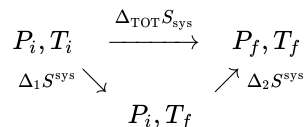


7.1: Calculation of ΔS_{sys}

In general ΔS^{sys} can be calculated using either its [Definition: Entropy](#), or its differential formula, [Equation 6.1.5](#). In practice, it is always convenient to keep in mind that entropy is a state function, and as such it does not depend on the path. For this reason, we can break every transformation into elementary steps, and calculate the entropy on any path that goes from the initial state to the final state, such as, for example:



$$\Delta_{\text{TOT}} S^{\text{sys}} = \Delta_1 S^{\text{sys}} + \Delta_2 S^{\text{sys}},$$

with $\Delta_1 S^{\text{sys}}$ calculated at constant P , and $\Delta_2 S^{\text{sys}}$ at constant T . The most important elementary steps from which we can calculate the entropy resemble the prototypical processes for which we calculated the energy in [section 3.1](#).

Entropy in isothermal processes

- For an ideal gas at constant temperature $\Delta U = 0$, and $Q_{\text{REV}} = -W_{\text{REV}}$. Using the formula for W_{REV} in either [Equation \(??\)](#) or [Equation \(??\)](#), we obtain:

$$\Delta S^{\text{sys}} = \int_i^f \frac{dQ_{\text{REV}}}{T} = \frac{-W_{\text{REV}}}{T} = \frac{nRT \ln \frac{V_f}{V_i}}{T} = nR \ln \frac{V_f}{V_i},$$

or, similarly:

$$\Delta S^{\text{sys}} = nR \ln \frac{P_i}{P_f}.$$

- A phase change is a particular case of an isothermal process that does not follow the formulas introduced above since an ideal gas never liquefies. The entropy associated with a phase change at constant pressure can be calculated from its definition, remembering that $Q_{\text{rev}} = \Delta H$. For example for vaporizations:

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_B},$$

with $\Delta_{\text{vap}} H$ being the enthalpy of vaporization of a substance, and T_B its boiling temperature.

It is experimentally observed that the entropies of vaporization of many liquids have almost the same value of:

$$\Delta_{\text{vap}} S \approx 10.5R, \quad (7.1.1)$$

which corresponds in SI to the range of about 85–88 J/(mol K). This simple rule is named **Trouton's rule**, after the French scientist that discovered it, Frederick Thomas Trouton (1863-1922).

? Exercise 7.1.1

Calculate the standard entropy of vaporization of water knowing $\Delta_{\text{vap}} H_{\text{H}_2\text{O}}^\ominus = 44 \text{ kJ/mol}$, as calculated in [Exercise 4.3.1](#).

Answer

Using [Equation 7.1.1](#)—and knowing that at standard conditions of $P^\ominus = 1 \text{ bar}$ the boiling temperature of water is 373 K—we calculate:

$$\Delta_{\text{vap}} S_{\text{H}_2\text{O}}^\ominus = \frac{44 \times 10^3 \text{ J/mol}}{373 \text{ K}} = 118 \text{ J/(mol K)}.$$

The entropy of vaporization of water is far from Trouton's rule range of 85–88 J/(mol K) because of the hydrogen bond interactions between its molecules. Other similar exceptions are ethanol, formic acid, and hydrogen fluoride.

Entropy in adiabatic processes

Since adiabatic processes happen without the exchange of heat, $dQ = 0$, it would be tempting to think that $\Delta S^{\text{sys}} = 0$ for every one of them. A transformation at constant entropy (isentropic) is always, in fact, a reversible adiabatic process. However, the opposite case is not always true, and an irreversible adiabatic transformation is usually associated with a change in entropy. To explain this fact, we need to recall that the definition of entropy includes the heat exchanged at reversible conditions only. Therefore, for irreversible adiabatic processes $\Delta S^{\text{sys}} \neq 0$. The calculation of the entropy change for an irreversible adiabatic transformation requires a substantial effort, and we will not cover it at this stage. The situation for adiabatic processes can be summarized as follows:

$$\begin{array}{ll} \text{reversible:} & \frac{dQ_{\text{REV}}}{T} = 0 \longrightarrow \Delta S^{\text{sys}} = 0 \quad (\text{isentropic}), \\ \text{irreversible:} & \frac{dQ_{\text{IRR}}}{T} = 0 \longrightarrow \Delta S^{\text{sys}} \neq 0. \end{array}$$

Entropy in isochoric processes

We can calculate the heat exchanged in a process that happens at constant volume, Q_V , using [Equation 2.3.2](#). Since the heat exchanged at those conditions equals the energy ([Equation 3.1.7](#)), and the energy is a state function, we can use Q_V regardless of the path (reversible or irreversible). The entropy associated with the process will then be:

$$\Delta S^{\text{sys}} = \int_i^f \frac{dQ_{\text{REV}}}{T} = \int_i^f nC_V \frac{dT}{T},$$

which, assuming C_V independent of temperature and solving the integral on the right-hand side, becomes:

$$\Delta S^{\text{sys}} \approx nC_V \ln \frac{T_f}{T_i}.$$

Entropy in isobaric processes

Similarly to the constant volume case, we can calculate the heat exchanged in a process that happens at constant pressure, Q_P , using [Equation 2.3.4](#). Again, similarly to the previous case, Q_P equals a state function (the enthalpy), and we can use it regardless of the path to calculate the entropy as:

$$\Delta S^{\text{sys}} = \int_i^f \frac{dQ_{\text{REV}}}{T} = \int_i^f nC_P \frac{dT}{T},$$

which, assuming C_P independent of temperature and solving the integral on the right-hand side, becomes:

$$\Delta S^{\text{sys}} \approx nC_P \ln \frac{T_f}{T_i}.$$

This page titled [7.1: Calculation of \$\Delta S^{\text{sys}}\$](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Roberto Peverati](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.