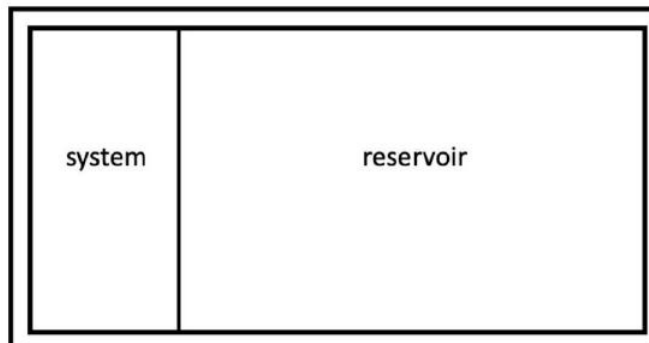


D: Energy Free to Do Work

An interesting question is how the work $\delta w'_{\text{actual}}$ that a system actually does on its surroundings differs from the work $\delta w'_{\text{rev}}$ that it would do if it operated in infinitesimal steps (i.e., reversibly). As in Appendix C, we consider an isolated composite system, comprising the working system and a large "reservoir". The difference is that we now posit perfect thermal contact ($T = T^r$) and any other contact that allows the system to do work.



An isolated composite system (with its rigid, impermeable and insulating boundaries represented by double lines according to convention) comprising our system of interest in contact with a "reservoir".

Since dE is independent of path

$$dE = \delta q_{\text{rev}} - \delta w'_{\text{rev}} = \delta q_{\text{actual}} - \delta w'_{\text{actual}} \quad (\text{D1})$$

Here δq continues to refer to heat taken up by the system while $\delta w'$ carries a prime to indicate that it refers to work done by the system (hence the negative sign in front of it). Rearranging,

$$\delta w'_{\text{actual}} - \delta w'_{\text{rev}} = \delta q_{\text{actual}} - \delta q_{\text{rev}} \quad (\text{D2})$$

By definition of entropy for each of the compartments,

$$dS = \frac{\delta q_{\text{rev}}}{T} \quad \text{and} \quad dS^r = \frac{-\delta q_{\text{actual}}}{T^r} = \frac{-\delta q_{\text{actual}}}{T} \quad (\text{D3})$$

Rearranging,

$$\delta q_{\text{actual}} - \delta q_{\text{rev}} = -T(dS + dS^r) \quad (\text{D4})$$

According to the 2nd Law for the isolated composite system

$$d(S + S^r) \geq 0 \quad (\text{D5})$$

where the equality applies only at equilibrium. Combining Equations D2, D4, and D5,

$$\delta w'_{\text{actual}} - \delta w'_{\text{rev}} \leq 0 \quad (\text{D6})$$

In other words, the actual path always produces less work than the reversible path (except at equilibrium where there is no distinction). Furthermore,

$$\begin{aligned} \delta w'_{\text{rev}} &= \delta q_{\text{rev}} - dE \\ &= -[dE - T^r dS] \\ &= -d(E - TS) \\ &= -dF \end{aligned} \quad (\text{D7})$$

Thus, at a fixed temperature, the maximum work that can be done **by a system on its surroundings** is done in a reversible process (i.e., against max resistance) and equals $-dF$ or the loss of the Helmholtz free energy of the system. In other words, F is a "free energy" in the sense that the change in F is the maximum energy available to do work at a given temperature. It is less than the change E by an amount equal to the change in TS .

When the contact between system and reservoir allows both PV work and other forms of work, we can isolate the latter by subtracting the former and then making use of Equation D7 to arrive at

$$\begin{aligned}\delta w'_{\text{rev-nonPV}} &= \delta w'_{\text{rev}} - p^r dV \\ &= -[dE + p^r dV - T^r dS] \\ &= -d(E + pV - TS) \\ &= -dG\end{aligned}\tag{D8}$$

In other words, at a given temperature and pressure, the maximum non-PV work that the system can do on its surroundings is done in a reversible process and equals $-dG$ or the loss of the Gibbs free energy of the system. This is useful for electrochemical work.

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