**Enthalpy** \( H(S, p, N) \)

Use pressure instead of volume

\[ E(S, V, N), \quad \phi = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \]

\[ H(S, p, N) = E + pV \]

\[ \left(\frac{\partial H}{\partial p}\right)_{SN} = V \]

\[ dH = TdS + Vdp + \mu dN \]

Since \( E = TS - pV + \mu N \)

\[ H = E + pV = TS + \mu N \]

**Gibbs Free Energy** \( G(T, p, N) \)

Use temperature and pressure instead of entropy and volume

\[ E(S, V, N), \quad \phi = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \quad \Rightarrow \quad T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \]

\[ G(T, p, N) = E - TS + \phi V \]

\[ \left(\frac{\partial G}{\partial T}\right)_{PN} = -S, \quad \left(\frac{\partial G}{\partial p}\right)_{T} = V \]

\[ dG = -SdT + Vdp + \mu dN \]
Since \( E = TS - pV + \mu N \)

\[
G = E - TS + pV = \mu N
\]

or \[
\frac{G}{N} = g = \mu
\]

the chemical potential is the Gibbs free energy per particle

From \( G = \mu N \) we get \( dG = \mu dN + N d\mu \)

Combining with \( dG = -S dT + V dp + \mu dp \)

\[
\mu dN + N d\mu = -S dT + V dp + \mu dp
\]

\[
\Rightarrow S dT - V dp + N d\mu = 0
\]

we regain the Gibbs - Duhamel relation

Note: If we are dealing with a system with more than one species of particles, \( N_1, N_2, \ldots \) then

\[
G(T, p, N_1, N_2, \ldots) = \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3 + \ldots
\]

where \( \mu_i = \left( \frac{dG}{dN_i} \right)_{T, p, N_j \neq i} \)
Grand potential $\Sigma(T, V, N)$

use temperature and chemical potential instead of entropy and particle number

$E(S, V, N), \quad T = \left( \frac{\partial E}{\partial S} \right)_{V, N} \quad \mu = \left( \frac{\partial E}{\partial N} \right)_{S, V}$

$\Sigma(T, V, \mu) = E - TS - \mu N$

$\left( \frac{\partial \Sigma}{\partial T} \right)_{V, \mu} = -S, \quad \left( \frac{\partial \Sigma}{\partial \mu} \right)_{T, V} = -N$

$d\Sigma = -SpdT - p\delta V - Nd\mu$

Since $E = TS - pV + \mu N$

$\Sigma = E - TS - \mu N = -pV$

$-\frac{\Sigma}{V} = \phi$

the pressure is $(-)$ the grand potential per unit volume.
Extremum Principles for Free Energies

Concept of a thermal reservoir

\[ \text{system of interest} \]

\[ \text{thermal reservoir} \quad \gg \quad \text{system of interest} \]

\[ \left( \frac{\partial E_R}{\partial S_R} \right)_{\text{sys}} = T_R \]

Suppose we add heat \( \Delta Q = T_R \Delta S \) to the reservoir.

The change in the reservoir's temperature \( T_R \) will be

\[ \Delta T_R = \left( \frac{\partial T_R}{\partial S_R} \right) \Delta S = \left( \frac{\partial^2 E_R}{\partial S_R^2} \right) \Delta S \]

Since \( E_R \) and \( S_R \) are both extensive variables, they scale with the number of particles in the reservoir \( N_R \).

So,

\[ \left( \frac{\partial^2 E_R}{\partial S_R^2} \right) \sim \frac{1}{N_R} \to 0 \]

for infinitely large reservoir

\[ \Rightarrow \Delta T_R \to 0 \]

Formally, a thermal reservoir is a system so large that its temperature does not change when it exchanges heat with the system of interest.
Consider a system in contact with a thermal reservoir. Only energy can be exchanged between system and reservoir. Temperature $T_r$ of reservoir is constant by definition.

Since system is in equilibrium with reservoir, the system temp $T = T_r$

If an internal constraint in the system is relaxed, what determines the new equilibrium state?

Use entropy formulation - total energy is conserved $E = E_r + E$

total entropy is maximized

$$S^{tot} = S_r(E_r) + S(E)$$
$$= S_r(E^{tot} - E) + S(E)$$

Since $E \ll E^{tot}$ (as $E_r \gg E$ by def of reservoir)

we can expand

$$S^{tot} = S_r(E^{tot}) - (\frac{\partial S_r}{\partial E_r})E + S(E)$$
$$= S_r(E^{tot}) - \frac{E}{T_r} + S(E)$$

$$= S_r(E^{tot}) - \left( E - T_rS \right) / T_r$$

$$= S_r(E^{tot}) - A / T_r$$

$T = \frac{1}{A}$

$T_r$ constant. Helmholtz free energy
\[ S_{\text{tot}} \text{ maximized } \Rightarrow A \text{ minimized} \]

\[ \Rightarrow \text{ the equilibrium state of a system in contact with a thermal reservoir will be the one that minimizes the Helmholtz free energy } A(T, V, N) \]

Now consider a system in contact with a thermal pressure reservoir pressure reservoir always has fixed pressure \( P_R \)

\[ \text{system } E, S, V \]

\[ \text{reservoir } E_R, S_R, V_R \]

Total energy conserved \( E^{\text{tot}} = E_R + E = \text{constant} \)

Total volume conserved \( V^{\text{tot}} = V_R + V = \text{constant} \)

System in equilibrium with reservoir \( \Rightarrow T = T_R, \ P = P_R \)

\[ S^{\text{tot}} = S_R(E_R, V_R) + S(E, V) \]

\[ = S_R(E^{\text{tot}}, V^{\text{tot}} - V) + S(E, V) \]

\[ \approx S_R(E^{\text{tot}}, V^{\text{tot}}) - \left( \frac{\partial S_R}{\partial E_R} \right) E - \left( \frac{\partial S_R}{\partial V_R} \right) V + S(E, V) \]

\[ = \text{constant} - \frac{E}{T_R} + \frac{P_R}{T_R} V + S \]

\[ \approx \text{constant} - \left( E + p_R V - s T \right) / T = \text{constant} - G/T \]

\[ S^{\text{tot}} \text{ maximized } \Rightarrow G, \text{ Gibbs Free energy is minimized} \]
The equilibrium state of a system in contact with a thermal and pressure reservoir will be the one that minimizes the Gibbs free energy $G(T, p, N)$.

Similarly, the equilibrium state of a system in contact with a pressure reservoir will be the one that minimizes the enthalpy $H(S, p, N)$.

And the equilibrium state of a system in contact with a thermal and a particle reservoir (a particle reservoir can exchange particles with the system, but is so large that its chemical potential $\mu$ stays constant) will be the one that minimizes the grand potential $\Sigma(T, V, \mu)$. 
Maxwell Relations

Follow from 2nd derivatives of the thermodynamic potential.

\[ E(S, V, N) \Rightarrow \left( \frac{\partial E}{\partial S} \right)_{V,N} = T(S, V, N) \]

So \[ \left( \frac{\partial^2 E}{\partial S \partial V} \right)_{N} = \left( \frac{\partial T}{\partial V} \right)_{S,N} \]

But \[ \left( \frac{\partial E}{\partial V} \right)_{S,N} = -p(S, V, N) \]

So \[ \left( \frac{\partial^2 E}{\partial V \partial S} \right)_{N} = -\left( \frac{\partial p}{\partial S} \right)_{V,N} \]

\[ \Rightarrow \left( \frac{\partial T}{\partial V} \right)_{S,N} = -\left( \frac{\partial p}{\partial S} \right)_{V,N} \]

Can do the same for any thermodynamic potential

Helmholtz free energy

\[ A(T, V, N) \Rightarrow -\left( \frac{\partial A}{\partial T} \right)_{V,N} = S(T, V, N) \]

So \[ -\left( \frac{\partial^2 A}{\partial T \partial V} \right)_{N} = \left( \frac{\partial S}{\partial V} \right)_{T,N} \]

But \[ -\left( \frac{\partial A}{\partial V} \right)_{T,N} = p(T, V, N) \]

So \[ -\left( \frac{\partial^2 A}{\partial V \partial T} \right)_{N} = \left( \frac{\partial p}{\partial V} \right)_{T,N} \]

\[ \Rightarrow \left( \frac{\partial S}{\partial V} \right)_{T,N} = \left( \frac{\partial p}{\partial T} \right)_{V,N} \]
Gibbs free energy

\[ G(T, p, N) = \frac{\partial G}{\partial p}_{T, N} = V(T, p, N) \]

so

\[ \frac{\partial^2 G}{\partial p \partial N} = \frac{\partial V}{\partial N} \] at \( T, p \)

but

\[ \frac{\partial G}{\partial N} = \mu(T, p, N) \] at \( T, \mu \)

so

\[ \frac{\partial^2 G}{\partial N \partial p} = \frac{\partial \mu}{\partial p} \] at \( T, N \)

\[ \Rightarrow \frac{\partial V}{\partial N} = \frac{\partial \mu}{\partial p} \] at \( T, N \)

These equalities, which follow from the independence of the order of taking 2nd derivatives, are called the Maxwell Relations.

See Callen Chpt 7 for a complete list.