7.3: Clausius Theorem

By replacing Equation 7.2.2 into 7.2 we can write the differential change in the entropy of the system as:

$$dS^{\text{sys}} = dS^{\text{universe}} - dS^{\text{surr}} = dS^{\text{universe}} + \frac{đQ_{\text{sys}}}{T}.$$

According to the second law, for any spontaneous process $dS^{\text{universe}} \geq 0$, and therefore, replacing it into Equation $7.3.1$:

$$dS^{\text{sys}} \geq \frac{đQ}{T},$$

which is the mathematical expression of the so-called **Clausius theorem**. Eq. $7.3.2$ distinguishes between three conditions:

$$\begin{aligned} dS^{\text{sys}} > \frac{đQ}{T} \qquad & \text{spontaneous, irreversible transformation} \\ dS^{\text{sys}} = \frac{đQ}{T} \qquad & \text{reversible transformation} \\ dS^{\text{sys}} < \frac{đQ}{T} \qquad & \text{non-spontaneous, irreversible transformation,} \end{aligned}$$

Clausius theorem provides a useful criterion to infer the spontaneity of a process, especially in cases where it's hard to calculate $\Delta S^{\text{universe}}$. Eq. $7.3.2$ requires knowledge of quantities that are dependent on the system exclusively, such as the difference in entropy, the amount of heat that crosses the boundaries, and the temperature at which the process happens.[1] If a process produces more entropy than the amount of heat that crosses the boundaries divided by the absolute temperature, it will be spontaneous. Vice versa, if the entropy produced is smaller than the amount of heat crossing the boundaries divided by the absolute temperature, the process will be non-spontaneous. The equality holds for systems in equilibrium with their surroundings, or for reversible processes since they happen through a series of equilibrium states. Measuring or calculating these quantities might not always be the simplest of calculations. We will return to the Clausius theorem in the next chapter when we seek more convenient indicators of spontaneity.

1. In cases where the temperature of the system changes throughout the process, T is just the (constant) temperature of its immediate surroundings, T_{surr}, as explained in section 7.2.