

1.3: Entropy Changes Associated with State Changes

Phase Changes

When a system receives an amount of energy q at a constant temperature, T , the entropy increase ΔS is defined by the following equation. Hence, the magnitude of ΔS for a reversible process such as a phase change is calculated

$$\Delta S = \frac{q_{rev}}{T} \quad (1.3.1)$$

with the temperature in Kelvin. Since entropy changes are much smaller than enthalpy changes, they are usually reported in $\text{J K}^{-1} \text{mol}^{-1}$.

Examples of reversible processes are

- **Boiling:** As temperature is constant,

$$\Delta S = \frac{\Delta H_{vap}}{T} \quad (1.3.2)$$

- **Melting:** As temperature is constant,

$$\Delta S = \frac{\Delta H_{fus}}{T} \quad (1.3.3)$$

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are significantly more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev} , and the second law may be stated as the following:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} \\ &= \Delta S_{sys} + \frac{q_{surr}}{T} \end{aligned} \quad (1.3.4)$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 1.3.1.

✓ Example 1.3.1: Will Ice Spontaneously Melt?

The entropy change for the process



is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at $-10.00 \text{ }^\circ\text{C}$? Is it spontaneous at $+10.00 \text{ }^\circ\text{C}$?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, $\Delta S_{sys} = 22.1 \text{ J/K}$ and $q_{surr} = -6.00 \text{ kJ}$.

At $-10.00 \text{ }^\circ\text{C}$ (263.15 K), the following is true:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} \\ &= \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 \text{ J}}{263.15 \text{ K}} \\ &= -0.7 \text{ J/K} \end{aligned}$$

Since $S_{univ} < 0$, melting is nonspontaneous (*not* spontaneous) at $-10.0 \text{ }^\circ\text{C}$.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 \text{ J}}{283.15 \text{ K}} \\ &= +0.9 \text{ J/K}\end{aligned}$$

Since $S_{\text{univ}} > 0$, melting of ice is spontaneous at **10.00 °C**.

? Example 1.3.2

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ} ?

Answer

Entropy is a state function, and freezing is the opposite of melting. At -10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, -0.9 J/K.

Ice Melting

Ice melting provides an example in which entropy increases in a small system, a thermodynamic system consisting of the surroundings (the warm room) and the entity of glass container, ice, water which has been allowed to reach thermodynamic equilibrium at the melting temperature of ice. In this system, some heat (δQ) from the warmer surroundings at 298 K (25 °C; 77 °F) transfers to the cooler system of ice and water at its constant temperature (T) of 273 K (0 °C; 32 °F), the melting temperature of ice. The entropy of the system, which is $\delta Q/T$, increases by $\delta Q/273\text{K}$. The heat δQ for this process is the energy required to change water from the solid state to the liquid state, and is called the enthalpy of fusion, i.e. ΔH for ice fusion.

It is important to realize that the entropy of the surrounding room decreases less than the entropy of the ice and water increases: the room temperature of 298 K is larger than 273 K and therefore the ratio, (entropy change), of $\delta Q/298\text{K}$ for the surroundings is smaller than the ratio (entropy change), of $\delta Q/273\text{K}$ for the ice and water system. This is always true in spontaneous events in a thermodynamic system and it shows the predictive importance of entropy: the final net entropy after such an event is always greater than was the initial entropy.

As the temperature of the cool water rises to that of the room and the room further cools imperceptibly, the sum of the $\delta Q/T$ over the continuous range, “at many increments”, in the initially cool to finally warm water can be found by calculus. The entire miniature ‘universe’, i.e. this thermodynamic system, has increased in entropy. Energy has spontaneously become more dispersed and spread out in that ‘universe’ than when the glass of ice and water was introduced and became a ‘system’ within it.

✓ Example 1.3.3

Calculate entropy change when 36.0 g of ice melts at 273 K and 1 atm.

Solution

This is a directly application of Equation 1.3.3, which requires the enthalpy of fusion for this reaction and the temperature is already given. If you look up the enthalpy of fusion for ice, you would get a molar enthalpy of 6.01 kJ/mol.

$$\Delta S = \left(\frac{6.01 \text{ kJ mol}^{-1}}{273 \text{ K}} \right)$$

This is a molar value that needs to be scaled by the amount of the material (36 g). So a standard mass-to-moles conversion factor is needed (along with the molar mass of water - 18.01 g/mol).

$$\begin{aligned}\Delta S &= \left(\frac{6.01 \text{ kJ } \cancel{\text{mol}^{-1}}}{273 \text{ K}} \right) \left(\frac{36 \text{ g}}{18.01 \text{ g } \cancel{\text{mol}^{-1}}} \right) \\ &= 0.044 \text{ kJ/K}\end{aligned}$$

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