Matter on Earth can exist in any of three states—gas, liquid, or solid—and can change from one state to another. Figure 4.1 lists the possible changes of state. In this section, you will examine these changes of state and the factors that cause them.

**Main Idea**

**Substances in equilibrium change back and forth between states at equal speeds.**

Some liquid chemical substances, such as rubbing alcohol, have an odor that is very easily detected. This is because some molecules at the upper surface of the liquid have enough energy to overcome the attraction of neighboring molecules, leave the liquid phase, and evaporate. A phase is any part of a system that has uniform composition and properties. In a closed bottle of rubbing alcohol, gas molecules under the cap strike the liquid surface and reenter the liquid phase through condensation. Condensation is the process by which a gas changes to a liquid. A gas in contact with its liquid or solid phase is often called a vapor.

If the temperature of the liquid remains constant and the cap remains closed, the rate at which molecules move from the liquid to vapor remains constant. Near the beginning of the evaporation process, very few molecules are in the gas phase, so the rate of condensation is very low.

### Table: Possible Changes of State

<table>
<thead>
<tr>
<th>Change of state</th>
<th>Process</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid → liquid</td>
<td>melting</td>
<td>ice → water</td>
</tr>
<tr>
<td>solid → gas</td>
<td>sublimation</td>
<td>dry ice → CO₂ gas</td>
</tr>
<tr>
<td>liquid → solid</td>
<td>freezing</td>
<td>water → ice</td>
</tr>
<tr>
<td>liquid → gas</td>
<td>vaporization</td>
<td>liquid bromine → bromine vapor</td>
</tr>
<tr>
<td>gas → liquid</td>
<td>condensation</td>
<td>water vapor → water</td>
</tr>
<tr>
<td>gas → solid</td>
<td>deposition</td>
<td>water vapor → ice</td>
</tr>
</tbody>
</table>
As more liquid evaporates, the increasing number of gas molecules causes the rate of condensation to increase until the rate of condensation equals the rate of evaporation and a state of equilibrium is established (see Figure 4.2). **Equilibrium** is a dynamic condition in which two opposing changes occur at equal rates in a closed system. Even though molecules are constantly moving between liquid and gas phases, there is no net change in the amount of substance in either phase.

**Equilibrium Vapor Pressure of a Liquid**

Vapor molecules in equilibrium with a liquid in a closed system exert a pressure proportional to the concentration of molecules in the vapor phase. The pressure exerted by a vapor in equilibrium with its corresponding liquid at a given temperature is called the **equilibrium vapor pressure** of the liquid.

The increase in equilibrium vapor pressure with increasing temperature can be explained in terms of the kinetic-molecular theory for the liquid and gaseous states. Increasing the temperature of a liquid increases the average kinetic energy of the liquid’s molecules. This increases the number of molecules that have enough energy to escape from the liquid phase into the vapor phase. The resulting increased evaporation rate increases the number of molecules in the vapor phase, which in turn increases the equilibrium vapor pressure.

Every liquid has a specific equilibrium vapor pressure at a given temperature. The stronger these attractive forces are, the smaller is the percentage of liquid particles that can evaporate at any given temperature. A low percentage of evaporation results in a low equilibrium vapor pressure. **Volatile liquids**, which are liquids that evaporate readily, have relatively weak forces of attraction between their particles.
Ether is a typical volatile liquid. Nonvolatile liquids, such as molten ionic compounds, do not evaporate readily and have relatively strong attractive forces between their particles.

**MAIN IDEA**  
TEKS 9C  

_A liquid boils when it has absorbed enough energy to evaporate._

Equilibrium vapor pressures can be used to explain and define the concept of **boiling**, which is the conversion of a liquid to a vapor within the liquid as well as at its surface.

If the temperature of the liquid is increased, the equilibrium vapor pressure also increases. The **boiling point** of a liquid is the temperature at which the equilibrium vapor pressure of the liquid equals the atmospheric pressure. The lower the atmospheric pressure is, the lower the boiling point is.

At the boiling point, all of the energy absorbed is used to evaporate the liquid, and the temperature remains constant as long as the pressure does not change. If the pressure above the liquid being heated is increased, the temperature of the liquid will rise until the vapor pressure equals the new pressure and the liquid boils once again. A pressure cooker is sealed so that steam pressure builds up over the surface of the boiling water inside. The boiling temperature of the water increases, resulting in shorter cooking times. A device called a **vacuum evaporator** causes boiling at lower-than-normal temperatures. Vacuum evaporators used to prepare evaporated and sweetened condensed milk remove water from milk and sugar solutions. Under reduced pressure, the water boils away at a temperature low enough to avoid scorching the milk or sugar.

At normal atmospheric pressure (1 atm, 760 torr, or 101.3 kPa), water boils at exactly 100°C. This is the _normal_ boiling point of water.

**Figure 4.3**

**Boiling Point**  
The vapor pressure of any liquid increases as its temperature increases. A liquid boils when its vapor pressure equals the pressure of the atmosphere.
Figure 4.4 shows that the normal boiling point of each liquid occurs when its equilibrium vapor pressure equals 760 torr. Energy must be added continuously in order to keep a liquid boiling. The temperature of a liquid and its vapor at the boiling point remains constant despite the continuous addition of energy. The added energy is used to overcome the attractive forces between molecules of the liquid during the liquid-to-gas change and is stored in the vapor as potential energy.

Molar Enthalpy of Vaporization

The amount of energy as heat that is needed to vaporize one mole of liquid at the liquid’s boiling point at constant pressure is called the liquid’s molar enthalpy of vaporization, $\Delta H_v$. Molar enthalpy of vaporization measures the attraction between particles of the liquid. The stronger the attraction is, the more energy is required to overcome it, resulting in a higher molar enthalpy of vaporization. Each liquid has a characteristic molar enthalpy of vaporization. Liquid water’s molar enthalpy of vaporization is very high, due to its extensive hydrogen bonding. This makes water an effective cooling agent. When water evaporates, the escaping molecules carry away with them a great deal of energy as heat. Figure 4.4 shows the distribution of the kinetic energies of molecules in a liquid at two different temperatures. At higher temperatures, a greater portion of the surface molecules have the kinetic energy required to escape and become vapor.

**Figure 4.3** (see previous page) shows that the normal boiling point of each liquid occurs when its equilibrium vapor pressure equals 760 torr. Energy must be added continuously in order to keep a liquid boiling. The temperature of a liquid and its vapor at the boiling point remains constant despite the continuous addition of energy. The added energy is used to overcome the attractive forces between molecules of the liquid during the liquid-to-gas change and is stored in the vapor as potential energy.

**Main Idea**

Freezing occurs when a substance loses enough heat energy to solidify.

The physical change of a liquid to a solid is called freezing. Freezing involves a loss of energy in the form of heat by the liquid.

\[
\text{liquid} \rightarrow \text{solid} + \text{energy}
\]
In the case of a pure crystalline substance, this change occurs at constant temperature. **The normal freezing point** is the temperature at which the solid and liquid are in equilibrium at 1 atm (760 torr, or 101.3 kPa) pressure. At the freezing point, particles of the liquid and the solid have the same average kinetic energy, and the energy lost during freezing is the potential energy that was present in the liquid. At the same time energy decreases, there is a significant increase in particle order, because the solid state of a substance is much more ordered than the liquid state, even at the same temperature.

Melting, the reverse of freezing, also occurs at constant temperature. As a solid melts, it continuously absorbs energy as heat, as represented by the following equation.

\[
\text{solid} + \text{energy} \rightarrow \text{liquid}
\]

For pure crystalline solids, the melting point and freezing point are the same. At equilibrium, melting and freezing proceed at equal rates. The following general equilibrium equation can be used to represent these states.

\[
\text{solid} + \text{energy} \rightleftharpoons \text{liquid}
\]

At normal atmospheric pressure, the temperature of a system containing ice and liquid water will remain at 0°C as long as both ice and water are present, no matter what the surrounding temperature. Adding energy in the form of heat to such a system shifts the equilibrium to the right. That shift increases the proportion of liquid water and decreases that of ice. Only after all the ice has melted will the addition of energy increase the temperature of the system.

**Molar Enthalpy of Fusion**

The amount of energy as heat required to melt one mole of solid at the solid's melting point is the solid's **molar enthalpy of fusion**, \(\Delta H_f\). The energy absorbed increases the solid's potential energy as its particles are pulled apart, overcoming the attractive forces holding them together. At the same time, there is a significant decrease in particle order as the substance makes the transformation from solid to liquid. Similar to the molar enthalpy of vaporization, the magnitude of the molar enthalpy of fusion depends on the attraction between the solid particles.

**Sublimation and Deposition**

At sufficiently low temperature and pressure conditions, a liquid cannot exist. Under such conditions, a solid substance exists in equilibrium with its vapor instead of its liquid, as represented by the following equation.

\[
\text{solid} + \text{energy} \rightleftharpoons \text{vapor}
\]

The change of state from a solid directly to a gas is known as **sublimation**. The reverse process is called **deposition**, the change of state from a gas directly to a solid. Among the common substances that sublime at ordinary temperatures are dry ice (solid CO\(_2\)) and iodine.
Ordinary ice sublimes slowly at temperatures lower than its melting point (0.°C). This explains how a thin layer of snow can eventually disappear, even if the temperature remains below 0.°C. Sublimation occurs in frost-free refrigerators when the temperature in the freezer compartment is periodically raised to cause any ice that has formed to sublime. A blower then removes the water vapor that has formed. The formation of frost on a cold surface is a familiar example of deposition.

**MAIN IDEA**

**Under certain conditions, water can exist in all three phases at the same time.**

A *phase diagram* is a graph of pressure versus temperature that shows the conditions under which the phases of a substance exist. A phase diagram also reveals how the states of a system change with changing temperature or pressure.

Figure 4.5 shows the phase diagram for water over a range of temperatures and pressures. Note the three curves, AB, AC, and AD. Curve AB indicates the temperature and pressure conditions at which ice and water vapor can coexist at equilibrium. Curve AC indicates the temperature and pressure conditions at which liquid water and water vapor coexist at equilibrium. Similarly, curve AD indicates the temperature and pressure conditions at which ice and liquid water coexist at equilibrium. Because ice is less dense than liquid water, an increase in pressure lowers the melting point. (Most substances have a positive slope for this curve.) Point A is the triple point of water. The **triple point** of a substance indicates the temperature and pressure conditions at which the solid, liquid, and vapor of the substance can coexist at equilibrium. Point C is the critical point of water. The **critical point** of a substance indicates the critical temperature and critical pressure. The **critical temperature** ($t_c$) is the temperature above which the substance cannot exist in the liquid state.

**FIGURE 4.5**

**Phase Diagram** This phase diagram shows the relationships between the physical states of water and its pressure and temperature.
Reviewing Main Ideas

1. What is equilibrium?
2. What happens when a liquid-vapor system at equilibrium experiences an increase in temperature? What happens when it experiences a decrease in temperature?
3. What would be an example of deposition?
4. What is the equilibrium vapor pressure of a liquid? How is it measured?
5. What is the boiling point of a liquid?
6. In the phase diagram for water, what is meant by the triple point and the critical point?

Critical Thinking

7. **INTERPRETING GRAPHICS** Refer to the phase diagram for water (Figure 4.5) to answer the following questions.
   a. Describe all the changes a sample of solid water would undergo when heated from −10°C to its critical temperature at a pressure of 1.00 atm.
   b. Describe all the changes a sample of water vapor would undergo when cooled from 110°C to 5°C at a pressure of 1.00 atm.
   c. At approximately what pressure will water be a vapor at 0°C?
   d. Within what range of pressures will water be a liquid at temperatures above its normal boiling point?

The critical temperature of water is 373.99°C. Above this temperature, water cannot be liquefied, no matter how much pressure is applied. The critical pressure \( P_c \) is the lowest pressure at which the substance can exist as a liquid at the critical temperature. The critical pressure of water is 217.75 atm.

The phase diagram in Figure 4.5 on the previous page indicates the normal boiling point and the normal freezing point of water. It also shows how boiling point and freezing point change with pressure. As shown by the slope of line AD, ice melts at a higher temperature with decreasing pressure. Below the triple point, the temperature of sublimation decreases with decreasing pressure. Figure 4.6 summarizes the changes of state of solids, liquids, and gases.