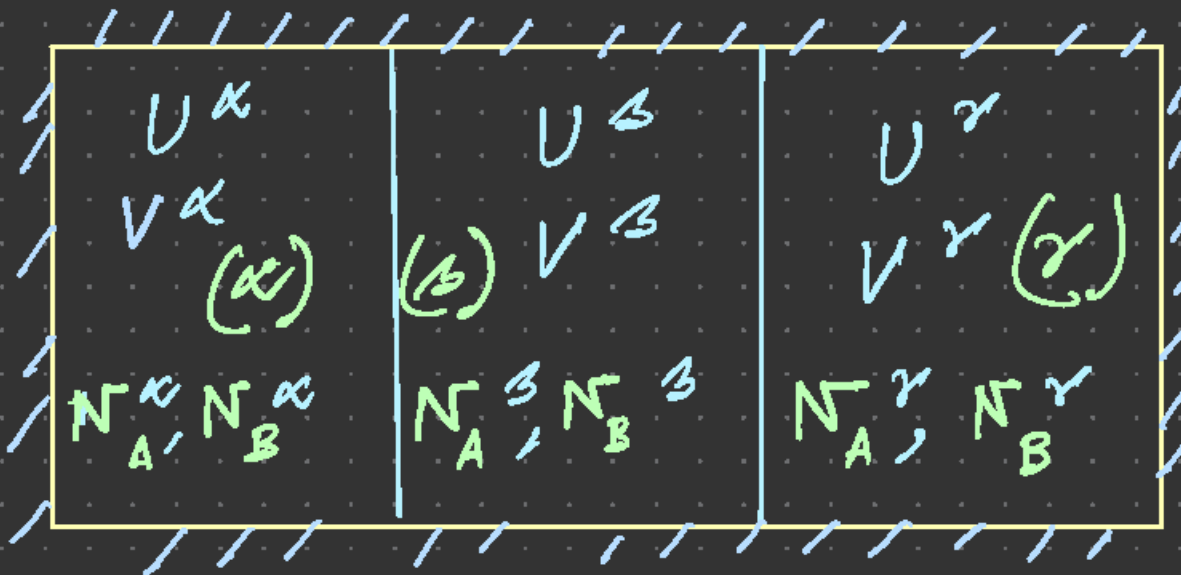
Thermal, Mechanical, Chemical

$dS = 0$




Two Components

Constraints

$$N_A = N_A^\alpha + N_A^\beta + N_A^\gamma$$

$$N_B = N_B^\alpha + N_B^\beta + N_B^\gamma$$

$$V = V^\alpha + V^\beta + V^\gamma$$

$$U = U^\alpha + U^\beta + U^\gamma$$

$$N = N_A + N_B$$

$$N = N_A + N_B$$

$$S = \sum_{q=\alpha,\beta,\gamma} S^q$$

$$S = S(U, V, N)$$

$$S^{\alpha} = S^{\alpha}\left(U^{\alpha}, V^{\alpha}, N_A^{\alpha}, N_B^{\alpha}\right)$$

$$S^{\beta} = S^{\beta}\left(U^{\beta}, V^{\beta}, N_A^{\beta}, N_B^{\beta}\right)$$

$$S^{\gamma} = S^{\gamma}\left(U^{\gamma}, V^{\gamma}, N_A^{\gamma}, N_B^{\gamma}\right)$$

$$dS^{\alpha} = \left(\frac{\partial S}{\partial U}\right)^{\alpha}_{V^{\alpha}, N_A^{\alpha}, N_B^{\alpha}} dU^{\alpha} + \left(\frac{\partial S}{\partial V}\right)^{\alpha}_{U^{\alpha}, N_A^{\alpha}, N_B^{\alpha}} dV^{\alpha} + \left(\frac{\partial S}{\partial N_A}\right)^{\alpha} dN_A^{\alpha} + \left(\frac{\partial S}{\partial N_B}\right)^{\alpha} dN_B^{\alpha}$$

$$dU = TdS - pdV + \mu dN$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$\left(\frac{\partial S}{\partial U}\right)^{\alpha} = \frac{1}{T^{\alpha}}$$

$$\left(\frac{\partial S}{\partial V}\right)^{\alpha} = \frac{p^{\alpha}}{T^{\alpha}}$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N_i} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N_i} = \frac{p}{T}$$

$$\left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} = -\frac{\mu_i}{T} \qquad \left(\frac{\partial S}{\partial N_i}\right)^{\alpha} = -\frac{\mu_i^{\alpha}}{T^{\alpha}}$$

$i = A, B$

$$
\begin{aligned}
dS &= dS^{\alpha} + dS^{\beta} + dS^{\gamma} \\
&= \frac{1}{T^{\alpha}} dU^{\alpha} + \frac{1}{T^{\beta}} dU^{\beta} + \frac{1}{T^{\gamma}} dU^{\gamma} \\
&\quad + \frac{P^{\alpha}}{T^{\alpha}} dV^{\alpha} + \frac{P^{\beta}}{T^{\beta}} dV^{\beta} + \frac{P^{\gamma}}{T^{\gamma}} dV^{\gamma} \\
&\quad - \frac{\mu_A^{\alpha}}{T^{\alpha}} dN_A^{\alpha} - \frac{\mu_A^{\beta}}{T^{\beta}} dN_A^{\beta} - \frac{\mu_A^{\gamma}}{T^{\gamma}} dN_A^{\gamma} \\
&\quad - \frac{\mu_B^{\alpha}}{T^{\alpha}} dN_B^{\alpha} - \frac{\mu_B^{\beta}}{T^{\beta}} dN_B^{\beta} - \frac{\mu_B^{\gamma}}{T^{\gamma}} dN_B^{\gamma}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{T^{\alpha}} dU^{\alpha} - \frac{1}{T^{\beta}} \left( dU^{\alpha} + dU^{\gamma} \right) + \frac{1}{T^{\gamma}} dU^{\gamma} \\
&\quad + \frac{P^{\alpha}}{T^{\alpha}} dV^{\alpha} - \frac{P^{\beta}}{T^{\beta}} \left( dV^{\alpha} + dV^{\gamma} \right) + \frac{P^{\gamma}}{T^{\gamma}} dV^{\gamma} \\
&\quad + \sum_{i=A,B} \left\{ - \frac{\mu_i^{\alpha}}{T^{\alpha}} dN_i^{\alpha} + \frac{\mu_i^{\beta}}{T^{\beta}} \left( dN_i^{\alpha} + dN_i^{\gamma} \right) - \frac{\mu_i^{\gamma}}{T^{\gamma}} dN_i^{\gamma} \right\}
\end{aligned}
$$

$$= \frac{1}{T^\alpha} dU^\alpha - \frac{1}{T^\beta} dU^\alpha - \frac{1}{T^\beta} dU^\gamma + \frac{1}{T^\gamma} dU^\gamma$$

$$+ \cdots$$

$$+ \cdots$$

$$dS = \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right) dU^\alpha + \left(\frac{1}{T^\gamma} - \frac{1}{T^\beta}\right) dU^\gamma$$

$$+ \left(\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}\right) dV^\alpha + \left(\frac{p^\gamma}{T^\gamma} - \frac{p^\beta}{T^\beta}\right) dV^\gamma$$

$$+ \left(\frac{\mu_A^\beta}{T^\beta} - \frac{\mu_A^\alpha}{T^\alpha}\right) dN_A^\alpha + \left(\frac{\mu_A^\beta}{T^\beta} - \frac{\mu_A^\gamma}{T^\gamma}\right) dN_A^\gamma$$

$$+ \left(\frac{\mu_B^\beta}{T^\beta} - \frac{\mu_B^\alpha}{T^\alpha}\right) dN_B^\alpha + \left(\frac{\mu_B^\beta}{T^\beta} - \frac{\mu_B^\gamma}{T^\gamma}\right) dN_B^\gamma$$

$$\frac{1}{T^\alpha} - \frac{1}{T^\beta} = 0 \qquad \frac{1}{T^\beta} - \frac{1}{T^\gamma} = 0$$

Thermal $\quad T^\alpha = T^\beta = T^\gamma$

Mechanical $\quad p^\alpha = p^\beta = p^\gamma$

Chemical Equilibrium $\quad \mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma \quad \mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma$

| $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|
| $T^\alpha$ | $T^\beta$ | $T^\gamma$ |
| $p^\alpha$ | $p^\beta$ | $p^\gamma$ |
| $x_A^\alpha$ | $x_A^\beta$ | $x_A^\gamma$ |
| $x_B^\alpha$ | $x_B^\beta$ | $x_B^\gamma$ |

What are the unknowns?

9

$$x_A^\alpha + x_B^\alpha = 1$$

$$x_A^\beta + x_B^\beta = 1$$

What are the equations?

$$x_A^\gamma + x_B^\gamma = 1$$

8

$$x_A^\alpha + x_B^\alpha$$

$n^\alpha \leftarrow$ # moles of A and B in $\alpha$ $= \dfrac{n_A^\alpha + n_B^\alpha}{n^\alpha}$

$$x + y = 3$$
$$x - y = 4$$
$$2x + 3y = 7$$
$$5x - 9y = 8$$

$$x + y - z = 3$$
$$x - y + z = 7$$
$$x + y + z = 10$$

$$A \begin{bmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 3 \\ 7 \\ 10 \end{bmatrix}$$

Degrees of freedom

= number of unknowns

− number of equations

All phases are condensed

$$p^{\alpha} = p^{\beta} = p^{\gamma} = p \text{ (known)}$$

No. of Variables — 6

No. of equations — 6

Gibbs phase Rule

No. of variables = No. of equations

$$\left.\begin{aligned} 2x+3y &= 5 \\ x-y &= 4 \\ x+3y &= 1 \end{aligned}\right\}$$

— An unique solution

No of variables > No. of equations

— Infinite solutions

No of variables < No of equations

— No solution

Entropy maximum principle

$S(U, V, N)$ $\quad dS = 0$ (Extremum condition)

$d^2S < 0$

$\Updownarrow$

Energy minimum principle

$U(S, V, N)$ $\quad dU = 0$

$d^2U > 0$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_A,N_B} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_A,N_B} dV + \left(\frac{\partial U}{\partial N_A}\right)_{S,V,N_B} dN_A + \left(\frac{\partial U}{\partial N_B}\right)_{S,V,N_A} dN_B$$




$S = S^\alpha + S^\beta$ — constant

$S = S(U, V, N)$

Isolated composite system with subsystems $\alpha$ and $\beta$

$S$ is continuous, differentiable function of $U$

$\left(\frac{\partial S}{\partial U}\right)_{V,N_i} > 0$ monotonic

$dU = 0$

$S = S(U, V, N)$

$\Downarrow$

$U = U(S, V, N)$

Constraints

$$\begin{cases} N_A^{\alpha} + N_A^{\beta} = N_A \\ V^{\alpha} + V^{\beta} = V \\ N_B^{\alpha} + N_B^{\beta} = N_B \\ S^{\alpha} + S^{\beta} = S \end{cases}$$

$dU = 0$

(constant for the isolated system if the processes are reversible)

$$T^{\alpha} = T^{\beta}$$
$$P^{\alpha} = P^{\beta}$$
$$\mu_A^{\alpha} = \mu_A^{\beta}$$
$$\mu_B^{\alpha} = \mu_B^{\beta}$$

$$dU = 0 \qquad d^2U > 0$$

Constraints

1. $S^\alpha + S^\beta = S$ (total)
2. $V^\alpha + V^\beta = V$ (total) does not change

Isolated system with constant $S \Rightarrow dS = 0$

constant $V \Rightarrow dV = 0$

3. $N_A^\alpha + N_A^\beta = N_A \Rightarrow dN_A = 0$
4. $N_B^\alpha + N_B^\beta = N_B \Rightarrow dN_B = 0$

$dU = 0 \longrightarrow$

$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu_A^\alpha = \mu_A^\beta, \quad \mu_B^\alpha = \mu_B^\beta$$

Equations of state

$$T = T(S, V, N)$$
$$P = P(S, V, N)$$
$$\mu_i = \mu_i(S, V, N) \qquad i = A, B, \ldots$$

Homogeneous zeroth order functions

$$T(\lambda S, \lambda V, \lambda N) = \lambda^0 T(S, V, N)$$
$$= T(S, V, N)$$

$$S = \left(\frac{R^2}{v_0 \theta}\right)^{1/3} (NVU)^{1/3}$$

$R, v_0, \theta$ are +ve constants

First order, homogeneous function (extensive)

$$S = S(U, V, N)$$

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

$$\frac{\partial S}{\partial U} > 0$$

$$(\lambda N \lambda V \lambda U)^{1/3} = \lambda (NVU)^{1/3}$$

$$S^3 = \frac{R^2}{v_0 \theta} NVU$$

or, $$U = \left(\frac{v_0 \theta}{R^2}\right) \frac{1}{NV} S^3$$

$$S(U,V,N) = \left(\frac{R^2}{v_0\theta}\right)^{1/3} (NVU)^{1/3}$$

$R > 0$
$v_0 > 0$
$\theta > 0$

$$S(\lambda U, \lambda V, \lambda N)$$

$$\lambda S(U,V,N) = \lambda \left(\frac{R^2}{v_0\theta}\right)^{1/3} (NVU)^{1/3}$$

$$\frac{\partial S}{\partial U}_{N,V} > 0$$

$$\frac{\partial S}{\partial U} = \left(\frac{R^2}{v_0\theta}\right)^{1/3} N^{1/3} V^{1/3} \frac{1}{3} U^{-2/3}$$

$$S = \left(\frac{R}{\theta^2}\right)^{1/3} \left(\frac{NU}{V}\right)^{2/3} N$$

$$S(\lambda U, \lambda V, \lambda N) = \left(\frac{R}{\theta^2}\right)^{1/3} \left(\frac{\lambda N \lambda U}{\lambda V}\right)^{2/3}$$

$$= \lambda^{2/3} \left(\frac{R}{\theta^2}\right)^{1/3} \left(\frac{NU}{V}\right)^{2/3}$$

Not first order homogeneous

$\Rightarrow$ not extensive ✗

## Euler equation

Homogeneous, first order function

$$U(\lambda S, \lambda V, \lambda N_1, \lambda N_2, \ldots) = \lambda U(S, V, N_1, N_2, \ldots)$$

$S$ — Entropy
$V$ — Volume
$N_i$ — mole number of component $i$

Differentiate w.r.t. $\lambda$

$$\frac{\partial U(\lambda S, \ldots)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \ldots)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} = U(S, V, N_1, \ldots)$$

$\frac{\partial \lambda S}{\partial \lambda} = S$

$= \frac{\partial U}{\partial S}$

True for any $\lambda$. Put $\lambda = 1$

$\lambda$ — arbitrary multiplier $> 0$

$$\frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \sum_{j=1}^{r} \frac{\partial U}{\partial N_j} N_j = U$$

$S, N_j$ | $S, V, N_{i \neq j}$

$$U = TS - PV + \mu_1 N_1 + \cdots + \mu_r N_r$$

$\frac{\partial \lambda V}{\partial \lambda} = V$

$\frac{\partial \lambda V}{\partial \lambda} = V$

$U(\lambda S, \lambda V, \lambda N_i) = \lambda U(S, V, N)$

$\frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial \lambda N}{\partial \lambda} = U(S, V, N)$

$$U = TS - PV + \mu_i N_i$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_i} dV + \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{i\neq j}} dN_j$$

$$= TdS - PdV + \mu_j dN_j$$

$$= TdS - PdV + \mu_i dN_i$$

$U = TS - PV + \mu_i N_i$ — Euler — (1)

$dU = TdS - PdV + \mu_i dN_i$ — (Exact differential) — (2)

$dU = TdS + SdT - PdV - VdP + \mu_i dN_i + N_i d\mu_i$ — (3)

Compare (2) and (3)

$SdT - VdP + N_i d\mu_i = 0$ — J W Gibbs

— Gibbs-Duhem Relation

## Gibbs-Duhem relation

$$\mathrm{dU} = T\,\mathrm{dS} - P\,\mathrm{dV} + \mu_i\,\mathrm{dN}_i \,(\text{from } U = U(S, V, N)) \tag{1}$$

$$U = TS - PV + \mu_i N_i \,(\text{from Euler relation}) \tag{2}$$

$$\mathrm{dU} = T\,\mathrm{dS} + S\,\mathrm{dT} - P\,\mathrm{dV} - V\,\mathrm{dP} + \mu_i\,\mathrm{dN}_i + N_i\,d\mu_i \quad (\text{from } (2)) \tag{3}$$

$$U = TS - PV + \sum_{i=1}^{n} \mu_i N_i$$

$$dU = T\,dS + S\,dT - P\,dV - V\,dP + \sum_{i=1}^{n} (N_i\,d\mu_i + \mu_i\,dN_i)$$

Compare equations (1) and (3):

$$S\,\mathrm{dT} - V\,\mathrm{dP} + N_i\,d\mu_i = 0 \,(\mathrm{Gibbs - Duhem})$$

$$H = U + PV \qquad F = U - TS$$

$$G = H - TS$$

Entropy maximum principle

$V^\alpha, V^\beta, N_1^\alpha, N_1^\beta, U^\alpha, U^\beta$

The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.

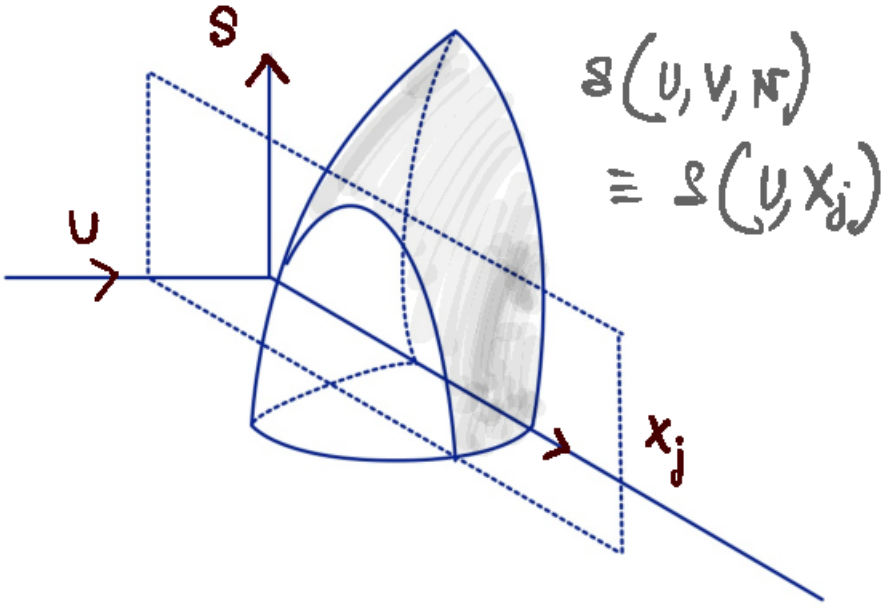
Energy minimum principle

$V^\alpha, V^\beta, N_1^\alpha, N_1^\beta, S^\alpha, S^\beta$

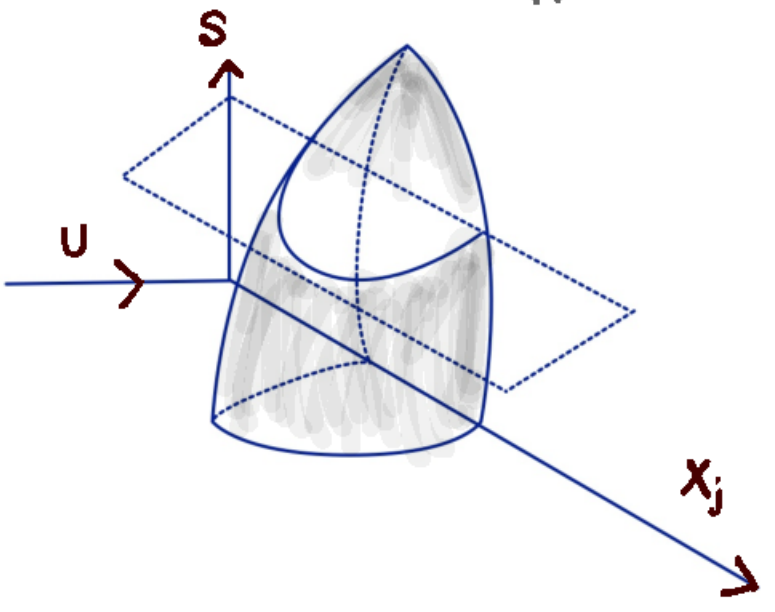
The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of total entropy.

$dS = 0 \quad d^2S < 0$ – Entropy maximum

$dU = 0 \quad d^2U > 0$ – Energy minimum




$S(U, V, N_j) \equiv S(U, X_j)$



$$S = S(U, V, N) \equiv S(U, Y) \qquad Y - V, N_1, N_2, \ldots$$

$$S = S(U, V)$$

Assume $\left(\frac{\partial S}{\partial V}\right)_U = 0 \qquad \left(\frac{\partial^2 S}{\partial V^2}\right)_U < 0$

— Entropy maximum principle

$U = U(S, V)$

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

$= 0$ (from our assumption)

$Z = Z(X, Y)$

$$\left(\frac{\partial Z}{\partial Y}\right)\left(\frac{\partial X}{\partial Z}\right)\left(\frac{\partial Y}{\partial X}\right) = -1$$

$$\frac{\partial Z}{\partial Y} = -\frac{\left(\frac{\partial X}{\partial Y}\right)_Z}{\left(\frac{\partial X}{\partial Z}\right)_Y}$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_U$$

$$P = P(U, V)$$

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial P}{\partial V}\right)_U \left(\frac{\partial V}{\partial V}\right)_S$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \qquad = \left(\frac{\partial P}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial P}{\partial V}\right)_U$$

$$= 0$$

$$= -P\left(\frac{\partial P}{\partial U}\right)_V + \left(\frac{\partial P}{\partial V}\right)_U$$

$$= \left(\frac{\partial P}{\partial V}\right)_U \qquad \text{at } P = 0$$

$$dP = \left(\frac{\partial P}{\partial U}\right)_V dU + \left(\frac{\partial P}{\partial V}\right)_U dV$$

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial P}{\partial V}\right)_U$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = \frac{\partial}{\partial V}\left[-\frac{\left(\partial S/\partial V\right)_U}{\left(\partial S/\partial U\right)_V}\right]_U$$

$$\frac{\partial}{\partial x}\left(-\frac{1}{x}\right) = +\frac{1}{x^2}$$

$$= -\frac{\partial^2 S}{\partial V^2}\Big/\frac{\partial S}{\partial U} + \left(\frac{\partial S}{\partial V}\right)_U \frac{\dfrac{\partial^2 S}{\partial U \partial V}}{\left(\dfrac{\partial S}{\partial U}\right)_V^2}$$

$$= -T\frac{\partial^2 S}{\partial V^2} \qquad \because \frac{\partial^2 S}{\partial V^2} < 0 \quad \left(\frac{\partial S}{\partial V}\right)_U = 0$$

$$> 0$$

$\therefore$ U is a minimum

$Y = Y(X) \Rightarrow \psi = \psi(P)$ Legendre transformation

$P = \frac{Y - \psi}{X - 0}$ or $\psi = Y - PX$

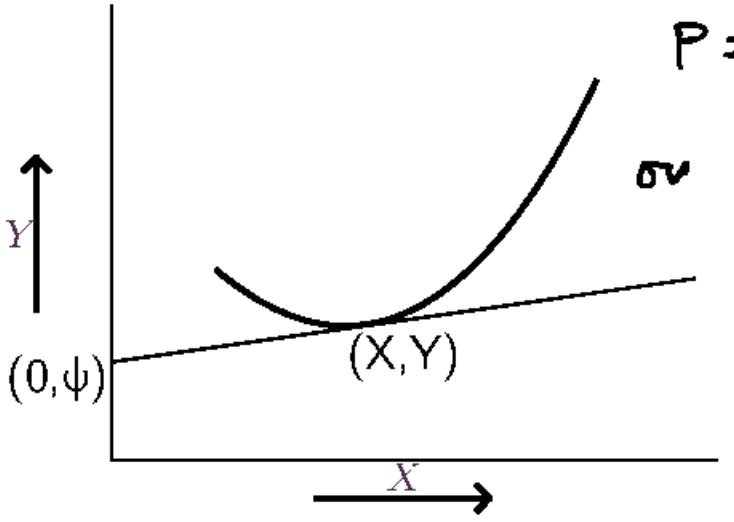
T ↔ S

V ↔ P

μ ↔ κ

$P = \frac{Y - \psi}{X}$ $y = f(x)$

or $\psi = Y - PX$ $Y = Y(X)$




$\psi = Y - PX$

— intercept

P — slope

$dY = P\,dX$

$d\psi = dY - P\,dX - X\,dP = -X\,dP$ or, $-X = \frac{d\psi}{dP}$

$-X = \frac{d\psi}{dP}$

$\frac{dY}{dX} = P$

$\Rightarrow dY = P\,dX$

## Legendre Transformation

$Y = Y(X)$

$P = \frac{dY}{dX}$

$\psi = -PX + Y$

Elimination of $X$ and $Y$ $\quad \psi = \psi(P)$

$\psi = \psi(P)$

$-X = \frac{d\psi}{dP}$

$Y = XP + \psi$

Elimination of $\psi$ and $P$ $\quad Y = Y(X)$

## Helmoltz potential or Helmoltz free energy

$U = U(S, V, N_1, ...)$

$T = \partial U / \partial S$

$F = U - TS$

Eliminate $U$ and $S$ to get

$F = F(T, V, N_1, ...)$

$F = F(T, V, N_1, ...)$

$S = -\partial F / \partial T$

$U = F + TS$

Elimiminate $F$ and $T$ to get

$U = U(S, V, N_1, ...)$

$$\mathrm{dF} = -S\,\mathrm{dT} - P\,\mathrm{dV} + \mu_1 \mathrm{dN}_1 + \mu_2\,\mathrm{dN}_2 + \cdots$$

$U = U(S, V, N_1, \cdots, N_k)$

$T = T(S, V, N_1, \cdots, N_k)$

$U = U(S, V, N_1, \cdots, N_k)$

$F = F(T, V, N_1, \cdots, N_k)$

$F = F(T, V, N_1, \cdots)$

## Enthalpy H≡U[P]

$U = U(S, V, N_1, \ldots)$

$-P = \partial U / \partial V$

$H = U + PV$

Eliminate $U$ and $V$ to get

$H = H(S, P, N_1, \ldots)$

$H = H(S, P, N_1, \ldots)$

$V = \partial H / \partial P$

$U = H - PV$

Eliminate $H$ and $P$ to get

$U = U(S, V, N_1, \ldots)$

$P = P(S, V, N_1, \ldots)$

$$\mathrm{dH} = T\,\mathrm{dS} + V\,\mathrm{dP} + \mu_1 \mathrm{dN}_1 + \mu_2\,\mathrm{dN}_2 + \cdots$$

## Gibbs Free Energy G≡U[T,P]

$U = U(S, V, N_1, \ldots)$

$T = \partial U / \partial S$ $\quad S \to T$

$-P = \partial U / \partial V$ $\quad V \to P$

$G = U - TS + PV + \mu N$

Eliminate $U$, $S$, and $V$ to get

$G = G(T, P, N_1, \ldots)$

$H = H(S, P, N_1, \ldots)$

$-S = \partial G / \partial T$

$V = \partial G / \partial P$

$U = G + TS - PV$

Eliminiminate $G$, $T$, and $P$ to get

$U = U(S, V, N_1, \ldots)$

$$dG = -S\,dT + V\,dP + \mu_1 dN_1 + \mu_2 dN_2 + \cdots \quad - (1)$$

$$G = U - TS + PV + \mu_i N_i$$

$$dG = dU - TdS - SdT + PdV + VdP + \mu_i dN_i + N_i d\mu_i \quad - (2)$$

$$dU + PdV = TdS$$

$$dU - TdS + PdV + N_i d\mu_i = 0$$

$$N_i d\mu_i = 0 \quad - \text{Gibbs Duhem relation}$$

Helmoltz potential minimum principle: *The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmoltz potential over the manifold of states for which* $T = T^{\text{reservoir}}$

Gibbs free energy minimum principle: *The equilibrium value of any unconstrained internal parameter in a system in contact with a thermal and a pressure reservoir miminimizes the Gibbs free energy at constant temperature and pressure* $T = T^r, P = P^r$

$$d(U + U^r) = \mathrm{dU} - T^r \mathrm{dS} + P^r \,\mathrm{dV} = 0$$

$\because T = T^r, P = P^r \qquad \mathrm{dG} = d(U - TS + PV) = 0$

$d^2G = d^2(U - T^rS + P^rV) = d^2U > 0$

$d(U + U^r) = 0$

$d^2(U + U^r) = d^2U > 0$

subject to

$d(S + S^r) = 0$

# System at constant T

System + Reservoir $\longrightarrow$ Isolated System

$$\Delta\left(U+U^{r}\right)=0$$

$U$ – Internal energy of System

$U^{r}$ – Internal energy of Reservoir

$$\Delta S+\Delta S^{r}\geq 0 \quad \text{(Second law)}$$

Assumption – Size of the reservoir is infinite compared to the size of the System

$$\Delta U^R = -\Delta U$$

Temperature of reservoir $T^R$ is kept constant

Reservoir – $\Delta U^r$ is infinitesemal change in energy

$$\Delta S^R = \frac{\Delta U^R}{T^R} = \frac{-\Delta U}{T^R}$$

$$\therefore \quad \Delta S + \Delta S^R \geq 0 \Rightarrow \quad \Delta S - \frac{\Delta U}{T^R} \geq 0$$

$$\frac{\Delta U}{T^{ir}} - \Delta S \leq 0$$

or, $$\Delta\left(U - T^{ir}\Delta S\right) \leq 0$$

$$T = T^{ir}$$

$$\therefore \quad \Delta\left(U - TS\right) \leq 0$$

or $$\Delta F \leq 0$$

$\Delta F = 0$ — reversible process

Closed composite system

$$\sum_{i=1}^{m} V^{(i)} = V \qquad \sum_{i=1}^{m} N_c^{(i)} = N_c$$

$c \to A, B, C, \cdots$

$$F\left(T^{\pi}, V^{(1)}, N_c^{(1)}, \cdots, V^{(m)}, N_c^{(m)}\right)$$

$$= \sum_{i=1}^{m} F^{(i)}\left(T^{\pi}, V^{(i)}, N_c^{(i)}\right)$$

$$dF = \sum_{i=1}^{m} \left[ -\left(p^{(i)} - p^{(i)}\right) dV + \left(\mu_c^{(i)} - \mu_c^{(i)}\right) dN_c \right]$$

$= 0$

$d^2F > 0$

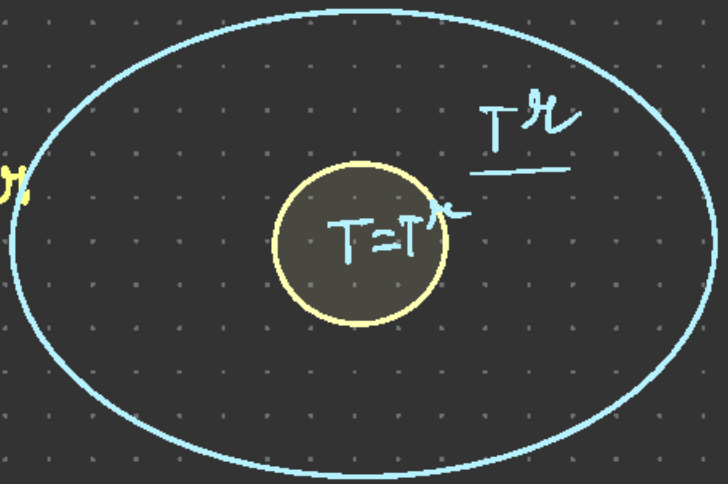
System + thermal reservoir — adiabatically isolated System

$$W = -\Delta\left(U + U^R\right)$$

$$\Delta U^R = T^R \Delta S^R$$

$$= -\Delta U - \Delta U^R$$

$$= -\Delta U - T^R \Delta S^R$$




$$\Delta S + \Delta S^R \geq 0$$

$$\Delta S^R = -\Delta S \quad \text{(reversible)}$$

$$W^{rev} = -\Delta U + T^R \Delta S$$

$$= -\left(\Delta U - T\Delta S\right) = -\Delta F$$

$$W^{irr} < W^{rev} = -\Delta F$$

$$W \leq -\Delta F$$

System in contact with a thermal reservoir and the wall is flexible so that volume adjusts such that

$$T = T^r \qquad P = P^r$$

$$\Delta\left(U + U^r\right) = 0$$

$$\Delta\left(V + V^r\right) = 0$$

$U + U^r$ = constant

$V + V^r$ = Constant

$\Delta U^r = -\Delta U$

Note $\Delta U = -\Delta U^r$

$\Delta V = -\Delta V^r$

But $\Delta V^r$, $\Delta U^r$ are infinitesimal and neglected due to infinite size of reservoir

$$\Delta U^{\gamma} = -\Delta U \sim 0$$

$$\Delta V^{\pi} = -\Delta V \sim 0$$

Thus, $P^{\pi}$, $T^{\pi}$ are constant

Now, $\Delta S + \Delta S^{\gamma} \geq 0$

$$\Delta S^{\pi} = \frac{\Delta U^{\pi}}{T^{\pi}} + \frac{P^{\pi}\Delta V^{\pi}}{T^{\pi}} = \frac{-\Delta U}{T^{\pi}} - \frac{P^{\pi}\Delta V}{T^{\pi}}$$

$$\therefore \quad \Delta\left(U - T^{\pi}S + P^{\pi}V\right) \leq 0$$

$T^{\pi} = T$

$P^{\pi} = P$

$$G_1 = U - T^{\pi}S + P^{\pi}V = U - TS + PV$$

$$\therefore \Delta G_1 \leq 0$$

# Maxwell Relations

$$dZ = M\,dx + N\,dy$$

$$M = \left(\frac{\partial Z}{\partial x}\right)_y \qquad N = \left(\frac{\partial Z}{\partial y}\right)_x$$

$$\frac{\partial M}{\partial y} = \frac{\partial^2 Z}{\partial y \partial x} \qquad \frac{\partial N}{\partial x} = \frac{\partial^2 Z}{\partial x \partial y}$$

$$dU = T\,dS - p\,dV + \mu\,dN$$

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

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

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

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

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

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

$$\left(\frac{\partial^2 F}{\partial T \partial V}\right)_N = \left(\frac{\partial^2 F}{\partial V \partial T}\right)_N \Rightarrow +\left(\frac{\partial S}{\partial V}\right)_{T,N} = +\left(\frac{\partial p}{\partial T}\right)_{V,N}$$

$$\left(\frac{\partial^2 H}{\partial S \partial P}\right)_N = \left(\frac{\partial^2 H}{\partial P \partial S}\right)_N \Rightarrow \left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$$

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right)_N = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_N \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N}$$

$$= V\alpha$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

$dH = TdS = C_P\,dT$ at const $P$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$dU = TdS = C_V dT$ at constant $V$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

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

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

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

Isothermal Compressibility $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Adiabatic Compressibility $K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

$$\ln\left(\frac{xe}{ze}\right) = \frac{\ln\left(\frac{xe}{ze}\right)}{1} = \ln\left(\frac{ze}{xe}\right)$$

$$\ln\left(\frac{xe}{ze}\right) \times \left(\frac{\ln e}{ze}\right) - =$$

$$\ln\left(\frac{ze}{xe}\right) \times \left(\frac{\ln e}{ze}\right) - =$$

$$\exists\left(\frac{\ln e}{me}\right) \exists\left(\frac{me}{xe}\right) = \exists\left(\frac{\ln e}{xe}\right)$$

$$z = z(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Put $dz = 0$

$$\left(\frac{\partial z}{\partial x}\right)_y dx = -\left(\frac{\partial z}{\partial y}\right)_x dy$$

or, $$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

or, $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial z}{\partial x}\right)_y^{-1}$

$S = S(T, P)$

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial S}{\partial T}\right)_P^{-1} = + \frac{TV\alpha}{C_P}$$

Maxwell

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

$$= -V\alpha$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$Z(x, y, w)$$

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_{y,w} dx + \left(\frac{\partial Z}{\partial y}\right)_{x,w} dy + \left(\frac{\partial Z}{\partial w}\right)_{x,y} dw$$

$$dw = 0$$

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_{y,w} dx + \left(\frac{\partial Z}{\partial y}\right)_{x,w} dy$$

$$\therefore \left(\frac{\partial Z}{\partial y}\right)_w = \left(\frac{\partial Z}{\partial x}\right)_{y,w} \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial Z}{\partial y}\right)_x$$

$$V(T, P, S)$$

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

$$-V K_S \qquad\qquad -V K_T \qquad\qquad -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = K_S$$

$$\therefore \quad K_T - K_S = \frac{TV\alpha^2}{C_P}$$

$$K_S < K_T$$

$$-V K_S = V\alpha \frac{TV\alpha}{C_P} - V K_T$$

Find $\Delta G$ for $MgO$ when 1 mole is heated from $25^\circ C$ to $1027^\circ C$ at 1 atm. pressure.

$298\,K$ $\quad$ $1300\,K$

$$C_p = 48.99 + 3.43 \times 10^{-3} T - \frac{11.34 \times 10^{-5}}{T^2} \quad \frac{J}{mol\text{-}K}$$

$$S^\circ_{298} = 26.9 \quad \frac{J}{mol\text{-}K}$$

$$T(K) = T(^\circ C) + 273$$

Identify variables

$$G = G(T, P)$$

$$dG = -S\,dT + V\,dP$$

$dP = 0$ ? Pressure is 1 atm. Constant

$$\therefore \quad dG = -S\,dT$$

$S(T,P)$

$dH = T\,dS$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT - \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \frac{C_P}{T} dT - V\alpha\, dP$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$$

$dP = 0$

$$\therefore \quad dS = \frac{C_P}{T} dT$$

$$\int_{298}^{T} dS = S(T) - S^{\circ}_{298} = \int_{298}^{T} \frac{C_P(T)}{T} dT$$

$$S(T) = S^{\circ}_{298} + \int_{298}^{T} \frac{C_p(T)}{T}\, dT$$

$$\therefore \quad \Delta G_T = \int_{298}^{T} dG_T$$

$$= -\int_{298}^{T} S(T)\, dT$$

$$= -\int_{298}^{T} \left\{ S^{\circ}_{298} + \int_{298}^{T} \frac{C_p(T)}{T}\, dT \right\}$$

Find $\left(\frac{\partial H}{\partial q}\right)_S$ in terms of experimental Variables

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$= \delta q + VdP$$

$$= TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

$$dG = V\,dP - S\,dT$$

$$S(T,P) = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$dS = \frac{C_P}{T}\,dT - V\alpha\,dP$$

$$\frac{C_p}{T} dT = dS + V\alpha\, dP$$

or, $$dT = \frac{T\,dS}{C_p} + \frac{TV\alpha}{C_p} dP$$

$$dG = V\,dP - S\,dT$$

$$= V\,dP - S\left(\frac{T\,dS}{C_p} + \frac{TV\alpha}{C_p} dP\right)$$

$$= \left(V - \frac{TSV\alpha}{C_p}\right) dP - \frac{TS}{C_p} dS$$

$$\left(\frac{\partial G}{\partial P}\right)_S = V - \frac{TSV\alpha}{C_p}$$

$$\left(\frac{\partial H}{\partial G}\right)_S = \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial G}\right)_S$$

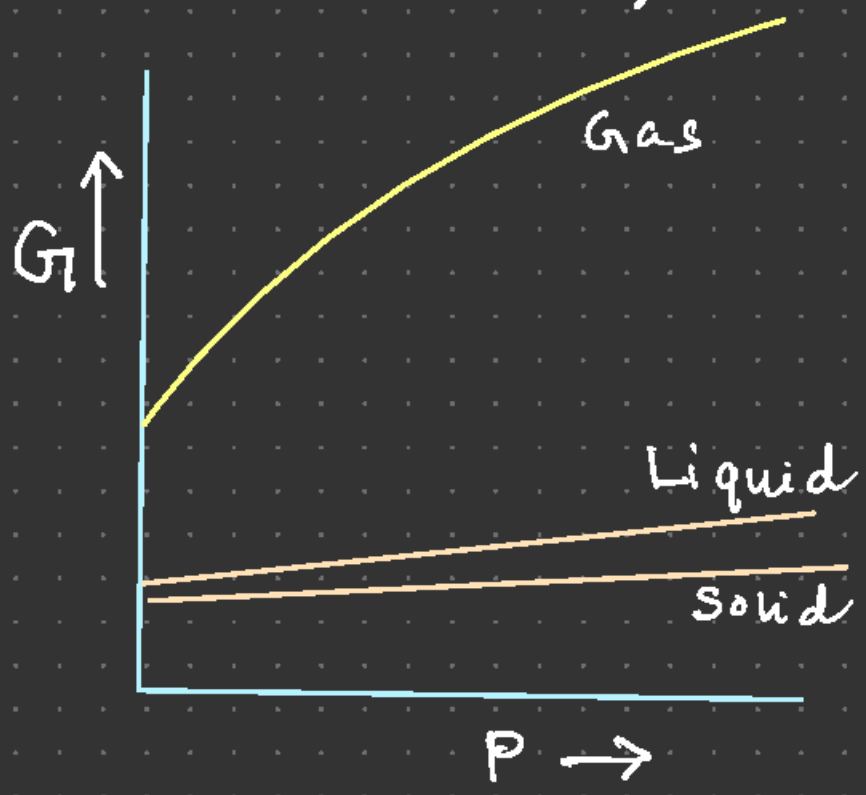
$$= \frac{V}{\frac{VC_P - TSV\alpha}{C_P}} = \frac{C_P V}{C_P V - TSV\alpha}$$

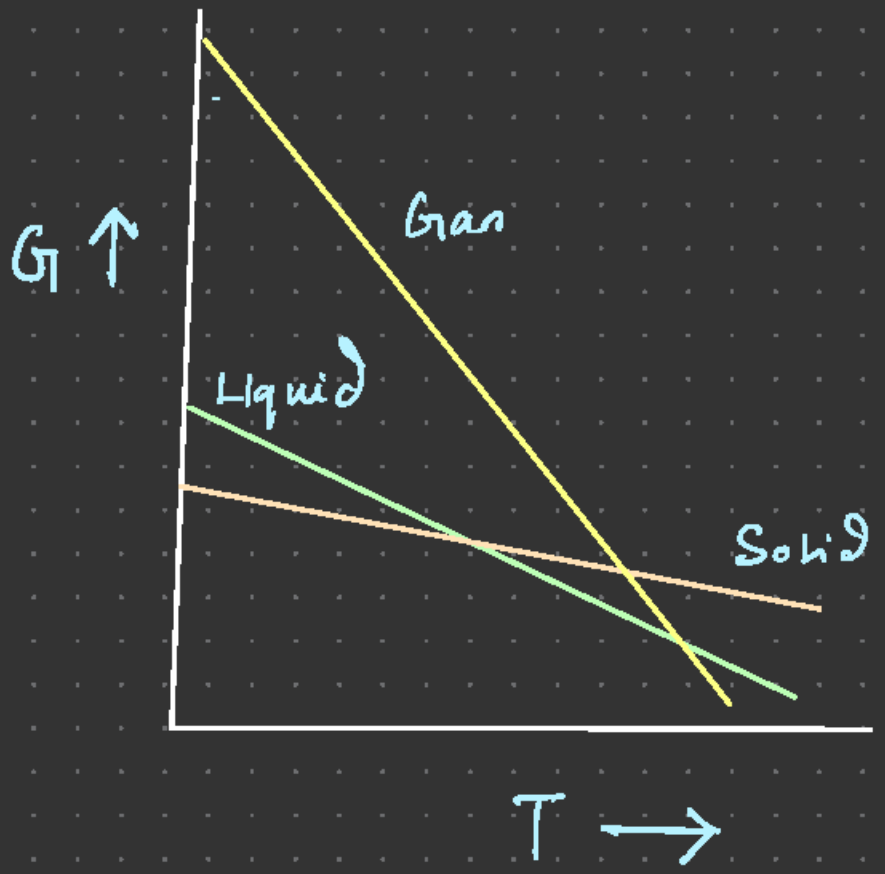
$$= \frac{C_P}{C_P - TS\alpha}$$

$$dG = V\,dP - S\,dT + \mu\,dN$$

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

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



Gibbs - Helmholtz equation $\quad G = H - TS$

$$S = \frac{H - G}{T}$$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G - H}{T}$$

$$\left(\frac{\partial}{\partial T}\ \frac{G}{T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\,\frac{d}{dT}\,\frac{1}{T}$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2}$$

$$= \frac{1}{T}\left\{\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right\}$$

$$= \frac{1}{T}\left(\frac{G - H}{T} - \frac{G}{T}\right) = -\frac{H}{T^2}$$

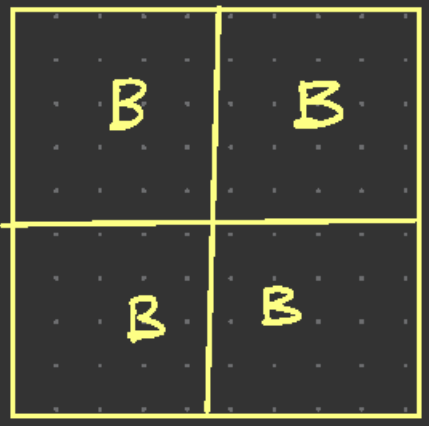
Phase change

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

Connection between the microscopic world of atoms & macroscopic thermodynamics




4 A atoms

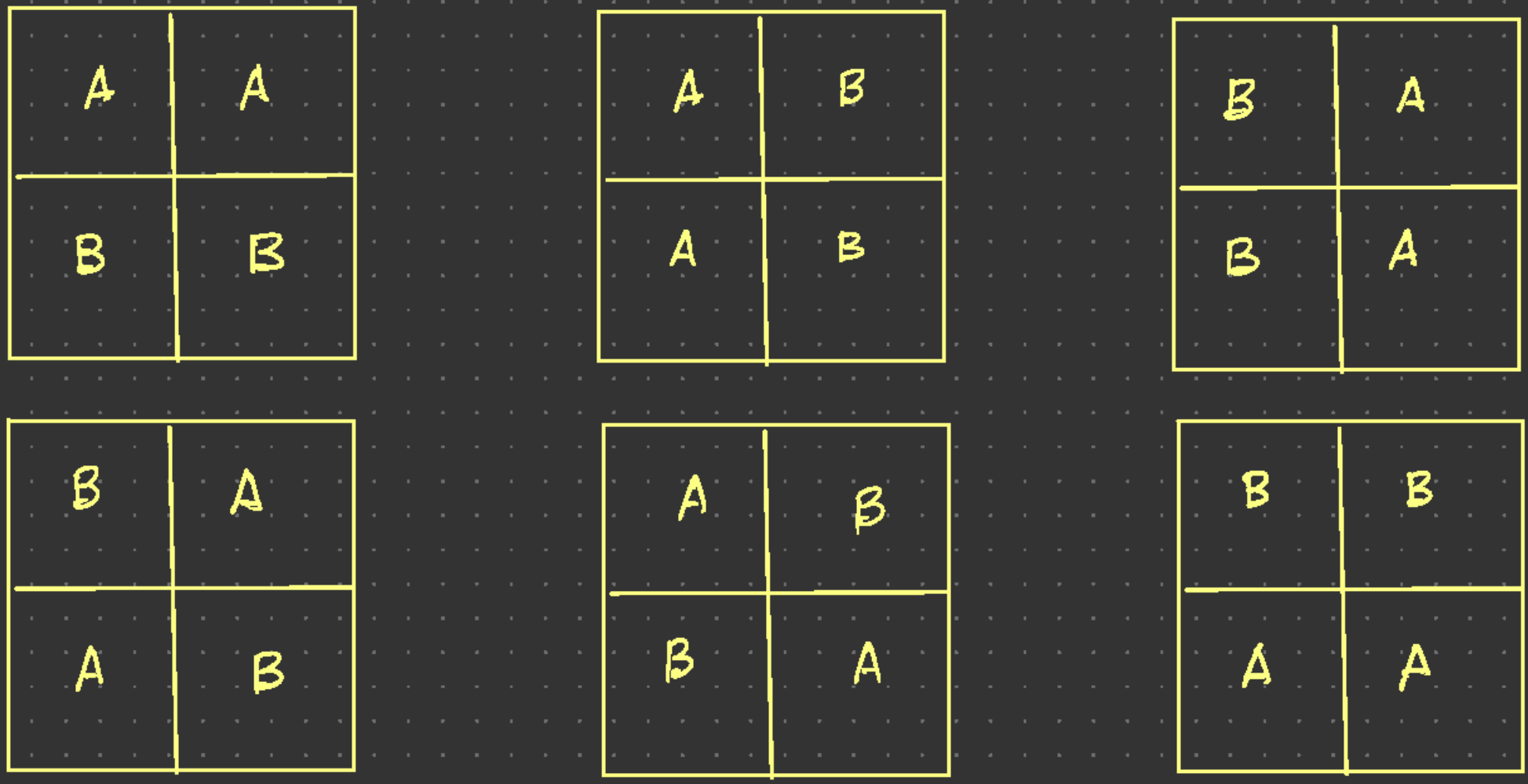



B atoms

4 A's are same type - identical

4 B's are same type - identical

A, B are distinct or distinguishable kinds




2 A's and 2 B's

4 placeholders

Problem

Arrange $n_1$ elements of type 1
$n_2$ elements of type 2
$n_3$ elements of type 3
$\vdots$
$n_k$ elements of type $k$
in $n$ positions.

Each type is distinct or distinguishable from the other

$$n_1 + n_2 + n_3 + \cdots + n_k = n$$

Arrange $n_1$ elements among $n$ places