Pearson

11.6: Sublimation and Fusion

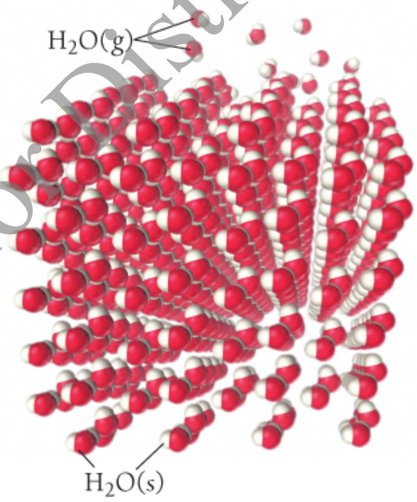
In Section 11.5, we examined a beaker of liquid water at room temperature from the molecular viewpoint. Now, let's examine a block of ice at −10 °C from the same molecular perspective, paying close attention to two common processes: sublimation and fusion.

Sublimation

Even though a block of ice is solid, the water molecules have thermal energy, which causes each one to vibrate about a fixed point. The motion is much less vigorous than in a liquid, but it is significant nonetheless. As in liquids, at any instant some molecules in the block of ice have more thermal energy than the average and some have less. The molecules with high enough thermal energy can break free from the ice surface—where, as in liquids, molecules are held less tightly than in the interior due to fewer neighbor–neighbor interactions—and transition directly into the gas state (Figure 11.30). This process is known as **sublimation**, the transition from solid to gas. Some of the water molecules in the gas state (those at the low end of the energy distribution curve for the gaseous molecules) collide with the surface of the ice and are captured by the intermolecular forces with other molecules. This process—the opposite of sublimation—is **deposition**, the transition from gas to solid. As is the case with liquids, the pressure of a gas in dynamic equilibrium with its solid is the vapor pressure of the solid.

Figure 11.30 **The Sublimation of Ice**

The water molecules at the surface of an ice cube can sublime directly into the gas state.



Although both sublimation and deposition occur on the surface of an ice block open to the atmosphere at −10 °C, sublimation usually occurs at a greater rate because most of the newly sublimed molecules escape into the surrounding atmosphere and never come back. The result is a noticeable decrease in the size of the ice block over time (even though the temperature is below the melting point).

If you live in a cold climate, you may have noticed the disappearance of ice and snow from the ground even though the temperature remains below 0 °C. Similarly, ice cubes left in the freezer for a long time slowly shrink, even though the freezer is always below 0 °C. In both cases, the ice is *subliming*, turning directly into water vapor. Ice also sublimes out of frozen foods. You may have noticed, for example, the gradual growth of ice crystals on the *inside* of airtight plastic food-storage bags in a freezer. The ice crystals are composed of water that has sublimed out of the food and redeposited on the surface of the bag or on the surface of the food.

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For this reason, food that remains frozen for too long becomes dried out. Such dehydration can be avoided to some degree by freezing foods to colder temperatures, a process called deep-freezing. The colder temperature lowers the vapor pressure of ice and preserves the food longer. Freezer burn on meats is another common manifestation of sublimation. When you improperly store meat (for example, in a container that is not airtight) sublimation continues unabated. The result is the dehydration of the surface of the meat, which becomes discolored and loses flavor and texture.

A substance commonly associated with sublimation is solid carbon dioxide or dry ice, which does not melt under atmospheric pressure no matter what the temperature is. However, at −78 °C the CO_2 molecules have enough energy to leave the surface of the dry ice and become gaseous through sublimation.

Dry ice (solid CO_2 sublimes but does not melt at atmospheric pressure.

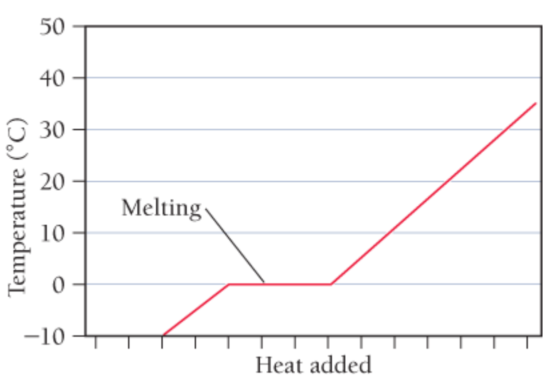
Fusion

Let's return to our ice block and examine what happens at the molecular level as we increase its temperature. The increasing thermal energy causes the water molecules to vibrate faster and faster. At the **melting point** (0 °C for water), the molecules have enough thermal energy to overcome the intermolecular forces that hold the molecules at their stationary points, and the solid turns into a liquid. This process is **melting** or **fusion**, the transition from solid to liquid. The opposite of melting is **freezing**, the transition from liquid to solid. Once the melting point of a solid is reached, additional heating only causes more rapid melting; it does not raise the temperature of the solid above its melting point (Figure 11.31). Only after all of the ice has melted does additional heating raise the temperature of the liquid water past 0 °C. A mixture of water *and* ice always has a temperature of 0 °C (at 1 atm pressure).

> The term *fusion* is used for melting because if we heat crystals of a solid, they *fuse* into a continuous liquid upon melting.

Figure 11.31 **Temperature during Melting**

The temperature of water during melting remains at 0.0 °C as long as both solid and liquid water remain.



Energetics of Melting and Freezing

The most common way to cool a beverage quickly is to drop several ice cubes into it. As the ice melts, the drink cools because melting is endothermic—the melting ice absorbs heat from the liquid. The amount of heat required to melt one mole of a solid is the **heat of fusion** (ΔH_{fus}). The heat of fusion for water is 6.02 kJ/mol:

$$H_2O\,(s) \rightarrow H_2O\,(l) \qquad \Delta H_{fus} = 6.02\ \mathrm{kJ/mol}$$

The heat of fusion is positive because melting is endothermic.

Freezing, the opposite of melting, is exothermic—heat is released when a liquid freezes into a solid. For example, as water in the freezer turns into ice, it releases heat, which must be removed by the refrigeration system of the freezer. If the refrigeration system did not remove the heat, the water would not completely freeze into ice. The heat released as the water began to freeze would warm the freezer, preventing further freezing. The change in enthalpy for freezing has the same magnitude as the heat of fusion but the opposite sign:

$$H_2O\,(l) \rightarrow H_2O\,(s) \qquad \Delta H = -\Delta H_{fus} = -6.02\ \mathrm{kJ/mol}$$

Different substances have different heats of fusion, as shown in Table 11.9.

Table 11.9 **Heats of Fusion of Several Substances**

Liquid	Chemical Formula	Melting Point (°C)	ΔH_{fus} (kJ/mol)
Water	H_2O	0.00	6.02
Rubbing alcohol (isopropyl alcohol)	C_3H_8O	−89.5	5.37
Acetone	C_3H_6O	−94.8	5.69
Diethyl ether	$C_4H_{10}O$	−116.3	7.27

In general, the heat of fusion for a substance is significantly less than its heat of vaporization, as shown in Figure 11.32. We have already seen that the solid and liquid states are closer to each other in many ways than they are to the gas state. It takes less energy to melt one mole of ice into liquid than it does to vaporize one mole of liquid water into gas because vaporization requires complete separation of molecules from one another, so the intermolecular forces must be completely overcome. Melting, however, requires that intermolecular forces be only partially overcome, allowing molecules to move around one another while still remaining in contact.

Figure 11.32 **Heat of Fusion and Heat of Vaporization**