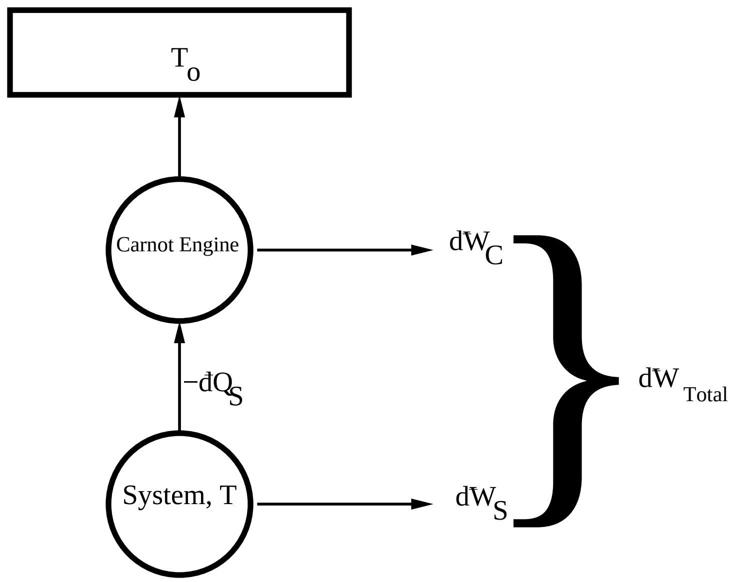
THE CLAUSIUS INEQUALITY AND THE MATHEMATICAL STATEMENT OF THE SECOND LAW

CHEMISTRY 213B

Here is a summary of the proof of the Clausius inequality given in class.



where C is a reversible Carnot engine which takes heat $-đQ_s$ from a part of the system at temperature T, produces work, $đW_c$, in the surroundings, and gives the remaining heat to a reservoir at temperature T_0. While this happens, the system absorbs heat $đQ_s$ and produces work $đW_s$.

From our definition of efficiency and the fact that the efficiencies of all reversible Carnot engine are the same (cf. previous handout), we have:

$$đW_c = -\eta_c đQ_s = \left[\frac{T_o}{T} - 1\right] đQ_s. \qquad (1)$$

From Thompson's principle and Eq. (1), it follows that

$$W_{Total} = \oint đW_s + đW_c = \oint đW_s + \left[\frac{T_o}{T} - 1\right] đQ_s \le 0. \qquad (2)$$

This inequality must hold if the process is to proceed as written. Now we integrate Eq. (2) around one cycle of the system (reversible or not) and use the fact that the system's energy is conserved; i.e.,

$$\oint đW_s = \oint đQ_s.$$

After a little algebra, this gives:

$$\oint \frac{đQ_s}{T} \le 0, \tag{3}$$

where the constant, positive multiplicative factor, T_0, has been dropped. This is the Clausius inequality.

Equation (3) holds for **any** spontaneous process which can occur in the system; although, all irreversible processes will require a net work input in order to run in the configuration depicted above. The inequality in Thompson's principle, cf. the last handout, becomes an equality only for reversible processes (no matter what the path) and thus Eq. (3) becomes:

$$0 = \oint \frac{đQ_{rev}}{T} \equiv \oint dS \tag{4}$$

where the entropy is defined along any reversible path (Eq. (4) is a proof that it is a state function) through

$$dS \equiv \frac{đQ_{rev}}{T} \tag{5}$$

Proof that $dS \ge \frac{đQ}{T}$

Consider some process whereby the system changes from state A to B along path I; it may be irreversible. After the process is finished, the system is restored to its initial state (A) along a reversible path II. If we apply the Clausius inequality to this cycle, we have

$$\int_{A,pathI}^{B} \frac{đQ_I}{T} + \int_{B,pathII}^{A} \frac{đQ_{rev}}{T} \le 0. \tag{1}$$

Since path II is reversible, the process can be carried out in reverse (*This is not necessarily true for path I*) and thus:

$$\int_{B,pathII}^{A} \frac{đQ_{rev}}{T} = -\int_{A,pathII}^{B} \frac{đQ_{rev}}{T} = -\Delta S_{A\to B} \tag{2}$$

By using Eq. (2) in Eq. (1) we conclude that

$$\Delta S_{A\to B} \ge \int_{A}^{B} \frac{đQ_I}{T},$$

or for infinitesimal changes

$$dS \ge \frac{đQ}{T}.$$

Note that the equality holds only for reversible processes.