Section 72 – The Second Law of Thermodynamics

72-1. HI has a normal boiling point of –35.4°C, and its ΔH_{vap} is 21.16 kJ mol^{-1}. Calculate the molar entropy of vaporization (ΔS_{vap}).

Solution:

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\Delta S_{\text{vap}} = \frac{(21.16\ \text{kJ mol}^{-1})}{(-35.4 + 273.15)\text{K}}$$

$$\Delta S_{\text{vap}} = \frac{(21.16\ \text{kJ mol}^{-1})}{237.8\ \text{K}}$$

$$\Delta S_{vap} = 0.08898\ \text{kJ mol}^{-1}\ \text{K}^{-1}$$

Normally molar entropies of vaporization are in units of J mol^{-1} K^{-1}, but the answer can be readily converted to these units if needed:

$$\Delta S_{\text{vap}} = 0.08898\ \text{kJ mol}^{-1}\text{K}^{-1} \times \frac{(1000\ \text{J})}{1\ \text{kJ}}$$

$$\Delta S_{vap} = 88.98\ \text{J mol}^{-1}\ \text{K}^{-1}$$

72-2. What is the total entropy change (i.e., system plus surroundings) when 17.9 g of water (ΔH_{fus} =6.01 kJ mol^{-1}) freezes at 0.0°C in a freezer compartment whose temperature is held at -29.0 °C? Is this process spontaneous?

Solution:

Approach: we know that $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$. Thus we need to calculate both the entropy change of the water as it freezes at 0.00 °C (the ΔS_{sys}) and the entropy change of the freezer compartment (held at -29.0 °C) as it absorbs the heat lost by the water (the ΔS_{surr}), and then add them together. From experience, we know that water will freeze in a freezer, so we know that the process is spontaneous (and so our answer for ΔS_{total} ought to be positive).

Note that we are provided with the value for ΔH_{fus}, which is the heat change that occurs when water changes from solid to liquid. However, since in this problem we are asked about the water is changing from liquid to solid we need ΔH_{sol}, which is equal in magnitude but opposite in sign ($\Delta H_{sol} = -\Delta H_{fus}$).

The heat change of the system can be calculated as follows:

$$\Delta \text{H}_{\text{sys}} = -6.01\ \text{kJ mol}^{-1} \times \left(17.9\ \text{g} \times \frac{1\ \text{mol H}_2\text{O}}{18.015\ \text{g H}_2\text{O}}\right) \times \frac{1000\ \text{J}}{1\ \text{kJ}}$$

$$\Delta H_{sys} = -6.01 \text{ kJ mol}^{-1} \times (0.9936 \text{ mol } H_2O) \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\Delta H_{sys} = -5.97 \text{ x } 10^3 \text{ J}$$

Thus,

$$\Delta S_{sys} = \frac{\Delta H_{sys}}{T} = \frac{-5.97 \times 10^3 \text{ J}}{(273.15 \text{ K})} = -21.9 \text{ J K}^{-1}$$

The sign of ΔS_{sys} is negative, as we would expect since the water is undergoing a phase change from liquid to solid.

The heat change of the surroundings would be equal in magnitude but opposite in sign to the heat change of the system, and so we can calculate ΔS_{surr} as follows:

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-(-5.97 \times 10^3 \text{ J})}{(273.15 - 29.0) \text{ K}} = \frac{5.97 \times 10^3 \text{ J}}{(244.2) \text{ K}} = 24.4 \text{ J K}^{-1}$$

Now we can calculate the total entropy change:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{total} = -21.9 \text{ J K}^{-1} + 24.4 \text{ J K}^{-1} = 2.5 \text{ J K}^{-1}.$$

The total entropy change is positive, which indicates that this is a spontaneous process. This answer "makes sense" since, from experience, we know that water will freeze in a freezer, so we know that the process is spontaneous.

72-3. What is the total entropy change (i.e. system plus surroundings) when 68.2 g of ice (ΔH_{fus} = 6.01 kJ mol^{-1}) melts at 0.0 ºC on a counter in the kitchen whose temperature is 20.0 ºC? Is this process spontaneous?

Solution:

The approach is the same as the previous question.

The heat change of the system can be calculated as follows:

$$\Delta H_{sys} = 6.01 \text{ kJ mol}^{-1} \times \left(68.2 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O}\right) \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\Delta H_{sys} = 6.01 \text{ kJ mol}^{-1} \times (3.79 \text{ mol } H_2O) \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\Delta H_{sys} = 2.28 \text{ x } 10^4 \text{ J}$$

Thus,

$$\Delta S_{sys} = \frac{\Delta H_{sys}}{T} = \frac{2.28 \times 10^4 \text{ J}}{(273.15 \text{ K})} = 83.5 \text{ J K}^{-1}$$

The heat change of the surroundings would be equal in magnitude but opposite in sign to the heat change of the system, and so we can calculate ΔS_{surr} as follows:

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-(2.28 \times 10^4 \text{ J})}{(273.15 + 20.0) \text{ K}} = \frac{-2.28 \times 10^4 \text{ J}}{(293.2) \text{ K}} = -77.8 \text{ J K}^{-1}$$

Now we can calculate the total entropy change:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$
$$\Delta S_{total} = 83.5 \text{ J K}^{-1} - 77.8 \text{ J K}^{-1} = 5.7 \text{ J K}^{-1}.$$

The total entropy change is positive, which indicates that this is a spontaneous process. This answer "makes sense" since, from experience, we know that ice will melt on a counter top in a kitchen (at room temperature), so we know that the process is spontaneous.

72-4. What is the total entropy change when 1.76 mol of water ($\Delta H_{fus} = 6.01 \text{ kJ mol}^{-1}$) melts at 0.0 ºC outside in Winnipeg when it is -35.0 ºC outside? Is this process spontaneous?

Solution:

The approach is the same as the previous questions.

The heat change of the system can be calculated as follows:

$$\Delta H_{sys} = 6.01 \text{ kJ mol}^{-1} \times (1.76 \text{ mol}) \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\Delta H_{sys} = 1.06 \text{ x } 10^4 \text{ J}$$

Thus,

$$\Delta S_{sys} = \frac{\Delta H_{sys}}{T} = \frac{1.06 \times 10^4 \text{ J}}{(273.15 \text{ K})} = 38.8 \text{ J K}^{-1}$$

The heat change of the surroundings would be equal in magnitude but opposite in sign to the heat change of the system, and so we can calculate ΔS_{surr} as follows:

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-(1.06 \times 10^4 \text{ J})}{(273.15 - 35.0) \text{ K}} = \frac{-1.06 \times 10^4 \text{ J}}{238.2 \text{ K}} = -44.5 \text{ J K}^{-1}$$

Now we can calculate the total entropy change:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{total} = 38.8 \text{ J K}^{-1} - 44.5 \text{ J K}^{-1} = -5.7 \text{ J K}^{-1}.$$

The total entropy change is negative, which indicates that this is a NOT spontaneous process. This answer "makes sense" since, from experience, we know that ice will NOT melt outside when it is that cold out, and so the process is not spontaneous.