9.23: The Reversible Work is the Minimum Work at Constant Tˆ

The Clausius inequality leads to an important constraint on the work that can be done on a system during a spontaneous process in which the temperature of the surroundings is constant. As we discuss in Section 9.7, the initial state of the spontaneous process cannot be a true equilibrium state. In our present considerations, we assume that the initial values of all the state functions of the spontaneously changing system are the same as those of a true equilibrium system. Likewise, we assume that the final state of the spontaneously changing system is either a true equilibrium state or a state whose thermodynamic functions have the same values as those of a true equilibrium system.

From the first law applied to any spontaneous process in a closed system, we have $\Delta E^{rev} = \Delta E^{spon}$ and $q^{rev} + w^{rev} = q^{spon} + w^{spon}$. Since the temperature of the system and its surroundings are equal and constant for the reversible process, we have $q^{rev} = T\Delta S = \hat{T}\Delta S$. So long as the temperature of the surroundings is constant, we have $q^{spon} < \hat{T}\Delta S$ for the spontaneous process. It follows that

$$\hat{T}\Delta S + w^{rev} - w^{spon} = q^{spon} < \hat{T}\Delta S$$

so that

$$w^{rev} < w^{spon}$$

($\hat{T}$ constant)

A given isothermal process does the minimum possible amount of work on the system when it is carried out reversibly. (In Section 7.20, we find this result for the special case in which the only work is the exchange of pressure–volume work between an ideal gas and its surroundings.) Equivalently, a given isothermal process produces the maximum amount of work in the surroundings when it is carried out reversibly: Since $w^{rev} = -\hat{w}^{rev}$ and $w^{spon} = -\hat{w}^{spon}$, we have $-\hat{w}^{rev} < -\hat{w}^{spon}$ or

$$\hat{w}^{rev} > \hat{w}^{spon}$$