

7.2: Calculation of ΔS_{surr}

While the entropy of the system can be broken down into simple cases and calculated using the formulas introduced above, the entropy of the surroundings does not require such a complicated treatment, and it can always be calculated as:

$$\Delta S^{\text{surr}} = \frac{Q_{\text{surr}}}{T_{\text{surr}}} = \frac{-Q_{\text{sys}}}{T_{\text{surr}}},$$

or, in differential form:

$$dS^{\text{surr}} = \frac{dQ_{\text{surr}}}{T_{\text{surr}}} = \frac{-dQ_{\text{sys}}}{T_{\text{surr}}},$$

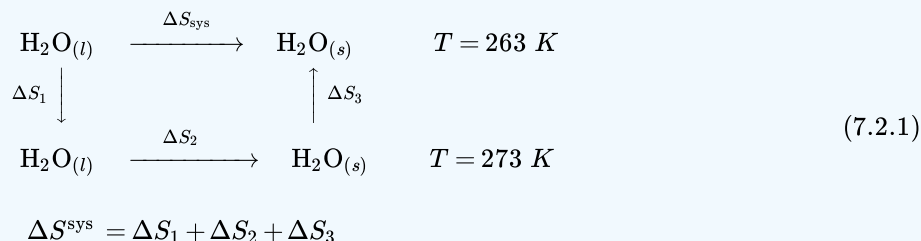
where the substitution $Q_{\text{surr}} = -Q_{\text{sys}}$ can be performed regardless of whether the transformation is reversible or not. In other words, the surroundings always absorb heat reversibly. To justify this statement, we need to restrict the analysis of the interaction between the system and the surroundings to just the vicinity of the system itself. Outside of a generally restricted region, the rest of the universe is so vast that it remains untouched by anything happening inside the system.¹ To facilitate our comprehension, we might consider a system composed of a beaker on a workbench. We can then consider the room that the beaker is in as the immediate surroundings. To all effects, the beaker+room combination behaves as a system isolated from the rest of the universe. The room is obviously much larger than the beaker itself, and therefore every energy production that happens in the system will have minimal effect on the parameters of the room. For example, an exothermal chemical reaction occurring in the beaker will not affect the overall temperature of the room substantially. When we study our reaction, T_{surr} will be constant, and the transfer of heat from the reaction to the surroundings will happen at reversible conditions.

? Exercise 7.2.1

Calculate the changes in entropy of the universe for the process of 1 mol of supercooled water, freezing at -10°C , knowing the following data: $\Delta_{\text{fus}}H = 6 \text{ kJ/mol}$, $C_P^{\text{H}_2\text{O}(l)} = 76 \text{ J/(mol K)}$, $C_P^{\text{H}_2\text{O}(s)} = 38 \text{ J/(mol K)}$, and assuming both C_P to be independent on temperature.

Answer

ΔS^{sys} for the process under consideration can be calculated using the following cycle:



ΔS_1 and ΔS_3 are the isobaric heating and cooling processes of liquid and solid water, respectively, and can be calculated filling the given data into [Equation 7.1.12](#). ΔS_2 is a phase change (isothermal process) and can be calculated translating [Equation 7.1.6](#) to the freezing transformation. Overall:

$$\begin{aligned}
 \Delta S^{\text{sys}} &= \int_{263}^{273} \frac{C_P^{\text{H}_2\text{O}(l)}}{T} dT + \frac{-\Delta_{\text{fus}}H}{273} + \int_{273}^{263} \frac{C_P^{\text{H}_2\text{O}(s)}}{T} dT \\
 &= 76 \ln \frac{273}{263} - \frac{6 \times 10^3}{273} + 38 \ln \frac{263}{273} = -20.6 \text{ J/K}.
 \end{aligned} \tag{7.2.2}$$

Don't be confused by the fact that ΔS^{sys} is negative. This is not the entropy of the universe! Hence it tells nothing about spontaneity! We can now calculate ΔS^{surr} from Q_{sys} , noting that we can calculate the enthalpy around the same cycle in [Equation 7.2.1](#). To do that, we already have $\Delta_{\text{fus}}H$ from the given data, and we can calculate ΔH_1 and ΔH_3 using [Equation 2.3.4](#).

$$\begin{aligned}
 Q^{\text{sys}} = \Delta H &= \int_{263}^{273} C_P^{\text{H}_2\text{O}(l)} dT + (-\Delta_{\text{fus}}H) + \int_{273}^{263} C_P^{\text{H}_2\text{O}(s)} dT \\
 &= 76 \times 10^{-3} (273 - 263) - 6 + 38 \times 10^{-3} (263 - 273) \\
 &= -5.6 \text{ kJ.}
 \end{aligned} \tag{7.2.3}$$

$$\Delta S^{\text{surr}} = \frac{-Q_{\text{sys}}}{T} = \frac{5.6 \times 10^3}{263} = +21.3 \text{ J/K.}$$

Bringing 7.2.1 and 7.2.3 results together, we obtain:

$$\Delta S^{\text{universe}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}} = -20.6 + 21.3 = +0.7 \text{ J/K.}$$

Since the entropy changes in the universe are positive, the process is spontaneous, as expected.

1. Even if we think at the most energetic event that we could imagine happening here on earth—such as the explosion of an atomic bomb or the hit of a meteorite from outer space—such an event will not modify the average temperature of the universe by the slightest degree.

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