poured in, particles begin to evaporate from it into the space above at a rate that is dependent on the surface area of the liquid, the strengths of attractions between the liquid particles, and the temperature. If these three factors remain constant, the rate of evaporation will be constant.

Imagine yourself riding on one of the particles in the vapor phase above the liquid. Your rapidly moving particle collides with other particles, with the container walls, and with the surface of the liquid. When it collides with the surface of the liquid and its momentum carries it into the liquid, your particle returns to the liquid state. The number of gas particles that return to liquid per second is called the **rate of condensation**.

Now let's go back to the instant the liquid is poured into the container. If we assume that the container initially holds no vapor particles, there is no condensation occurring when the liquid is first added. As the liquid evaporates, however, particles of vapor gradually collect in the space above the liquid, and the condensation process slowly begins. As long as the rate of evaporation of the liquid is greater than the rate of condensation of the vapor, the concentration of vapor particles above the liquid will increase. However, as the concentration of vapor particles increases, the rate of collisions of vapor particles with the liquid increases, boosting the rate of condensation.

If there is enough liquid in the container, not all of it will evaporate. Instead, the rising rate of condensation will eventually become equal to the rate of evaporation.

OBJECTIVE 10

OBJECTIVE 10

At this point, for every particle that leaves the liquid, a particle somewhere else in the container returns to the liquid. Thus there is no net change in the amount of substance in the liquid state or the amount of substance in the vapor state (Figures 14.5 and 14.6). There is no change in volume either (because our system is enclosed in a container), so there is no change in the concentration of vapor above the liquid and no change in the rate of collision with the surface of the liquid. Therefore, the rate of condensation stays constant.

OBJECTIVE 11

When two opposing rates of change are equal—such as the rate of evaporation and the rate of condensation in our closed system—we say the system has reached a **dynamic equilibrium**. Dynamic equilibrium is found in many of the systems that you will encounter in chemistry, so it is important to have a general understanding of the conditions necessary to create it. First, the system must exhibit two ongoing, opposing changes, from state A to state B and from state B to state A. In our example, state A is the liquid, state B is the vapor, and the two opposing changes are evaporation and condensation. For a dynamic equilibrium to exist, the rates of the two opposing changes must be equal, so that there are constant changes between state A and state B but no net change in the components of the system. In the dynamic equilibrium of our liquid-vapor system, the liquid is constantly changing to vapor, and the vapor is constantly changing to liquid, but no net change in the amounts of liquid and vapor is observed (Figure 14.6).

Figure 14.5
Rate of Evaporation, Rate of Condensation, and the Liquid-Vapor Equilibrium

OBJECTIVE 10

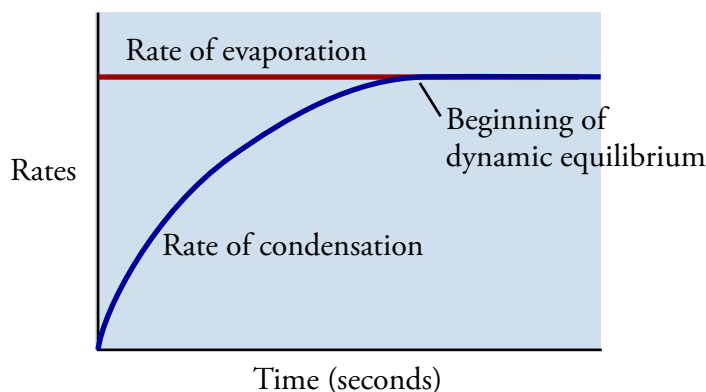
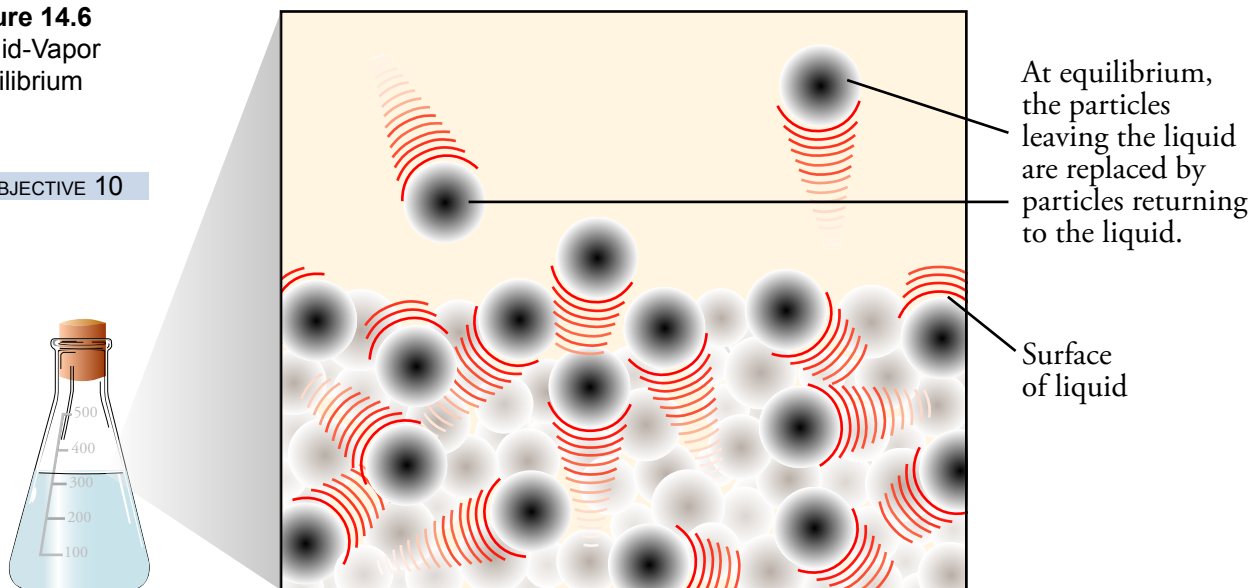


Figure 14.6
Liquid-Vapor Equilibrium

OBJECTIVE 10



An analogy might help with this visualization of dynamic equilibrium. It is common these days for children's indoor play areas to have a large bin filled with plastic balls. The bin is like a wading pool where the kids do not get wet. Picture two kids in a bin throwing balls at one another. Most of the balls they throw hit the nets surrounding the bin, but a few escape through the openings and fall onto the floor. The escape of the balls can be likened to particles evaporating from the surface of a liquid.

The escaping balls attract the attention of an attendant, who rushes over to return them to the bin. At first, there are only a few balls on the floor, so the attendant has to move a relatively long way to get from one ball to another and throw them back in the bin. This makes the rate of return rather low, and the kids are able to throw the balls out faster than he can return them, resulting in a steady increase in the number of balls on the floor. Now there is less distance between the balls, and the attendant is able to return them to the bin at a faster and faster rate. This situation is like the increasing rate of condensation that results from an increase in the concentration of gas above a liquid.

Eventually the attendant is reaching the balls quickly enough to return them to the bin just as quickly as the kids can throw them out. At this point, the process continues at a frantic pace but with no net change in the numbers of balls in the bin and on the floor. This is like the dynamic equilibrium reached between the rates of evaporation and condensation of liquid and vapor in a closed container. When the rates are equal, there is no net change in the amount of liquid or vapor in the system.

The dynamic equilibrium lasts until something happens to disrupt the system in a way that changes one or both of the rates. For example, the liquid vapor system would be disrupted if the top were removed from the closed container, allowing vapor to escape and decreasing the rate of condensation. The plastic ball equilibrium could be disrupted when a mother comes over to rescue the attendant by convincing the kids to stop throwing balls and go get ice cream.



Equilibrium Vapor Pressure

When a liquid is placed in a closed container and begins to evaporate, the vapor exerts a pressure against the container's walls (and against the surface of the liquid). When this system reaches a dynamic equilibrium between the rates of evaporation and condensation, the amount of vapor above the liquid remains constant. According to the ideal gas equation, the pressure of the vapor (or gas) is dependent on the vapor's concentration (moles divided by volume or n/V) and its temperature:

$$PV = nRT \quad P = \frac{n}{V}RT = [\text{concentration}]RT$$

If the temperature of the system, as well as the concentration of the vapor, remains constant, the pressure of the vapor stays constant as well.

The space above a liquid in a closed container usually contains substances other than the vapor of the evaporating liquid. The pressure exerted by the vapor that has escaped the liquid is therefore the partial pressure of that substance in the total amount of gas

OBJECTIVE 12

OBJECTIVE 12

inside the container. For example, if the container held both air and liquid at the time we closed it, any vapor that escapes the liquid will mix with the oxygen, nitrogen, and other gases in the air and contribute only a portion of the total pressure. The partial pressure of vapor above a liquid in a closed system with a dynamic equilibrium between the rate of evaporation and the rate of condensation is called the **equilibrium vapor pressure**, P_{vap} .

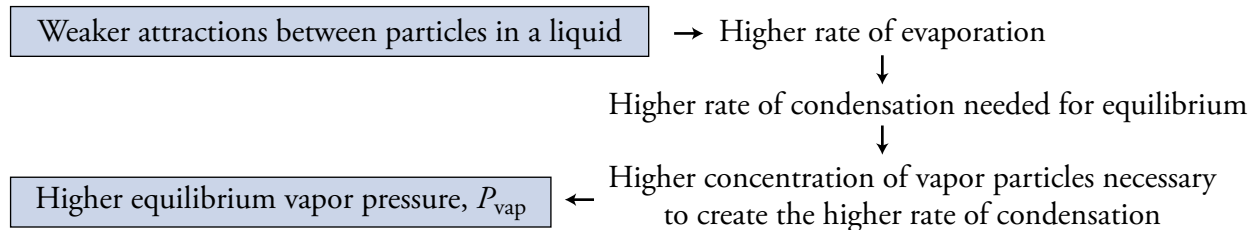
OBJECTIVE 13

Different substances have different equilibrium vapor pressures at the same temperature. For example, the vapor pressure above liquid acetone in a closed container is higher than for water at the same temperature. Because the attractions between acetone molecules are weaker than the attractions between water molecules, it is easier for an acetone molecule to break them and move into the vapor phase. Therefore, the rate of evaporation from liquid acetone is greater than for water at the same temperature. When the dynamic equilibrium between evaporation and condensation for each liquid is reached, the rate of condensation for the acetone is higher than for water. The rate of condensation is higher because the concentration of vapor above the liquid is higher. The higher concentration of acetone particles creates a higher equilibrium vapor pressure. This logic is summarized in Figure 14.7. The weaker the attractions between particles of a substance, the higher the equilibrium vapor pressure for that substance at a given temperature.

Figure 14.7

Relative Equilibrium Vapor Pressures

OBJECTIVE 13



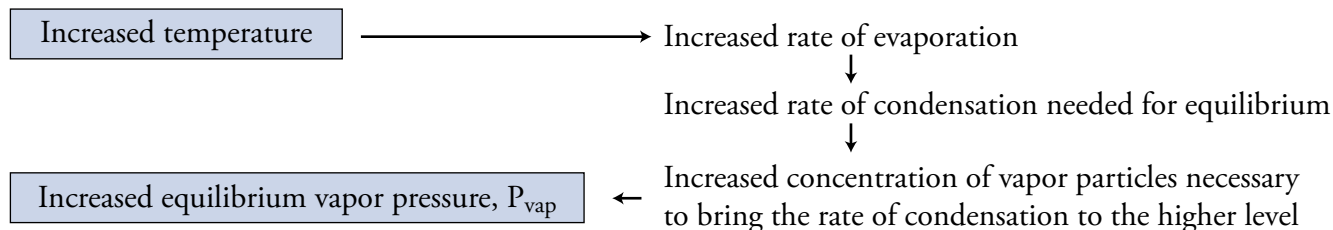
OBJECTIVE 14

The equilibrium vapor pressure of a liquid increases with increased temperature. At a higher temperature, the faster-moving particles can escape from the liquid more easily, so the rate of evaporation increases, leading to a higher rate of condensation at equilibrium. To reach this higher rate of condensation, the concentration of vapor above the liquid must rise to yield a higher rate of collisions with the surface of the liquid. A higher concentration of vapor leads to a higher vapor pressure (Figure 14.8). Figure 14.9 shows how the equilibrium vapor pressure varies with temperature for acetone and water.

Figure 14.8

Effect of Temperature on Equilibrium Vapor Pressure

OBJECTIVE 14



A similar situation can arise in our children's play area. Seeing that the attendant is trying to return the balls to the bin, the kids might take on the challenge and begin to try to throw the balls out the opening. This increases the rate of escape and at first allows them to get ahead of the poor attendant, but as the concentration of the balls on the floor increases, his rate of return increases until the two rates are again equal.

We can now explain why high temperature can cause an aerosol can to explode. If you leave an aerosol can in the hot sun, the temperature of the substances in the can will go up, and the rates of evaporation of the liquids that it contains will increase. The concentration of vapor in the can will rise accordingly, and the vapor pressure will increase. If the pressure becomes too high, the can will explode. A typical aerosol can is built to withstand pressures up to about 10 to 12 times normal room pressure.

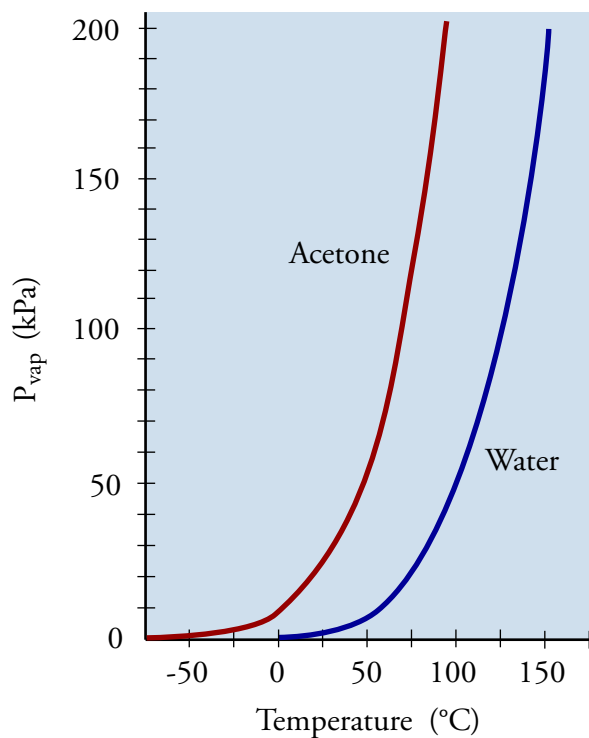


Figure 14.9
Equilibrium Vapor Pressure, P_{vap} , and Temperature

SPECIAL TOPIC 14.1 Chemistry Gets the Bad Guys

We've all seen it on TV and in the movies... the detective arrives at the crime scene and stalks into the room wearing a trench coat. The area is taped off, and the experts from the crime lab are already "dusting for fingerprints." In the movies, this usually means spreading black powder that will stick to the fingerprints, but in the real world, forensic scientists have developed new and better ways to make fingerprints visible and help identify the "perp."

There are three types of fingerprints. If the people investigating a crime are lucky, the fingerprints will be either plastic, impressions left in soft material like wax or paint, or visible, imprints made by blood, dirt, ink, or grease. However, usually the fingerprints are latent, invisible patterns that must be made visible before they can be of use. Latent fingerprints are composed of perspiration, oils, amino acids, proteins, inorganic salts (such as sodium and potassium chloride), and many other substances. In order to make latent fingerprints visible, the investigator covers the area with a substance that either sticks to them more than to the surfaces they're sitting on or, in some cases, reacts chemically with the fingerprint components.

A 1993 kidnapping case provided forensic chemists



with a puzzling problem. An 8-year-old was kidnapped in Knoxville, Tennessee, but, fortunately, she was able to escape and identify the car used in the kidnapping. When the car was checked for fingerprints, the investigators found many latent prints of the car's owner, but they could not find any fingerprints of the kidnapped girl. Knowing that this would raise doubts in the minds of the jury, they began to study the differences between the fingerprints of children and adults in hopes of finding an explanation. They found that an adult's fingerprints contain a relatively high concentration of molecules called esters produced by the oil glands on a grown person's face and then transferred to the fingers when they touch the face. These esters are not produced until after puberty, so they are not found in a child's fingerprints. The ester molecules are very large with strong attractions that lead to low rates of evaporation. This discovery explained why the car owner's fingerprints could be found even after the child's prints had evaporated and helped convince the jury that the car's owner was guilty.

Source: Doris R. Kimbrough and Ronald DeLorenzo, "Solving the Mystery of Fading Fingerprints with London Dispersion Forces." *Journal of Chemical Education*, 75, 10 (October 1998), pp. 1300-1301.

14.2 Boiling Liquids

Why do bubbles form in very hot water but not in water that is cold or even warm? Why does it take longer to boil your potatoes on a backpacking trip to the high Sierras? This section presents a model for visualizing the process of boiling and then uses it to answer questions such as these.

How Do Bubbles Form in Liquids?

OBJECTIVE 15

To understand why bubbles form in a boiling liquid, picture yourself riding on particle 1 in the liquid shown in Figure 14.10. Your particle is moving constantly, sometimes at very high velocity. When it collides with particles 2 and 3, it pushes them aside and moves in between them, leaving a small space in your wake. If at the same time particle 4 moves across this space and collides with particles 5 and 6, the space will grow in volume. Collisions such as these are continuously causing spaces to form within the liquid. These spaces can be thought of as tiny bubbles (Figure 14.10).

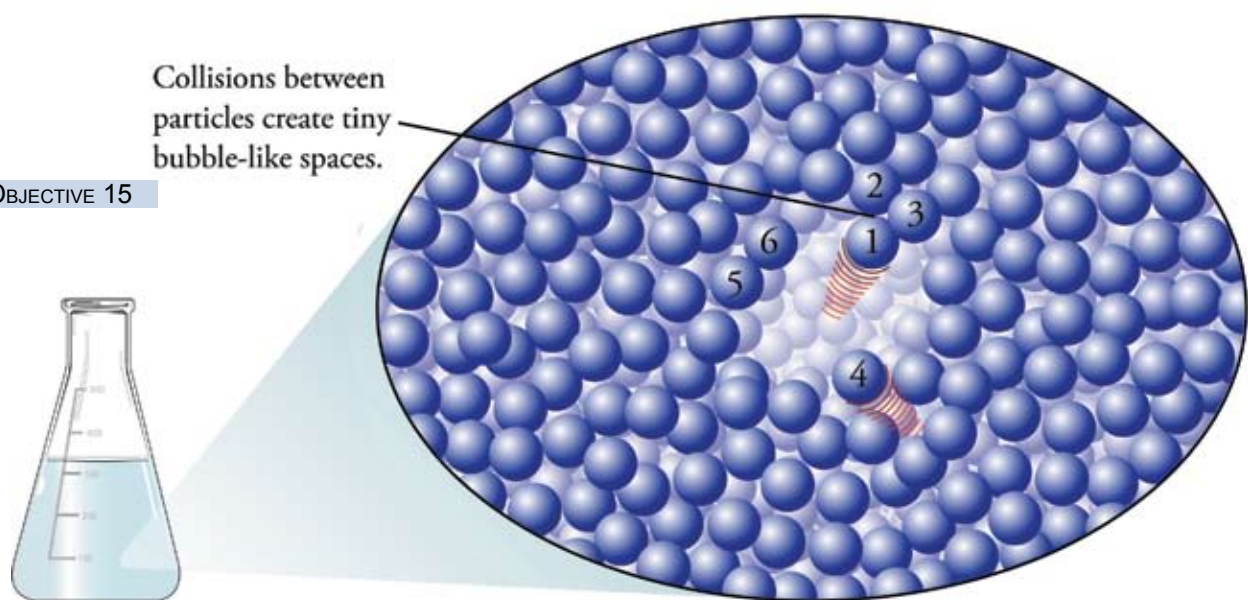


Figure 14.10
Spaces in Liquids

Each of these tiny bubbles is enclosed in a spherical shell of liquid particles. The shell acts as a surface that, except for its shape, is the same as the surface at the top of the liquid. Particles can escape from the surface (evaporate) into a vapor phase inside the bubble, and when particles in that vapor phase collide with the surface of the bubble, they return to the liquid state (condense). A dynamic equilibrium can form in the bubble between the rate of evaporation and the rate of condensation, just like the liquid-vapor equilibrium above the liquid in the closed container (Figure 14.11).

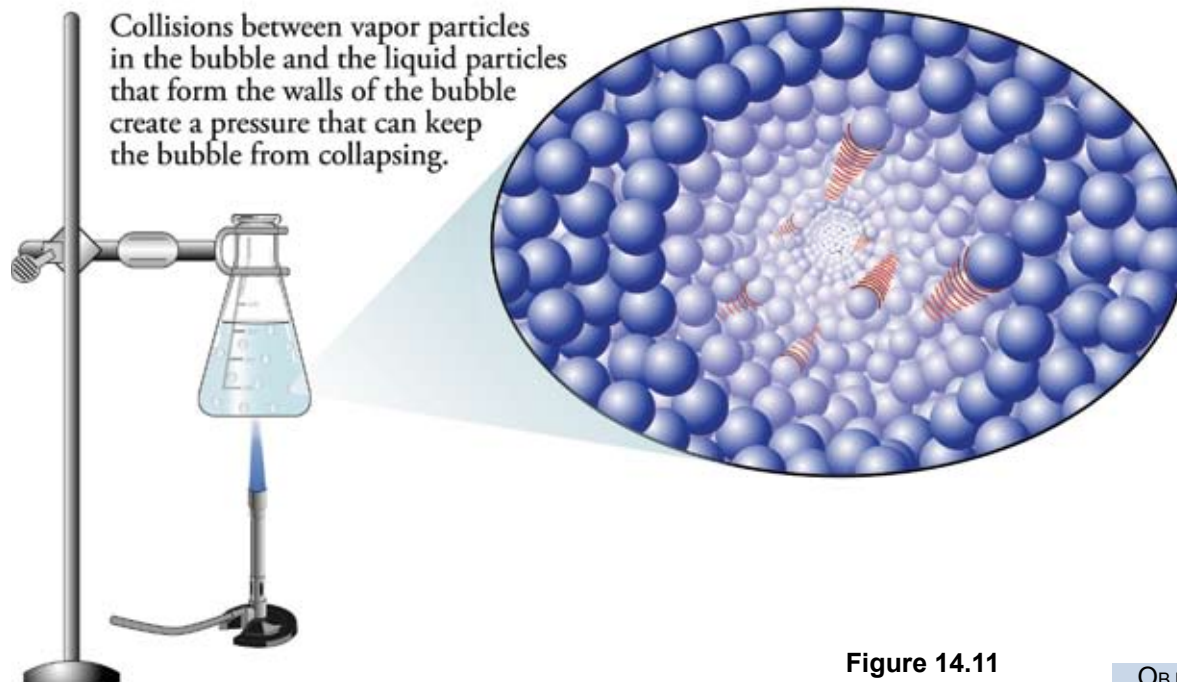


Figure 14.11
Bubble in a Liquid

OBJECTIVE 15

Each time a particle moves across a bubble's interior and collides with the bubble's surface, it exerts a tiny force pushing the wall of the bubble outward. All such collisions with the shell of the bubble combine to produce a gas pressure inside the bubble. This pressure is the same as the equilibrium vapor pressure for the vapor above the liquid in a closed container.

There is an opposing pressure pushing inward on the bubble equal to the sum of the gas pressure on the upper surface of the liquid and the weight of the liquid above the bubble. You can view this external pressure as competing with the equilibrium vapor pressure inside the bubble. If the external pressure pushing in on the bubble is greater than the bubble's vapor pressure, the liquid particles of the bubble surface are pushed closer together, and the bubble collapses. If the vapor pressure of the bubble is greater than the external pressure, the bubble will grow. If the two pressures are equal, the bubble maintains its volume (Figure 14.12).

OBJECTIVE 16

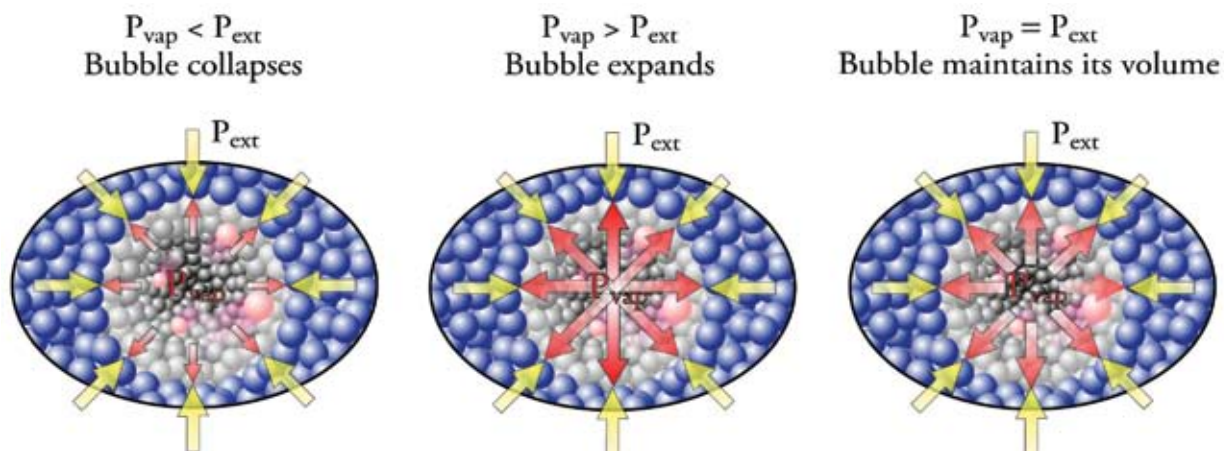


Figure 14.12
Bubble formation

OBJECTIVE 16

Therefore, if the vapor pressure of the bubble is greater than or equal to the external pressure acting on it, the bubble continues to exist. Because the vapor in bubbles is less dense than the liquid, the bubble will rise through the liquid and escape from its upper surface. When this happens, the liquid is boiling. **Boiling** can be defined as the conversion of liquid into vapor anywhere in the liquid rather than just at the top surface. The temperature at which a liquid boils is called the **boiling-point temperature**, or often just *boiling point*.

OBJECTIVE 16

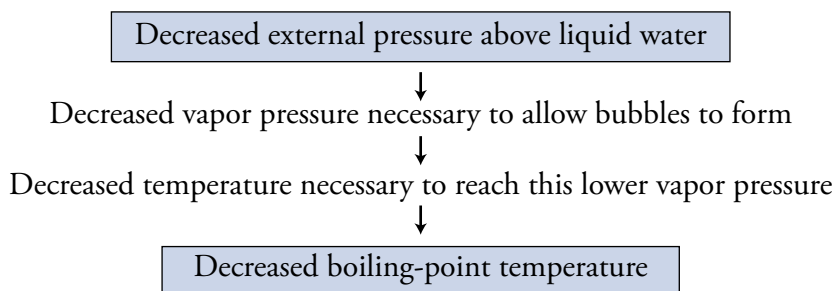
Remember that an increase in temperature increases the equilibrium vapor pressure, which is also the pressure of bubbles as they form in the liquid. Below the boiling-point temperature, the vapor pressure is too low to counteract the greater external pressure, so our tiny bubbles that are always forming will quickly collapse. They do not last long enough to move to the surface, so the liquid does not boil. As the liquid is heated, the vapor pressure of the liquid increases until the temperature gets high enough to make the pressure within the bubble equal to the external pressure. At this temperature, the bubbles can maintain their volume, and the liquid boils. The **boiling-point temperature** can therefore be defined as the temperature at which the equilibrium vapor pressure of the liquid becomes equal to the external pressure acting on the liquid.

Response of Boiling-Point Temperature to External Pressure Changes

OBJECTIVE 17

If the external pressure acting on a liquid changes, then the internal vapor pressure needed to preserve a bubble changes, and therefore the boiling-point temperature changes. For example, if water is placed in a sealed container, and if the pressure above the water is decreased by pumping some of the gas out of the space above the water, the water can be made to boil at room temperature (Figure 14.13). If the external gas pressure is lowered sufficiently, the particles have enough energy even at room temperature to escape into bubbles and maintain sufficient pressure inside them to keep them from collapsing (remember, the external pressure pushing in on them is now lower).

Figure 14.13
Effect of Changing External Pressure on Boiling-Point Temperatures



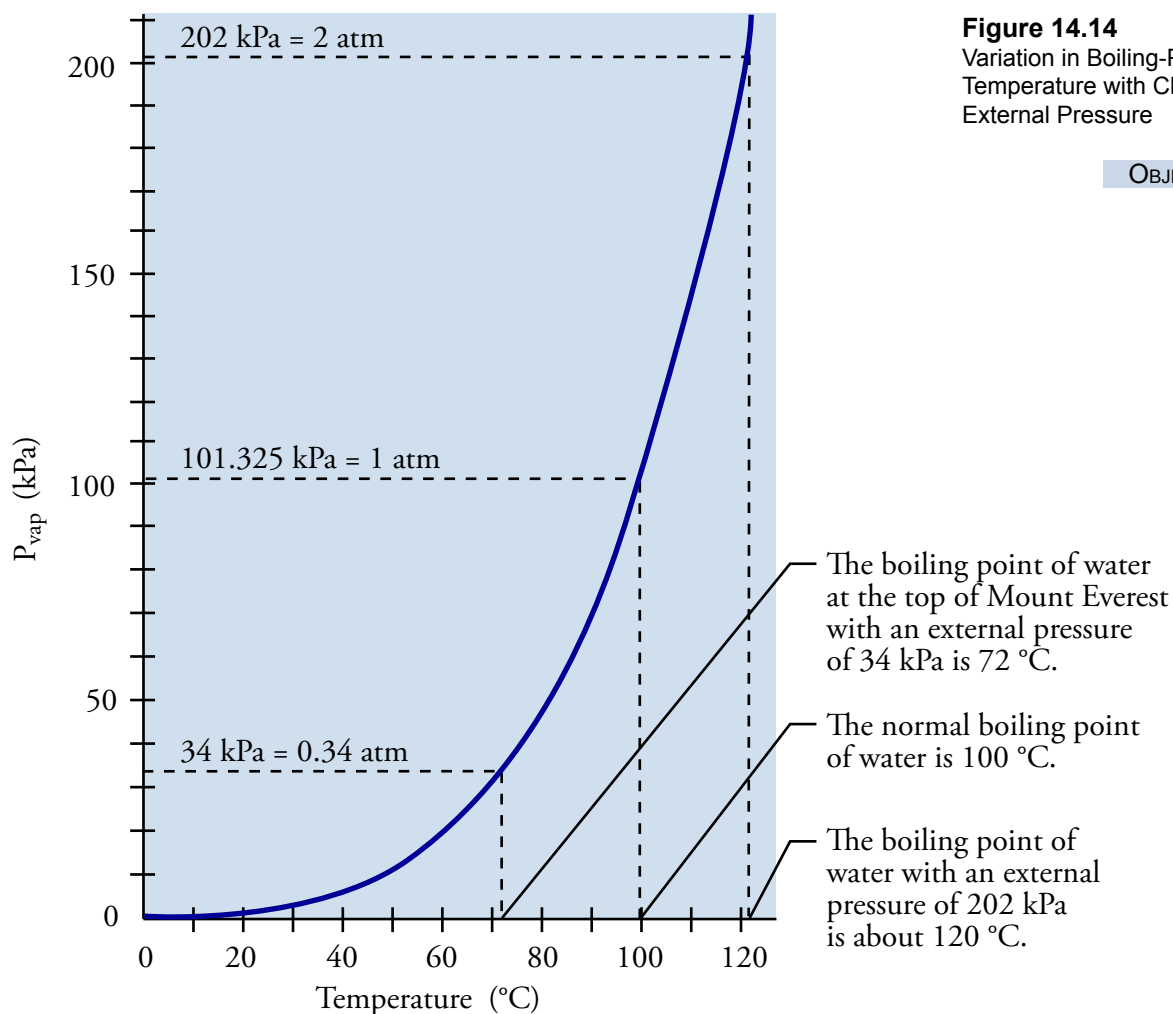
OBJECTIVE 17

OBJECTIVE 18

This helps us to explain why potatoes take longer to cook in boiling water in the mountains than at the seashore, and why they cook much faster in a pressure cooker. When pure water begins to boil at a constant external pressure, its temperature levels off and stays constant at the boiling temperature as long as there is liquid in the container. (The heat being added to keep the liquid boiling works to increase the potential energy of the gas compared to that of the liquid, instead of increasing the kinetic energy of the liquid. If the average kinetic energy of the liquid is constant, the temperature remains constant.)

At 8840 meters above sea level, on the top of Mount Everest, the atmospheric pressure is about 34 kPa (0.34 atm). At this pressure, water boils at about 72 °C, and as we have just learned, the water remains at that temperature until all of it has boiled away. The potatoes will take much longer to cook at this temperature, which is 28 °C lower than the normal boiling temperature. If we could heat the water in a pressure cooker, however, the pressure above the water could increase to higher than the atmospheric pressure, causing the boiling point of the water to increase. For example, water boils at about 120 °C when the pressure above the water is 202 kPa (2 atm). Potatoes cook much faster at this temperature (Figure 14.14).

OBJECTIVE 18



OBJECTIVE 18

Because the external pressure determines the temperature at which a liquid boils, we need to specify the external pressure associated with a reported boiling point. If the pressure is not specified, it is understood to be 1 atmosphere. The temperature at which the equilibrium vapor pressure of a liquid equals 1 atmosphere is called its **normal boiling-point temperature** or just its **normal boiling point**. If a liquid has an external

pressure of 1 atmosphere acting on it, the normal boiling point is the temperature at which the liquid will boil.

For example, if you are told that the boiling point of hexane is $69\text{ }^{\circ}\text{C}$, you can assume that this is the temperature at which the equilibrium vapor pressure of the hexane reaches 1 atm. If the pressure acting on the liquid hexane is 1 atm, it will boil at $69\text{ }^{\circ}\text{C}$. If the pressure acting on the hexane is less than 1 atm, it will boil at a lower temperature. If the pressure acting on the hexane is greater than 1 atm, it will not boil until it is heated to a temperature above $69\text{ }^{\circ}\text{C}$.

Relative Boiling-Point Temperatures and Strengths of Attractions

OBJECTIVE 19

We can predict which of two substances has a higher boiling point by comparing the relative strengths of the attractions between the particles. We know that increased strength of attractions leads to decreased rate of evaporation, decreased rate of condensation at equilibrium, decreased concentration of vapor, and decreased vapor pressure at a given temperature. This leads to an increased temperature necessary to reach a vapor pressure of 1 atmosphere. Thus stronger attractions holding the particles in the liquid lead to higher normal boiling points. For example, because the attractions between water molecules are stronger than the attractions between acetone molecules, the normal boiling point of water ($100\text{ }^{\circ}\text{C}$) is higher than the normal boiling point of acetone ($56.5\text{ }^{\circ}\text{C}$). Figure 14.15 summarizes this reasoning, and Figure 14.16 shows graphs of the change in equilibrium vapor pressure with changes in temperature for acetone and water.

Figure 14.15
Strengths of Attractions and Boiling-Point Temperatures

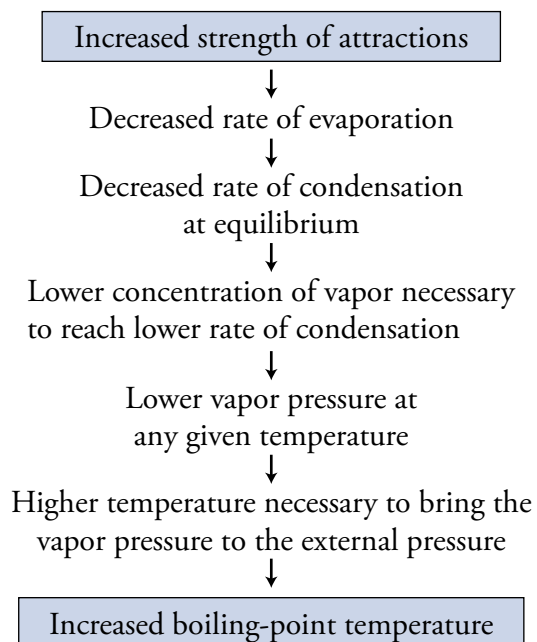
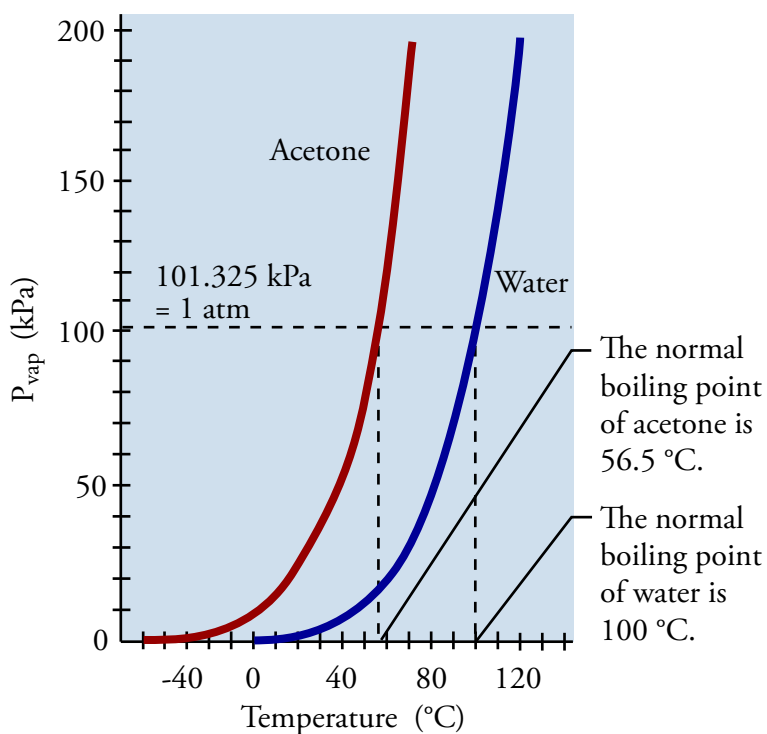


Figure 14.16
Boiling-Point Temperatures for Acetone and Water

OBJECTIVE 19



14.3 Particle-Particle Attractions

When you look at a glass of water or a teaspoon of salt, what do you see? A colorless liquid? A mound of white crystals? A chemist sees much, much more. Chemists may think of water, for example, as a vast crowd of jostling H_2O molecules, constantly breaking away from and attracting one another as they tumble throughout their container. They may see a salt crystal as a system of alternating cations and anions held together by ionic bonds. The purpose of this section is to expand your ability to visualize the particle nature of substances by introducing you to the ways that particles are bound together in the liquid form.

Dipole-Dipole Attractions

We know from Chapter 3 that because hydrogen chloride consists of two nonmetallic elements, it is a molecular compound: it is composed of molecules, which are groups of atoms held together by covalent bonds. Because chlorine atoms attract electrons more strongly than hydrogen atoms do, the covalent bond in each HCl molecule is a polar covalent bond. The chlorine atom has a partial minus charge, and the hydrogen atom has a partial positive charge. A molecule that contains a partial positive charge at one end and a partial negative charge at the other is called a **molecular dipole**, or often just a dipole.

Under normal pressure, HCl gas condenses to a liquid at $-84.9\text{ }^\circ\text{C}$. This is the temperature at which the attractions between the HCl molecules are strong enough to keep the molecules close together. The attraction between one HCl molecule and another is a **dipole-dipole attraction**, which is an attraction between the partial negative end of one molecule and the partial positive end of another molecule (Figure 14.17).

OBJECTIVE 20

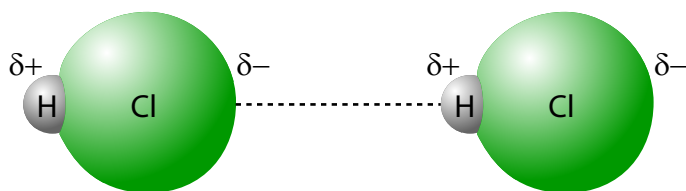


Figure 14.17
Dipole-Dipole Attractions
Between HCl Molecules

OBJECTIVE 20

If you were riding on a molecule in a sample of liquid hydrogen chloride, you would see several other HCl molecules close by, and your particle would be attracted to each of them. You would move constantly from place to place, breaking old dipole-dipole attractions and making new ones (Figure 14.18).

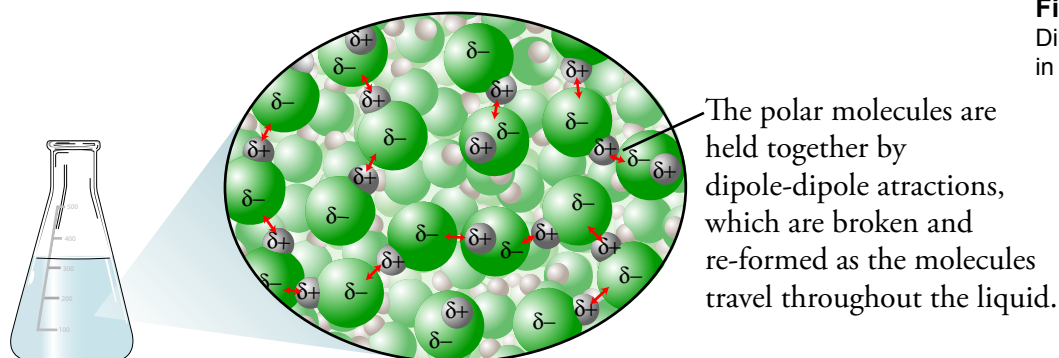


Figure 14.18
Dipole-Dipole Attractions
in a Liquid

OBJECTIVE 21

When a polar molecular substance, such as hydrogen chloride, is heated to convert it from liquid to gas, dipole-dipole attractions are broken. The molecules themselves remain unchanged. For example, when liquid HCl is boiled, the dipole-dipole attractions between HCl molecules are broken, but the covalent bonds between the hydrogen atoms and the chlorine atoms within the HCl molecules are unaffected.

Predicting Bond Type

To predict whether molecules are polar or nonpolar, we need first to predict whether the bonds within them are polar or nonpolar. Remember that atoms form nonpolar covalent bonds, polar covalent bonds, or ionic bonds depending on the relative electron attracting ability of the atoms in the bond (Section 3.2). If the two atoms forming a bond have very different electron-attracting abilities, one or more electrons will be transferred between the atoms, forming ions and an ionic bond. At the other extreme, if there is no significant difference in the electron-attracting ability of the two atoms forming a chemical bond, the bond they form is a nonpolar covalent bond, with no significant transfer of electrons from one atom to another and therefore no significant charges on either of the atoms. Polar covalent bonds lie between these two extremes. The atoms differ just enough in their electron attracting ability to result in a transfer that is significant but not complete. This leads to partial charges on the atoms and a polar covalent bond.

Electronegativity, EN, is a term chemists use to describe the electron-attracting ability of an atom in a chemical bond. Figure 14.19 shows the electronegativities for many of the elements. The higher an element's electronegativity, the greater its ability to attract electrons from other elements. For example, because chlorine has a higher electronegativity (3.16) than hydrogen (2.20), we expect chlorine atoms to attract electrons more strongly than hydrogen atoms do. Comparing electronegativities allows us to predict whether a covalent bond is nonpolar covalent, polar covalent, or ionic.

Figure 14.19

A Table of Average Electronegativities

																	18		
																	8A		
1	2											13	14	15	16	17			
1A	2A											3A	4A	5A	6A	7A			
2	0.98 Li	1.57 Be											2.20 H	2.04 B	2.55 C	3.04 N	3.44 O	3.98 F	
3	0.93 Na	1.31 Mg	3	4	5	6	7	8	9	10	11	12	1.61 Al	1.90 Si	2.19 P	2.58 S	3.16 Cl		
4	0.82 K	1.00 Ca	1.36 Sc	1.54 Ti	1.63 V	1.66 Cr	1.55 Mn	1.83 Fe	1.88 Co	1.91 Ni	1.90 Cu	1.65 Zn	1.81 Ga	2.01 Ge	2.18 As	2.55 Se	2.96 Br	3.00 Kr	
5	0.82 Rb	0.95 Sr	1.22 Y	1.33 Zr	1.6 Nb	2.16 Mo	1.9 Tc	2.2 Ru	2.28 Rh	2.20 Pd	1.93 Ag	1.69 Cd	1.78 In	1.96 Sn	2.05 Sb	2.1 Te	2.66 I	2.6 Xe	
6	0.79 Cs	0.89 Ba	1.27 Lu	1.3 Hf	1.5 Ta	2.36 W	1.9 Re	2.2 Os	2.20 Ir	2.28 Pt	2.54 Au	2.00 Hg	1.62 Tl	2.33 Pb	2.02 Bi	2.0 Po	2.2 At		
7	0.7 Fr	0.9 Ra																	

OBJECTIVE 22A

If the difference in electronegativity (ΔEN) between the atoms in the bond is less than 0.4, we expect them to share electrons more or less equally, forming a nonpolar covalent bond. For example, hydrogen has an electronegativity of 2.20, and carbon has an electronegativity of 2.55. The difference in electronegativity (ΔEN) is 0.35, which is

less than 0.4. We expect the bond between carbon and hydrogen to be a nonpolar covalent bond.

If the difference in electronegativity (ΔEN) between two atoms is between 0.4 and 1.7, we expect the bond between them to be a polar covalent bond. For example, hydrogen has an electronegativity of 2.20, and chlorine has an electronegativity of 3.16. The difference in electronegativity (ΔEN) is 0.96, so the bond is a polar covalent bond, which is sometimes called a **bond dipole**.

OBJECTIVE 22A

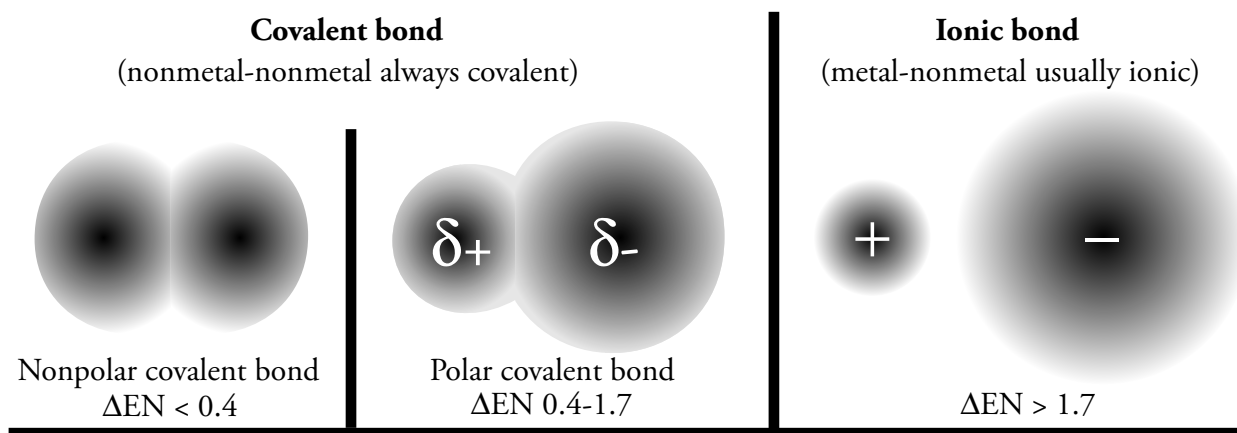
If the difference in electronegativity (ΔEN) between two atoms is greater than 1.7, we expect the bond between them to be ionic. For example, sodium has an electronegativity of 0.93, and chlorine has an electronegativity of 3.16. The difference in electronegativity (ΔEN) is 2.23, so we predict their bond to be ionic.

OBJECTIVE 22A

There are exceptions to these guidelines. For example, the electronegativity difference is 1.78 in the H–F bond and 1.79 in the P–F bond. Our electronegativity guidelines lead us to predict that these would be ionic bonds, but experiments show them to be covalent bonds. Exceptions such as these will not confuse you if you remember that the bond between two nonmetallic atoms is always a covalent bond. (Figure 14.20).

OBJECTIVE 22A

Figure 14.20
Identification of Bond Type



Electronegativities also give us a simple way of predicting which atom in a polar covalent bond has the partial negative charge and which has the partial positive charge. *In a polar covalent bond, the atom with the higher electronegativity has the partial negative charge, and the atom with the lower electronegativity has the partial positive charge.* For example, the electronegativity of chlorine (3.16) is higher than for hydrogen (2.20). In an H–Cl bond, we predict that the chlorine atom attracts electrons more strongly than the hydrogen atom and gets a partial negative charge. Due to its lower electronegativity, the hydrogen atom has a partial positive charge.

OBJECTIVE 22B

Similar logic allows us to predict which atom in an ionic bond forms the positive cation and which forms the negative anion. *In an ionic bond between monatomic ions, the nonmetallic element has the higher electronegativity and forms the anion, and the metallic element has the lower electronegativity and forms the cation.*

OBJECTIVE 22C

OBJECTIVE 22D

We can use another simple guideline to predict which of two bonds is more polar. *The bond with the greater difference in electronegativity (ΔEN) is likely to be the more polar bond.*

For example, ΔEN for the H–Cl bond is 0.96. The ΔEN for the H–F bond is 1.78. Because there is a greater difference between the electron-attracting abilities of hydrogen atoms and fluorine atoms than between hydrogen atoms and chlorine atoms, we expect larger partial charges in the H–F bond. That is, we expect the H–F bond to be more polar than the H–Cl bond.

The following sample study sheet summarizes the guidelines for using electronegativity to make predictions about bonds.

Sample Study Sheet 14.1

Electronegativity, Types of Chemical Bonds, and Bond Polarity

OBJECTIVE 22

TIP-OFF – You wish to (1) classify a chemical bond as nonpolar covalent, polar covalent, or ionic, (2) identify which element in a polar covalent bond is partially negative and which is partially positive, (3) identify which element in an ionic bond forms the anion and which forms the cation, or (4) identify which of two bonds is more polar.

GENERAL STEPS

- Use the following guidelines to identify a chemical bond as ionic, nonpolar covalent, or polar covalent.

$\Delta EN < 0.4 \rightarrow$ nonpolar covalent

$\Delta EN 0.4\text{--}1.7 \rightarrow$ polar covalent

$\Delta EN > 1.7 \rightarrow$ ionic

- Use the following guidelines to identify which element in a polar covalent bond is partially negative and which is partially positive.

Higher electronegativity \rightarrow partial negative charge

Lower electronegativity \rightarrow partial positive charge

- Use the following guidelines to identify which element in an ionic bond between monatomic ions forms the anion and which forms the cation.

Nonmetal, which has a higher electronegativity \rightarrow anion

Metal, which has the lower electronegativity \rightarrow cation

- Use the following guideline to decide which of two bonds is likely to be more polar.

The greater the ΔEN , the more polar the bond.

EXAMPLE See Examples 14.1 and 14.2.

EXAMPLE 14.1 - Using Electronegativities

OBJECTIVE 22

Classify the following bonds as nonpolar covalent, polar covalent, or ionic. If a bond is polar covalent, identify which atom has the partial negative charge and which has the partial positive charge. If the bond is ionic, identify which element is negative and which is positive.

- O bonded to H
- C bonded to S
- Li bonded to Cl
- H bonded to F

Solution

- Both O and H represent nonmetallic elements, so the bond is covalent. Because oxygen's electronegativity is 3.44 and hydrogen's is 2.20, the difference in electronegativity (ΔEN) is 1.24, so this is a **polar covalent bond**. The higher electronegativity of the oxygen tells us that oxygen atoms attract electrons more strongly than hydrogen atoms. Therefore, the oxygen atom in the O–H bond is δ^- , and the hydrogen atom in the O–H bond is δ^+ .
- Both C and S represent nonmetallic elements, so the bond is covalent. The electronegativity of carbon is 2.55, and the electronegativity of sulfur is 2.58. The ΔEN is only 0.03, so the bond is a **nonpolar covalent bond**.
- Lithium is a metal, and chlorine is a nonmetal. Bonds between metallic atoms and nonmetallic atoms are expected to be ionic. Because lithium's electronegativity is 0.98 and chlorine's is 3.16, the ΔEN is 2.18, so again we would predict the bond to be best described as an **ionic bond**. The nonmetallic chlorine has the negative charge, and the metallic lithium has the positive charge.
- On the basis of the hydrogen's electronegativity being 2.20 and fluorine's being 3.98, for a ΔEN of 1.78, we might expect these elements to form an ionic bond. However, because both of these elements are nonmetallic, the bond is instead a very **polar covalent bond**. The higher electronegativity of the fluorine tells us that fluorine atoms attract electrons more strongly than hydrogen atoms. The fluorine atom in the H–F bond is δ^- , and the hydrogen atom in the H–F bond is δ^+ .

EXAMPLE 14.2 - Using Electronegativities

OBJECTIVE 22

Which bond would you expect to be more polar, H–S or H–Cl?

Solution

The ΔEN for the H–S bond is 0.38, and the ΔEN for the H–Cl bond is 0.96. We expect the bond with the greater difference, the H–Cl bond, to be more polar. The Cl in the H–Cl bond would have a larger δ^- charge than the S in the H–S bond.

EXERCISE 14.1 - Using Electronegativities

OBJECTIVE 22

Classify the following bonds as nonpolar covalent, polar covalent, or ionic. If a bond is polar covalent, identify which atom has the partial negative charge and which has the partial positive charge. If a bond is ionic, identify which atom is negative and which is positive.

- N bonded to H
- N bonded to Cl
- Ca bonded to O
- P bonded to F

EXERCISE 14.2 - Comparing Bond Polarities

OBJECTIVE 22

Which bond would you expect to be more polar, P–H or P–F? Why?

Predicting Molecular Polarity

Now that we can predict whether covalent bonds are polar or nonpolar, we can continue our discussion of polar molecules. Three questions will help you predict whether substances are composed of polar or nonpolar molecules. First,

Is the substance molecular?

If a substance is composed of all nonmetallic elements and does not contain the ammonium ion, you can assume that the answer to the first question is yes.

For reasons that we explore below, molecules are polar if they have an asymmetrical arrangement of polar covalent bonds, so another question is

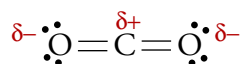
If the substance is molecular, do the molecules contain polar covalent bonds?

When there are no polar bonds in a molecule, there is no permanent charge difference between one part of the molecule and another, and the molecule is nonpolar. For example, the Cl₂ molecule has no polar bonds because the two atoms in each Cl–Cl bond attract electrons equally. It is therefore a nonpolar molecule. None of the bonds in hydrocarbon molecules, such as hexane, C₆H₁₄, are significantly polar, so hydrocarbons are nonpolar molecular substances. Lastly,

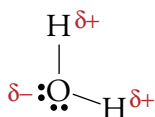
If the molecules contain polar covalent bonds, are these bonds asymmetrically arranged?

OBJECTIVE 23

A molecule can possess polar bonds and still be nonpolar. If the polar bonds are evenly (or symmetrically) distributed, the bond dipoles cancel and do not create a molecular dipole. For example, the two bonds in a molecule of CO₂ are significantly polar, but they are symmetrically arranged around the central carbon atom. No one side of the molecule has more negative or positive charge than another side, and so the molecule is nonpolar:



A water molecule is polar because (1) its O–H bonds are significantly polar, and (2) its bent geometry makes the distribution of those polar bonds asymmetrical. The side of the water molecule containing the more electronegative oxygen atom is partially negative, and the side of the molecule containing the less electronegative hydrogen atoms is partially positive.



You can see a more complete description of the procedure used to predict whether molecules are polar or nonpolar at the web address below. For now, it will be useful to remember that the following substances have polar molecules: water, H_2O ; ammonia, NH_3 ; oxyacids (such as nitric acid, HNO_3); hydrogen halides (HCl , HF , HBr , and HI); methanol, CH_3OH ; and ethanol, $\text{C}_2\text{H}_5\text{OH}$. You will also be expected to recognize the following as composed of nonpolar molecules: the elements composed of molecules (H_2 , N_2 , O_2 , F_2 , Cl_2 , Br_2 , I_2 , P_4 , S_8 , and Se_8); carbon dioxide, CO_2 ; and hydrocarbons (such as pentane, C_5H_{12} , and hexane, C_6H_{14}).

A description of a procedure for determining whether molecules are polar can be found at the textbook's Web site.

Hydrogen Bonds

Now, let's return to our discussion of attractions between molecules (**intermolecular attractions**). Hydrogen fluoride, HF , is used to make uranium hexafluoride, UF_6 , a chemical that plays an important role in the production of nuclear reactor fuel. Chemists have learned that gaseous hydrogen fluoride condenses to a liquid at 19.54°C , a much higher temperature than the one at which hydrogen chloride condenses to a liquid (-84.9°C). This difference suggests that the attractions between HF molecules are much stronger than the attractions between HCl molecules. (It is common to consider room temperature to be 20°C , or 68°F , so HF is a liquid at just slightly below room temperature.)

One reason the attractions are so much stronger between HF molecules than between HCl molecules is that the HF molecules have much higher partial positive and negative charges on the atoms. The difference in electronegativity between hydrogen and chlorine is 0.96, while the difference in electronegativity between hydrogen and fluorine is 1.78. As a result, the $\text{H}-\text{F}$ bond is far more polar, with a very large partial positive charge on each hydrogen atom and a very large partial negative charge on each fluorine atom. These relatively large charges on HF molecules lead to such strong intermolecular attractions that chemists place them in a special category and call them hydrogen bonds. **Hydrogen bonds** are attractions that occur between a nitrogen, oxygen, or fluorine atom of one molecule and a hydrogen atom bonded to a nitrogen,

OBJECTIVE 23

OBJECTIVE 24

OBJECTIVE 25

OBJECTIVE 26

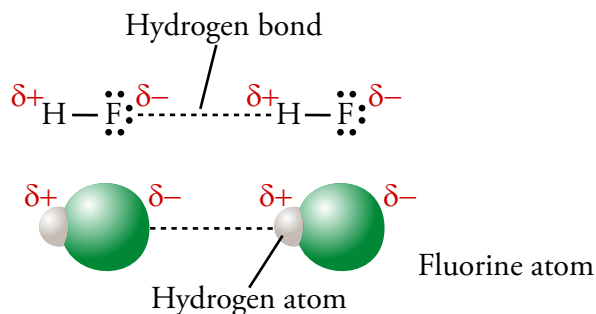
oxygen, or fluorine atom in another molecule. Hydrogen fluoride is the only fluorine containing compound that is capable of hydrogen bonding (Figure 14.21).

Figure 14.21

Two Ways to Illustrate Hydrogen Bonding in HF

In HF, the hydrogen bond is the attraction between the partial negative charge of a fluorine atom in one HF molecule and the partial positive charge of a hydrogen atom attached to a fluorine atom in another HF molecule.

OBJECTIVE 26



Hydrogen bonds are very important in the chemistry of life. The strands of DNA that carry our genetic information are held together by hydrogen bonds, and hydrogen bonds help to give the enzymes that regulate our body chemistry their characteristic shapes. Hydrogen bonding also explains the physical characteristics of water.

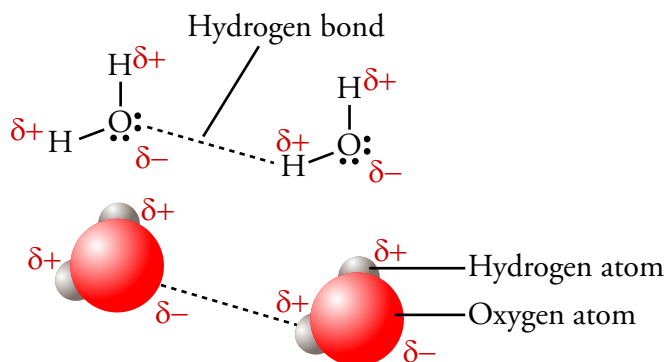
Life on Earth, if it existed at all, would be far different if water were a gas at normal temperatures, like other similar substances. For example, hydrogen sulfide, H_2S (the substance that gives rotten eggs their distinctive smell) has a structure that is very similar to water, but it is a gas above -60.7°C . The fact that water is a liquid suggests that the attractions between H_2O molecules are stronger than the attractions in H_2S . Hydrogen sulfide molecules have relatively weak dipole-dipole attractions between them, but H_2O molecules have strong hydrogen bonds between them owing to the attraction between the partial negative charge on an oxygen atom of one water molecule and the partial positive charge on a hydrogen atom of another molecule (Figure 14.22).

Figure 14.22

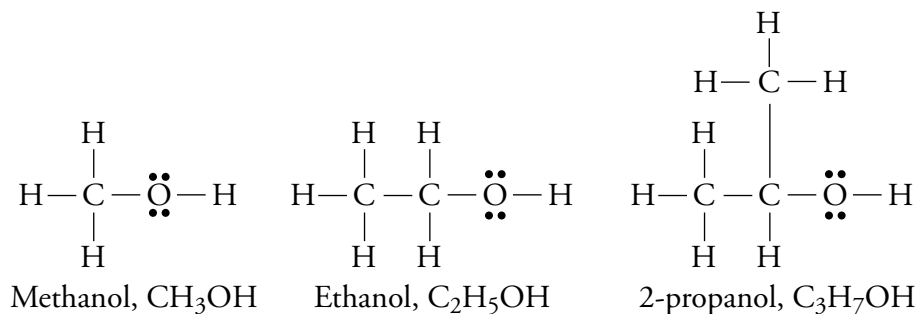
Hydrogen Bonding Between Water Molecules

In water, the hydrogen bond is the attraction between the partial negative charge of an oxygen atom in one molecule and the partial positive charge of a hydrogen atom attached to an oxygen atom in another molecule.

OBJECTIVE 26



As you discovered in Chapter 3, the three most common alcohols are methanol, CH_3OH , ethanol, $\text{C}_2\text{H}_5\text{OH}$, and 2-propanol, $\text{C}_3\text{H}_7\text{OH}$.



Like water, alcohol molecules contain the O–H bond and therefore experience hydrogen bonding of their molecules in the liquid and solid form (Figure 14.23).

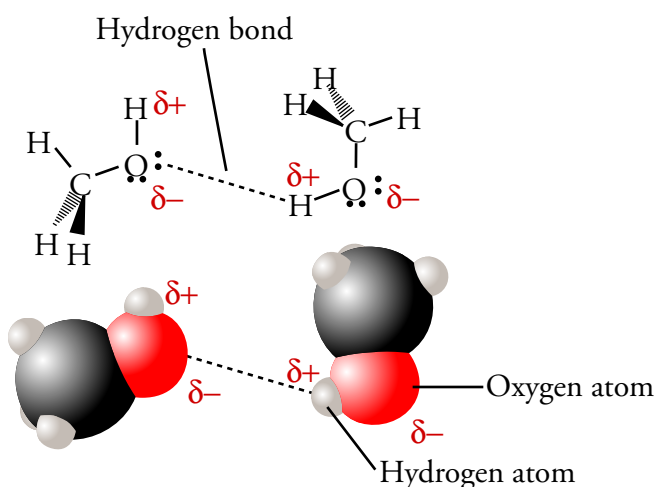


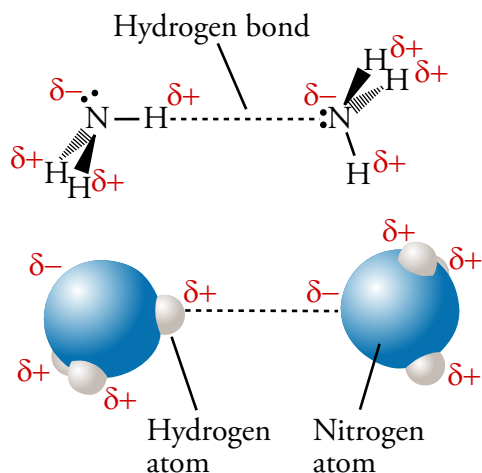
Figure 14.23

Hydrogen Bonding in Methanol

In methanol, the hydrogen bond is the attraction between the partial negative charge of an oxygen atom in one molecule and the partial positive charge of a hydrogen atom attached to an oxygen atom in another molecule.

OBJECTIVE 26

Ammonia, NH_3 , a gas at room temperature, is used to make fertilizers, explosives, rocket fuel, and other nitrogen containing products. Dissolved in water, it is used as a household cleaner. When NH_3 gas is cooled below -33.35°C , the molecules slow down to the point where the hydrogen bonds they form during collisions keep them together long enough to form a liquid (Figure 14.24).



OBJECTIVE 26

Figure 14.24

Hydrogen Bonding in Ammonia

In ammonia, the hydrogen bond is the attraction between the partial positive charge of a hydrogen atom attached to a nitrogen atom in one molecule and the partial negative charge of a nitrogen atom.

London Forces



OBJECTIVE 27

Are you old enough to remember tincture of iodine? Before the introduction of antibacterial ointments and sprays for the treatment of minor cuts and burns, tincture of iodine, a mixture of iodine and alcohol, was a common disinfectant for the skin. The pure iodine used to make this solution consists of diatomic molecules, I_2 , whose mutual attractions are strong enough to form a solid at room temperature. Because the only bond within the I_2 molecule is the nonpolar I–I bond, we do not expect normal dipole-dipole attractions between iodine molecules. Why, then, do they attract each other strongly?

Although we expect the I–I bond to be nonpolar, with a symmetrical distribution of the electrons, this arrangement is far from static. Even though the most probable distribution of charge in an isolated I_2 molecule is balanced, a sample of iodine that contains many billions of molecules will always include, by chance, some molecules whose electron clouds are shifted more toward one iodine atom than toward the other. The resulting dipoles are often called *instantaneous dipoles* because they may be short-lived (Figure 14.25). The constant collisions between molecules contribute to the formation of instantaneous dipoles. When I_2 molecules collide, the repulsion between their electron clouds will distort the clouds and shift them from their nonpolar state.

An instantaneous dipole can create a dipole in the molecule next to it. For example, the negative end of one instantaneous dipole will repel the negative electron cloud of a nonpolar molecule next to it, pushing the cloud toward the far side of the neighboring molecule. The new dipole is called an *induced dipole*. The induced dipole can then induce a dipole in another neighboring molecule. This continues until there are many polar molecules in the system. The resulting partial charges on instantaneous and induced dipoles lead to attractions between the opposite charges on the molecules (Figure 14.25). These attractions are called **London dispersion forces**, **London forces**, or **dispersion forces**.

OBJECTIVE 28

The larger the molecules of a substance, the stronger the London forces between them. A larger molecule has more electrons and a greater chance of having its electron

cloud distorted from its nonpolar shape. Thus instantaneous dipoles are more likely to form in larger molecules. The electron clouds in larger molecules are also larger, so the average distance between the nuclei and the electrons is greater; as a result, the electrons are held less tightly and shift more easily to create a dipole.

The increased strength of London forces with increased size of molecules explains a trend in the properties of halogens. Fluorine, F_2 , and chlorine, Cl_2 , which consist of relatively small molecules, are gases at room temperature and pressure. Bromine, Br_2 , with larger molecules and therefore stronger London forces between them, is a liquid. Iodine, I_2 , with still larger molecules, is a solid.

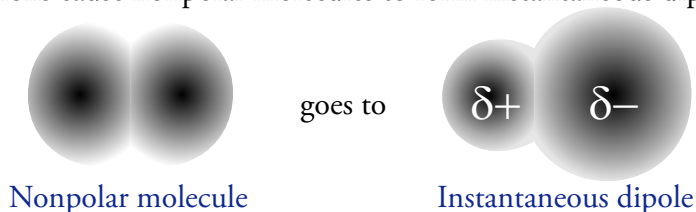
The effect of molecular size on the strengths of London forces can also be used to explain the different states observed among the byproducts of crude oil. Crude oil is a mixture of hydrocarbon molecules that can be separated into natural gas, gasoline, kerosene, lubricating oils, and asphalt by heating it and isolating

Increasing size of molecules leads to increasing strengths of London forces.

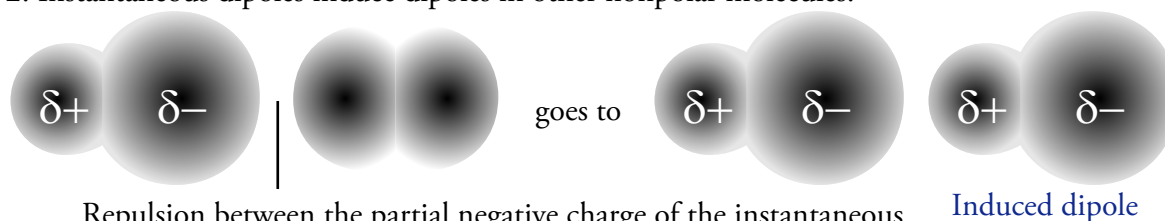
Gas	9 F 18.9984
Gas	17 Cl 35.4527
Liquid	35 Br 79.904
Solid	53 I 126.9045

OBJECTIVE 29

1. Chance or collisions cause nonpolar molecules to form instantaneous dipoles.

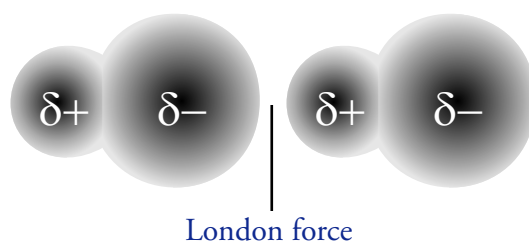


2. Instantaneous dipoles induce dipoles in other nonpolar molecules.



Repulsion between the partial negative charge of the instantaneous dipole and the negative charge of the electrons in the nonpolar molecule pushes the electrons in the nonpolar molecule to the right, forming an induced dipole.

3. Induced dipoles can induce dipoles in other nonpolar molecules, resulting in many molecules with partial charges. London forces are the attractions between the partial positive and partial negative charges in these instantaneous and induced dipoles.



OBJECTIVE 27

Figure 14.25
London Dispersion Forces

different substances as they evaporate from the mixture. The smallest hydrocarbons, with up to four carbon atoms, have the weakest London forces between molecules, so they evaporate from the crude oil mixture first and can be piped to our homes as natural gas. Hydrocarbons with 5 to 25 carbons have strong enough London forces to remain liquids at room temperature and pressure. After removal of the natural gas molecules, further heating of the remaining mixture drives off molecules with 6 to 12 carbon atoms, which can be used as gasoline. Kerosene, a mixture of hydrocarbon molecules with 11 to 16 carbon atoms, evaporates next. Lubricating oils, which contain hydrocarbon molecules with 15 to 25 carbon atoms, are then driven off at an even higher temperature. Hydrocarbons with more than 25 carbons remain solid throughout this process. When the liquid components of crude oil have been separated, the solid asphalt that is left behind can be used to build roads.



Hydrocarbons have many uses. Natural gas is used to heat our homes, cars require liquid gasoline and lubricating oils, and solid asphalt is used to make roads and driveways.

We know that polar molecules are attracted to each other by dipole-dipole attractions or hydrogen bonds. Experiments have shown, though, that the actual strengths of the attractions between polar molecules are greater than we would predict from the polarity of the isolated molecules. A description of why this is true can be found at the textbook's Web site.

Particle Interaction in Pure Elements

As we have noted, the I_2 molecules in solid iodine are held together by London forces, but what about the solid forms of other elements? Let's review what we discovered in Section 2.5 about the particles that form the structures of the pure elements and find out more about the attractions that hold them together.

OBJECTIVE 30

Most of the elements are metallic and their pure solids are held together by metallic bonds. According to the sea of electrons model described in Section 2.5, the fundamental structure of a solid metal consists of cations that have lost one or more electrons. The lost electrons are free to move throughout the solid, so our image of the particles in a solid metal is one of island-like cations in a sea of electrons. **Metallic bonds** can be described as the attractions between the positive metal cations and negative electrons that surround them.

OBJECTIVE 30

The nonmetallic elements exhibit more variety in the types of particles their solids are made of and the types of attractions between them. The particles making up the solid structure of diamond are carbon atoms, and the attractions that hold them in the solid form are covalent bonds (Section 2.5). The noble gases are composed of separate atoms. When a noble gas is cooled enough to form a liquid, London forces hold the particles together.

OBJECTIVE 30

Pure samples of all the other nonmetallic elements consist of molecules. Hydrogen, nitrogen, oxygen, and all of the halogens (group 17) are composed of diatomic molecules: H_2 , N_2 , O_2 , F_2 , Cl_2 , Br_2 , and I_2 . Sulfur and selenium can take different forms, but the most common form for each is a molecule with eight atoms, S_8 and Se_8 . Phosphorus also has different forms, but the most important forms consist of P_4 molecules. All of the molecules of these elements are nonpolar, and the attractions holding their solids together are London forces.

Summary of the Types of Particles and the Attractions Between Them

Table 14.1 summarizes the kinds of particles that make up different substances and the attractions between them. Figure 14.26 shows a scheme for predicting the types of attractions between particles.

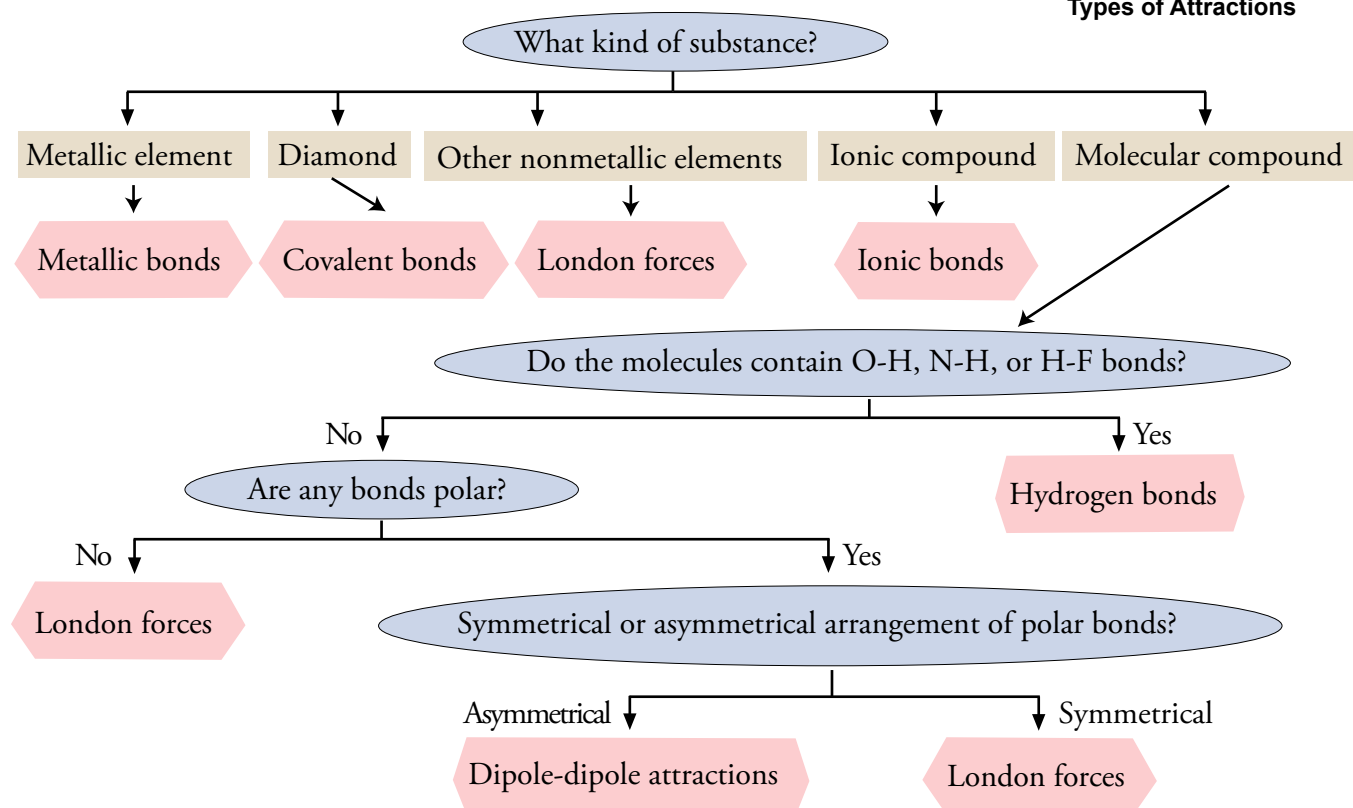
Table 14.1

The Particles in Different Types of Substances and the Attractions that Hold Them in the Solid and Liquid Form

OBJECTIVE 30

Type of substance	Particles	Examples	Attraction
Elements			
Metal	Cations in a sea of electrons	Au	Metallic bond
Noble gases	Atoms	Xe	London forces
Carbon (diamond)	Carbon atoms	C(dia)	Covalent bonds
Other nonmetal elements	Molecules	H ₂ , N ₂ , O ₂ , F ₂ , Cl ₂ , Br ₂ , I ₂ , S ₈ , Se ₈ , P ₄	London forces
Ionic compounds	Cations and anions	NaCl	Ionic bond
Molecular compounds			
Nonpolar molecular	Molecules	CO ₂ and hydrocarbons	London forces
Polar molecules without H-F, O-H, or N-H bond	Molecules	HF, HCl, HBr, and HI	Dipole-dipole forces
Molecules with H-F, O-H or N-H bond	Molecules	HF, H ₂ O, alcohols, NH ₃	Hydrogen bonds

OBJECTIVE 30

Figure 14.26
Scheme for Predicting
Types of Attractions

EXAMPLE 14.3 - Types of Particles and Types of Attractions**OBJECTIVE 30**

For (a) C_8H_{18} , (b) aluminum, (c) Br_2 , (d) $LiBr$, (e) ethanol, and (f) CH_3NH_2 , specify (1) the type of particle that forms the substance's fundamental structure and (2) the name of the type of attraction holding these particles in the solid and liquid form.

Solution

- The compound C_8H_{18} is a hydrocarbon, so it is composed of C_8H_{18} **molecules** held together by **London forces**.
- Aluminum is a metallic element, so it is composed of **Al cations in a sea of electrons**. The particles are held together by **metallic bonds**.
- The formula Br_2 describes bromine, a nonmetallic element. Except for carbon and the noble gases, the nonmetallic elements are composed of **molecules** held together by **London forces**.
- Because $LiBr$ consists of a metal and a nonmetal, we assume it is an ionic compound with **cations and anions** held together by **ionic bonds**.
- The formula for ethanol is C_2H_5OH . Ethanol, like all alcohols, has a structure formed by **molecules** held together by **hydrogen bonds**.
- Because all of the symbols in the formula CH_3NH_2 represent nonmetallic elements, we assume that CH_3NH_2 has all covalent bonds and therefore is a molecular substance composed of CH_3NH_2 **molecules**. The $-NH_2$ in the formula suggests that the molecules have an N-H bond, which leads to **hydrogen bonding** between molecules.

EXERCISE 14.3 - Types of Particles and Types of Attractions**OBJECTIVE 30**

For (a) iron, (b) iodine, (c) CH_3OH , (d) NH_3 , (e) hydrogen chloride, (f) KF , and (g) carbon in the diamond form, specify (1) the type of particle that forms the substance's fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

If you can predict the types of attractions between particles in two different substances, you can also predict the relative strengths of those attractions, and then the relative boiling-point temperatures for the substances. The textbook's Web site shows a general procedure for making these predictions.

Condensation The change from vapor to liquid.

Evaporation The change from liquid to vapor.

Vapor A gas derived from a substance that is liquid at normal temperatures and pressures. It is also often used to describe gas that has recently come from a liquid.

Rate of evaporation The number of particles moving from liquid to gas per second.

Rate of condensation The number of particles moving from gas to liquid per second.

Dynamic equilibrium A system that has two equal and opposing rates of change, from state A to state B and from state B to state A. There are constant changes between state A and state B but no net change in the amount of components in either state.

Equilibrium vapor pressure, P_{vap} The partial pressure of vapor above a liquid in a closed system with a dynamic equilibrium between the rate of evaporation and the rate of condensation.

Boiling The conversion of liquid to vapor anywhere in the liquid rather than just at the top surface.

Boiling-point temperature The temperature at which a liquid boils. It is also the temperature at which the equilibrium vapor pressure of the liquid becomes equal to the external pressure acting on the liquid.

Normal boiling point The temperature at which the equilibrium vapor pressure of the liquid equals one atmosphere.

Molecular dipole (or often just **dipole**) A molecule that contains an asymmetrical distribution of positive and negative charges.

Dipole-dipole attraction The intermolecular attraction between the partial negative end of one polar molecule and the partial positive end of another polar molecule.

Electronegativity A measure of the electron attracting ability of an atom in a chemical bond.

Bond dipole A polar covalent bond, which has an atom with a partial positive charge and an atom with a partial negative charge.

Intermolecular attraction Attraction between molecules.

Hydrogen bond The intermolecular attraction between a nitrogen, oxygen, or fluorine atom of one molecule and a hydrogen atom bonded to a nitrogen, oxygen, or fluorine atom in another molecule.

London dispersion forces, London forces, or dispersion forces The attractions produced between molecules by instantaneous and induced dipoles.

Metallic bond The attraction between the positive metal cations that form the fundamental structure of a solid metal and the negative charge from the mobile sea of electrons that surround the cations.

Chapter Objectives

The goal of this chapter is to teach you to do the following.

1. Define all of the terms in the Chapter Glossary.

Section 14.1 Change from Gas to Liquid and from Liquid to Gas—An Introduction to Dynamic Equilibrium

2. Describe the submicroscopic changes occurring when gas is converted from high temperature gas to lower temperature gas to liquid.
3. Describe the process of evaporation from the surface of a liquid.
4. List three criteria that a particle must meet to escape from the surface of a liquid and move into the gas phase.
5. Explain why liquids cool as they evaporate.
6. List the three factors that affect the rate of evaporation of a liquid.
7. Explain why increased surface area of a liquid leads to a higher rate of evaporation.
8. Explain why weaker strength of attractions between particles in a liquid leads to a higher rate of evaporation.
9. Explain why increasing a liquid's temperature causes an increase in the rate of evaporation.
10. Describe the process by which a dynamic equilibrium is established between the rates of evaporation and condensation for a liquid in a closed container.
11. Write a general description of dynamic equilibrium.
12. Explain why the vapor pressure is constant above a liquid in a system that has a dynamic equilibrium between the rate of evaporation and the rate of condensation.
13. Explain why weaker attractions between particles in a liquid lead to higher equilibrium vapor pressures.
14. Explain why increasing a liquid's temperature leads to an increase in equilibrium vapor pressure.

Section 14.2 Boiling Liquids

15. Describe how a bubble can form in a liquid.
16. Explain why boiling does not take place in a liquid until the liquid reaches its boiling-point temperature.
17. Explain why a change in the external pressure acting on a liquid will change its boiling-point temperature.
18. Explain why potatoes take longer to cook in boiling water on the top of Mount Everest than at sea level and why they cook faster in water boiled in a pressure cooker.
19. Explain why liquids whose particles experience stronger mutual attractions will have higher boiling points than liquids whose particles experience weaker mutual attractions.

Section 14.3 Particle-Particle Attractions

20. Describe dipole-dipole attractions between polar molecules.
21. Draw a sketch of polar molecules, such as HCl molecules, in the liquid form showing the dipole-dipole attractions that hold the particles together.

22. Given a table of electronegativities, do the following:
 - a. Classify chemical bonds as nonpolar covalent, polar covalent, or ionic.
 - b. Identify which of two atoms in a polar covalent bond has a partial negative charge, and which atom has a partial positive charge.
 - c. Identify which of two atoms in an ionic bond has a negative charge, and which atom has a positive charge.
 - d. Given two bonds, determine which of the bonds would be expected to be more polar.
23. Explain why hydrocarbon molecules are nonpolar, why carbon dioxide, CO_2 , molecules are nonpolar, and why water molecules are polar.
24. Identify the following substances as composed of polar molecules: water, H_2O ; ammonia, NH_3 ; oxyacids (such as nitric acid, HNO_3); hydrogen halides (HF , HCl , HBr , and HI); methanol, CH_3OH ; and ethanol, $\text{C}_2\text{H}_5\text{OH}$.
25. Identify the following substances as composed of nonpolar molecules: elements composed of molecules (H_2 , N_2 , O_2 , F_2 , Cl_2 , Br_2 , I_2 , P_4 , S_8 , and Se_8); carbon dioxide, CO_2 ; and hydrocarbons (such as hexane, C_6H_{14}).
26. Describe hydrogen bonds between molecules of HF , H_2O , CH_3OH , and NH_3 .
27. Describe London dispersion forces between nonpolar molecules, including how the attractions form between molecules that initially have no polarity.
28. Explain why larger molecules have stronger London forces.
29. Describe the similarities and differences between natural gas, gasoline, kerosene, lubricating oils, and asphalt.
30. Given the name or chemical formula for a substance, (1) categorize the substance as a metallic element, carbon in the diamond form, another nonmetallic element, an ionic compound, a polar molecular compound with hydrogen bonds, a polar molecular compound without hydrogen bonds, or a nonpolar molecular compound; (2) identify the type of particle that forms its fundamental structure; and (3) identify the type of attraction holding its particles in the solid and liquid form.

1. For each of the following pairs of elements, decide whether a bond between them would be covalent or ionic.
 - a. Ni and F
 - b. S and O
2. Classify each of the following as either a molecular compound or an ionic compound.
 - a. oxygen difluoride
 - b. Na_2O
 - c. calcium carbonate
 - d. C_3H_8
3. Classify each of the following compounds as either (1) a binary ionic compound, (2) an ionic compound with polyatomic ion(s), (3) a binary covalent compound, (4) a binary acid, (5) an alcohol, or (6) an oxyacid. Write the chemical formula that corresponds to each name.
 - a. magnesium chloride
 - b. hydrogen chloride
 - c. sodium nitrate
 - d. methane
 - e. ammonia
 - f. hydrochloric acid
 - g. nitric acid
 - h. ethanol

4. Classify each of the following compounds as either (1) a binary ionic compound, (2) an ionic compound with polyatomic ion(s), (3) a binary covalent compound, (4) a binary acid, (5) an alcohol, or (6) an oxyacid. Write the name that corresponds to each chemical formula.
- | | |
|-----------------------|-----------------------------------|
| a. HF | e. C ₂ H ₆ |
| b. CH ₃ OH | f. BF ₃ |
| c. LiBr | g. H ₂ SO ₄ |
| d. NH ₄ Cl | |
5. For each of the formulas listed below, draw a reasonable Lewis structure, write the name of the electron group geometry around the central atom, draw the geometric sketch of the molecule, including bond angles, and write the name of the molecular geometry around the central atom.
- | | |
|---------------------|---------------------|
| a. CCl ₄ | c. PF ₃ |
| b. SF ₂ | d. BCl ₃ |

Key Ideas

Complete the following statements by writing one of these words or phrases in each blank.

1 atmosphere	molecular compound
anywhere	momentum
attract	more
cancel	more rapidly
chance	negative
collisions	net
difference	number
dipole-dipole	nonpolar
direction of motion	opposing
equilibrium vapor	partial negative
external pressure	partial positive
greater than 1.7	partial pressure
higher	percentage
higher electronegativity	polar
hydrogen	positive
increase	remain
increased temperature	repel
induced	significant
internal vapor pressure	strength of attractions
large	stronger
less than	surface
less tightly	surface area
lower	temperature
lower electronegativity	top surface
molecular	weaker

6. Gases can be converted into liquids by a decrease in temperature. At a high temperature, there are no _____ attractions between particles of a gas. As the temperature is lowered, attractions between particles lead to the formation of very small clusters that _____ in the gas phase. As the temperature is lowered further, the particles move slowly enough to form clusters so _____ that they drop to the bottom of the container and combine to form a liquid.
7. For a particle to escape from the surface of a liquid, it must be at the liquid's _____, its _____ must take it beyond the liquid's surface, and its _____ must be great enough to overcome the backward pull of the other particles at the surface.
8. During the evaporation of a liquid, the _____ moving particles escape, leaving the particles left in the liquid with a lower average velocity, and lower average velocity means _____ temperature.
9. The rate of evaporation—the _____ of particles moving from liquid to gas per second—depends on three factors: _____ of the liquid, _____ between the particles in the liquid, and _____ of the liquid.
10. Greater surface area means _____ particles at the surface of a liquid, which leads to a greater rate of evaporation.
11. Weaker attractions between particles lead to a(n) _____ rate of evaporation.
12. Increased temperature increases the average velocity and momentum of the particles. As a result, a greater _____ of particles will have the minimum momentum necessary to escape, so the liquid will evaporate more quickly.
13. As long as the rate of evaporation of the liquid is greater than the rate of condensation of the vapor, the concentration of vapor particles above the liquid will _____. However, as the concentration of vapor particles increases, the rate of _____ of vapor particles with the liquid increases, boosting the rate of condensation.
14. For a dynamic equilibrium to exist, the rates of the two _____ changes must be equal, so that there are constant changes between state A and state B but no _____ change in the components of the system.
15. The _____ of vapor above a liquid in a closed system with a dynamic equilibrium between the rate of evaporation and the rate of condensation is called the equilibrium vapor pressure, P_{vap} .
16. The _____ the attractions between particles of a substance, the higher the equilibrium vapor pressure for that substance at a given temperature.
17. Boiling can be defined as the conversion of liquid into vapor _____ in the liquid rather than just at the _____.
18. As a liquid is heated, the vapor pressure of the liquid increases until the temperature gets high enough to make the pressure within the bubbles that form equal to the _____. At this temperature, the bubbles can maintain their volume, and the liquid boils.

19. The boiling-point temperature can be defined as the temperature at which the _____ pressure of the liquid becomes equal to the external pressure acting on the liquid.
20. If the external pressure acting on a liquid changes, then the _____ needed to preserve a bubble changes, and therefore the boiling-point temperature changes.
21. The temperature at which the equilibrium vapor pressure of a liquid equals _____ is called its normal boiling-point temperature or just its normal boiling point.
22. We know that increased strength of attractions leads to decreased rate of evaporation, decreased rate of condensation at equilibrium, decreased concentration of vapor, and decreased vapor pressure at a given temperature. This leads to a(n) _____ necessary to reach a vapor pressure of 1 atmosphere.
23. A molecule that contains a partial positive charge at one end and a partial negative charge at the other is called a(n) _____ dipole, or often just a dipole.
24. A dipole-dipole attraction is an attraction between the _____ end of one molecule and the _____ end of another molecule.
25. When a polar molecular substance, such as hydrogen chloride, is heated to convert it from liquid to gas, _____ attractions are broken.
26. The higher an element's electronegativity, the greater its ability to _____ electrons from other elements.
27. If the difference in electronegativity (ΔEN) between the atoms in the bond is _____ 0.4, we expect them to share electrons more or less equally, forming a nonpolar covalent bond.
28. If the difference in electronegativity (ΔEN) between two atoms is between 0.4 and 1.7, we expect the bond between them to be a(n) _____ covalent bond.
29. If the difference in electronegativity (ΔEN) between two atoms is _____, we expect the bond between them to be ionic.
30. The atom with the higher electronegativity has the partial _____ charge. The atom with the lower electronegativity has the partial _____ charge.
31. The nonmetallic element in a bond between a metallic atom and a nonmetallic atom has the _____ and forms the anion. The metallic element has the _____ and forms the cation.
32. When comparing two covalent bonds, the bond with the greater _____ in electronegativity (ΔEN) between the atoms in the bond is likely to be the more polar bond.
33. If a substance is composed of all nonmetallic elements and does not contain the ammonium ion, you can assume that it is a(n) _____.
34. When there are no polar bonds in a molecule, there is no permanent charge difference between one part of the molecule and another, and the molecule is _____.
35. If the polar bonds in a molecule are evenly (or symmetrically) distributed, the bond dipoles _____ and do not create a molecular dipole.

36. _____ bonds are attractions that occur between a nitrogen, oxygen, or fluorine atom of one molecule and a hydrogen atom bonded to a nitrogen, oxygen, or fluorine atom in another molecule.
37. An instantaneous dipole can create a dipole in the molecule next to it. For example, the negative end of one instantaneous dipole will _____ the negative electron cloud of a nonpolar molecule next to it, pushing the cloud toward the far side of the neighboring molecule. The new dipole is called a(n) _____ dipole.
38. The larger the molecules of a substance, the _____ the London forces between them. A larger molecule has more electrons and a greater _____ of having its electron cloud distorted from its nonpolar shape. Thus instantaneous dipoles are more likely to form in larger molecules. The electron clouds in larger molecules are also larger, so the average distance between the nuclei and the electrons is greater; as a result, the electrons are held _____ and shift more easily to create a dipole.

Section 14.1 Change From Gas to Liquid and from Liquid to Gas—An Introduction to Dynamic Equilibrium

Chapter Problems

39. A batch of corn whiskey is being made in a backwoods still. The ingredients are mixed and heated, and because the ethyl alcohol, C_2H_5OH , evaporates more rapidly than the other components, the vapor that forms above the mixture is enriched in C_2H_5OH . When the vapor is captured and condensed, the liquid it forms has a higher percentage of ethyl alcohol than the original mixture. Describe the submicroscopic changes occurring when pure, gaseous C_2H_5OH is converted to a liquid, including a description of the transitions from a high temperature gas to a lower temperature gas to a liquid.
40. Why is dew more likely to form on a lawn at night than in the day? Describe the changes that take place as dew forms.
41. Acetone, CH_3COCH_3 , is a laboratory solvent that is also commonly used as a nail polish remover.
- Describe the submicroscopic events taking place at the surface of liquid acetone when it evaporates.
 - Do all of the acetone molecules moving away from the surface of the liquid escape? If not, why not? What three criteria must be met for a molecule to escape from the surface of the liquid and move into the gas phase?
 - If you spill some nail polish remover on your hand, the spot will soon feel cold. Why?
 - If you spill some acetone on a lab bench, it evaporates much faster than the same amount of acetone in a test tube. Why?
 - If you spill acetone on a hot plate in the laboratory, it evaporates much more quickly than the same amount of acetone spilled on the cooler lab bench. Why?

OBJECTIVE 2

OBJECTIVE 3

OBJECTIVE 4

OBJECTIVE 5

OBJECTIVE 7

OBJECTIVE 9

42. Consider two test tubes, each containing the same amount of liquid acetone. A student leaves one of the test tubes open overnight and covers the other one with a balloon so that gas cannot escape. When the student returns to the lab the next day, all of the acetone is gone from the open test tube, but most of it remains in the covered tube.
- Explain why the acetone is gone from one test tube and not from the other.
 - Was the initial rate at which liquid changed to gas (the rate of evaporation) greater in one test tube than the other? Explain your answer.
 - Consider the system after 30 minutes, with liquid remaining in both test tubes. Is condensation (vapor to liquid) taking place in both test tubes? Is the rate of condensation the same in both test tubes? Explain your answer.
 - Describe the submicroscopic changes in the covered test tube that lead to a constant amount of liquid and vapor.
 - The balloon expands slightly after it is placed over the test tube, suggesting an initial increase in pressure in the space above the liquid. Why? After this initial expansion, the balloon stays inflated by the same amount. Why doesn't the pressure inside the balloon change after the initial increase?
 - If the covered test tube is heated, the balloon expands. Part of this expansion is due to the increase in gas pressure owing to the rise in temperature of the gas, but the increase is greater than expected from this factor alone. What other factor accounts for the increase in pressure? Describe the submicroscopic changes that take place that lead to this other factor.
43. The attractions between ethanol molecules, C_2H_5OH , are stronger than the attractions between diethyl ether molecules, $CH_3CH_2OCH_2CH_3$.
- Which of these substances would you expect to have the higher rate of evaporation at room temperature? Why?
 - Which of these substances would you expect to have the higher equilibrium vapor pressure? Why?
44. Why do caregivers rub alcohol on the skin of feverish patients?
45. Picture a half empty milk bottle in the refrigerator. The water in the milk will be constantly evaporating into the gas-filled space above the liquid, and the water molecules in this space will be constantly colliding with the liquid and returning to the liquid state. If the milk is tightly closed, a dynamic equilibrium forms between the rate of evaporation and the rate of condensation. If the bottle is removed from the refrigerator and left out in the room with its cap still on tightly, what happens to the rates of evaporation and condensation? An hour later when the milk has reached room temperature, will a dynamic equilibrium exist between evaporation and condensation?

OBJECTIVE 10

OBJECTIVE 12

OBJECTIVE 14

OBJECTIVE 13



Section 14.2 Boiling Liquids

46. Describe the difference between boiling point temperature and normal boiling point temperature.

47. The normal boiling point of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 78.3°C .
- a. Describe the submicroscopic events occurring when a bubble forms in liquid ethanol. OBJECTIVE 15
 - b. Consider heating liquid ethanol in a system where the external pressure acting on the liquid is 1 atm. Explain why bubbles cannot form and escape from the liquid until the temperature reaches 78.3°C . OBJECTIVE 16
 - c. If the external pressure on the surface of the ethanol is increased to 2 atm, will its boiling-point temperature increase, decrease, or stay the same? Why? OBJECTIVE 17
48. Explain why potatoes take longer to cook in boiling water on top of Mount Everest than at sea level and why they cook faster in water boiled in a pressure cooker. OBJECTIVE 18
49. At 86 m below sea level, Death Valley is the lowest point in the western hemisphere. The boiling point of water in Death Valley is slightly higher than water's normal boiling point. Explain why.
50. Butane is a gas at room temperature and pressure, but the butane found in some cigarette lighters is a liquid. How can this be?
51. Explain why liquid substances with stronger interparticle attractions will have higher boiling points than liquid substances whose particles experience weaker interparticle attractions. OBJECTIVE 19

Section 14.3 Particle-Particle Attractions

52. Bromine monofluoride, BrF , a substance that liquefies at -20°C , consists of polar molecules that are very similar to HCl molecules. Each BrF molecule consists of a bromine atom with a polar covalent bond to a fluorine atom. (a) Describe what you would see if you were small enough to ride on a BrF molecule in gaseous bromine monofluoride. (b) Describe the process that takes place when bromine monofluoride gas is cooled enough to form a liquid. (c) What type of attraction holds the molecules together in the liquid form? (d) Draw a rough sketch of the structure of liquid bromine monofluoride. (e) Describe what you would see if you were small enough to ride on a BrF molecule in liquid bromine monofluoride. OBJECTIVE 20
53. Do the electronegativities of the elements in a column on the periodic table increase or decrease from top to bottom? Do the electronegativities of the elements in a period on the periodic table increase or decrease from left to right? In general, the greater the separation of two elements on the periodic table, the greater the difference in electronegativity and the greater the expected polarity of the bond they form. Is this always true? If it is not always true, when is it true and when is it not necessarily true? OBJECTIVE 21
54. Classify each of the following bonds as nonpolar covalent, polar covalent, or ionic. If a bond is polar covalent, identify the atom that has the partial negative charge and the atom that has the partial positive charge. If a bond is ionic, identify the ion that has the negative charge and the ion that has the positive charge. OBJECTIVE 22
- | | | | |
|---------|---------|--------|--------|
| a. C–N | d. Li–F | g. F–S | j. F–H |
| b. C–H | e. C–Se | h. O–P | |
| c. H–Br | f. Se–S | i. O–K | |

OBJECTIVE 22

55. Classify each of the following bonds as nonpolar covalent, polar covalent, or ionic. If a bond is polar covalent, identify the atom that has the partial negative charge and the atom that has the partial positive charge. If a bond is ionic, identify the ion that has the negative charge and the ion that has the positive charge.

- | | | | |
|----------|----------|---------|--------|
| a. N–O | d. H–I | g. Se–I | j. F–P |
| b. Al–Cl | e. Br–Cl | h. N–Sr | |
| c. Cl–N | f. Cl–S | i. O–F | |

OBJECTIVE 22

56. Identify the bond in each pair that you would expect to be more polar.

- a. C–O or C–H b. P–H or H–Cl

OBJECTIVE 22

57. Identify the bond in each pair that you would expect to be more polar.

- a. P–F or N–Cl b. S–I or Se–F

OBJECTIVE 23

58. Explain why water molecules are polar, why ethane, C_2H_6 , molecules are nonpolar, and why carbon dioxide, CO_2 , molecules are nonpolar.

59. The C–F bond is more polar than the N–F bond, but CF_4 molecules are nonpolar and NF_3 molecules are polar. Explain why.

OBJECTIVE 26

60. Ammonia has been used as a refrigerant. In the cooling cycle, gaseous ammonia is alternately compressed to a liquid and allowed to expand back to the gaseous state. What are the particles that form the fundamental structure of ammonia? What type of attraction holds these particles together? Draw a rough sketch of the structure of liquid ammonia.

OBJECTIVE 26

61. Methanol can be used as a home heating oil extender. What are the particles that form the fundamental structure of methanol? What type of attraction holds these particles together? Draw a rough sketch of the structure of liquid methanol.

OBJECTIVE 27

62. Bromine, Br_2 , is used to make ethylene bromide, which is an antiknock additive in gasoline. The Br_2 molecules have nonpolar covalent bonds between the atoms, so we expect isolated Br_2 molecules to be nonpolar. Despite the nonpolar character of isolated Br_2 molecules, attractions form between bromine molecules that are strong enough to hold the particles in the liquid form at room temperature and pressure. What is the nature of these attractions? How do they arise? Describe what you would see if you were small enough to ride on a Br_2 molecule in liquid bromine.

OBJECTIVE 28

63. Carbon tetrabromide, CBr_4 , is used to make organic compounds, and carbon tetrachloride, CCl_4 , is an industrial solvent whose use is diminishing due to its toxicity. Both CCl_4 and CBr_4 molecules are nonpolar. Carbon tetrachloride is a liquid at room temperature, but carbon tetrabromide is a solid, suggesting that the attractions between CCl_4 molecules are weaker than between CBr_4 molecules. Explain why.

64. Carbon disulfide, CS_2 , which is used to make rayon, is composed of nonpolar molecules that are similar to carbon dioxide molecules, CO_2 . Unlike carbon dioxide, carbon disulfide is liquid at room temperature. Why?

65. Milk bottles are often made of polyethylene plastic, which is composed of extremely large, nonpolar molecules. What type of attraction holds these molecules together in the solid form? In general, would you expect this type of attraction to be stronger or weaker than the hydrogen bonds that hold water molecules together? Because polyethylene is a solid at room temperature and water is a liquid, the attractions between polyethylene molecules must be stronger than those between water molecules. What makes the attractions between polyethylene molecules so strong?
66. Methanol, CH_3OH , is used to make formaldehyde, CH_2O , which is used in embalming fluids. The molecules of these substances have close to the same atoms and about the same molecular mass, so why is methanol a liquid at room temperature and formaldehyde a gas?
67. Describe the similarities and differences between natural gas, gasoline, and asphalt. Explain why the substances in natural gas are gaseous, why the substances in gasoline are liquid, and why the substances in asphalt are solid.
68. Complete the following table by specifying (1) the name for the type of particle viewed as forming the structure of a solid, liquid, or gas of each of the following substances and (2) the name of the type of attraction holding these particles in the solid and liquid form.
- | | | |
|-----------|------------------------------------|------------------------------|
| a. silver | c. $\text{C}_2\text{H}_5\text{OH}$ | e. C_5H_{12} |
| b. HCl | d. carbon (diamond) | f. water |
69. Complete the following table by specifying (1) the name for the type of particle viewed as forming the structure of a solid, liquid, or gas of each of the following substances and (2) the name of the type of attraction holding these particles in the solid and liquid form.
- | | | |
|------------|------------------------------|------------------------------------|
| a. ammonia | c. C_6H_{14} | e. hydrogen bromide |
| b. KCl | d. iodine | f. $\text{C}_3\text{H}_7\text{OH}$ |
70. Have you ever broken a mercury thermometer? If you have, you probably noticed that the mercury forms droplets on the surface on which it falls rather than spreading out and wetting it like water. Describe the difference between liquid mercury and liquid water that explains this different behavior. (Hint: Consider the attractions between particles.)

OBJECTIVE 28

OBJECTIVE 29

OBJECTIVE 30

OBJECTIVE 30

Discussion Topic

71. Chlorofluorocarbons, CFCs, were used for years as aerosol propellants (Section 7.4). Although CFCs, such as CFC-12, are gases at normal pressure, under high pressures they can be converted to liquid. The liquid CFC in an aerosol can evaporates, and the resulting vapor pressure pushes substances out of the can. When the valve on the top of the can is pressed and substances escape, the pressure inside the can decreases at first, but it quickly returns to the pressure that existed before the valve was pushed. Describe what happens at the “submicroscopic” level as the pressure returns to its original value. Why does the pressure return to the same value as long as any liquid CFC remains in the can? If you were looking for a replacement for CFCs in aerosol cans, what are the criteria you might consider?