Thermodynamic Potentials

1) Internal Energy : $U(V, S, N)$

natural variables or control parameters

1st Law $$dU = \underbrace{-p\,dV}_{dW} + \underbrace{T\,dS}_{dQ_{reversible}} + \mu\,dN$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_{SN} dV + \left(\frac{\partial U}{\partial S}\right)_{VN} dS + \left(\frac{\partial U}{\partial N}\right)_{VS} dN$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_{SN}, \quad T = \left(\frac{\partial U}{\partial S}\right)_{VN}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{VS}$$

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2) Enthalpy : $H(P, S, N) = \underline{U + PV}$

(Heat function)

Legendre Transform

$$dH = dU + d(PV) = dU + p\,dV + V\,dP$$

$$= (-\cancel{p\,dV} + T\,dS + \mu\,dN) + \cancel{p\,dV} + V\,dP$$

$$= V\,dp + T\,dS + \mu\,dN$$

$$dH = \left(\frac{\partial H}{\partial p}\right)_{SN} dp + \left(\frac{\partial H}{\partial S}\right)_{PN} dS + \left(\frac{\partial H}{\partial N}\right)_{PS} dN$$

$$V = \left(\frac{\partial H}{\partial p}\right)_{SN}, \quad T = \left(\frac{\partial H}{\partial S}\right)_{PN}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{PS}$$

3) Helmholtz Free Energy A, F

$$F(V,T,N) = U - TS$$

"Free" $\equiv$ T is a control parameter

$$dF = dU + -TdS - SdT$$

$$= (-pdV + \cancel{TdS} + \mu dN) - \cancel{TdS} - SdT$$

$$= -pdV - SdT + \mu dN$$

$$dF = \left(\frac{\partial F}{\partial V}\right)_{TN} dV + \left(\frac{\partial F}{\partial T}\right)_{VN} dT + \left(\frac{\partial F}{\partial N}\right)_{VT} dN$$

$$-p = \left(\frac{\partial F}{\partial V}\right)_{TN}, \quad -S = \left(\frac{\partial F}{\partial T}\right)_{VN}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{VT}$$

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4) Gibbs Free Energy: $G(P,T,N)$

$$G = U + PV - TS = H - TS = F + PV$$

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

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

$$V = \left(\frac{\partial G}{\partial P}\right)_{TN}, \quad -S = \left(\frac{\partial G}{\partial T}\right)_{PN}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{PT}$$

Gibbs-Duhem Relation

Only applies if the system is extensive.

$U(S,V,N)$

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S,V,N) \quad \text{take } \left.\frac{d}{d\lambda}\right|_{\lambda=1}$$

$$\frac{d}{d\lambda} U(\lambda S, \lambda V, \lambda N) = \left(\frac{\partial U}{\partial S}\right)_{VN} \underbrace{\frac{d(\lambda S)}{\partial \lambda}}_{S} + \left(\frac{\partial U}{\partial V}\right)_{SN} \underbrace{\frac{d(\lambda V)}{d\lambda}}_{V} + \left(\frac{\partial U}{\partial N}\right)_{SV} \underbrace{\frac{d(\lambda N)}{d\lambda}}_{N}$$

$$= \left(\frac{\partial U}{\partial S}\right)_{VN} S + \left(\frac{\partial U}{\partial V}\right)_{SN} V + \left(\frac{\partial U}{\partial N}\right)_{SV} N = U$$

$$= (T) S + (-p) V + (\mu) N = U$$

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extensive: $U = -pV + TS + \mu N$

$$dU = -p\,dV - V\,dp + T\,dS + S\,dT + \mu\,dN + N\,d\mu$$

1st Law $\quad dU = -p\,dV + T\,dS + \mu\,dN$

$$0 = -V\,dp + S\,dT + N\,d\mu$$ Gibbs Duhem

New Potential: $X(P,T,\mu) \equiv \varnothing$

Use Gibbs-Duhem: $\quad S\,dT = V\,dp - N\,d\mu$

$$dG = V\,dp - S\,dT + \mu\,dN = N\,d\mu + \mu\,dN$$

$$d(\mu N) = N\,d\mu + \mu\,dN$$

integrate

$$G = \mu N \Rightarrow \mu = \frac{G}{N}$$

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5) Grand Potential

Grand Canonical Potential

<u>The</u> thermodynamic Potential

Landau Potential

$$\Omega = \Phi = F - \mu N = F - G = -pV$$

if extensive

$$\Phi(V, T, \mu)$$

Maxwell Relations (fixed N)

Mixed partial derivatives must be equal

* not always

$$f(x,y) \implies \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \cdot \partial y}$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_S \quad , \quad T = \left(\frac{\partial U}{\partial S}\right)_V$$

$$\left(-\frac{\partial p}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial V}{\partial S}\right)_P$$

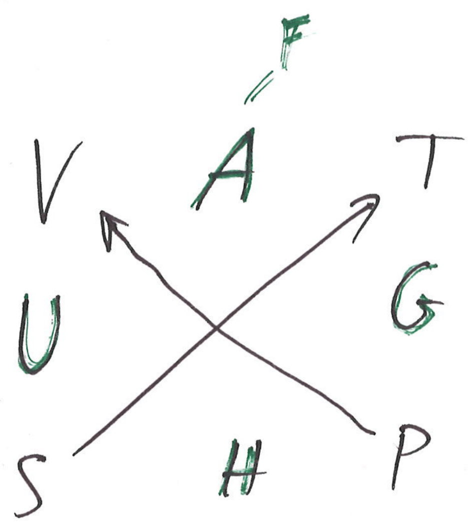
$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

$$-\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial p\,\partial T} = \frac{\partial^2 G}{\partial T\,\partial p} = \left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p}$$



Thermodynamic Square

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50 small number

10^{50} large number

$10^{(10^{50})}$ very large number

large + small = large

$10^{50} + 50 \approx 10^{50}$

100000000000000000000000000
000000000000000050

Mass of multiverse $10^{(10^{50})}$ $\underbrace{\text{g a tonnes}}_{10^6}$

$$10^6 \cdot 10^{(10^{50})} = 10^{1000000000000000000000000000000000006} \simeq 10^{10^{50}}$$