

particularly convenient for comparing the different phases of a substance. Figure 13–20 is the phase diagram for water. The curve labeled  $l-v$  represents those points where the liquid and vapor phases are in equilibrium—it is thus a graph of the boiling point versus pressure. Note that the curve correctly shows that at a pressure of 1 atm the boiling point is  $100^\circ\text{C}$  and that the boiling point is lowered for a decreased pressure. The curve  $s-l$  represents points where solid and liquid exist in equilibrium and thus is a graph of the freezing point versus pressure. At 1 atm, the freezing point of water is  $0^\circ\text{C}$ , as shown. Notice also in Fig. 13–20 that at a pressure of 1 atm, the substance is in the liquid phase if the temperature is between  $0^\circ\text{C}$  and  $100^\circ\text{C}$ , but is in the solid or vapor phase if the temperature is below  $0^\circ\text{C}$  or above  $100^\circ\text{C}$ . The curve labeled  $s-v$  is the *sublimation point* versus pressure curve. **Sublimation** refers to the process whereby at low pressures a solid changes directly into the vapor phase without passing through the liquid phase. For water, sublimation occurs if the pressure of the water vapor is less than 0.0060 atm. Carbon dioxide, which in the solid phase is called dry ice, sublimates even at atmospheric pressure.

The intersection of the three curves (in Fig. 13–20) is the **triple point**. For water this occurs at  $T = 273.16\text{ K}$  and  $P = 6.03 \times 10^{-3}\text{ atm}$ . It is only at the triple point that the three phases can exist together in equilibrium. Because the triple point corresponds to a unique value of temperature and pressure, it is precisely reproducible and is often used as a point of reference. For example, the standard of temperature is usually specified as exactly 273.16 K at the triple point of water, rather than 273.15 K at the freezing point of water at 1 atm.

Notice that the  $s-l$  curve for water slopes upward to the left. This is true only of substances that *expand* upon freezing; at a higher pressure, a lower temperature is needed to cause the liquid to freeze. More commonly, substances contract upon freezing and the  $s-l$  curve slopes upward to the right, as shown for carbon dioxide ( $\text{CO}_2$ ) in Fig. 13–21.

The phase transitions we have been discussing are the common ones. Some substances, however, can exist in several forms in the solid phase. A transition from one phase to another occurs at a particular temperature and pressure, just like ordinary phase changes. For example, ice has been observed in at least eight forms at very high pressure. Ordinary helium has two distinct liquid phases, called helium I and II. They exist only at temperatures within a few degrees of absolute zero. Helium II exhibits very unusual properties referred to as **superfluidity**. It has essentially zero viscosity and exhibits strange properties such as climbing up the sides of an open container.

## \* 13–13 Vapor Pressure and Humidity

### Evaporation

If a glass of water is left out overnight, the water level will have dropped by morning. We say the water has evaporated, meaning that some of the water has changed to the vapor or gas phase.

This process of **evaporation** can be explained on the basis of kinetic theory. The molecules in a liquid move past one another with a variety of speeds that follow, approximately, the Maxwell distribution. There are strong attractive forces between these molecules, which is what keeps them close together in the liquid phase. A molecule near the surface of the liquid may, because of its speed, leave the liquid momentarily. But just as a rock thrown into the air returns to the Earth, so the attractive forces of the other molecules can pull the vagabond molecule back to the liquid surface—that is, if its velocity is not too large. A molecule with a high enough velocity, however, will escape the liquid entirely, like a rocket escaping the Earth, and become part of the gas phase. Only those molecules that have kinetic energy above a particular value can escape to the gas phase. We have already seen that kinetic theory predicts that the relative number of molecules with kinetic energy above a particular value (such as  $E_A$  in Fig. 13–18) increases with temperature. This is in accord with the well-known observation that the evaporation rate is greater at higher temperatures.

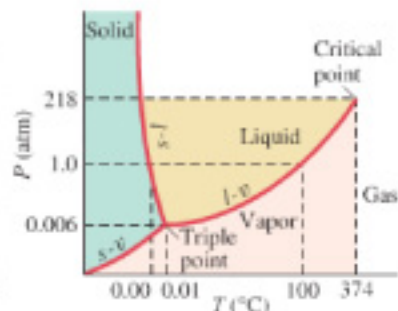
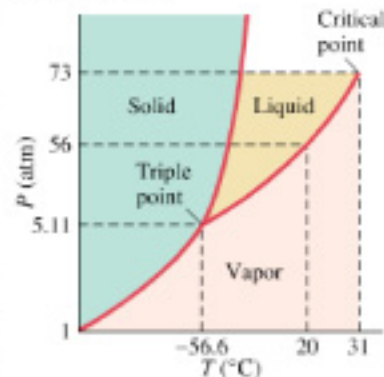


FIGURE 13–20 Phase diagram for water (note that the scales are not linear).

### Triple point

FIGURE 13–21 Phase diagram for carbon dioxide.



### Superfluidity

### Evaporation