.4.2 Enthalpy H

$$H = H(S, Y, \{N_j\})$$

example: chemical reactions

fast → $dQ = 0 \Rightarrow dS = 0$

open vessel → $dp = 0$ ($dY = 0$)

$$H = U - XY = TS + \sum_j \mu_j' N_j$$ "Legendre transformation"

$$dH = dU - YdX - XdY \leq TdS - XdY + \sum_j \mu_j' dN_j$$

extremal principle:

For any change of a system at constant $S, Y, \{N_j\}$

$\Delta H = \int dH \leq 0$

⇒ Irreversible processes at constant $S, Y, \{N_j\}$ decrease the enthalpy H. In thermodynamic equilibrium the enthalpy H ~~takes~~ is minimized at fixed $S, Y, \{N_j\}$

again chemical reaction:

H_{before} = enthalpy of unreacted reagents

H_{after} = enthalpy of reacted reagents

$H_{before} > H_{after}$ ⇒ reaction will occur <u>spontaneously</u> irreversibly

$H_{after} < H_{before}$ ⇒ reaction will not occur spontaneously

E.o.S. $T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_j\}}$, $X = -\left(\frac{\partial H}{\partial Y}\right)_{S,\{N_j\}}$, $\mu_j' = \left(\frac{\partial H}{\partial N_j}\right)_{S,Y,\{N_{i\neq j}\}}$

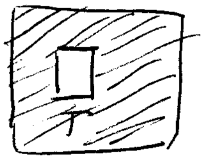
Maxwell relations:

$$\left(\frac{\partial T}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial X}{\partial S}\right)_{Y,\{N_j\}} \qquad \left(\frac{\partial T}{\partial N_j}\right)_{S,Y,\{N_{\ell\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial S}\right)_{Y,\{N_j\}}$$

$$\left(\frac{\partial X}{\partial N_j}\right)_{S,Y,\{N_{\ell\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial Y}\right)_{S,\{N_j\}} \qquad \left(\frac{\partial \mu_j'}{\partial N_i}\right)_{S,Y,\{N_{\ell\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{S,Y,\{N_{\ell\neq j}\}}$$

I. 4.3 Helmholtz Free Energy F (A)

$$F = F(T, V, N)$$



$$F = U - TS = XY + \sum_j \mu_j' N_j$$

$$dF \leq -S\,dT + Y\,dX + \sum_j \mu_j'\,dN_j$$

Irreversible processes at constant T, X, N_j decrease the Helmholtz Free Energy. In thermodynamic equilibrium the Helmholtz Free Energy is minimized at fixed $T, X, \{N_j\}$

E.o.S. $S = -\left(\frac{\partial F}{\partial T}\right)_{X,\{N_j\}}$ $Y = \left(\frac{\partial F}{\partial X}\right)_{T,\{N_j\}}$ $\mu_j' = \left(\frac{\partial F}{\partial N_j}\right)_{T,X,\{N_{\ell\neq j}\}}$

Maxwell relations

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}} \qquad \left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial T}\right)_{X,\{N_j\}}$$

$$\left(\frac{\partial Y}{\partial N_j}\right)_{T,X,\{N_{\ell\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial X}\right)_{T,\{N_j\}} \qquad \left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,X,\{N_{\ell\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{T,X,\{N_{\ell\neq j}\}}$$

I. 4.4 Gibbs Free Energy (G)

$$G = G(T, Y, \{N_j\})$$

$$G = U - TS - XY = H - TS = F - XY = \sum_j \mu_j' N_j$$

$$dG \leq -S\,dT - X\,dY + \sum_j \mu_j'\,dN_j$$

Irreversible processes at constant $T, Y, \{N_j\}$ decrease the Gibbs Free Energy. In thermodynamic equilibrium the Gibbs Free Energy is minimal at fixed $T, Y, \{N_j\}$.

$$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_j\}} \qquad X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_j\}} \qquad \mu_j' = \left(\frac{\partial G}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}$$

Maxwell relations:

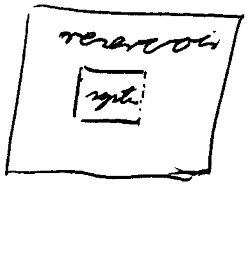
$$\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \qquad \left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial T}\right)_{Y,\{N_j\}}$$

$$\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial Y}\right)_{T,\{N_j\}} \qquad \left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}$$

I. 4.5 Grand Potential

Want to fix μ_j' instead of N_j

→ also fix T



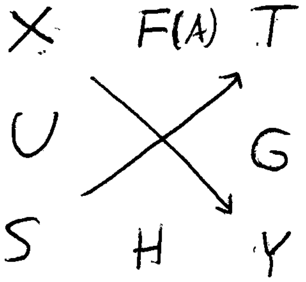
$$\Omega = \Omega(T, X, \{\mu_j'\})$$

$$\Omega = \quad - TS - \sum_j \mu_j' N_j = XY$$

I.4.5 How to memorize thermodynamic potentials?

$\{N_j\}$ fixed

The thermodynamic square



- the variables next to a potential are its natural variables
- Equations of state

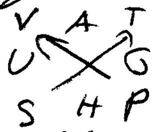
$$\left(\frac{\partial\,\text{potential}}{\partial\,\text{variable}}\right)_{\text{other variable},\,\{N_j\}} = \underset{\text{if going against arrow}}{-}\ \text{variable at the end of arrow}$$

- Maxwell relations

$$\left(\frac{\partial\,\text{variable}}{\partial\,\text{variable along edge}}\right)_{\partial\,\text{variable along diagonal}} \overset{\text{diagonal}}{} = \underset{\text{if one of the diagonals is crossed against arrow}}{-} \left(\frac{\partial\,\text{variable along other edge}}{\partial\,\text{variable along diagonal}}\right)_{\partial\,\text{variable along edge}} \overset{\text{diagonal}}{}$$

derivative ↓ ⋯→ constant   constant ← ↓ derivative

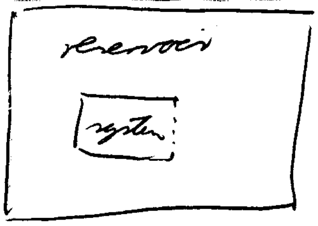
"Violets Are Tricky Unless Grown in Specially Heated Pots"



D.E. Christie, Am. J. Phys. 25 486 (1957)

"Good Physicists Have Studied Under Very Fine Teachers"

I.4.6 Grand Potential



Want to fix μ_j instead of N_j

→ also fix T

$$\Omega = \Omega(T, X, \{\mu_j\})$$

$$\Omega = U - TS - \sum_j \mu_j N_j = F - \sum_j \mu_j N_j = XY$$

$$d\Omega \leq -S\,dT + Y\,dX - \sum_j N_j\,d\mu_j'$$

Ω is minimized in thermodynamic equilibrium at fixed $T, X, \{\mu_j\}$.

E.o.S. $$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{X,\{\mu_j'\}} \qquad Y = \left(\frac{\partial \Omega}{\partial X}\right)_{T,\{\mu_j'\}} \qquad N_j = -\left(\frac{\partial \Omega}{\partial \mu_j'}\right)_{T,X,\{\mu_{\ell\neq j}'\}}$$

Maxwell relations:

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{\mu_j'\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{\mu_j'\}} \qquad \left(\frac{\partial S}{\partial \mu_j'}\right)_{T,X,\{\mu_{\ell\neq j}'\}} = \left(\frac{\partial N_j}{\partial T}\right)_{X,\{\mu_i'\}}$$

$$\left(\frac{\partial Y}{\partial \mu_j'}\right)_{T,X,\{\mu_{\ell\neq j}'\}} = -\left(\frac{\partial N_j}{\partial X}\right)_{T,\{\mu_j'\}} \qquad \left(\frac{\partial N_i}{\partial \mu_j'}\right)_{T,V,\{\mu_{\ell\neq j}\}} = \left(\frac{\partial N_j}{\partial \mu_i'}\right)_{T,V,\{\mu_{\ell\neq i}\}}$$

What about fixing all intensive variables $T, Y, \{\mu_j\}$

$$V = V(T, Y, \{\mu_j\})$$

$$V = U - TS - XY - \sum_j \mu_j N_j = 0 \quad \ddot{\nabla}\,\ddot{\nabla}\,\ddot{\nabla}$$

It does not make sense to prescribe values of all intensive variables independently since they are all coupled by the Gibbs-Duhem relation.

$\underline{\downarrow}$ 10/9