6.3: The Second Law of Thermodynamics

Now we can consider an isolated system undergoing a cycle composed of an irreversible forward transformation ($1 \rightarrow 2$) and a reversible backward transformation ($2 \rightarrow 1$), as in Figure $6.3.1$.

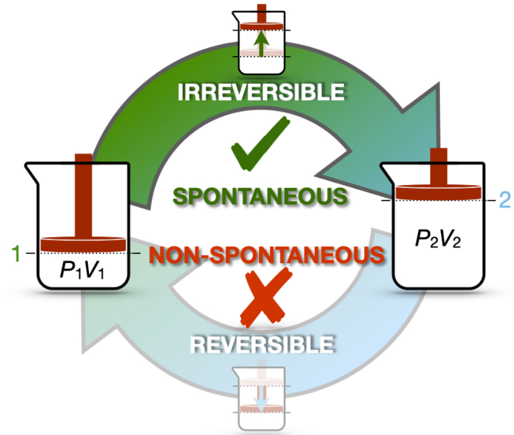

Figure $6.3.1$: Spontaneous and Non-Spontaneous Transformations in a Cycle.

This cycle is similar to the cycle depicted in Figure $6.3.1$ for the Joule's expansion experiment. In this case, we have an intuitive understanding of the spontaneity of the irreversible expansion process, while the non-spontaneity of the backward compression. Since the cycle has at least one irreversible step, it is overall irreversible, and we can calculate:

$$\oint \frac{đQ_{\mathrm{IRR}}}{T} = \int_1^2 \frac{đQ_{\mathrm{IRR}}}{T} + \int_2^1 \frac{đQ_{\mathrm{REV}}}{T}.$$

We can then use Clausius inequality (Equation 6.2.4) to write:

$$\int_1^2 \frac{đQ_{\mathrm{IRR}}}{T} + \int_2^1 \frac{đQ_{\mathrm{REV}}}{T} < 0,$$

which can be rearranged as:

$$\underbrace{\int_1^2 \frac{đQ_{\mathrm{REV}}}{T}}_{\int_1^2 dS = \Delta S} > \underbrace{\int_1^2 \frac{đQ_{\mathrm{IRR}}}{T}}_{=0}, \tag{6.3.1}$$

where we have used the fact that, for an isolated system (the universe), $đQ_{\mathrm{IRR}} = 0$. Equation $6.3.1$ can be rewritten as:

$$\Delta S > 0, \tag{6.3.2}$$

which proves that for any irreversible process in an isolated system, the entropy is increasing. Using Equation $6.3.2$ and considering that the only system that is truly isolated is the universe, we can write a concise statement for a new fundamental law of thermodynamics:

Definition: Second Law of Thermodynamics

For any spontaneous process, the entropy of the universe is increasing.