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

which is one of the Hamilton dynamic equations (the other is $\frac{\partial \mathcal{H}}{\partial q} = -\dot{p}$)

Legendre transform and Thermodynamics

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

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

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

$$\Rightarrow \quad A(T,V,N) \equiv E - TS$$

Helmholtz Free Energy
sometimes written as $F(T,V,N)$

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

$$\underset{\parallel}{\left(\frac{\partial E}{\partial V}\right)_{S,N}} \qquad \underset{\parallel}{\left(\frac{\partial E}{\partial N}\right)_{S,\mu}}$$

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

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

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

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

checking the derivatives more carefully

$A = E - TS$ to take Legendre transform we in principal compute $T(S,V,N) = \left(\frac{\partial E}{\partial S}\right)_{N,V}$ and invert it to get $S(T,V,N)$

then substitute into the above

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

then

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

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

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

Similarly

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

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

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

Similarly

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

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

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

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

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

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

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

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

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

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

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

where $\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, P, N_{j \neq i}}$

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

use temperature ad chemical potential instead of entropy ad particle number

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

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

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

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

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

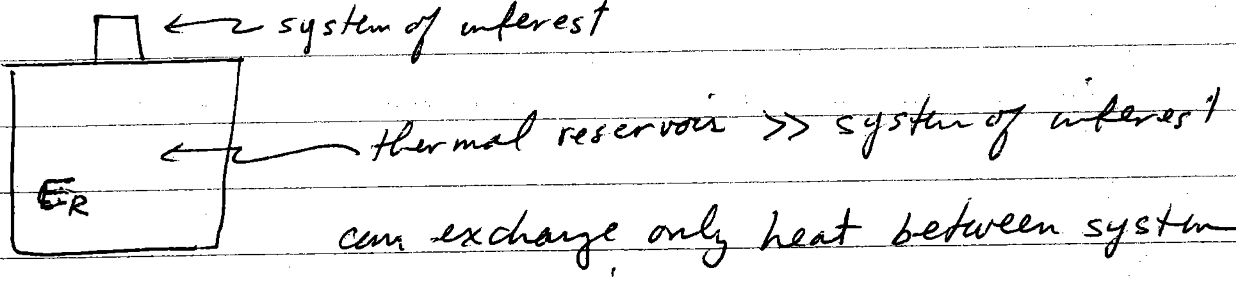
$$\Sigma = E - TS - \mu N = -pV$$

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

the pressure is (−) the grand potential per unit volume.

Extremum Principles for Free Energies

Concept of a thermal reservoir



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

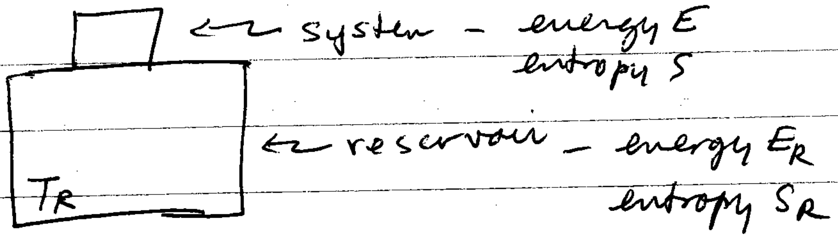
$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R}\right) dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS$$

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

So
$$\left.\begin{aligned} \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) &\sim \frac{1}{N_R} \to 0 \\ \Rightarrow \quad \Delta T_R &\to 0 \end{aligned}\right\} \text{ for infinitely large reservoir}$$

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



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

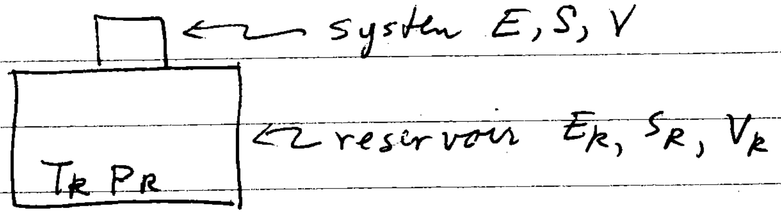
$$S^{tot} \simeq S_R(E^{tot}) - \left(\frac{\partial S_R}{\partial E_R}\right) E + S(E)$$
$$= S_R(E^{tot}) - \frac{E}{T_R} + S(E)$$
$$= S_R(E^{tot}) - (E - T_R S)/T_R \qquad \underset{\text{system temp}}{\underset{\uparrow}{T_R = T}}$$
$$= \underset{\text{constant}}{\underset{\uparrow}{S_R(E^{tot})}} - \underset{\text{Helmholtz free energy}}{\underset{\nearrow}{A}}/T_R$$

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

$\Rightarrow$ the equilib state of a system in contact with a <u>thermal reservoir</u> will be the one the <u>minimizes the Helmholtz free energy</u> $A(T,V,N)$

<u>Now consider a system in contact with a thermal + pressure reservoir</u>

pressure reservoir always has fixed pressure 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 $\Rightarrow T = T_R$, $p = p_R$

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

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

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

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

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

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

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

and - the equilib 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:

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

$$\text{so} \quad \left(\frac{\partial^2 E}{\partial S \partial V}\right)_N = \left(\frac{\partial T}{\partial V}\right)_{S,N}$$

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

$$\text{so} \quad \left(\frac{\partial^2 E}{\partial V \partial S}\right)_N = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

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

Can do the same for any thermodynamic potential

Helmholtz free energy

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

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

$$\text{but:} \quad -\left(\frac{\partial A}{\partial V}\right)_{T,N} = p(T,V,N)$$

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

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

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

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