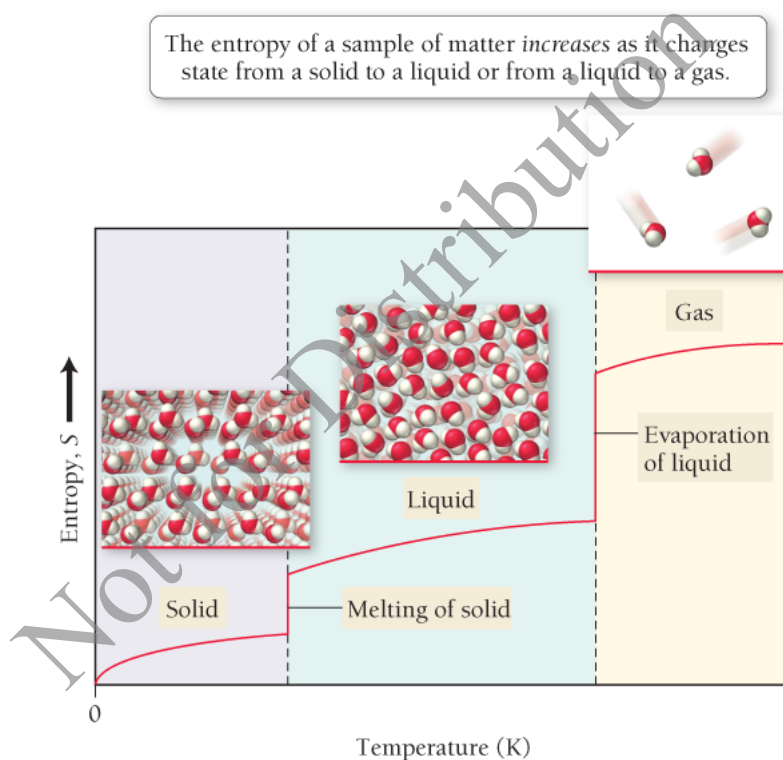


18.4: Entropy Changes Associated with State Changes

Key Concept Video Standard Molar Entropies

The entropy of a sample of matter *increases* as it changes state from a solid to a liquid or from a liquid to a gas (Figure 18.2). We first consider this idea conceptually, and then we turn to actually calculating the value of ΔS for this change. Recall that, in Chapter 9, we distinguished between a thermodynamic system and its surroundings. This distinction is useful in our discussion of entropy. For a change of state in a substance, we consider the substance to be the system. The surroundings are then the rest of the universe. Here, we focus on the entropy of the *system* undergoing the change of state (not the surroundings, which we address in Section 18.5).

Figure 18.2 Entropy and State Change



Entropy and State Change: The Concept

We can informally think of the increase in entropy in going from a solid to a gas or from a liquid to a gas by analogy with macroscopic disorder. The gaseous state is more disorderly than the liquid state, which is in turn more disorderly than the solid state. More formally, however, the differences in entropy are related to the number of energetically equivalent ways of arranging the particles in each state—there are more in the gas than in the liquid and more in the liquid than in the solid.

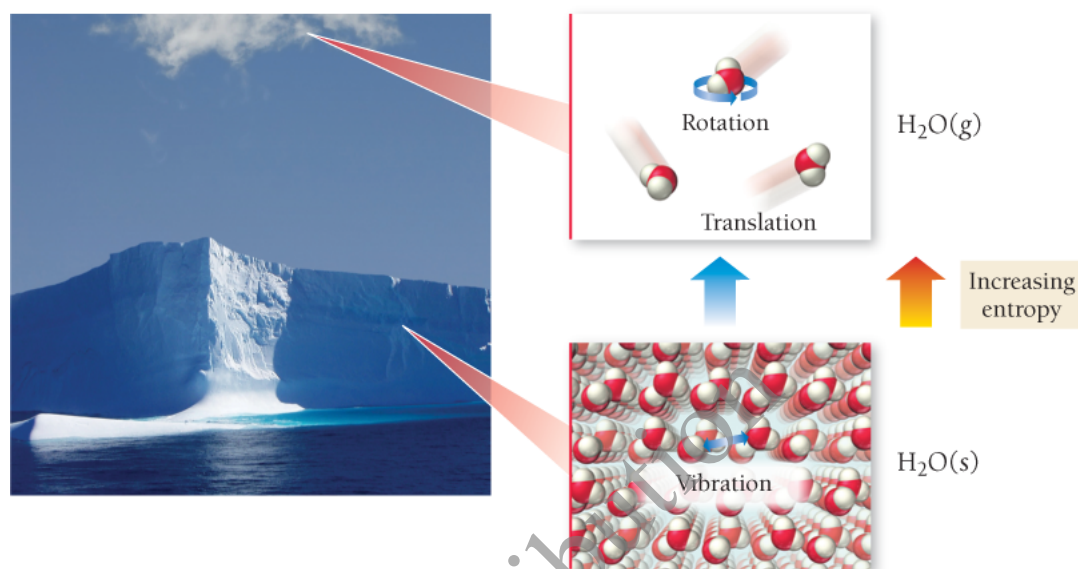
A gas has more energetically equivalent configurations because it has more ways to distribute its energy than a solid. The energy in a molecular solid consists largely of the vibrations between its molecules. If the same

substance is in its gaseous state, however, the energy can take the form of straight-line motions of the molecules (called translational energy) and rotations of the molecules (called rotational energy). In other words, when a solid sublimates into a gas, there are new “places” to put energy (Figure 18.3). The gas thus has more possible microstates (more energetically equivalent configurations) than the solid and therefore a greater entropy.

Figure 18.3 “Places” for Energy

In the solid state, energy is contained largely in the vibrations between molecules. In the gas state, energy can be contained in both the straight-line motion of molecules (translational energy) and the rotation of molecules (rotational energy).

Additional “Places” for Energy



We can now predict the sign of ΔS for processes involving changes of state (or phase). In general, entropy increases ($\Delta S > 0$) for each of the following:

- the phase transition from a solid to a liquid
- the phase transition from a solid to a gas
- the phase transition from a liquid to a gas
- an increase in the number of moles of a gas during a chemical reaction

Example 18.1 Predicting the Sign of Entropy Change

Predict the sign of ΔS for each process.

- $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$
- Solid carbon dioxide sublimates.
- $2\text{N}_2\text{O}(g) \rightarrow 2\text{N}_2(g) + \text{O}_2(g)$

SOLUTION

- ΔS is negative.
- Because a solid has a lower entropy than a gas, the entropy increases and ΔS is positive.
- Because the number of moles of gas increases, the entropy increases and ΔS is positive.

FOR PRACTICE 18.1 Predict the sign of ΔS for each process.

a. the boiling of water

- a. the boiling of water
- b. $I_2(g) \rightarrow I_2(s)$
- c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Entropy and State Changes: The Calculation

We have just seen how the entropy of a system increases with the transition from a solid to a liquid and from a liquid to a gas. We can calculate the actual changes in entropy that occur in the system during these state transitions. Recall from [Sections 11.5](#) and [11.6](#) that a change in state is accompanied by an exchange of heat between the system and surroundings. For example, melting and vaporization are endothermic (they absorb heat from the surroundings), while fusion and condensation are exothermic (they give off heat to the surroundings).

The definition of entropy that we introduced in [Section 18.3](#) ($S = k \ln W$) shows how entropy is related to the distribution of energy among the particles that compose matter. On a macroscopic scale, we can define the change in entropy that occurs when a system exchanges a quantity of heat (q) with its surroundings at a constant temperature (T) with the following equation:

[18.1]

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ (constant temperature)}$$

In this equation, ΔS is the entropy change of the system, q_{rev} is the heat exchanged with the surroundings in a *reversible* process (more on this to come), and T is the temperature in K. The temperature must be constant throughout the change—the process must be *isothermal*. Let's address two important concepts related to this equation, the units of entropy and reversible processes.

Units of Entropy

In [Section 18.3](#), we saw that the units of entropy are J/K. We can now better understand these units. Entropy is a measure of energy dispersal per unit temperature and therefore has the units of energy (J) over temperature (K). For example, when a substance melts (an endothermic process), it absorbs a certain amount of energy from the surroundings. That energy becomes dispersed into the system (as the substance changes state from a solid to a liquid) and the entropy of the substance increases. The change in entropy is related to the amount of energy the substance absorbs (units of J) divided by the temperature of the substance (units of K).

Reversible Processes

A **reversible process** reverses direction upon an infinitesimally small change in some property. The melting of ice when the ice and its surroundings are both at exactly 0 °C is an example of a reversible process. An infinitesimally small *removal* of heat reverses the melting and causes freezing instead. An infinitesimally small *addition* of heat causes the melting to resume. All reversible processes are in a constant state of equilibrium and represent highly idealized conditions. In contrast, the melting of ice that happens when we set an ice cube on a countertop at room temperature is *irreversible*. In this case, the countertop and the surrounding air are at 25.0 °C and an infinitesimally small removal of heat does not reverse the melting.

We can use [Equation 18.1](#) to calculate the change in the entropy of a system that undergoes a state change. For example, when ice melts at its melting point, the heat exchanged with the surroundings is ΔH_{fus} and the temperature is 273 K:

$$\begin{aligned} q_{\text{rev}} &= \Delta H_{\text{fus}} = 6.02 \text{ kJ/mol} \\ T &= 273 \text{ K} \end{aligned}$$

We substitute these quantities into [Equation 18.1](#) to determine the change in entropy of the system when 1 mol of ice melts at its melting point:

$$\begin{aligned}
 \Delta S &= \frac{q_{\text{rev}}}{T} \\
 &= \frac{(1 \text{ mol}) \frac{6.02 \times 10^3 \text{ J}}{\text{mol}}}{273 \text{ K}} \\
 &= 22.1 \text{ J/K}
 \end{aligned}$$

The value of ΔS is positive, as we would expect for a transition from solid to liquid.

Example 18.2 Calculating ΔS for a Change of State

Calculate the change in entropy that occurs in the system when 25.0 g of water condenses from a gas to a liquid at the normal boiling point of water (100.0 °C).

SOLUTION

Because the condensation is occurring at the boiling point of water and the temperature is constant, you can use Equation 18.1 to calculate the change in entropy of the system.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Gather the necessary quantities. Look up the value of the enthalpy of vaporization for water at its boiling point in Table 11.7. The enthalpy of condensation is the same in value but opposite in sign. Calculate the temperature in K.

$$\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$$

$$\Delta H_{\text{condensation}} = -40.7 \text{ kJ/mol}$$

$$\begin{aligned}
 T(\text{K}) &= T(^{\circ}\text{C}) + 273.15 \\
 &= 100.0 + 273.15 \\
 &= 373.15 \text{ K}
 \end{aligned}$$

Substitute into Equation 18.1 to calculate the change in entropy for the system.

$$\begin{aligned}
 \Delta S &= \frac{q_{\text{rev}}}{T} \\
 &= \frac{25.0 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times \left(\frac{-40.7 \times 10^3 \text{ J}}{\text{mol}} \right)}{373.15 \text{ K}} \\
 &= -151 \text{ J/K}
 \end{aligned}$$

CHECK The answer has the correct units for entropy (J/K). The answer is negative, as you would expect for the condensation of a gas to a liquid.

FOR PRACTICE 18.2 Calculate the change in entropy that occurs in the system when 10.0 g of acetone ($\text{C}_3\text{H}_6\text{O}$) vaporizes from a liquid to a gas at its normal boiling point (56.1 °C).

Not for Distribution

Not for Distribution