12.3: Helmholtz Free Energy

The Helmholtz free energy A is defined as

$$A = U - TS. \tag{12.3.1}$$

As when we first defined enthalpy, this doesn't seem to mean much until we write it in differential form:

$$dA = dU - TdS - SdT. \tag{12.3.2}$$

On substitution from equation 12.1.6 ($dU = TdS - PdV + \sum XdY$), this becomes

$$dA = -SdT - PdV + \sum XdY. \tag{12.3.3}$$

This tells us that in an isothermal process (in which $dT = 0$), the **increase** in the Helmholtz function of a system is equal to all the reversible work ($-PdV + \sum XdY$) done **on** it. Conversely, if a machine does any reversible work at constant temperature, the Helmholtz function decreases, and the **decrease** in the Helmholtz function is equal (if the temperature is held constant) to the reversible work (of all types) done **by** the machine. It is in this sense that the Helmholtz function is called the “free energy”. It is the energy, so to speak, that is free for the performance of external reversible (i.e. useful) work.