# 5.1: Basic Thermodynamics

The Helmholtz free energy $A(N, V, T)$ is a natural function of $N, V$ and $T$. The isothermal-isobaric ensemble is generated by transforming the volume $V$ in favor of the pressure $P$ so that the natural variables are $N$, $P$, and $T$ (which are conditions under which many experiments are performed, e.g., `standard temperature and pressure'. Performing a Legendre transformation of the Helmholtz free energy

$$\tilde{A}(N, P, T) = A(N, V(P), T) - V(P)\frac{\partial A}{\partial V}$$

But

$$\frac{\partial A}{\partial V} = -P$$

Thus,

$$\tilde{A}(N, P, T) = A(N, V(P), T) + PV \equiv G(N, P, T)$$

where $G(N, P, T)$ is the Gibbs free energy. The differential of $G$ is

$$dG = \left(\frac{\partial G}{\partial P}\right)_{N,T} dP + \left(\frac{\partial G}{\partial T}\right)_{N,P} dT + \left(\frac{\partial G}{\partial N}\right)_{P,T} dN$$

But from $G = A + PV$ , we have

$$dG = dA + PdV + VdP$$

but $dA = -SdT - PdV + \mu dN$ , thus

$$dG = -SdT + VdP + \mu dN$$

Equating the two expressions for $dG$, we see that

$$V = \left(\frac{\partial G}{\partial P}\right)_{N,T}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$