6.1: Entropy

Let's return to the definition of efficiency of a Carnot cycle and bring together eqs. 5.3.2 and 5.3.3:

$$\varepsilon = 1 + \frac{Q_3}{Q_1} = 1 - \frac{T_l}{T_h}.$$

Simplifying this equality, we obtain:

$$\frac{Q_3}{T_l} = -\frac{Q_1}{T_h}, \tag{6.1.1}$$

or alternatively:

$$\frac{Q_3}{T_l} + \frac{Q_1}{T_h} = 0. \tag{6.1.2}$$

The left hand side of Equation 6.1.2 contains the sum of two quantities around the Carnot cycle, each calculated as $\frac{Q_{\text{REV}}}{T}$, with Q_{REV} being the heat exchanged at reversible conditions (recall that according to Definition: Carnot Cycle each transformation in a Carnot cycle is reversible). Equation 6.1.1 can be generalized to a sequence of connected Carnot cycles joining more than two isotherms by taking the summation across different temperatures:

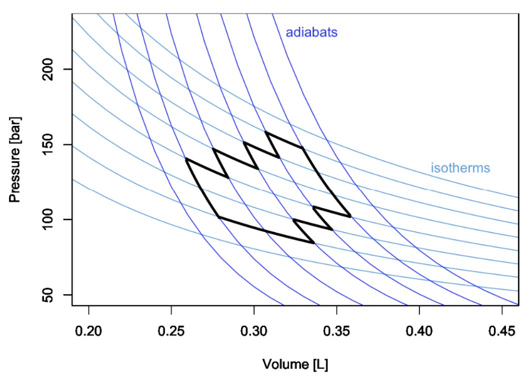

Figure 6.1.1

$$\sum_i \frac{Q_{\text{REV}}}{T_i} = 0, \tag{6.1.3}$$

where the summation happens across a sequence of Carnot cycles that connects different temperatures. Eqs. \label{6.1.3} and 6.1.3 show that for a Carnot cycle—or a series of connected Carnot cycles—there exists a conserved quantity obtained by dividing the heat associated with each reversible stage and the temperature at which such heat is exchanged. If a quantity is conserved around a cycle, it must be independent on the path, and therefore it is a state function. Looking at similar equations, Clausius introduced in 1865 a new state function in thermodynamics, which he decided to call entropy and indicate with the letter S:

Definition: Entropy

$$S = \frac{Q_{\text{REV}}}{T}.$$

We can use the new state function to generalize Equation 6.1.3 to any reversible cycle in a PV-diagram by using the rules of calculus. First, we will slice S into an infinitesimal quantity:

$$dS = \frac{đQ_{\text{REV}}}{T},$$

then we can extend the summation across temperatures of Equation 6.1.3 to a sum over infinitesimal quantities—that is the integral —around the cycle:

$$\oint dS = \oint \frac{đQ_{\mathrm{REV}}}{T} = 0.$$