$$\frac{\partial(-H)}{\partial p} = -\dot{q} \quad \text{or} \quad \frac{\partial H}{\partial p} = \dot{q}$$

which is one of Hamilton's dynamic equations

$$\left(\text{the other is } \frac{\partial H}{\partial q} = -\dot{p} \right)$$

Legendre transformation and Thermodynamics

Helmholtz Free Energy $\quad A(T, V, N)$

If we want a formulation of thermodynamics in which temperature T rather than entropy S is regarded as an independent variable, we take the Legendre transform of the energy, transforming from S to the conjugate variable T.

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

$$A(T, V, N) = E - TS \qquad \underline{\text{Helmholtz Free Energy}}$$

sometimes written as $F(T, V, N)$

From our results for Legendre transforms, we then have

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

To see this more clearly, we proceed as follows:

From $\left(\frac{\partial E}{\partial S} \right)_{V, N} = T(S, V, N)$ we invert this function with respect to S to get

$$S(T, V, N)$$

Then we substitute this $S(T, V, N)$ into the Legendre transform

$$A(T,V,N) = E(S(T,V,N),V,N) - TS(T,V,N)$$

Now by the chain rule

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

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

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

So

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

Similarly we can consider the other first partial derivatives of A

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = \left(\frac{\partial E}{\partial S}\right)_{V,N}\left(\frac{\partial S}{\partial V}\right)_{T,N} + \left(\frac{\partial E}{\partial V}\right)_{S,N} - T\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

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

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

So $\left(\frac{\partial A}{\partial V}\right)_{T,N} = -p(T,V,N)$

Similarly we can show,

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

So now we can write

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN$$

$$= -S\,dT - p\,dV + \mu\,dN$$

Also, since the Euler relation gives

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

and

$$A = E - TS$$

(follows from fact that E is a homogeneous function of first degree)

we have

$$A = -pV + \mu N$$

Enthalpy $H(S, p, N)$

use pressure instead of volume

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

$$H(S, p, N) \equiv E + pV$$

$$\left(\frac{\partial H}{\partial p}\right)_{S,N} = V$$

$$dH = TdS + Vdp + \mu dN$$

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

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

$$G(T, p, N) = E - TS + pV$$

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

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

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

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

or $$\boxed{\frac{G}{N} \equiv g = \mu}$$

the chemical potential is the Gibbs free energy per particle

From $G = \mu N$ we get $dG = \mu dN + N d\mu$
Combining with $dG = -SdT + V dp + \mu dN$

$$\mu dN + N d\mu = -SdT + V dp + \mu dN$$

$$\Rightarrow \quad SdT - Vdp + N d\mu = 0$$

we regain the Gibbs - Duhem 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 $\mu_i = \left(\dfrac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}}$

Grand potential $\Sigma (T, V, \mu)$

use temperature and chemical potential instead of entropy and particle number

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

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

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

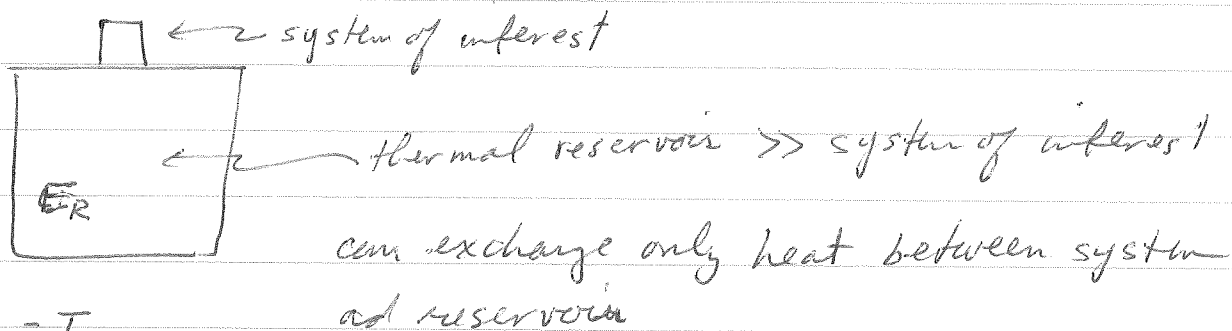$$d\Sigma = -S dT - p dV - N d\mu$$

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

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

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

the pressure is $(-)$ the grand potential per unit volume.

Extremum Principles for Free Energies

Concept of a thermal reservoir

← system of interest

thermal reservoir ≫ system of interest

can exchange only heat between system and reservoir

$$\left(\frac{\partial E_R}{\partial S_R}\right)_{V,N} = T_R$$

Suppose we add heat $dQ = TdS$ to the reservoir. The change in the reservoirs temperature T_R will be

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R}\right)dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right)dS$$

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

So

$$\left(\frac{\partial^2 E_R}{\partial S_R^2}\right) \sim \frac{1}{N_R} \to 0 \left.\begin{array}{c}\\ \\ \\ \end{array}\right\} \text{ for infinitely large reservoir}$$

$$\Rightarrow \quad \Delta T_R \to 0$$

· 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 + reservoir.
Temperature T_R of reservoir is const by definition

← system - energy E
entropy S

← reservoir - energy E_R
entropy S_R
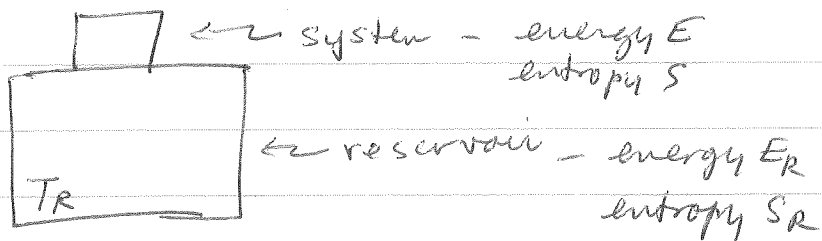
Since system is in equilib with reservoir, the system temp $T = T_R$

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

Use entropy formulation - total energy is conserved $E^{tot} = E_R + E$
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

$$S^{tot} \simeq S_R(E^{tot}) - \left(\frac{\partial S_R}{\partial E_R}\right) E + S(E)$$

$$= S_R(E^{tot}) - \frac{E}{T_R} + S(E)$$

$$= S_R(E^{tot}) - (E - T_R S)/T_R \qquad T_R = T$$
$\uparrow$
system
temp

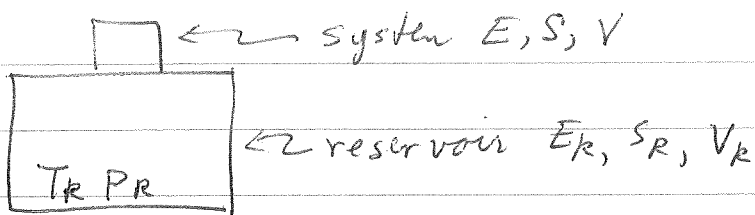$$= \underbrace{S_R(E^{tot})}_{\text{constant}} - \underbrace{A}_{\text{Helmholtz free energy}}/T_R$$

S^{tot} maximized $\Rightarrow$ A minimized

$\Rightarrow$ the equilib state of a system in contact with a thermal reservoir will be the one the 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

system E, S, V
reservoir E_R, S_R, V_R
$T_R \ P_R$

total energy conserved $E^{tot} = E_R + E = $ constant
total volume conserved $V^{tot} = V_R + V = $ const

system in equilib with reservoir $\Rightarrow T = T_R, \quad p = p_R$

$$S^{tot} = S_R(E_R, V_R) + S(E,V)$$

$$= S_R(E^{tot} - E, V^{tot} - V) + S(E,V)$$

$$\simeq S_R(E^{tot}, V^{tot}) - \left(\frac{\partial S_R}{\partial E_R}\right)E - \left(\frac{\partial S_R}{\partial V_R}\right)V + S(E,V)$$

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

$$= \text{const} - (E + pV - ST)/T = \text{const} - G/T$$

S^{tot} maximized $\Rightarrow$ G, Gibbs Free energy is minimized

$\Rightarrow$ the equilb state of a system in contact with a thermal & pressure reservoir will be the one that minimizes the Gibbs free energy $G(T, p, N)$

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

and — the equilb 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 μ_R stays constant) will be the one that minimizes the grand potential $\Sigma(T, V, \mu)$

Maxwell Relations

Follow from 2nd derivatives of the thermodynamic potentials

Energy:

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

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

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

Or   Gibbs free energy

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

so
$$\left(\frac{\partial^2 G}{\partial p \, \partial N}\right)_T = \left(\frac{\partial V}{\partial N}\right)_{T,p}$$

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

so
$$\left(\frac{\partial^2 G}{\partial N \, \partial p}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_{T,N}$$

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

These equivalences, 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