Thermodynamics & Kinetics of Materials

Week 12

Sondata Bhattacharya

Phase Equilibrium Conditions

$$P^{\alpha} = P^{\beta} = P^{\gamma}$$

$$\mu_A^{\alpha} = \mu_A^{\beta} = \mu_A^{\gamma}$$

$$\mu_B^{\alpha} = \mu_B^{\beta} = \mu_B^{\gamma}$$

$$T^{\alpha} = T^{\beta} = T^{\gamma}$$

Stability

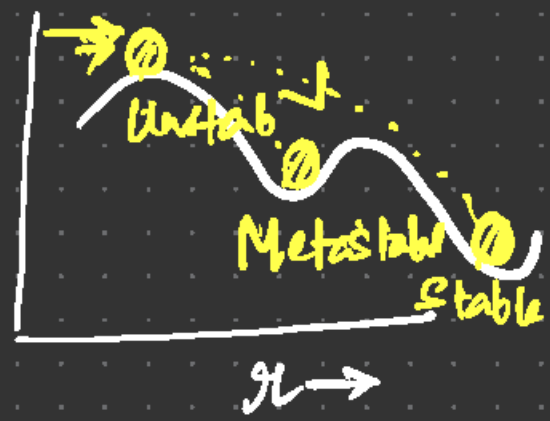
Numerical Modeling – G-X curves

Thermodynamics of reacts

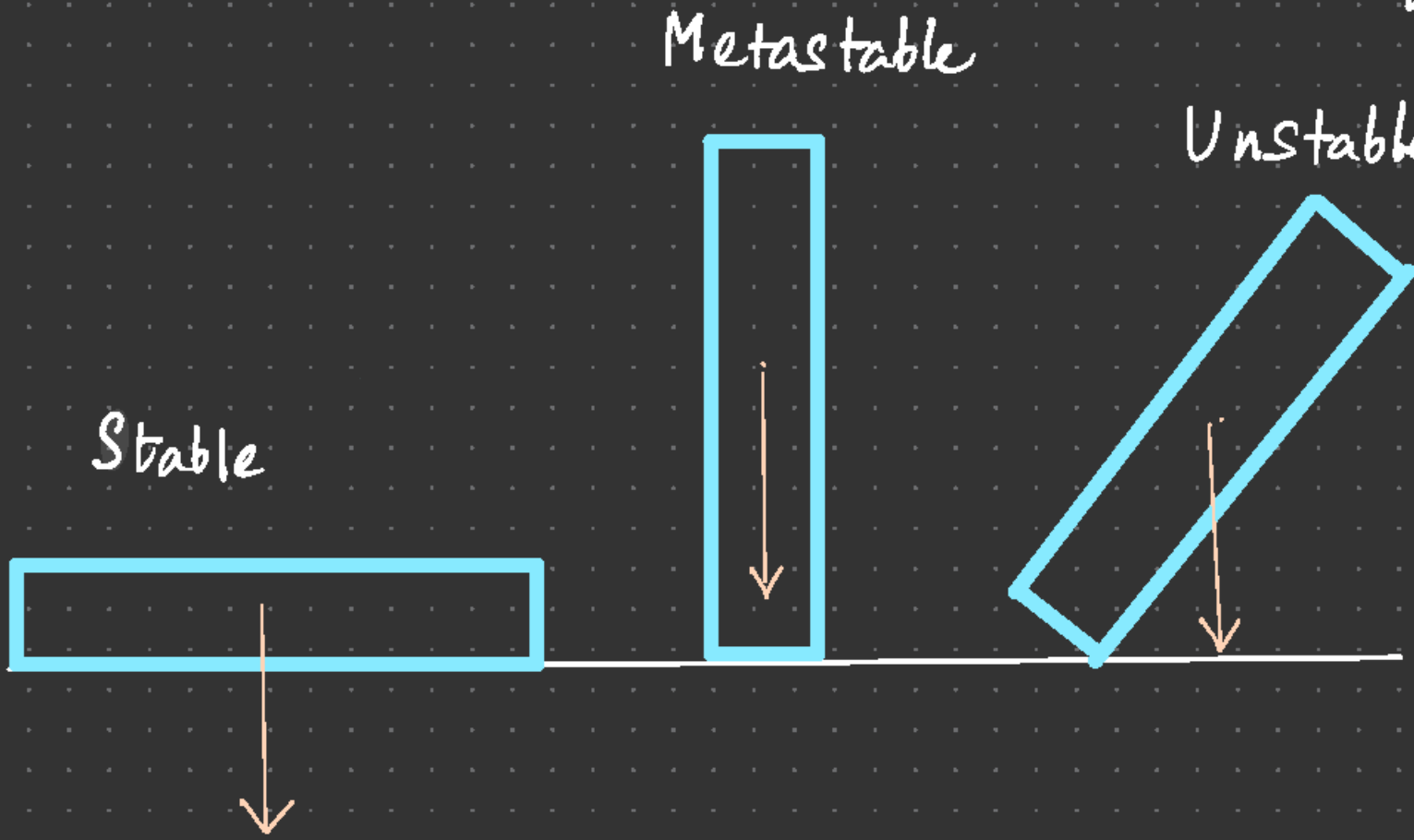
Interfacial thermodynamics

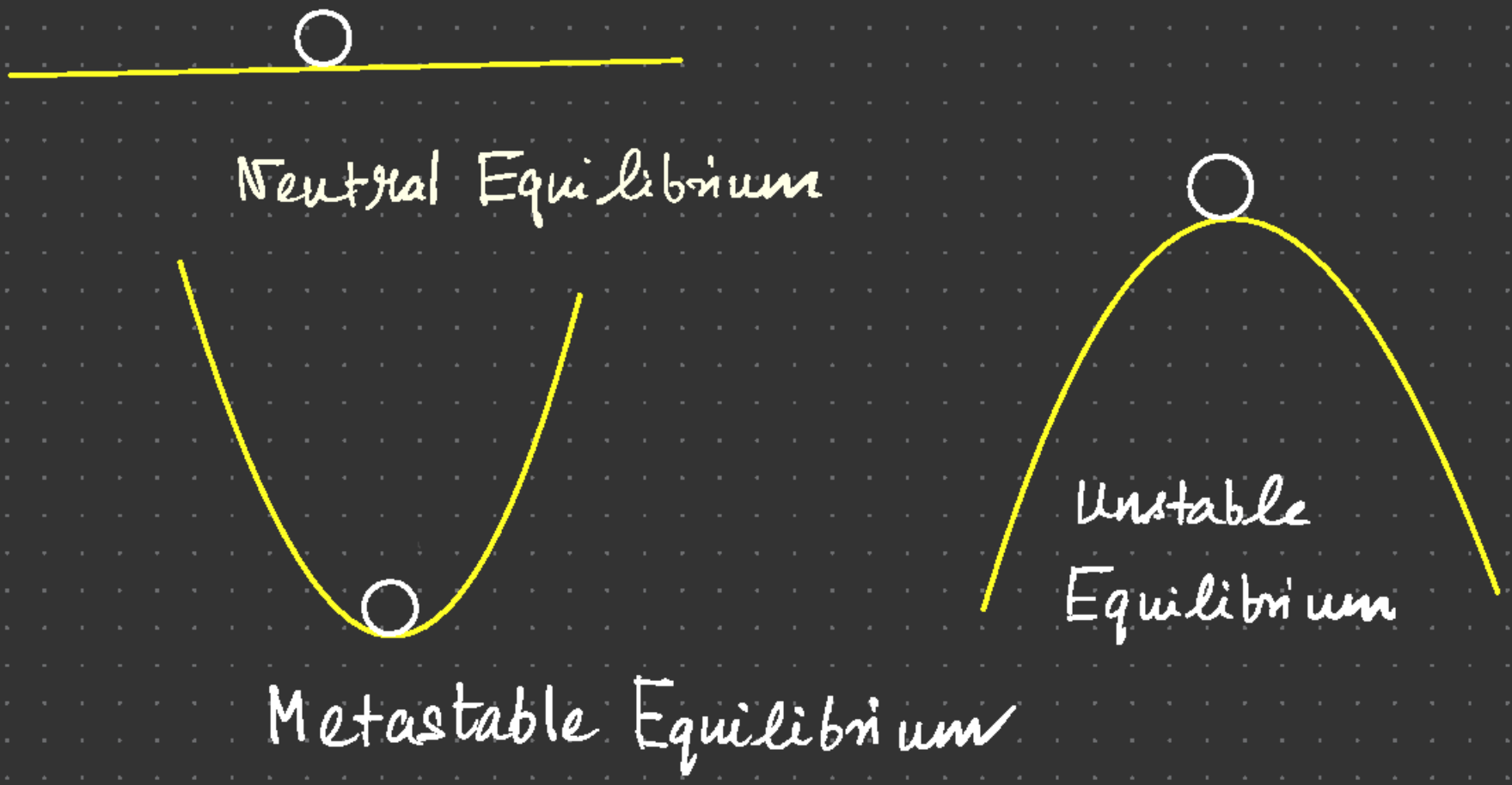
Irreversible thermodynamics – Flux-force relations

Criteria for phase stability



Mechanical Analogue



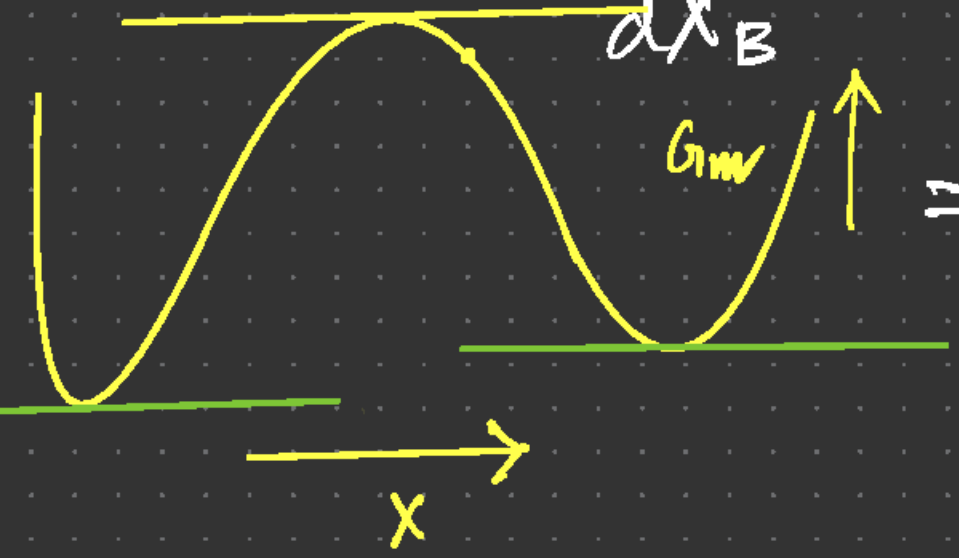

Neutral Equilibrium
Unstable Equilibrium
Metastable Equilibrium

$$G_{m,mix} = RT\left(x_A \ln x_A + x_B \ln x_B\right) + \omega x_A x_B$$

$x_A + x_B = 1$

$(1-x) \quad x$

$$= RT\{(1-x)\ln(1-x) + x\ln x\} + \omega x(1-x)$$



$$\frac{dG_{m,mix}}{dx_B} = \frac{dG_{m,mix}}{dx}$$

$$= RT\{-1 - \ln(1-x) + 1 + \ln x\} + \omega - 2\omega x$$

$$= RT\ln\left(\frac{x}{1-x}\right) + \omega(1-2x)$$

$$\frac{dG_{m,mix}}{dx} = RT\left\{\ln x - \ln(1-x)\right\} + \omega(1-2x)$$

$$\frac{d^2G_{m,mix}}{dx^2} = RT\left\{\frac{1}{x} + \frac{1}{1-x}\right\} - 2\omega$$

$$= 4RT - 2\omega \quad \text{at } x = 1/2$$

$$\frac{d^3G_{m,mix}}{dx^3} = RT\left\{\frac{1}{(1-x)^2} - \frac{1}{x^2}\right\}$$

$$4RT - 2\omega < 0$$

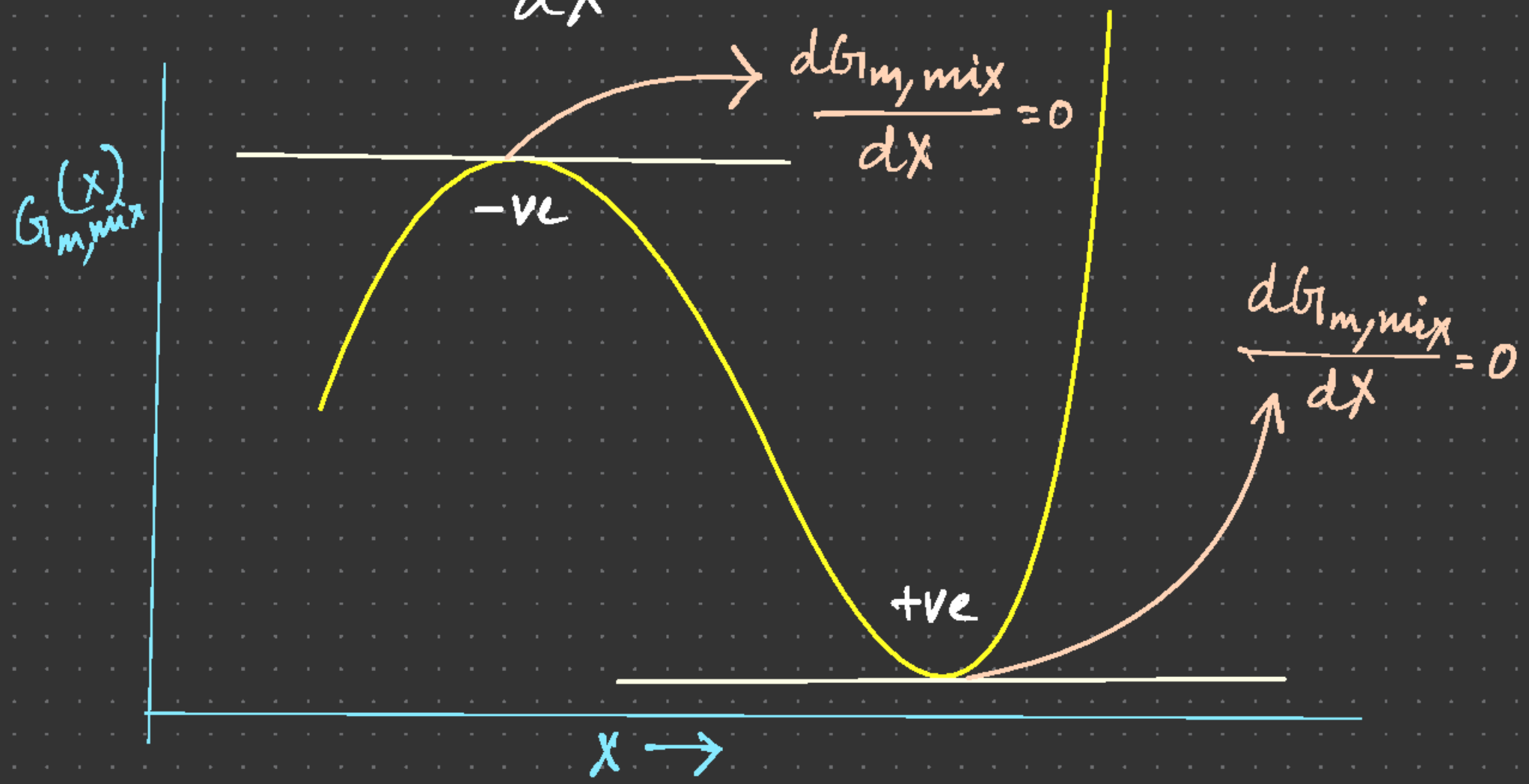
$$2\omega > 4RT \quad \omega > 2RT$$

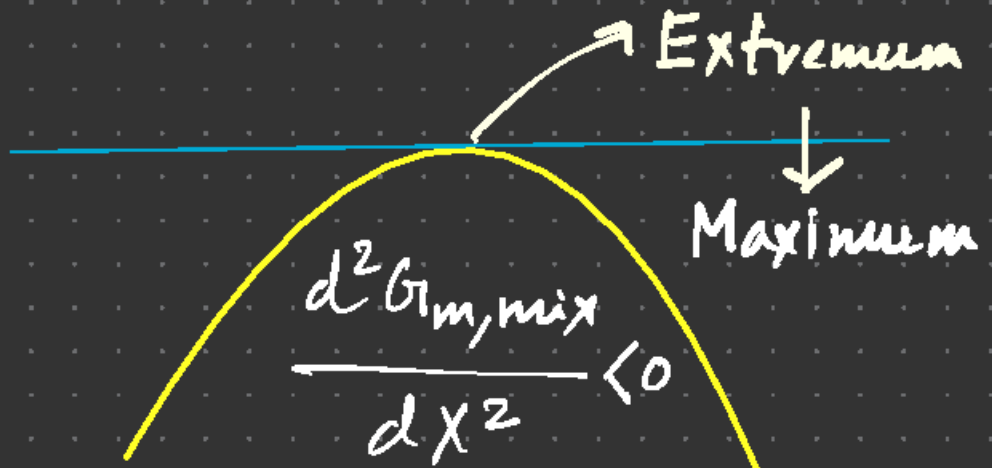
When $X = 0.5$

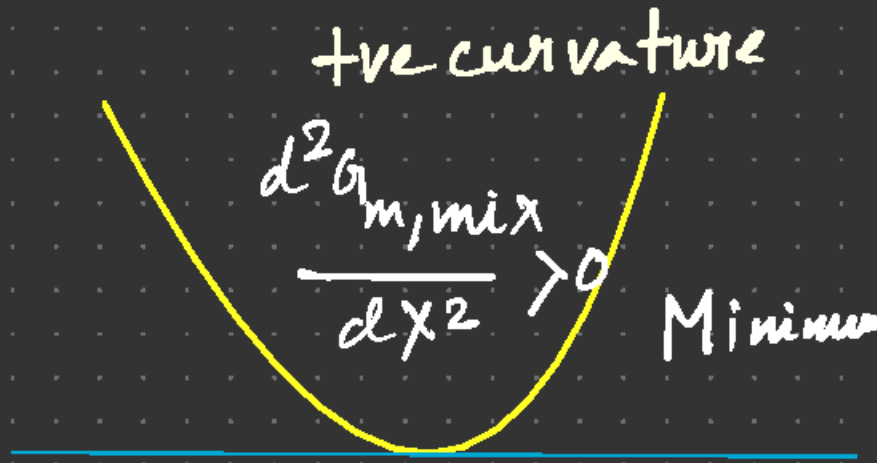
$G_{m,mix}(X)$

$= \Delta G_{mix}^{mix}(X)$

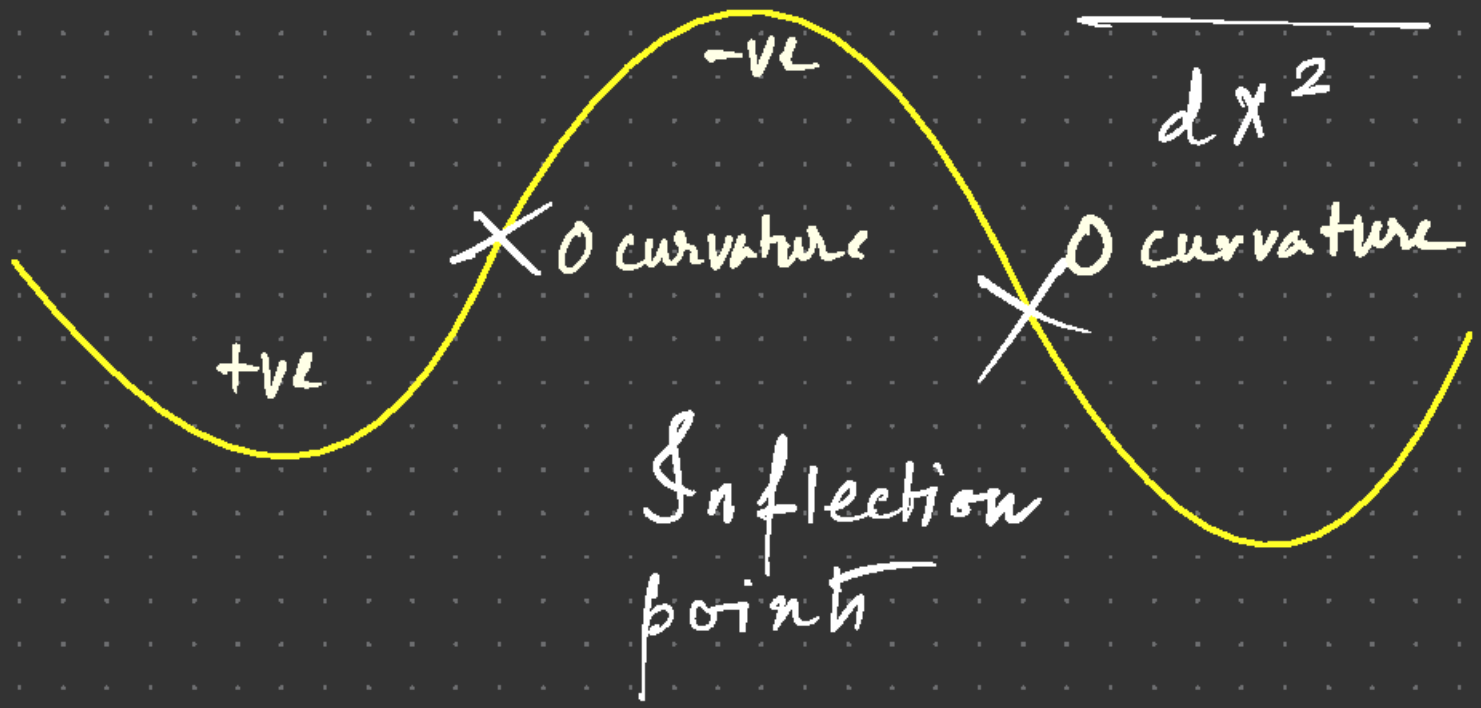
$$\frac{d^3 G_{m,mix}}{dX^3} = 0$$







What about $\frac{d^2G_{m,mix}}{dx^2} = 0$?



$$\frac{d^2 G_{m,mix}}{dx^2} = 0$$

$$\Rightarrow RT\left\{\frac{1}{x} + \frac{1}{1-x}\right\} - 2\omega = 0$$

$$\Rightarrow \frac{1}{x} + \frac{1}{1-x} = \frac{2\omega}{RT}$$

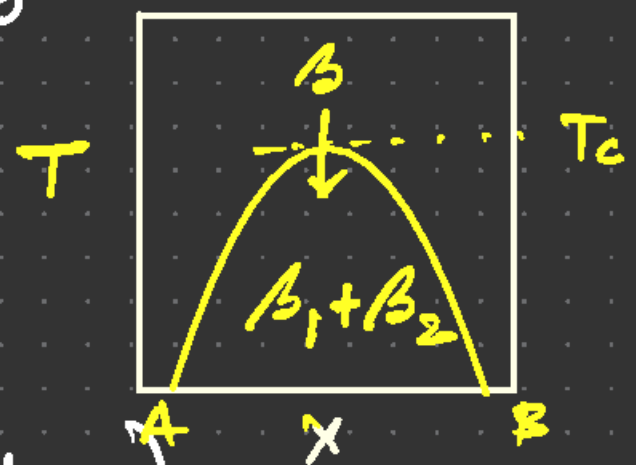
$$\Rightarrow \frac{RT}{2\omega} = x(1-x)$$

$$x = \frac{1}{2}$$

When $X = 0.5$

B – homogeneous solid sol^{n}. of A+B

$$\frac{RT}{2\omega} = \frac{1}{2} \cdot \frac{1}{2} = 0.25$$



$$\Rightarrow \frac{2\omega}{RT} = 4$$

$$\Rightarrow \frac{\omega}{RT} = 2 \quad \text{(Critical value)}$$

$$T_c = \frac{\omega}{2R}$$

$\alpha = \frac{\omega}{RT}$ $\alpha_c = 2$ $\frac{\omega}{RT} > 2$ $\omega > 2RT$

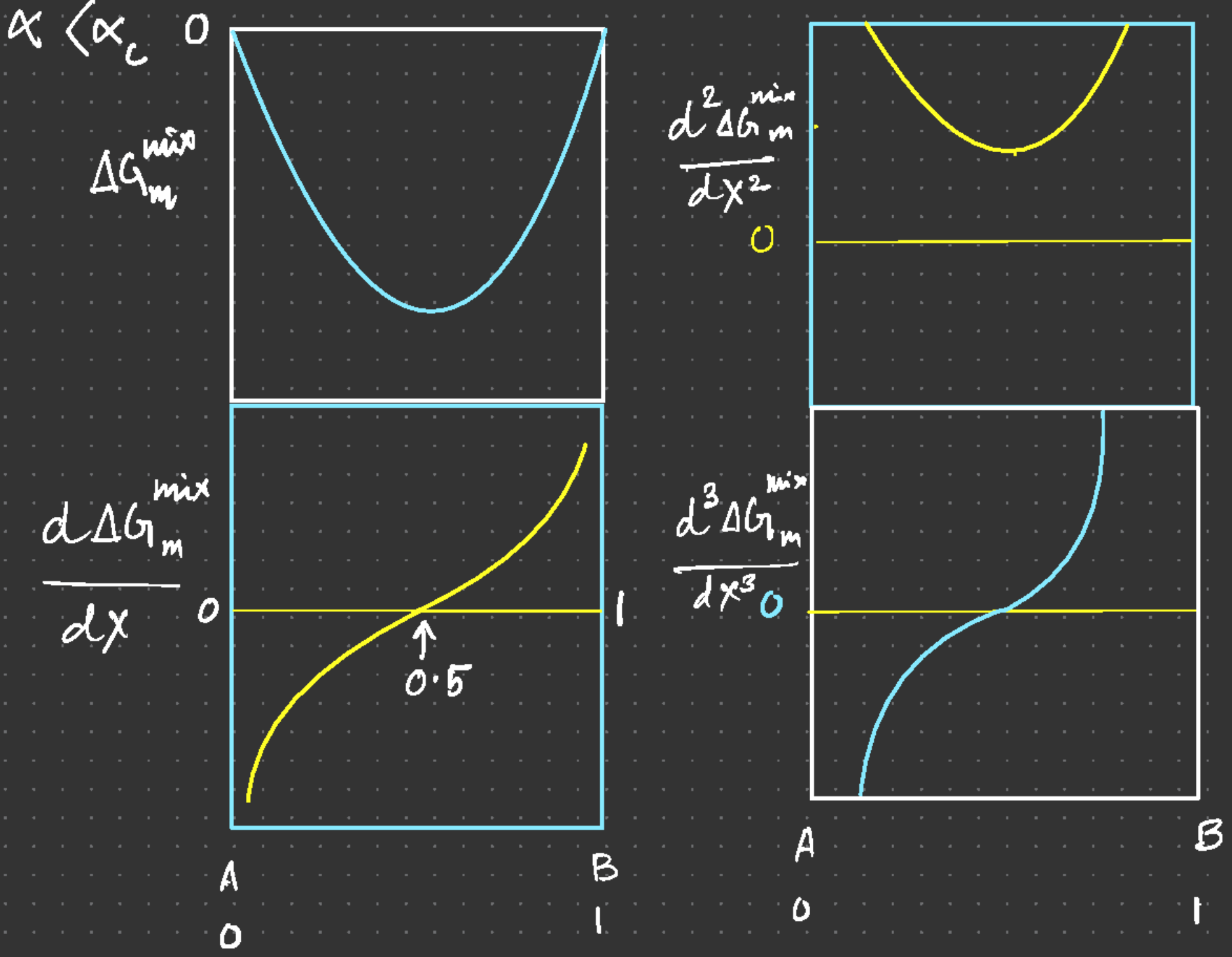
$\alpha > \alpha_c$ phase separation

$\alpha = \alpha_c$ Critical point

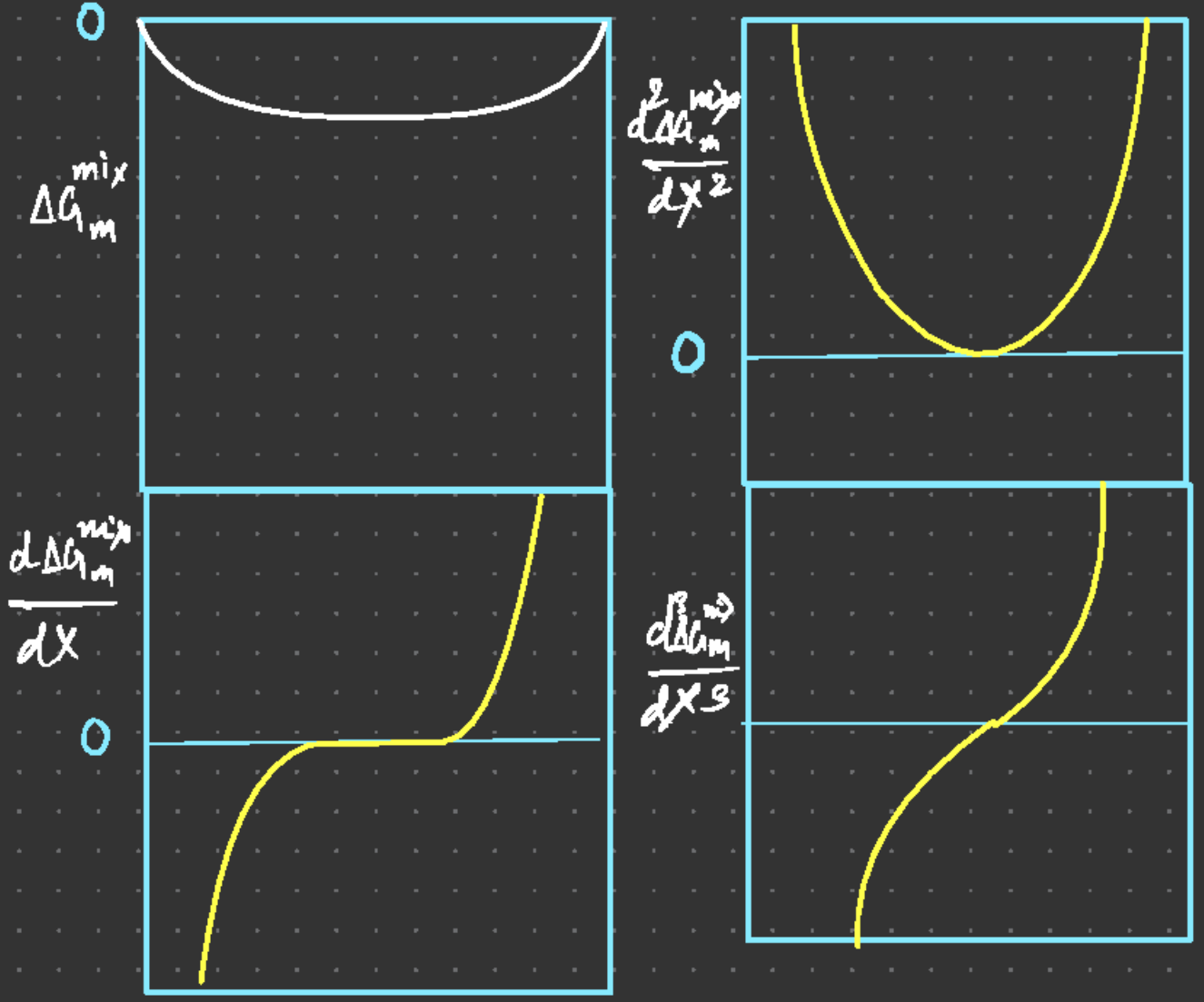
$\alpha < \alpha_c$ Homogeneous single phase

$\frac{\omega}{RT} < 2$

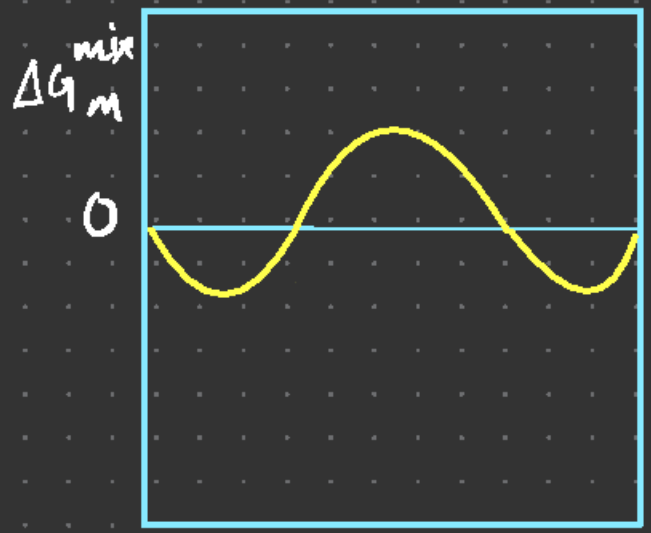
$\omega - 2RT < 0$

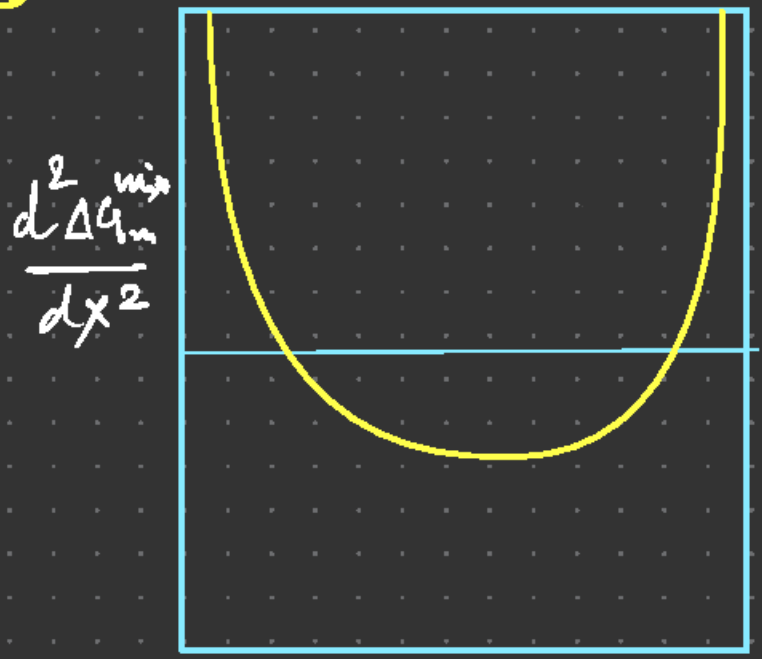

$\alpha < \alpha_c$
0
ΔG_m^{mix}
$\frac{d\Delta G_m^{mix}}{dx}$
0
0·5
1
A
B
0
1
$\frac{d^2\Delta G_m^{mix}}{dx^2}$
0
$\frac{d^3\Delta G_m^{mix}}{dx^3}$
0
A
B
0
1

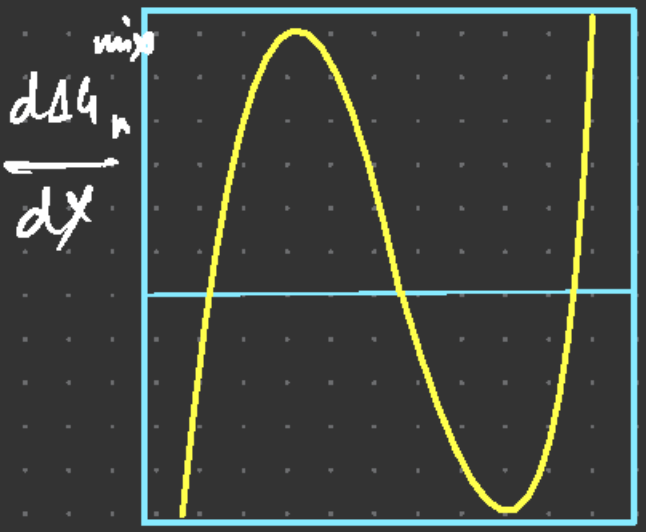
$\alpha = \alpha_c$

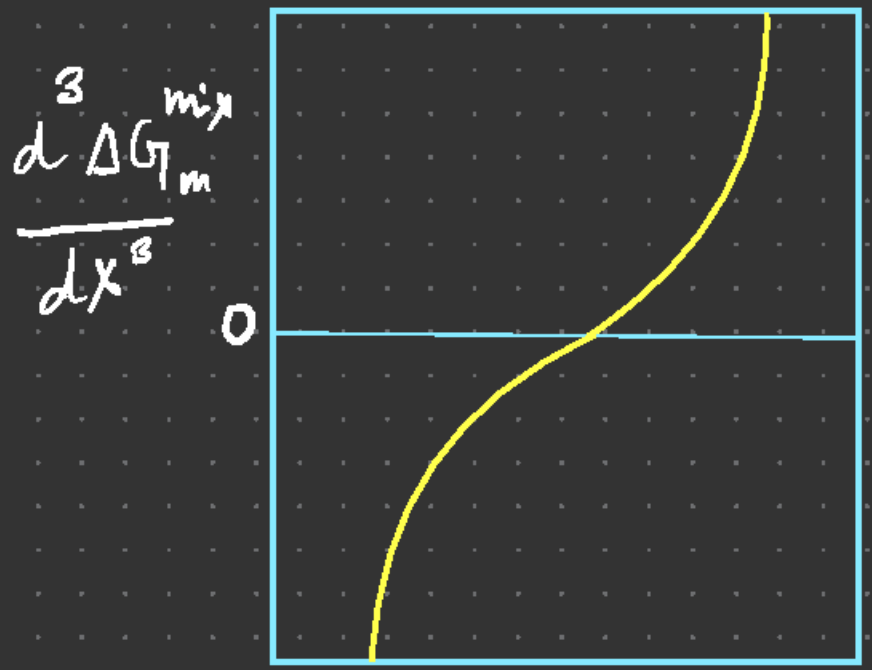


$\alpha > \alpha_c$









$$\Delta\mu_B = \Delta\bar{G}_B^{mix} = \Delta G_m^{mix} + (1-x_B)\frac{d\Delta G_m^{mix}}{dx_B} = RT\ln a_B$$

$$\therefore \frac{d\Delta\bar{G}_B^{mix}}{dx_B} = (1-x_B)\frac{d^2\Delta G_m^{mix}}{dx_B^2} = RT\frac{d\ln a_B}{dx_B}$$

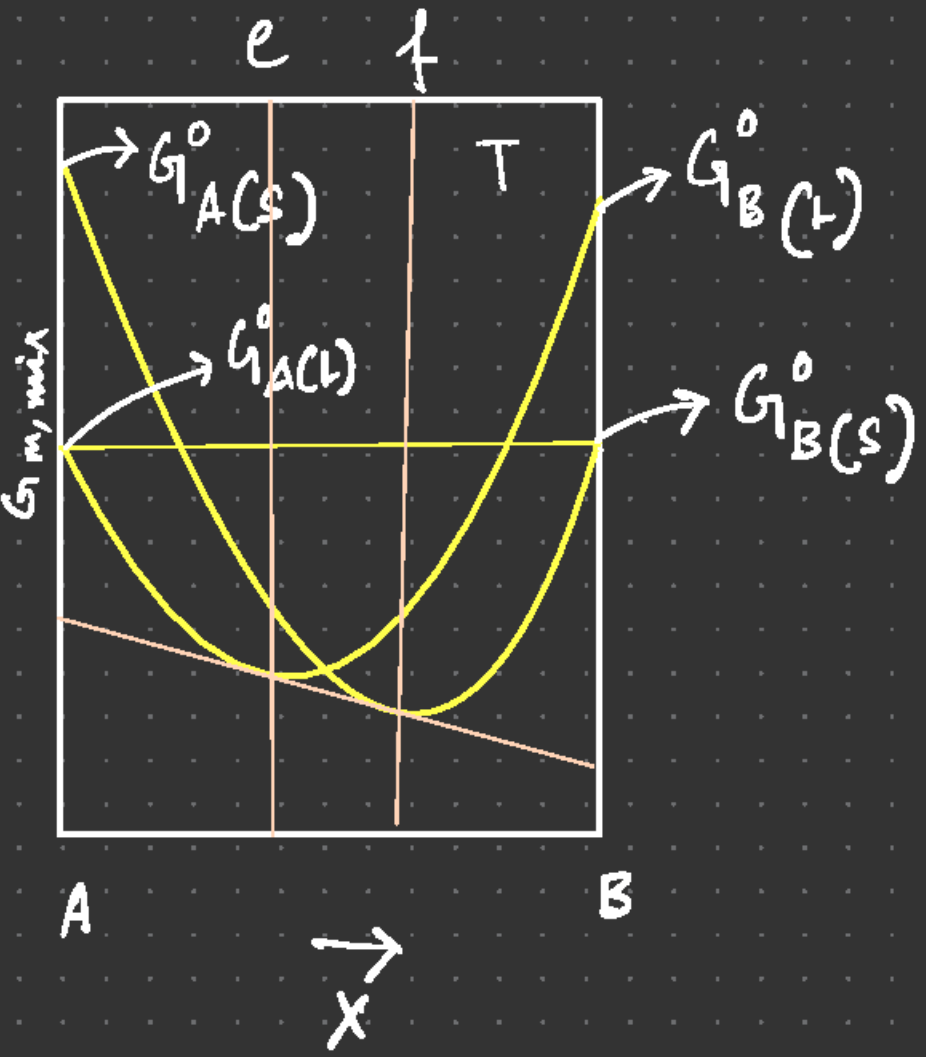
$$\frac{d\Delta\bar{G}_B^{mix}}{dx_B} = x_A\frac{d^2\Delta G_m^{mix}}{dx_B^2} = \frac{RT}{a_B}\frac{da_B}{dx_B}$$

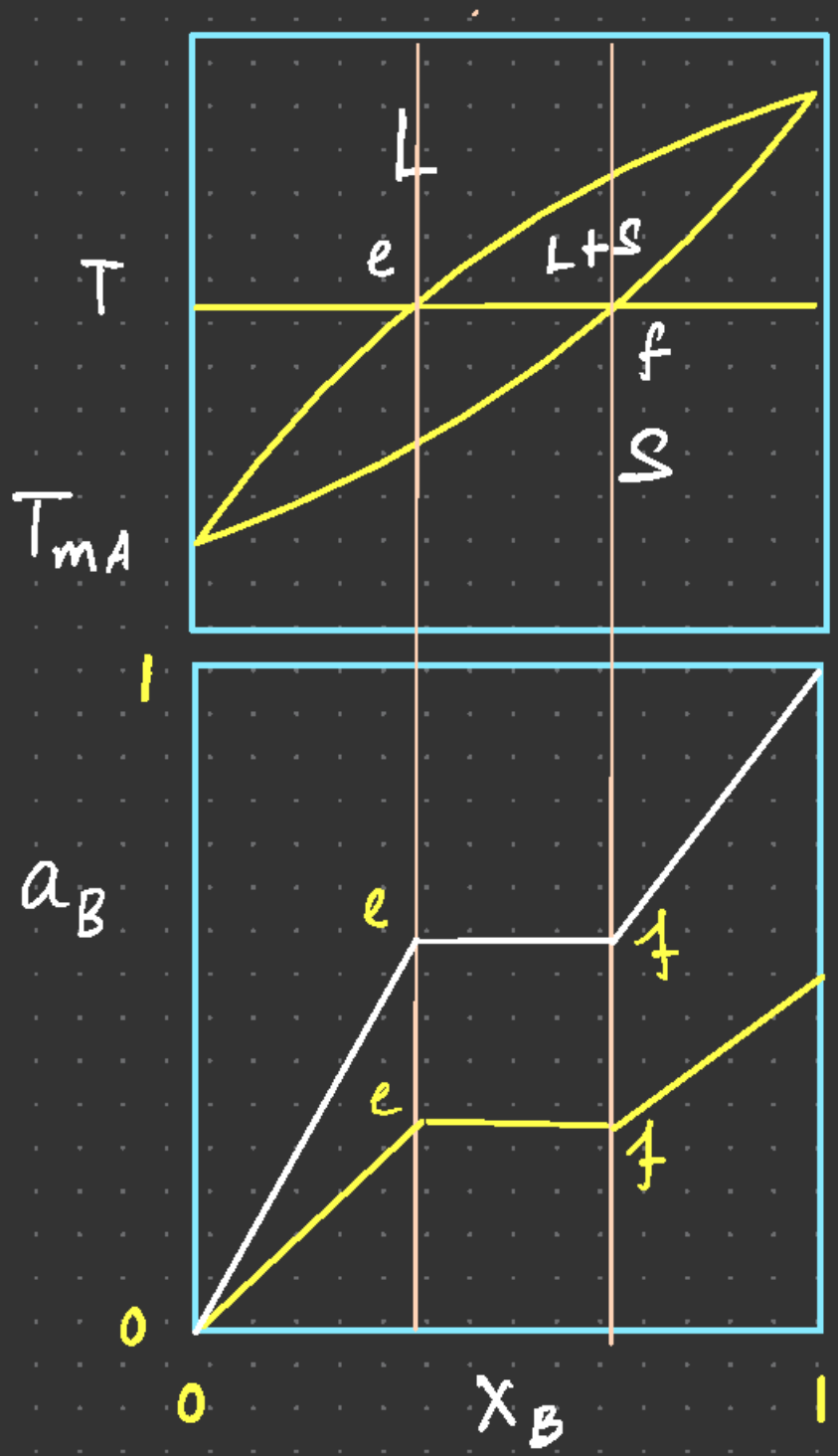
$$\mu_B^L = \mu^{\circ}_{B(l)} + RT \ln a_{B(l)}$$

$$\mu_B^S = \mu^{\circ}_{B(s)} + RT \ln a_{B(s)}$$

$$\mu_B^S = \mu_B^L$$

$$\mu^{\circ}_{B(l)} - \mu^{\circ}_{B(s)} = RT \ln \frac{a_{B(s)}}{a_{B(l)}}$$





(Solid as standard state)

(Liquid as standard state)

$T_{mA} = 800\,K$ (melting point of pure A)

$T_{mB} = 1200\,K$ (melting point of pure B)

$G^{0}_{mA} = 8000 - 10T$ (free energy of pure A)

$G^{0}_{mB} = 12000 - 10T$ (free energy of pure B)

$\omega_L = -20000\ J$ (Liquid) {Regular solution}

$\omega_s = 0$ (Solid) {Ideal solution since $\omega_s = 0$}

$$G_m(\text{solid}) = -X_A G^{\circ}_{m_A} + RT\left(X_A \ln X_A + X_B \ln X_B\right) + \omega_S X_A X_B \left(\Delta H_m^{mix}\right) - T\Delta S_m^{mix}$$

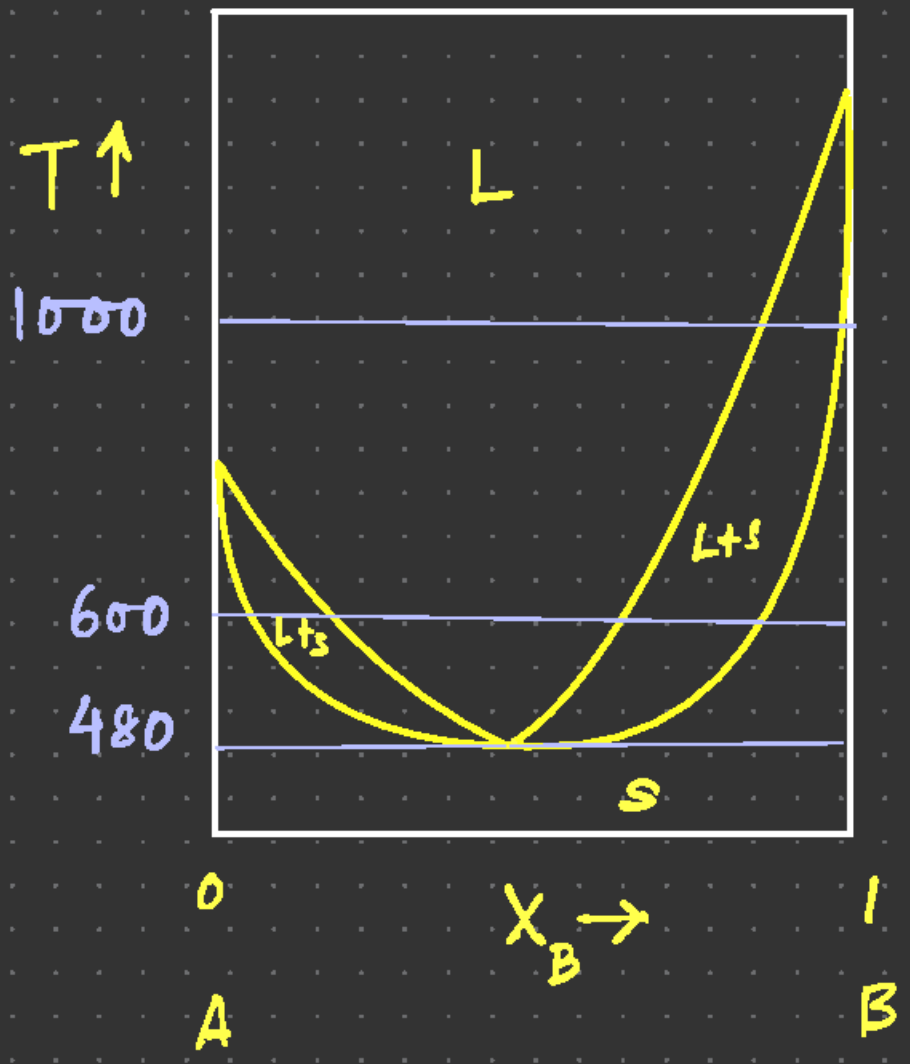
$$G_m(\text{liquid}) = X_B G^{\circ}_{m_B} + RT\left(X_A \ln X_A + X_B \ln X_B\right) + \omega_L X_A X_B \left(\Delta H_m^{mix} = 0\right)$$

$$\mu_A^L = \mu_A^S$$
$$\mu_B^L = \mu_B^S$$

1000, 800, 600, 480, 450

pycalphad – Open source

Thermo Calc – Academic free edition


T ↑
L
1000
600
480
L+S
L+S
S
0
X_B →
1
A
B

$$\mu_A = \bar{G}_A = G_m + (1 - X_A)\frac{dG_m}{dX_A} = G_m - X_B\frac{dG_m}{dX_B}$$

$$\underbrace{\mu_A}_{\text{Solution}} = \underbrace{\mu_A^\circ}_{\text{pure}} + RT \ln a_A$$

$$\mu_A - \mu_A^\circ = \Delta\bar{G}_A = \Delta\mu_A = RT \ln a_A$$

$$\mu_B = \bar{G}_B = G_m + (1 - X_B)\frac{dG_m}{dX_B}$$

$$\mu_B = \mu_B^\circ + RT \ln a_B$$

$$\mu_B - \mu_B^\circ = RT \ln a_B = \Delta\mu_B = \Delta\bar{G}_B$$

$$\Delta G_m^{mix} = G_m^{soln} - G_m^{pure}$$

$$= X_A \mu_A + X_B \mu_B - \left(X_A \mu_A^\circ + X_B \mu_B^\circ \right)$$

$$= X_A \left(\mu_A - \mu_A^\circ \right) + X_B \left(\mu_B - \mu_B^\circ \right)$$

$$= X_A \Delta \mu_A + X_B \Delta \mu_B$$

$$= X_A \Delta \bar{G}_A + X_B \Delta \bar{G}_B$$

$$= RT \left(X_A \ln a_A + X_B \ln a_B \right)$$

$$\Delta \bar{G}_A = \Delta G_m^{mix} - X_B \frac{d \Delta G_m^{mix}}{d X_B}$$

$$\Delta \bar{G}_B = \Delta G_m^{mix} + (1 - X_B) \frac{d \Delta G_m^{mix}}{d X_B}$$

$$RT \ln a_A = \omega x_B (1-x_B) + RT\{(1-x_B)\ln(1-x_B) + x_B \ln x_B\}$$
$$- x_B\{\omega(1-2x_B) + RT \ln x_B - RT \ln(1-x_B)\}$$

$$= \omega x_B - \omega x_B^2 + RT x_B \ln x_B + RT \ln(1-x_B)$$
$$- RT x_B \ln(1-x_B) - \omega x_B$$
$$+ 2\omega x_B^2 - RT x_B \ln x_B + RT x_B \ln(1-x_B)$$

$$= \omega x_B^2 + RT \ln x_A$$

$$RT \ln \gamma_A x_A = \omega x_B^2 + RT \ln x_A$$

$$RT \ln \gamma_A + RT \ln x_A = \omega x_B^2 + RT \ln x_A$$

$$\ln \gamma_A = \omega x_B^2 / RT$$

$$\gamma_A = \exp\left(\omega x_B^2 / RT\right)$$

What is γ_A at the critical temperature $T_c = \frac{\omega}{2R}$

Reacting systems. $aA + bB \rightleftharpoons cC + dD$

Gibbs phase Rule for non-reacting systems

$$f = c - p + 2$$

For reacting systems, $f = s - p - r + 2$

s — no. of different species or constituent

r — no. of independent (Reaction) relations among intensive variables of individual phases other than thermal, mechanical, chemical equilibr

Species is an entity distinguishable from other species by its chemical formula (can be charged or uncharged)

H_2O and OH^- are different species, CO_2 and CO_3^{2-} are different species.

$H_2O(g)$ and $H_2O(l)$: same species in different phases

Example: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$S = 3$

$P = 3$

$R = 1$

$S \quad P \quad R \quad 2$

$f = 3 - 3 - 1 + 2$

$= 1$

Reaction equilibria

$$aA + bB \rightarrow cC + dD$$

$-a \quad -b \quad +c \quad +d$

$\nu_i > 0$ for products

$\nu_i < 0$ for reactants

$\nu_i = 0$ for inert species

$$\Delta G_{reaction} = \sum \nu_i \mu_i$$

or,

$$K = \prod_i (a_i)^{\nu_i}$$

Equilibrium constant

$$\Delta_r G = \sum \nu_i \mu_i = 0$$

- reaction equilibrium

$$A(g) + B(g) = 2C(g)$$

Total energy

$$\mu_A + \mu_B - 2\mu_C = 0$$

or,

$$\mu_A^\circ + RT \ln f_A + \mu_B^\circ + RT \ln f_B = 2\mu_C^\circ + 2RT \ln f_C$$

$$2\mu_C^\circ - \mu_A^\circ - \mu_B^\circ = \Delta G^\circ = -RT \ln \frac{p_C^2}{p_A\, p_B}$$

$$= -RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G^\circ}{RT}$$

$$K_p = \frac{p_C^2}{p_A\, p_B} = \frac{x_C^2\, P^2}{x_A P\; x_B P} = \frac{x_C^2}{x_A\, x_B}$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_{i=1}^{c} \mu_k dn_k$$

Isolated System

$$dU = 0$$
$$dV = 0$$

} Isolation Constraints

$$dn_k = 0 \quad \text{(non-Reacting)}$$

$dn_k \neq 0$ Reacting system

$dN_{a,e} = 0$ Total no. of atoms of each element in the system is conserved

$(i = 1, 2, \ldots, s)$

$$\underset{1}{A} + \underset{1}{B} \longrightarrow \underset{0}{C} \qquad 2$$

$$1-\eta \quad 1-\eta \quad \eta \qquad 2-2\eta+\eta = 2-\eta$$

$$\Delta Z_{i \to f} = Z(T_f, P_f, N_1, N_2) - Z(T_i, P_i, N_1, N_2)$$

$$\{N_1, N_2\}_i = \{N_1, N_2\}_f$$

1, 2 – inert species

Let us suppose a dissociation reaction

$$I_2 \rightleftharpoons 2I$$

$I_2 \rightarrow$ Constituent 1

$I \rightarrow$ Constituent 2

Initial state T_i, P_i, n_1^0, n_2^0

Final state T_f, P_f, n_1, n_2

$$n_1 = n_1^f \neq n_1^0$$

$$n_2 = n_2^f \neq n_2^0$$

Stoichiometrically balanced chemical reaction

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$\nu_{CH_4} = -1$ $\quad$ $\nu_{H_2O} = -1$

$\nu_{CO} = 1$ $\quad$ $\nu_{H_2} = 3$

If 1 mole of CH_4 disappears,

Then, 1 mole of H_2O must disappear

1 mole of CO must appear

3 moles of H_2 must appear

$$\frac{\Delta N_{CH_4}}{\nu_{CH_4}} = \frac{\Delta N_{H_2O}}{\nu_{H_2O}} = \frac{\Delta N_{CO}}{\nu_{CO}} = \frac{\Delta N_{H_2}}{\nu_{H_2}}$$

$$|\nu_1| A_1 + |\nu_2| A_2 + \cdots \rightleftharpoons |\nu_3| A_3 + |\nu_4| A_4 + \cdots$$

or

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \frac{dN_3}{\nu_3} = \cdots = \frac{dN_n}{\nu_n}$$

Define $d\xi$ as extent of reaction

Then $dN_i = \nu_i \, d\xi \quad i = 1, 2, \cdots, n$

Multiple reactions, say m reactions

$$d\Sigma_{ir} = \nu_{ir}\, d\xi_r \qquad r = 1, 2, \cdots, m$$

$$d\Sigma_i = \sum_{r=1}^{m} d\Sigma_{ir} = \sum_{r=1}^{m} \nu_{ir}\, d\xi_r$$

Integrate from $\left(\xi_r = 0,\ \Sigma_i = \Sigma_{i0}\right)$

to $\left(\xi_r = \xi_r,\ \Sigma_i = \Sigma_i\right)$

$$\Sigma_i = \Sigma_{i0} + \sum_{r=1}^{m} \nu_{ir}\, \xi_r$$

Sum over all species

$$N = \sum_{i=1}^{n} N_i = \sum_{i=1}^{n} \left(N_{i0} + \sum_{r=1}^{m} \nu_{ir} \xi_r \right)$$

$$= \sum_{i=1}^{n} N_{i0} + \sum_{i=1}^{n} \sum_{r=1}^{m} \nu_{ir} \xi_r$$

$$\sum_{i=1}^{n} \nu_{ir} = \nu_r$$

$$\therefore \quad N = N_0 + \sum_{r=1}^{m} \nu_r \xi_r$$

$$N = \sum_{i=1}^{n} N_i, \quad N_0 = \sum_{i=1}^{n} N_{i0}, \quad \sum_{i=1}^{n} \nu_{ir} = \nu_r$$

$N^0_{a,i}$ = Constant

$N_{a,i}$ — individual atoms of each element

$$x_i = \frac{N_i}{N} = \frac{N_{i0} + \sum_{r=1}^{m} \nu_{ir} \xi_r}{N_0 + \sum_{r=1}^{m} \nu_r \xi_r}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad r = 1$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad r = 2$$

$N^0_{CH_4} = 2 \text{ mol}$ $\qquad N^0_{CO_2} = 0 \qquad N^0_{H_2} = 0$

$N^0_{H_2O} = 3 \text{ mol}$ $\qquad N^0_{CO} = 0$

i \ r	$r = 1, \nu_{i1}$	$r = 2, \nu_{i2}$
$CH_4 \equiv 1$	$\nu_{11} = -1$	$\nu_{12} = -1$
$H_2O \equiv 2$	$\nu_{21} = -1$	$\nu_{22} = -2$
$CO \equiv 3$	$\nu_{31} = +1$	$\nu_{32} = 0$
$CO_2 \equiv 4$	$\nu_{41} = 0$	$\nu_{42} = +1$
$H_2 \equiv 5$	$\nu_{51} = +3$	$\nu_{52} = +4$

$$\therefore \quad \nu_1 = \sum_{i=1}^{5} \nu_{i1} = +2$$

$$\nu_2 = \sum_{i=1}^{5} \nu_{i2} = +2$$

$$N^0_{CH_4} = 2 \equiv N^0_1$$

$$N^0_{H_2O} = 3 \equiv N^0_2$$

$$N^0_{CO} = N^0_{CO_2} = N^0_{H_2} = 0$$

$$\| \qquad \| \qquad \|$$

$$N^0_3 \qquad N^0_4 \qquad N^0_5$$

$$N_i = N_i^0 + \sum_{R=1}^{2} \nu_{iR}\, \xi_R$$

$$\therefore N_{CH_4} \equiv N_1 = 2 - \xi_1 - \xi_2$$

$$N_{H_2O} \equiv N_2 = 3 - \xi_1 - 2\xi_2$$

$$N_{CO} \equiv N_3 = 0 + \xi_1 + 0\,\xi_2 = \xi_1$$

$$N_{CO_2} \equiv N_4 = 0 + 0\,\xi_1 + \xi_2 = \xi_2$$

$$N_{H_2} \equiv N_5 = 0 + 3\xi_1 + 4\xi_2$$

$$N = 5 + 2\xi_1 + 2\xi_2$$

$$X_{CH_4} \equiv X_1 = \frac{2 - \xi_1 - \xi_2}{5 + 2\xi_1 + 2\xi_2}$$

$$X_{H_2O} \equiv X_2 = \frac{3 - \xi_1 - 2\xi_2}{5 + 2\xi_1 + 2\xi_2}$$

.

.

$$X_1 + X_2 + X_3 + X_4 + X_5 = 1$$

$$dG = VdP - SdT + \sum_{j=1}^{n} \mu_j dN_j$$

$$\sum_{j=1}^{n} dN_j \neq 0$$

$$dN_j = \sum_{r=1}^{m} \nu_{jr} d\xi_r$$

$$\therefore \quad dG = VdP - SdT + \sum_{r=1}^{m} \left[\sum_{j=1}^{n} \nu_{jr} \mu_j \right] d\xi_r$$

$$G = G(T, P, \xi_1, \xi_2, \cdots, \xi_m)$$

$$\left(\frac{\partial G}{\partial \xi_i}\right)_{T,P,\xi_{n\neq i}} = 0 \quad \text{at equilibrium}$$

$$= \sum_{j=1}^{n} \nu_{ji}\mu_j$$

$$\therefore \sum_{j=1}^{n} \nu_{jn}\mu_j = 0$$

How to determine $\mathcal{R}$?

If a system consists of e elements and S constituents or species, the no. of independent conservation relations or reactions that can be written for the system are

$$\mathcal{R} = S - e$$

$$2\,CO + O_2 = 2\,CO_2$$

Elements $e = 2$ $(C + O)$

Species $s = 3$ (CO, O_2, CO_2)

$$\mathcal{R} = s - e = 1$$

$$f = 3 - 3 - 1 + 2 = 1$$

$$C + O_2 = CO_2 \quad -(1)$$

$$2C + O_2 = 2CO \quad -(2)$$

$$C + CO_2 = 2CO \quad -(3)$$

$S = C, O_2, CO_2, CO$

$e = C, O$

$$\mathcal{R} = S - e = 4 - 2 = 2$$

Gibbs phase rule

$$f = 4 - 4 - 2 + 2 = 0$$

$S \quad P \quad \mathcal{R}$

$$CO_2 = C + O_2 \quad -(1{\cdot}1)$$

$$(3) = (2) - (1)$$

$$(3) = (1{\cdot}1) + (2)$$

$$CO_2 + 2C + O_2 = C + O_2 + 2CO$$

$$\Rightarrow \quad CO_2 + C = 2CO$$

$\mathcal{R} = 1$ univariant

$\mathcal{R} > 1$ multivariant

$$CO + \frac{1}{2} O_2 = CO_2$$

Linear combination of chemical potentials

$$A = \sum_{j=1}^{n} \nu_{jr} \mu_j$$

$$A = \mu_{CO_2} - \mu_{CO} - \frac{1}{2} \mu_{O_2}$$

$$dN_j = \sum_{r=1}^{m} \nu_{jr} \xi_r$$

$$dN_{CO} = -\xi_1 \qquad dN_{O_2} = -\frac{1}{2} \xi_1$$

$$dN_{CO_2} = \xi_1$$

$$dN_{CO} = -dN_{CO_2}$$

$$dN_{O_2} = -\frac{1}{2}\left[\underset{-\xi}{dN_{CO}} + \underset{+2\xi}{2\,dN_{CO_2}}\right]$$

$$= -\frac{1}{2}\,dN_{CO_2}$$

Three components, but only one can be varied independently.

Condition of equilibrium

$$A = \mu_{CO_2} - \left(\mu_{CO} + \frac{1}{2}\mu_{O_2}\right) = 0$$

$$\mu_{products} = \mu_{reactants} \quad \text{(Equilibrium)}$$

$$\ell L + m M = r R + s S \qquad r \ln a_R = \ln a_R^r$$

$$A = \mu_{products} - \mu_{reactants}$$

$$A = \left(r \mu_R + s \mu_S \right) - \left(\ell \mu_L + m \mu_M \right)$$

$$\mu_k = \mu_k^\circ + RT \ln a_k = G_k^\circ + RT \ln a_k$$

$$A = \left[\left(r G_R^\circ + s G_S^\circ \right) - \left(\ell G_L^\circ + m G_M^\circ \right) \right] + RT \ln \left[\frac{a_R^r \, a_S^s}{a_L^\ell \, a_M^m} \right]$$

$$A = \Delta G^\circ + RT \ln \left[\frac{a_R^r \, a_S^s}{a_L^l \, a_M^m} \right]$$

$$Q = \frac{a_R^r \, a_S^s}{a_L^l \, a_M^m}$$

$$A = \Delta G^\circ + RT \ln Q$$

$$K = Q_{equilibrium} \equiv Q_e = \left[\frac{a_R^r \, a_S^s}{a_L^l \, a_M^m} \right]_e$$

At equilibrium

$$A = 0 = \Delta G^\circ + RT \ln K$$

or, $$\Delta G^\circ = -RT \ln K$$

$$A = -RT \ln K + RT \ln Q$$

$$= RT \ln \frac{Q}{K}$$

Van't Hoff isotherm

P1. A gas mixture at 1 atm. pressure and 700°C temperature has the following composition

Components	H_2	O_2	H_2O
Mole fraction	0.01	0.01	0.96

At 700°C $2H_2 + O_2 = 2H_2O \quad \Delta G^\circ = -440\ kJ$

$$K = e^{-(\Delta G^\circ / RT)} = e^{-\left(\frac{-440\,000}{8.314 \times 973}\right)}$$

$$= 4.2 \times 10^{23}$$

If ideal solution,

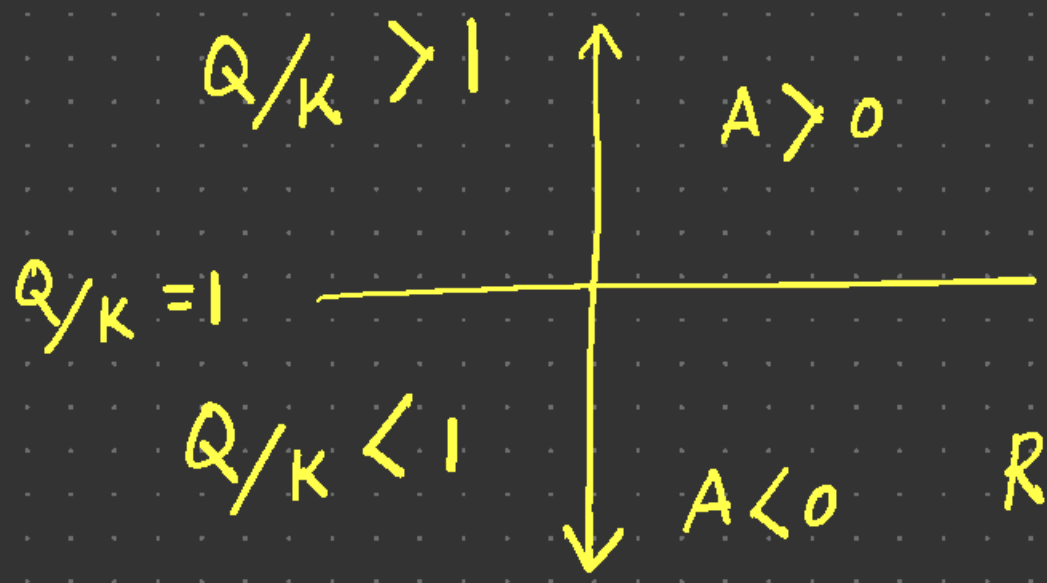
$$Q = \frac{a^2_{H_2O}}{a^2_{H_2}\, a_{O_2}} = \frac{X^2_{H_2O}}{X^2_{H_2}\, X_{O_2}} = \frac{(0.96)^2}{(0.01)^2\, 0.03}$$

$$= 3.1 \times 10^5$$

$$Q/K = \frac{3.1 \times 10^5}{4.2 \times 10^{23}} = 7.2 \times 10^{-19}$$

$$\ll 1$$

Strong tendency for products to form



Decomposition

Products → Reactants

A = 0 (reversible)

Formation

Reactants → Products

Extent of reaction

$$\Delta\nu = b + c - a$$

$$aA \longrightarrow bB + cC$$

$$RT \ln K_p = -\Delta G^\circ$$

$$K_p = \frac{p_B^{\,b}\, p_C^{\,c}}{p_A^{\,a}} = \frac{P^b x_B^{\,b}\, P^c x_C^{\,c}}{P^a x_A^{\,a}}$$

$$= P^{b+c-a}\, \frac{x_B^{\,b}\, x_C^{\,c}}{x_A^{\,a}}$$

$$= P^{\Delta\nu} \frac{\left(\frac{N_B}{N}\right)^b \left(\frac{N_B}{N}\right)^c}{\left(\frac{N_A}{N}\right)^a}$$

$$K_p = P^{\Delta\nu} \frac{N_B^{\,b} N_C^{\,c}}{N_A^{\,a}} \left(\frac{1}{N}\right)^{b+c-a}$$

$$= P^{\Delta\nu} \frac{N_B^{\,b} N_C^{\,c}}{N_A^{\,a}} \frac{1}{N^{\Delta\nu}}$$

$$= \left(\frac{P}{N}\right)^{\Delta\nu} \frac{N_B^{\,b} N_C^{\,c}}{N_A^{\,a}}$$

$$\left[\frac{\partial (G_1/T)}{\partial T}\right]_P = -\frac{H}{T^2} \quad \text{or,} \quad \left[\frac{\partial (\Delta G^\circ/T)}{\partial T}\right]_P = -\frac{\Delta H^\circ}{T^2}$$

$$RT \ln K_p = -\Delta G^\circ$$

$$\therefore \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Let $a = b = c = 1$

$$\Delta\nu = b + c - a = 1$$

$$A \rightarrow B + C$$

Moles of Species

Species	A	B	C
Initial	1	0	0
Equilibrium	$1-\eta$	η	η

$$\sum_{i=A,B,C} n_i \qquad 1 - \eta + 2\eta = 1 + \eta$$

$$K_p = \left(\frac{P}{1+\eta}\right)^1 \frac{\eta \cdot \eta}{1-\eta} = \frac{P\eta^2}{1-\eta^2}$$

$$\frac{p\eta^2}{1-\eta^2} = K_p$$

$\eta \rightarrow$ extent of dissociation

$\downarrow$

does not depend on the total no. of moles

$$\frac{\eta^2}{1-\eta^2} = \frac{K_p}{P}$$

$$\left(1 + \frac{K_p}{P}\right)\eta^2 = K_p/P$$

$$\eta^2 = \frac{K_p/P}{1 + K_p/P} = \frac{1}{1 + P/K_p}$$

$$\eta = \sqrt{\frac{1}{1 + P/K_p}}$$

Gas mixture

H_2	O_2	H_2O	CO	CO_2	CH_4
0.05	0.05	0.15	0.25	0.4	0.1

600°C

$S = 6 \quad e = 3 \quad \therefore \quad \mathcal{R} = 3$

R1 $\quad 2H_2 + O_2 = 2H_2O$

R2 $\quad 2CO + O_2 = 2CO_2$

R3 $\quad CH_4 + 2O_2 = CO_2 + 2H_2O$

} non redundant eqn, with all 6 constituent

$$\Delta G^{\circ}_{R1} = -406200 \text{ J}$$

$$\Delta G^{\circ}_{R2} = -414500 \text{ J}$$

$$\Delta G^{\circ}_{R3} = -797900 \text{ J}$$

Assume ideal

$$K_{R1} = \frac{X^2_{H_2O}}{X^2_{H_2} X_{O_2}} = 2.02 \times 10^{24} \quad -(1)$$

$$K_{R2} = \frac{X_{CO_2}^2}{X_{CO_2}^2 X_{O_2}} = 6.34 \times 10^{24} \quad -(2)$$

$$K_{R3} = \frac{X_{H_2O}^2 X_{CO_2}}{X_{CH_4} X_{O_2}^2} = 5.53 \times 10^{47} \quad -(3)$$

$$X_K = \frac{N_K}{N_T}$$

$$N_T = N_{H_2} + N_{O_2} + N_{H_2O} + N_{CO} + N_{CO_2} + N_{CH_4}$$

No. of gm atoms of element are conserved

e elements — e conservation conditions

$$m_j = \sum_{k=1}^{s} b_{jk} n_k$$

b_{jk} is the atoms of element j contained in a molecule of k

X_j = mole fraction of element j

$$X_j = \frac{m_j}{\sum_{j=1}^{e} m_j}$$

$$m_C = 0\,N_{H_2} + 0\,N_{O_2} + 0\,N_{H_2O} + 1\,N_{CO} + 1\,N_{CO_2} + 1\,N_{CH_4}$$

$$m_O = 0\,N_{H_2} + 2\,N_{O_2} + 1\,N_{CO} + 2\,N_{CO_2} + 0\,N_{CH_4}$$

$$m_H = 2\,N_{H_2} + 0\,N_{O_2} + 2\,N_{H_2O} + 0\,N_{CO} + 4\,N_{CH_4}$$

$$N_T = 1 \text{ mole of gas}$$

Numerically solve the equations to obtain the composition of gas mixture at equilibrium

$$\Delta G^{0} = -RT \ln K_p = -RT \ln \left[\frac{p_R^{r}\, p_S^{s}}{p_L^{l}\, p_M^{m}} \right]$$

$$l L + m M \rightarrow r R + s S$$

$$\Delta \nu = \sum_{i=1}^{c} \nu_i = +r + s - l - m$$

$$K_p = \left[\frac{p_R^{r}\, p_S^{s}}{p_L^{l}\, p_M^{m}} \right]_{\text{equilibrium}}$$

Law of mass action

$$\Delta \nu = (r + s) - (l + m)$$

$$A = -RT \ln K_p + RT \underbrace{\Delta \ln p_i}_{Q_p}$$

$$K_p = p^{\Delta\nu} \frac{x_R^r \, x_S^s}{x_L^l \, x_M^m}$$

$$= \left(\frac{p}{N_t}\right)^{\Delta\nu} \frac{n_R^r \, n_S^s}{n_L^l \, n_M^m}$$

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}$$

Gibbs-Helmholtz equation

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ_T}{T^2}$$

$$\Delta G^\circ = -RT \ln K_p$$

$$\therefore \quad \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$K_p = \frac{p_R^{\,n}\, p_S^{\,s}}{p_L^{\,l}\, p_M^{\,m}} = (RT)^{\Delta\nu} \frac{C_R^{\,n}\, C_S^{\,s}}{C_L^{\,l}\, C_M^{\,m}}$$

$$p_i V = n_i RT$$

$$p_i = c_i RT$$

Heterogeneous Reaction

$A = \sum \nu_i \mu_i$

$$CaCN_2 + 3H_2O(g) \rightleftharpoons CaCO_3 + 2NH_3(g)$$

$\mu_0 + RT \ln p_{NH_3}$

Gas

$$\mu_i = \mu_i^0 + RT \ln p_i \qquad \mu_0 + RT \ln p_{H_2O}$$

$$= G_i^0 + RT \ln p_i \qquad -3\mu_0^{H_2O} - 3RT \ln p_{H_2O}$$

$$+ 2\mu_0^{NH_3} + 2RT \ln p_{NH_3}$$

Solid/liquid

$$\mu_i \approx \mu_i^0 = G_i^0$$

Affinity

$$\Delta G = A = \Delta G^{0} + RT \ln \frac{p_{NH_3}^{2}}{p_{H_2O}^{3}}$$

$$\Delta G^{0} = 2G^{0}_{NH_3} + G^{0}_{CaCO_3} - 3G^{0}_{H_2O} - G^{0}_{CaCN_2}$$

$$K_p = \frac{p_{NH_3}^{2}}{p_{H_2O}^{3}}$$

$$K = \exp\left[-\frac{\Delta G^\circ}{RT}\right]$$

$$\Delta G^\circ(T, P^\circ) = \sum_{i=1}^{n} \nu_i G_i^\circ(T, P^\circ)$$

$$= \Delta H^\circ(T, P^\circ) - T\Delta S^\circ(T, P^\circ)$$

$$\Delta H_i^\circ = \Delta H_{f,i}^\circ \quad \therefore \Delta H^\circ = \sum_{j=1}^{n} \nu_j \Delta H_{f,j}^\circ$$

For pure elements $\Delta G_{f,i}^\circ = 0, \Delta H_{f,i}^\circ = 0$

$$dH_i^\circ = C_{Pi}^\circ \, dT$$

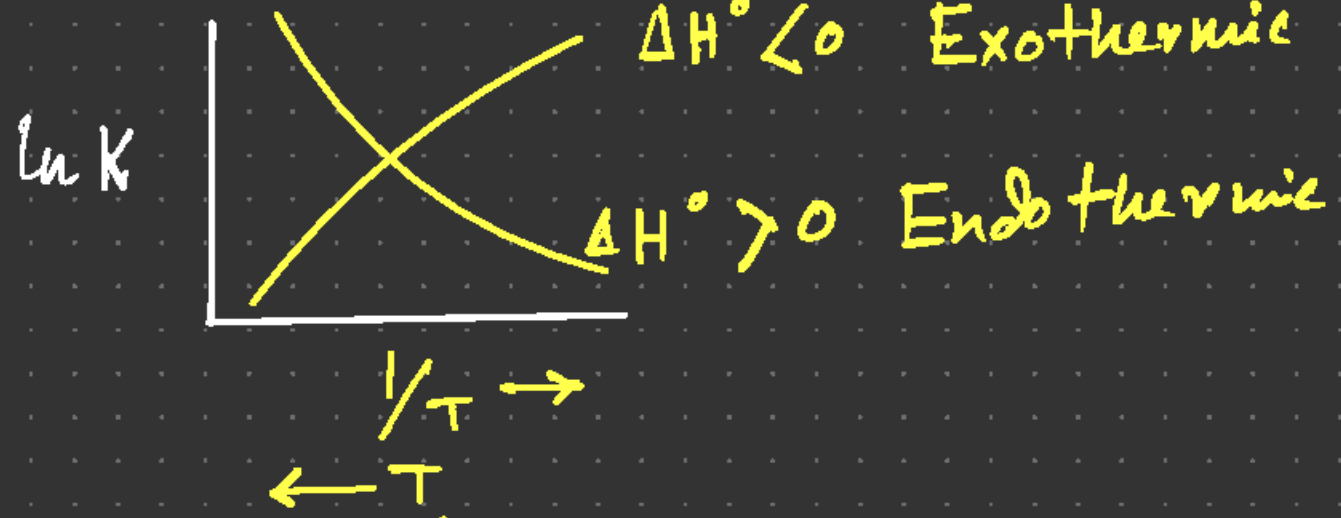
$$\nu_j \, dH_j^\circ = \nu_j \, C_{Pj}^\circ \, dT$$

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

$$\left.\frac{\partial \ln K}{\partial T}\right|_{p^\circ} = -\frac{1}{R}\left[\frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{T}\right)\right]$$

$$= \frac{\Delta H^\circ}{RT^2}$$

$$\left[\frac{\partial \ln K}{\partial (1/T)}\right]_{p^\circ} = -\frac{\Delta H^\circ}{R}$$



Le Chatelier's principle

A system at equilibrium, when subjected to a perturbation, responds in a manner that tends to eliminate the effect of perturbation

Endothermic Reaction

Perturb by increasing the temperature

→ Reaction shifts towards reactants which have higher enthalpy than the products

Why?

Heat provided to increase the temperature goes into the reaction thereby cooling the system and reducing T

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\therefore \left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{1}{RT}\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T$$

$P = P^\circ$ P is chosen to be 1 bar

Vapour pressure of component i at temperature T

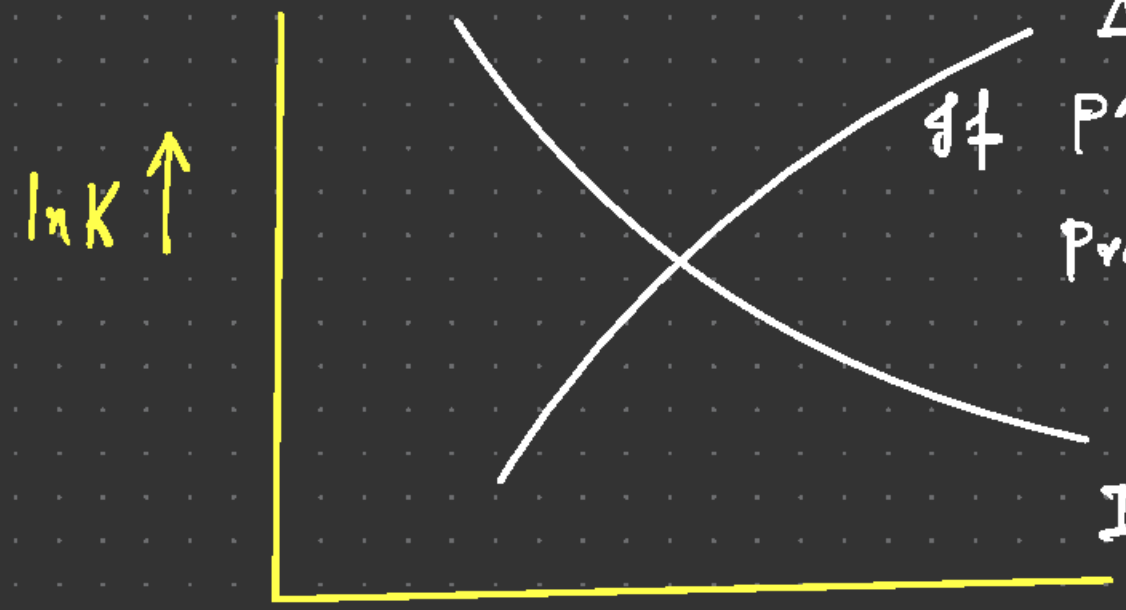
then $\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = 0$

$$\Delta G^\circ(T,P) = \sum_{i=1}^{n} \nu_i G_i^\circ(T,P)$$

$$\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = \sum_{i=1}^{n} \nu_i \left(\frac{\partial G_i^\circ(T,P)}{\partial P}\right)_T$$

$$= \sum_{i=1}^{n} \nu_i V_i^\circ(T,P)$$

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^\circ}{RT}$$



$\Delta V^\circ < 0$

If P↑, K↑

Products are favored

$\Delta V^\circ > 0$

If P↑, K↓

Reactants are favored

$$\Delta V^\circ = \sum_{i=1}^{w} \nu_i V_i^\circ \qquad P \rightarrow$$

Richardson - Ellingham chart for oxidation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$A + B \rightarrow C$$

$$\Delta G = G_C - G_A - G_B$$

$$= \Delta G^\circ + RT \ln\left(\frac{p_C}{p_A\, p_B}\right)$$

$$= 0 \quad \text{at equilibrium}$$

$$\Delta G^0 = - RT \ln K_p$$

$$K_p = \frac{p_c}{p_A \, p_B}$$

$$2\,M(s) + O_2(g) \longrightarrow 2\,MO(s)$$

$$K = \frac{a_c}{a_A \, a_B}$$

Metal and oxide are assumed to be pure solids - they are in their standard state - their activity is 1

$$K_p = \frac{1}{p_{O_2}} \quad \Big| \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\left. p_{O_2} \right|_{eq,T} = \exp\left(\frac{\Delta G^\circ}{RT}\right)$$

$$\Delta G^\circ = RT \ln p_{O_2}$$

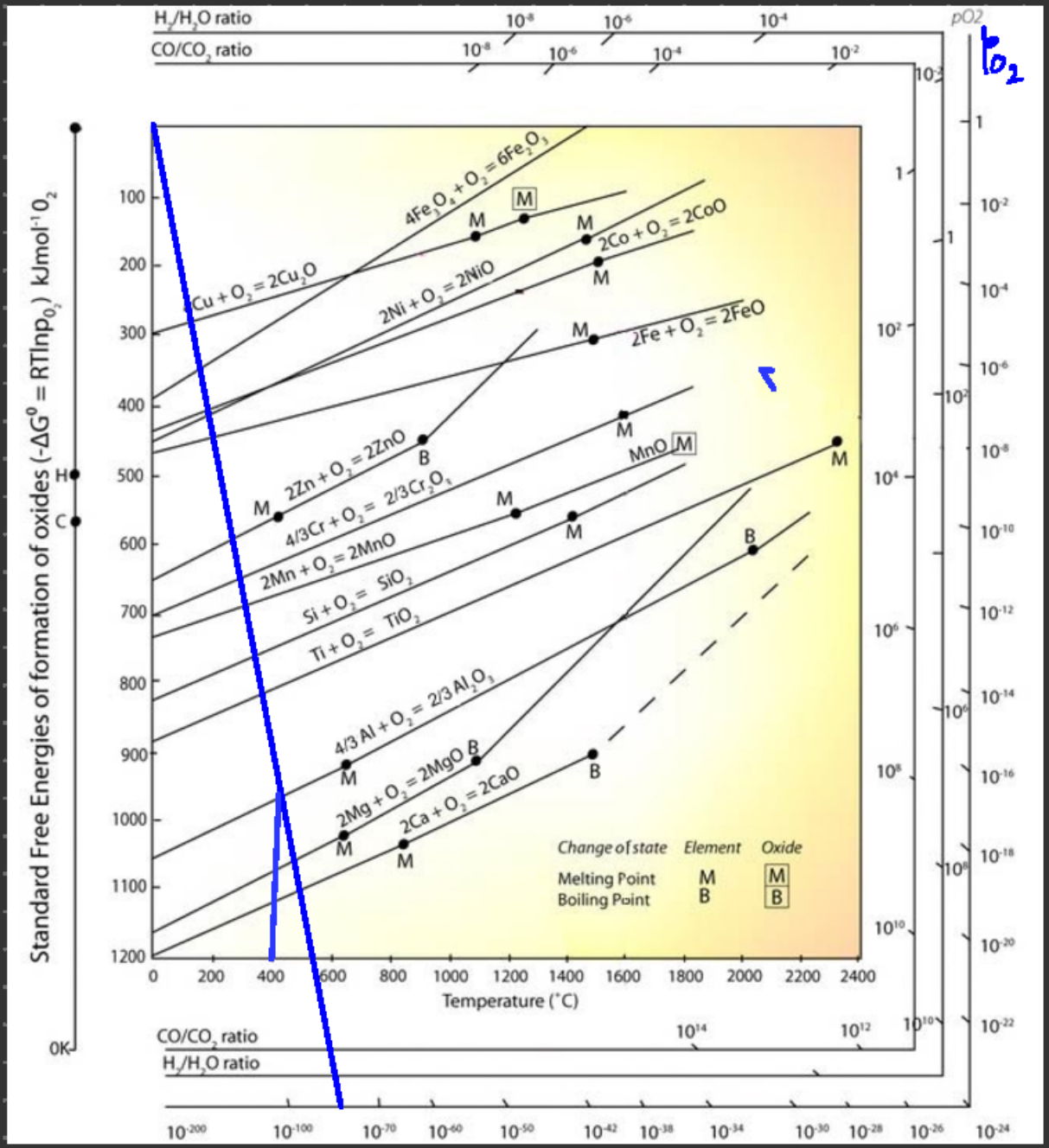
$$\left. \Delta G^\circ \right|_{0K} = \Delta H^\circ$$

$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$$

ΔS° is negative since there is elimination of oxygen gas during oxidation

$$\therefore \frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$$ is positive for metal oxidation

Ellingham diagram (courtesy: doitpoms.ac.uk)



$$\Delta G^\circ = RT \ln \left| p_{O_2} \right.$$

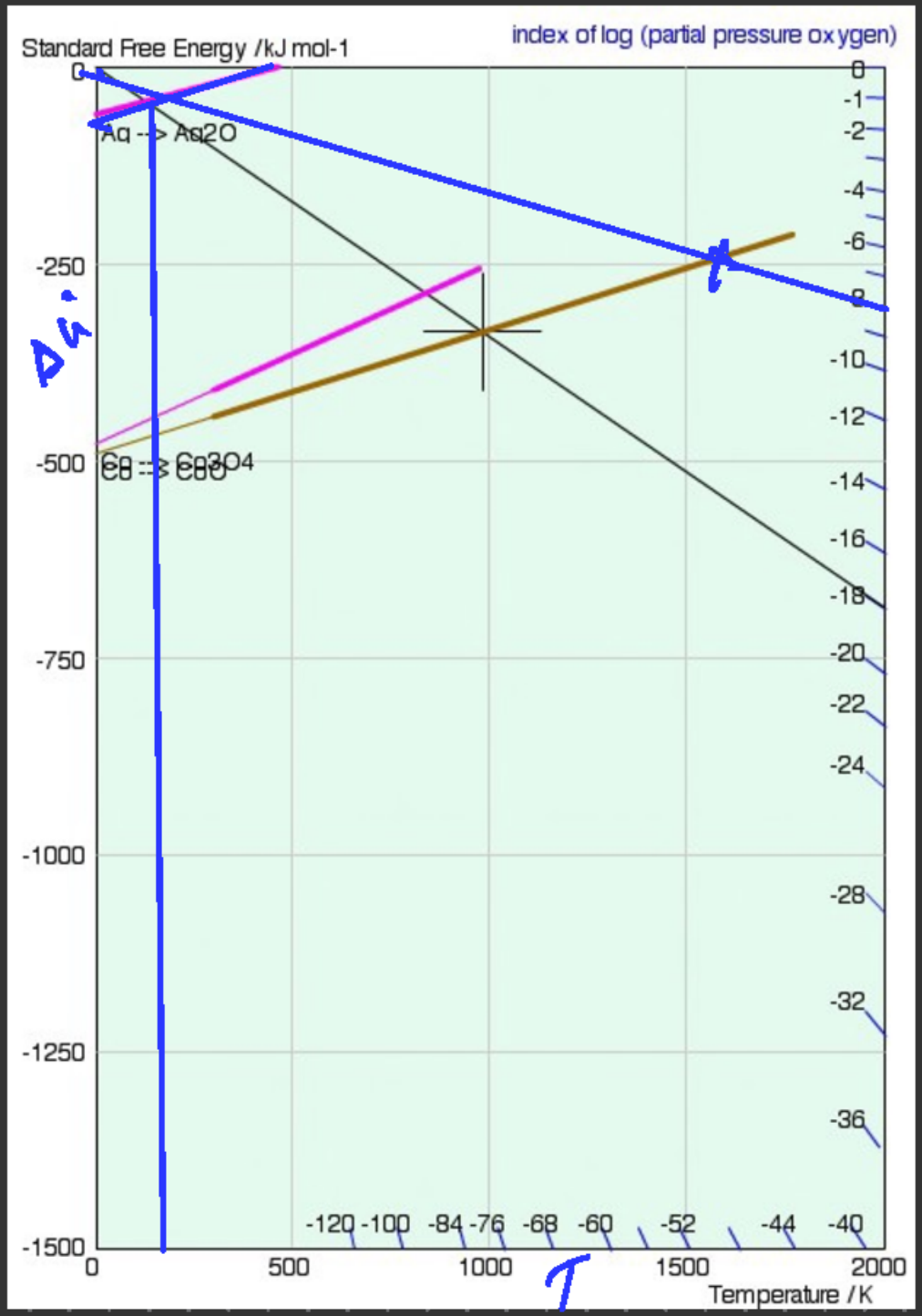
$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$$

At constant T,

$$G = G^\circ + RT \ln \frac{P}{P^\circ}$$

Put $P^\circ = 1\ atm$

$$\Delta G = RT \ln P$$



Courtesy:

doitpoms.ac.uk

Richardson's nomographic scale

$\Delta G = RT \ln P$

$(T = 0, \Delta G = 0)$

Equilibrium partial pressure

— pressure at which driving force for oxidation drops to zero

equilibrium

If $p_{O_2} > p_{O_2}^{equi}$

$2M + O_2 \rightarrow 2MO$

then $\Delta G^{oxidation} < 0$

$$p_{O_2}^{equi} = \exp\left(\frac{\Delta G^{\circ}}{RT}\right)$$

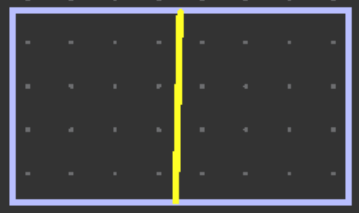
$$2M + O_2 \rightarrow 2MO$$

$\Delta G < 0$ if $p_{O_2} > p_{O_2}^{eq}$

$\Delta G = 0$ if $p_{O_2} = p_{O_2}^{eq}$

$\Delta G > 0$ if $p_{O_2} < p_{O_2}^{eq}$

Interfacial phenomena



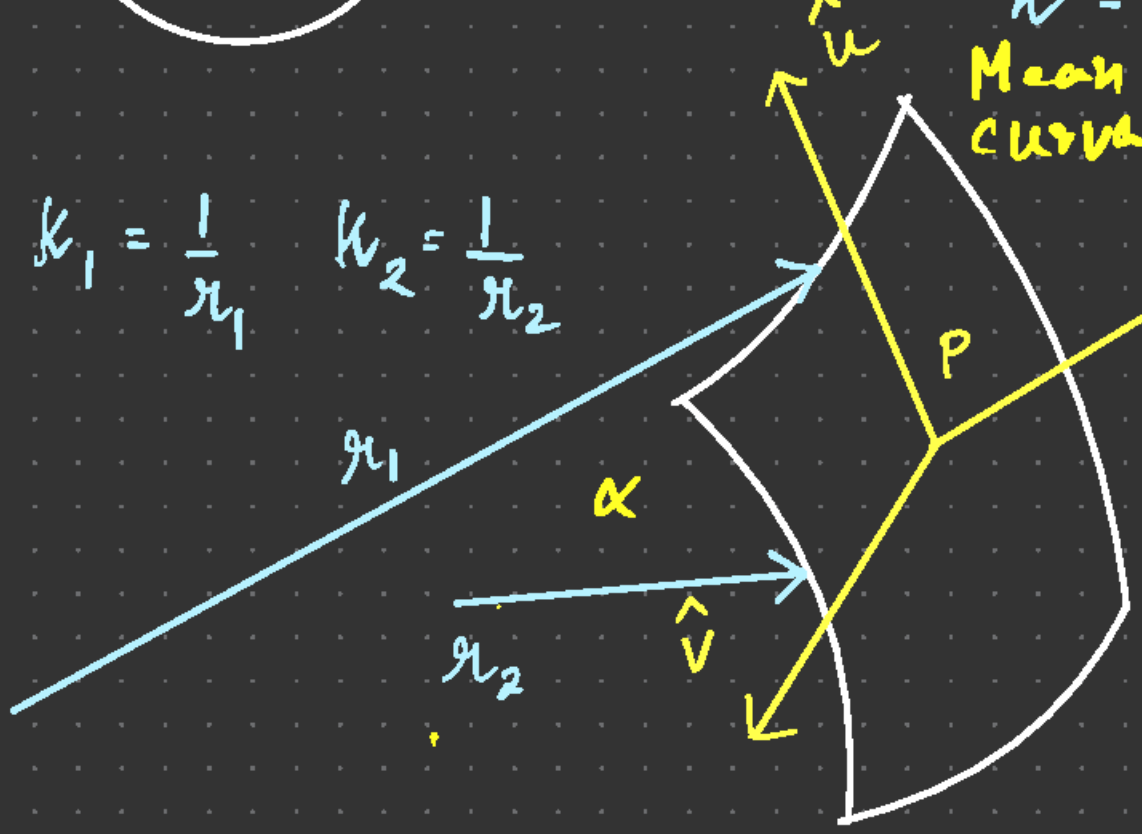


R - Radius of curvature

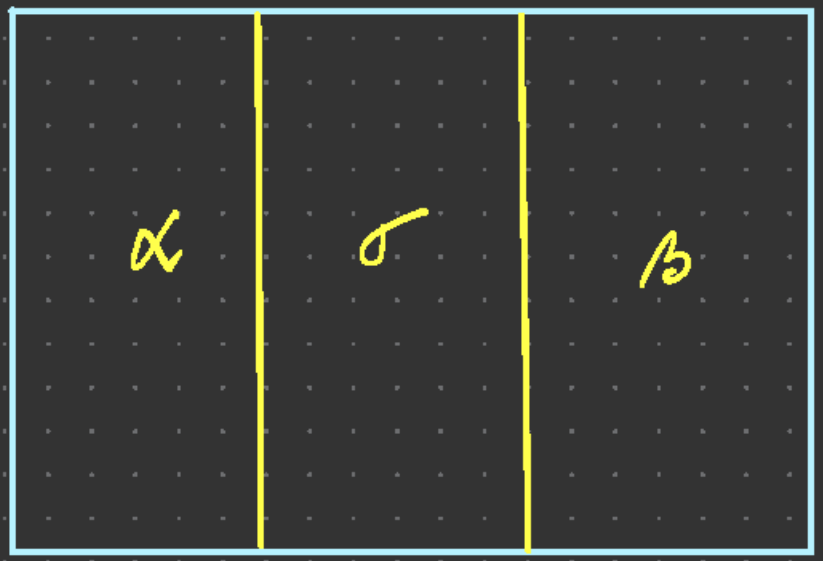
$k = \frac{1}{R}$ curvature

$h = \frac{1}{2}(K_1 + K_2)$ Mean curvature

$K_1 = \frac{1}{R_1}$ $K_2 = \frac{1}{R_2}$



$\delta A = 2h\,\delta V$

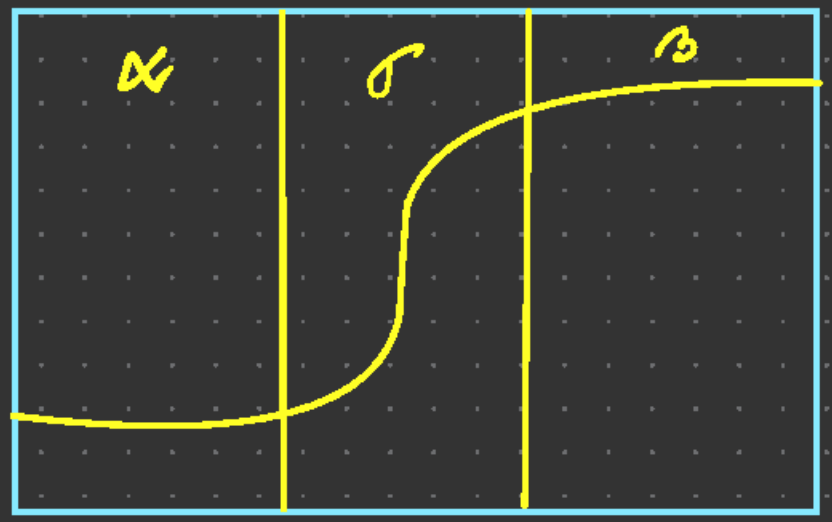


Physical Surface of discontinuity

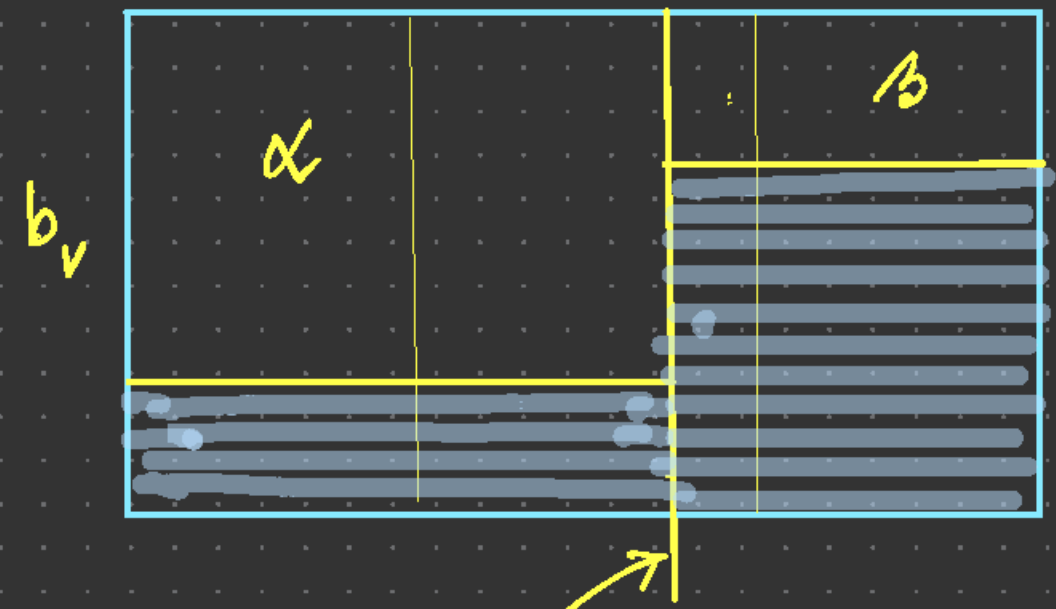
$B \rightarrow$ extensive property

$$b_v = \lim_{V \to 0} \frac{B}{V}$$

$$B = \int_V b_v \, dv$$



b_v



$$B^{xs} = B_{sys} - B_{bulk}$$

$$b^s = \frac{B^{xs}}{A}$$

$$dS_{сум} = dS^{\alpha} + dS^{\beta} + S^{s} dA$$

$$dS_{сум} = \left[\frac{1}{T^{\alpha}} dU^{\alpha} + \frac{P^{\alpha}}{T^{\alpha}} dV^{\alpha} - \sum_{k=1}^{C} \frac{\mu_k^{\alpha}}{T^{\alpha}} dN_k^{\alpha} \right]$$

$$+ \left[\frac{1}{T^{\beta}} dU^{\beta} + \frac{P^{\beta}}{T^{\beta}} dV^{\beta} - \sum_{k=1}^{C} \frac{\mu_k^{\beta}}{T^{\beta}} dN_k^{\beta} \right]$$

$$+ S^{s} dA$$

Isolation constraint

$$dV_{sys} = dV^{\alpha} + dV^{\beta} + V^{s} dA = 0$$

$$dV_{sys} = dV^{\alpha} + dV^{\beta} + V^{s} dA = 0$$

$V^{s} \rightarrow$ excess volume due to surface

$$= 0$$

$$dN_{k,sys} = dN_{k}^{\alpha} + dN_{k}^{\beta} + N_{k}^{s} dA$$

$$= 0$$

$$dS_{sys} = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \sum_{k=1}^{C} \frac{\mu_k^\alpha}{T^\alpha} dN_k^\alpha$$

$$+ \frac{1}{T^\beta}\left(-dU^\alpha - U^s dA\right) + \frac{P^\beta}{T^\beta}\left(-dV^\alpha\right)$$

$$- \sum_{k=1}^{C} \frac{\mu_k^\beta}{T^\beta}\left(-dN_k^\alpha - N_k^s dA\right) + S^s dA$$

$$= \left[\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right] dU^\alpha + \left[\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta}\right] dV^\alpha$$

$$- \sum_{k=1}^{C} \left[\frac{\mu_k^\alpha}{T^\alpha} - \frac{\mu_k^\beta}{T^\beta}\right] dN_k^\alpha +$$

$$\left[S^s - \frac{1}{T^\beta} U^s + \sum_{k=1}^{C} \frac{\mu_k^\beta}{T^\beta} N_k^s\right] dA$$

$$dA = 2h\,dV^{\alpha} = -2h\,dV^{\beta}$$

$$\therefore dS_{sys} = \left[\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right] dU^{\alpha}$$

$$+ \left[\left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\beta}}{T^{\beta}}\right) - \left(S^{s} - \frac{1}{T^{\beta}} U^{s} + \sum_{k=1}^{C} \frac{\mu_k^{\beta}}{T^{\beta}} N_k^{s}\right) 2h\right] dV^{\alpha}$$

$$- \sum_{k=1}^{C} \left[\frac{\mu_k^{\alpha}}{T^{\alpha}} - \frac{\mu_k^{\beta}}{T^{\beta}}\right] dN_k^{\alpha}$$

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

$$\frac{\mu_k^{\alpha}}{T^{\alpha}} - \frac{\mu_k^{\beta}}{T^{\beta}} = 0 \Rightarrow \mu_k^{\alpha} = \mu_k^{\beta}$$

$$\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) - \left(s^s - \frac{1}{T^{\beta}} U^s + \sum_{k=1}^{c} \frac{\mu_k^{\beta}}{T^{\beta}} \Gamma_k^s\right) 2h$$

$$= 0$$

$$\gamma = U^s - TS^s - \sum \mu_k \Gamma_k^s$$

— Interfacial energy

$$T^{\alpha} = T^{\beta} = T$$

$$\therefore \quad \frac{p^{\alpha}}{T} - \frac{p^{\beta}}{T} = -\frac{\gamma}{T} \cdot 2h$$

$$\therefore \quad P^{\beta} - P^{\alpha} = 2\gamma h$$

$$\Delta P = 2\gamma h$$

H ↑ as particle size decreases

— Capillarity

Unary two phase system

$$T^{\beta} = T^{\alpha}$$

$$P^{\beta} = P^{\alpha} + 2\gamma h$$

$$\mu^{\beta} = \mu^{\alpha}$$

$$d\mu^{\alpha} = -S^{\alpha} dT^{\alpha} + V^{\alpha} dP^{\alpha}$$

$$d\mu^{\beta} = -S^{\beta} dT^{\beta} + V^{\beta} dP^{\beta}$$

$$\therefore d\mu^{\beta} = -S^{\beta} dT + V^{\beta}\left(dP^{\alpha} + 2\gamma dh\right)$$

$$= d\mu^{\alpha} = -S^{\alpha} dT + V^{\alpha} dP^{\alpha}$$

$$\therefore \left(S^{\alpha} - S^{\beta}\right) dT - \left(V^{\alpha} - V^{\beta}\right) dP^{\alpha}$$

$$+ 2\gamma V^{\beta} dh = 0$$

$$\Delta S = S^{\alpha} - S^{\beta}$$

$$\Delta V = V^{\alpha} - V^{\beta}$$

$$\Delta S\, dT - \Delta V dP^{\alpha} + 2\gamma V^{\Delta} d h = 0$$

liquid / vapour interface

α (g)

β (l)

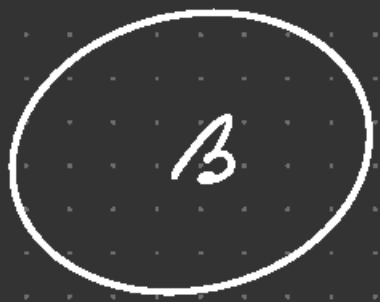
$dT = 0$

$$\therefore \quad -\Delta V\, dP + 2\gamma V^{l} d h = 0$$

$$\Delta V = V^{g} - V^{L} \simeq V^{g} = \frac{RT}{P}$$

Melting

β – solid
α – liquid



$$\Delta S\, dT + 2\gamma V^{\beta}\, dh = 0$$

$$dT = -\frac{2\gamma V^{\beta}}{\Delta S}\, dh$$

$$\int_{T(h=0)}^{T_h} dT = -\int_{H=0}^{H} \frac{2\gamma V^{\beta}}{\Delta S}\, dh$$

$$= -\frac{2\gamma V^{\beta}}{\Delta S}\, h$$

$$T_h = T_0 - \frac{2\gamma V^s}{\Delta S} h$$

$$= T_0 \left(1 - \lambda_m h\right)$$

$$\lambda_m = \frac{2\gamma V^s}{T_0 \Delta S}$$

$$= \frac{2\gamma V^s}{\Delta H}$$ (Capillary length)

$T_0 = T_m(H=0)$

$T_0 \Delta S = \Delta H$

Chemical potential in unary system

$$d\mu^{\alpha} = V^{\alpha} dP^{\alpha}$$

$$d\mu^{\beta} = V^{\beta} dP^{\beta}$$

$$= V^{\beta}\left(dP^{\alpha} + 2\gamma dh\right)$$

$$d\mu^{\alpha} = d\mu^{\beta} \qquad V^{\alpha} dP^{\alpha} = V^{\beta}\left(dP^{\alpha} + 2\gamma dh\right)$$

$$dP^{\alpha} = \frac{2\gamma V^{\beta}}{V^{\alpha} - V^{\beta}} dh$$

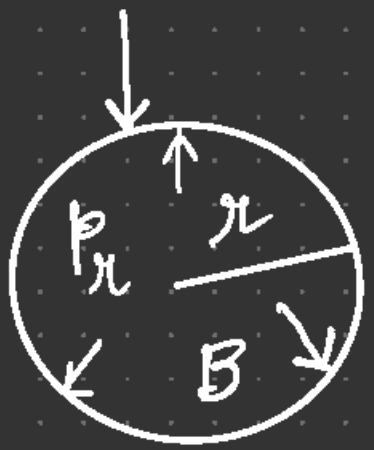
$$d\mu^{\alpha} = V^{\alpha} dP^{\alpha} = V^{\alpha} \frac{2\gamma V^{\beta}}{V^{\alpha} - V^{\beta}} dh$$

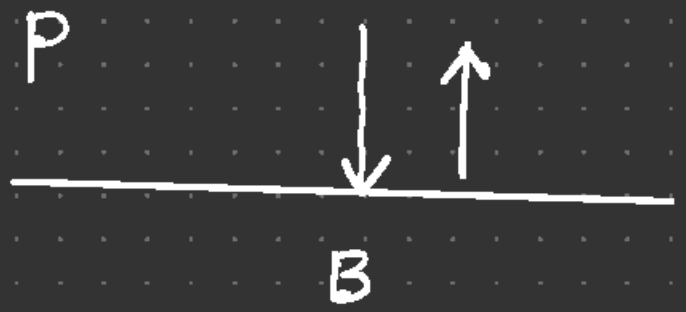
$$\mu_h^\alpha = \mu_{h=0}^\alpha + \frac{2\gamma v^\kappa v^\beta}{v^\alpha - v^\beta} h$$

Spherical particle of B immersed in A-rich α matrix

γ is the interfacial free energy between particle and matrix

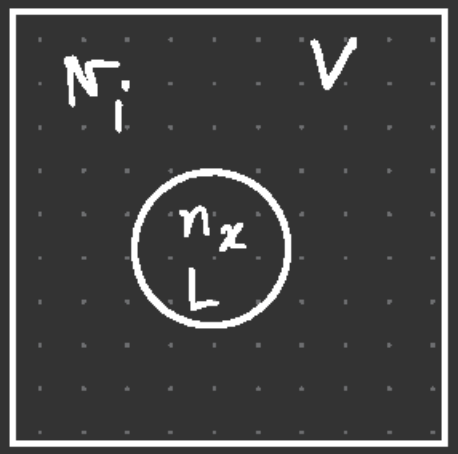
Find the vapour pressure of B as a function of its radius of curvature





$$G = U + pV - TS$$

$$dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dN_i$$



Liquid particle containing n_x molecules form in a vapour containing N_i molecules

$$\Delta G = G_{drop} - G_{vapour}$$

$$N_f = N_i - n_x$$

g_v – free energy per molecule of vapour

g_l – free energy per molecule of liquid drop

$$\Delta G = N_f g_v + n_x g_l + 4\pi r^2 \gamma - N_i g_v$$

$$= (N_i - n_x) g_v + n_x g_l + 4\pi r^2 \gamma - N_i g_v$$

$$= n_x (g_l - g_v) + 4\pi r^2 \gamma$$

$v_l \rightarrow$ volume occupied per molecule of liquid

$v_v \rightarrow$ volume occupied per molecule of Vapour

$$n_x v_l = \frac{4}{3}\pi r^3$$

$$n_x = \frac{4\pi r^3}{3 v_l}$$

$$\Delta G_1 = \frac{4\pi r^3}{3v_l}\left(g_l - g_v\right) + 4\pi r^2 \gamma$$

$$dg = \underbrace{\left(v_l - v_v\right)}_{\text{(per molecule)}} dP \qquad \text{at const. } T$$

$$v_v \gg v_l$$

$$dg = -v_v\, dP$$

$$v_v = \frac{kT}{P}$$

$$\Delta g = -k_B T \int_{P(r=0) \text{ ou } P_\infty}^{r} \frac{dP}{P}$$

$$\Delta g = -k_B T \ln\left(\frac{P}{P_\infty}\right)$$

$$\Delta G = -\frac{4\pi r^3}{3 v_l} \ln\left(\frac{P}{P_\infty}\right) + 4\pi r^2 \gamma$$

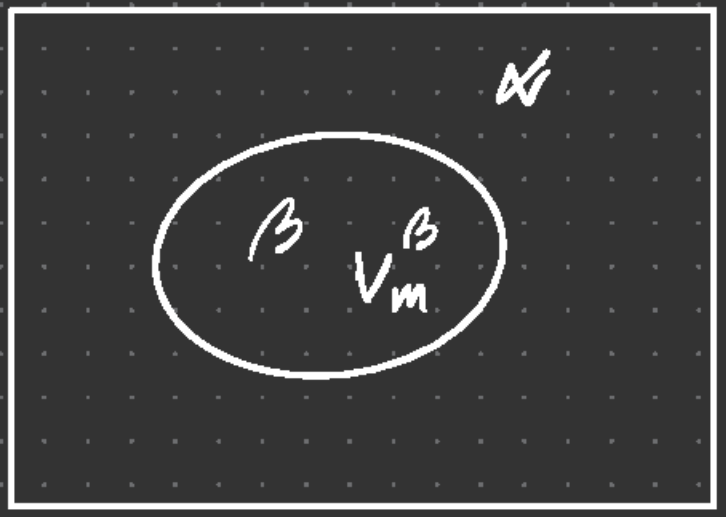
$$\frac{\partial \Delta G}{\partial r} = 0 \Rightarrow \ln\left(\frac{P}{P_\infty}\right) = \frac{2 v_L \gamma}{r k_B T}$$

$$= \frac{2 V_m \gamma}{r R T}$$

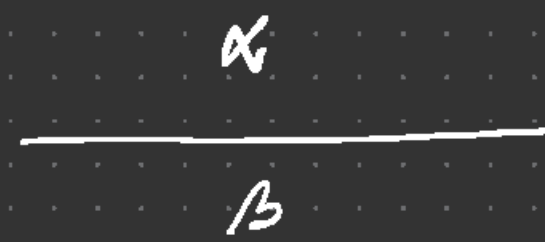
Ostwald - Freundlich equation

$$\frac{p}{p_\infty} = \exp\left(\frac{R_{critical}}{R}\right)$$

$$R_{critical} = \frac{2\gamma v_a}{k_B T}$$

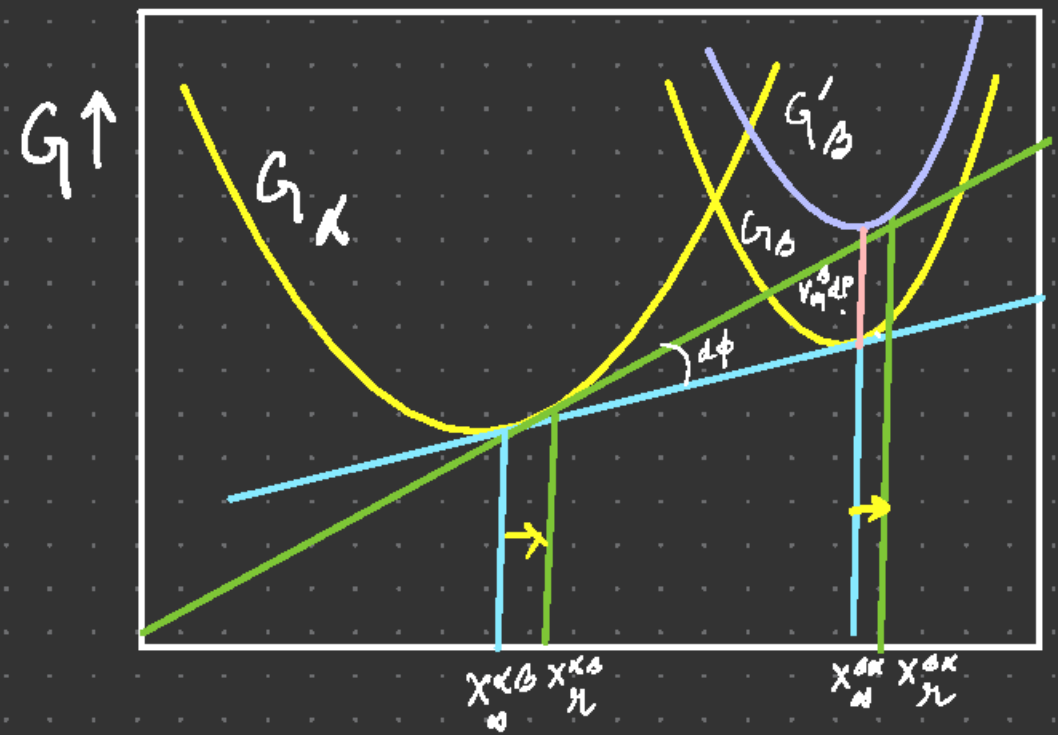


ΔP



$$dG = V\,dP$$

$$\Delta P = \frac{2\gamma}{r} \qquad dG = V dP$$



$$\left(x^{\alpha\beta} - x^{\beta\alpha}\right) d\phi = V_m^\beta dP$$

$$d\phi = \left.\frac{\partial G^\alpha}{\partial x^\alpha}\right|_{x_r^{\alpha\beta}} - \left.\frac{\partial G'}{\partial x'}\right|_{x_\alpha^{\alpha\beta}}$$

$$= \frac{\partial^2 G^\alpha}{\partial x^{\alpha 2}} dx^{\alpha\beta}$$

$$dx^{\alpha\beta} = x_r^{\alpha\beta} - x_\alpha^{\alpha\beta}$$

$$\frac{\partial^2 G^{\alpha}}{\partial X^{\alpha 2}} = \frac{RT}{X^{\alpha}} \quad \left(\text{dilute solution limit}\right)$$

$$dX^{\alpha\beta} = \frac{X^{\alpha\beta}}{X^{\beta\alpha} - X^{\alpha\beta}} \frac{V_m^{\beta} dP}{RT}$$

$$\ln \frac{X^{\alpha\beta}(P)}{X^{\alpha\beta}(P_{\alpha})} = \frac{V_m^{\beta} \Delta P}{RT\left(X^{\beta\alpha} - X^{\alpha\beta}\right)}$$

$$\Delta P = \frac{2\gamma}{r}$$

$$\ln \frac{x^{\alpha\beta}(r)}{x^{\alpha\beta}(r=\infty)} = \frac{2 V_m^{\beta} \gamma}{r} \frac{1}{RT\left(x^{\beta\alpha} - x^{\alpha\beta}\right)}$$

Thermodynamics of irreversible process

Flux $\leftrightarrow$ driving force

X – driving force

Onsager's postulates

1. $$j_i = \sum_k L_{ik} X_k$$

L_{ik} – kinetic coefficients

$\nabla \mu$

$$j_i = \sum M_{ik} \nabla \mu_k$$

j_i compositional flux

At steady state

$$\frac{\text{length}}{\text{time}} \frac{\text{Moles}}{\text{volume}} = \frac{\text{Moles}}{\text{Time Area}}$$

$$j = vc$$

↓ steady state velocity

$$c = \frac{\text{no. of moles}}{\text{volume}}$$

F = drag force

$$\delta W = \underline{F}\, vc\, dt = \vec{F} \cdot \vec{j}\, dt$$

↓ converted to heat

$$T\, dS_{irr} = \vec{F} \cdot \vec{j}\, dt$$

$$T \frac{\partial S_{irr}}{\partial t} = \vec{F} \cdot \vec{j}$$

$$T \frac{\partial S_{irr}}{\partial t} = \sum j_i X_i$$

$$T dS = dU + p dV - \sum_{i=1}^{k} \mu_i dN_i$$

$$d\left(\frac{Z}{V}\right) = \frac{dZ}{V} - Z \frac{dV}{V^2}$$

$$T \frac{dS}{V} = \frac{dU}{V} + p \frac{dV}{V} - \sum_{i=1}^{k} \mu_i \frac{dN_i}{V}$$

$$T ds = du - \sum_{i=1}^{k} \mu_i dc_i + \frac{dV}{V^2}$$

$$(U + pV - TS - \Sigma \mu_i N_i)$$

$$G = U + pV - TS$$

$$= \sum \mu_i N_i$$

$$\therefore \quad T ds = du - \sum_{i=1}^{k} \mu_i \, dc_i$$

$$T \frac{\partial s}{\partial t} = \frac{\partial U}{\partial t} - \sum_{i=1}^{k} \mu_i \frac{\partial c_i}{\partial t}$$

Continuity Eqn $\rightarrow$ $\dfrac{\partial c_i}{\partial t} + \nabla \cdot \vec{J}_i = 0$

Quantity in $-$ Quantity out $=$ Rate of accumulation/depletion

$+$ Quantity generated $-$ Quantity

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{j}_v = 0$$ — continuity equation

$$\frac{\partial s_{rev}}{\partial t} + \vec{\nabla} \cdot \vec{j}_s = 0$$

$$j_i = -D_i \nabla c_i$$

$$j_i = -L_{ii} \nabla \mu_i$$

$$\nabla \mu_i = RT \ln \nabla c_i$$

$$\therefore \quad j_i = -L_{ii} RT \nabla \ln c_i$$

$$M_i = L_{ii} RT$$

$$j_i = -M_i \nabla \ln c_i$$

$$= -\frac{M_i}{c_i} \nabla c_i = -D_i \nabla c_i$$