9.6: Entropy Changes for A Reversible Process

Let us consider a closed system that undergoes a reversible change while in contact with its surroundings. Since the change is reversible, the portion of the surroundings that exchanges heat with the system is at the same temperature as the system: $T = \hat{T}$. From $q^{rev} = -\hat{q}^{rev}$ and the definition, $dS = dq^{rev}/T$, the entropy changes are

$$\Delta S = q^{rev}/T$$

and

$$\Delta \hat{S} = \hat{q}^{rev}/T = -q^{rev}/T = -\Delta S$$

Evidently, for any reversible process, we have

$$\Delta S_{universe} = \Delta S + \Delta \hat{S} = 0$$

Note that these ideas are not sufficient to prove that the converse is true. From only these ideas, we cannot prove that $\Delta S_{universe} = 0$ for a process means that the process is reversible; it remains possible that there could be a spontaneous process for which $\Delta S_{universe} = 0$. However, our entropy-based statement of the second law does assert that the converse is true, that $\Delta S_{universe} = 0$ is necessary and sufficient for a process to be reversible.

In the next section, we use the machine-based statement of the second law to show that $\Delta S \geq 0$ for any spontaneous process in an isolated system. We introduce heuristic arguments to infer that $\Delta S = 0$ is not possible for a spontaneous process in an isolated system. From this, we show that $\Delta S_{universe} > 0$ for any spontaneous process and hence that $\Delta S_{universe} = 0$ is not possible for any spontaneous process. We conclude that $\Delta S_{universe} = 0$ is sufficient to establish that the corresponding process is reversible.