15–7 Entropy and the Second Law of Thermodynamics

We have seen several aspects of the second law of thermodynamics; and the different statements of it that we have discussed can be shown to be completely equivalent. But what we really need is a general statement of the second law of thermodynamics. It was not until the latter half of the nineteenth century that the *second law of thermodynamics* was finally stated in a general way—namely, in terms of a quantity called **entropy**, introduced by Clausius in the 1860s. Entropy, unlike heat, is a function of the state of a system. That is, a system in a given state has a temperature, a volume, a pressure, and so on, and also has a particular value of entropy. In the next Section, we will see that entropy can be interpreted as a measure of the order or disorder of a system.

Entropy

When we deal with entropy—as with potential energy—it is the *change* in entropy during a process that is important, not the absolute amount. According to Clausius, the change in entropy S of a system, when an amount of heat Q is *added* to it by a reversible† process at constant temperature, is given by

Entropy change

$$\Delta S = \frac{Q}{T}, \qquad \textbf{(15–8)}$$

where T is the kelvin temperature.

EXAMPLE 15–14 **Entropy change in melting.** An ice cube of mass 56 g is taken from a storage compartment at 0°C and placed in a paper cup. After a few minutes, exactly half of the mass of the ice cube has melted, becoming water at 0°C. Find the change in entropy of the ice/water.

APPROACH We consider the 56 g of water, initially in the form of ice, as our system. To determine the entropy change, we first must find the heat needed to melt the ice, which we do using the latent heat of fusion of water, $L = 333\,\text{kJ/kg}$ (Section 14–5).

SOLUTION The heat required to melt 28 g of ice (half of the 56-g ice cube) is

$$Q = mL = (0.028\,\text{kg})(333\,\text{kJ/kg}) = 9.3\,\text{kJ}.$$

The temperature remains constant in our process, so we can find the change in entropy from Eq. 15–8:

$$\Delta S = \frac{Q}{T} = \frac{9.3\,\text{kJ}}{273\,\text{K}} = 34\,\text{J/K}.$$

NOTE The change in entropy of the surroundings (cup, air) has not been computed.

The temperature in Example 15–14 was constant, so the calculation was easy. If the temperature varies during a process, a summation of the heat flow over the changing temperature can often be calculated using calculus or a computer. However, if the temperature change is not too great, a reasonable approximation can be made using the average value of the temperature, as indicated in the next Example.

EXAMPLE 15–15 **ESTIMATE** **Entropy change when mixing water.** A sample of 50.0 kg of water at 20.00°C is mixed with 50.0 kg of water at 24.00°C. Estimate the change in entropy.

APPROACH The final temperature of the mixture will be 22.00°C, since we started with equal amounts of water. We use the specific heat of water and the methods of calorimetry (Sections 14–3 and 14–4) to determine the heat transferred. Then we use the average temperature of each sample of water to estimate the entropy change ($\Delta Q/T$).

† Real processes are irreversible. Because entropy is a state variable, the change in entropy ΔS for an irreversible process can be determined by calculating ΔS for a reversible process between the same two states.