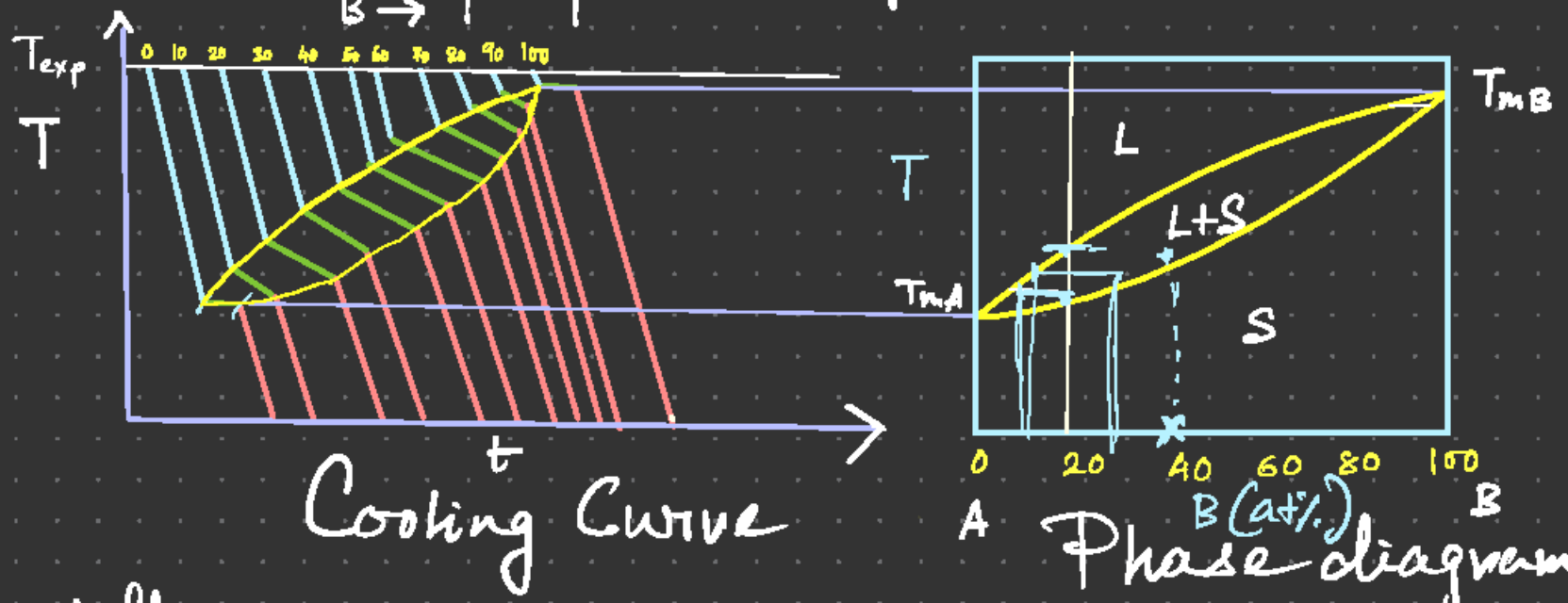
Determination of phase diagrams — Cooling curves, Vegard's Law

Determination of phase diagram



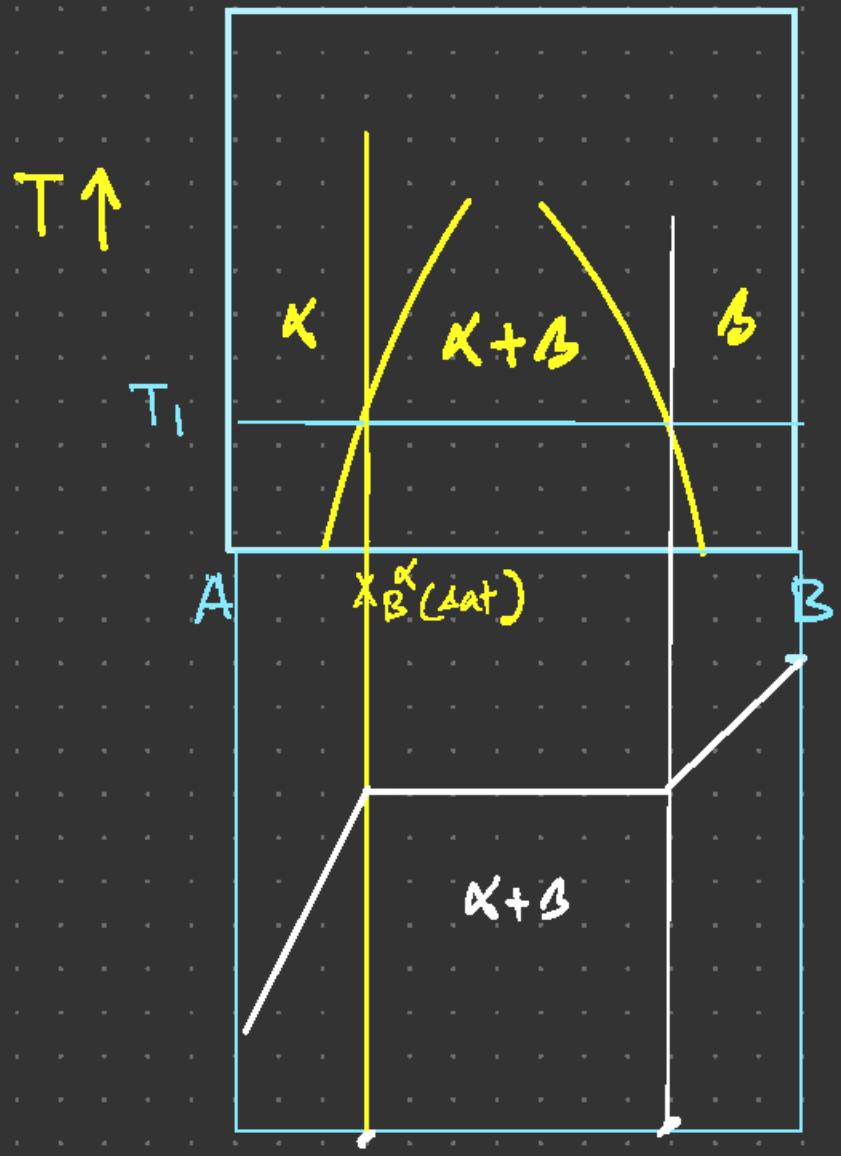
X-ray diffraction

Type II

Vegard's law $a - a_0 = K(c - c_0)$

$\frac{1}{a}\frac{da}{dc}$

a – lattice parameter


T ↑
α
α+β
β
T1
A
x_B^{α}(sat)
B
α+β

III A-B alloy

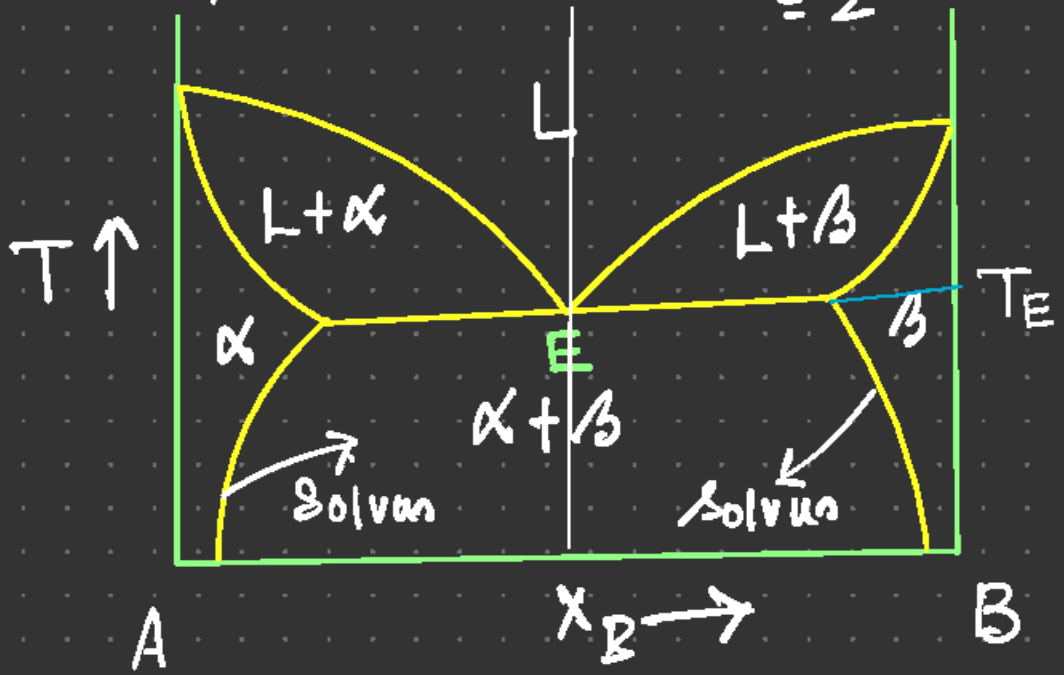
Solubility of A & B in liquid is infinite

Solubility of A & B in solid is limited or finite

Gibbs phase rule: $f = c - p + 1$

$= 2$

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



Eutectic phase diagram

At E: $f = c - p + 1$

$= 2 - 3 + 1$

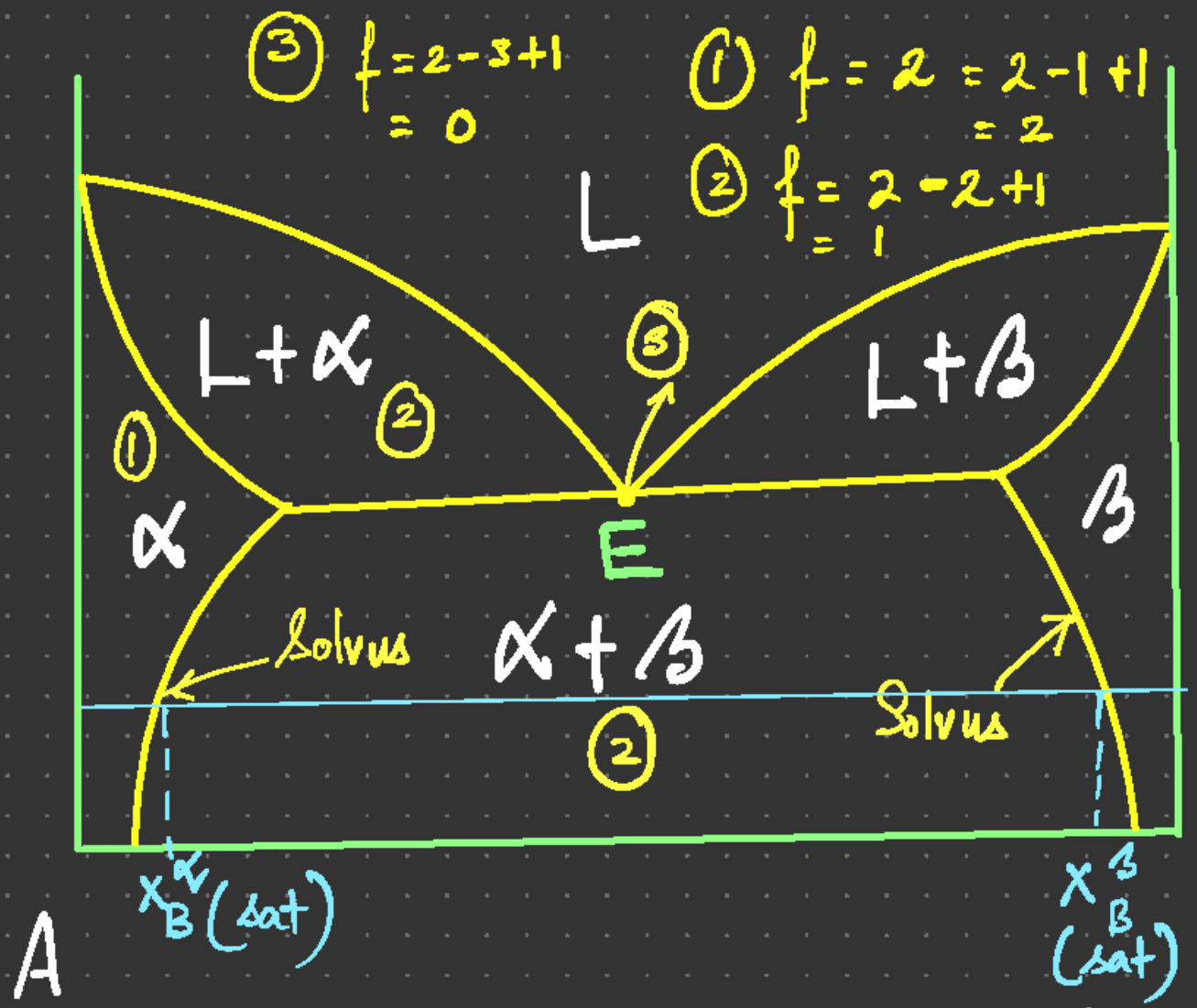
$= 0$

α - solid solution of B solute in A solvent

β - solid solution of A solute in B solvent

$L \rightarrow \alpha + \beta$

Invariant point E below the melting points of pure A and pure B



T_1

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

at x_B^{α}(sat), x_B^{β}(sat)

Let α and β be dilute solutions at T_1

Henry's law obeyed by solute

Raoult's law obeyed by solvent

In saturated α,

B - Solute, A - Solvent

$$\mu_B^{\alpha} = \mu_B^{\circ} + RT \ln X_{B(sat)}^{\alpha} + RT \ln \gamma_B^{\circ} \quad \text{— (1)}$$

In saturated β, $\mu_B^{\alpha} = \mu_B^{\beta}$

B - solvent

$$\mu_B^{\beta} = \mu_B^{\circ} + RT \ln a_B^{\beta} = \mu_B^{\circ} + RT \ln X_{B(sat)}^{\beta} \quad \text{— (2)}$$

$$\therefore \ln X_{B(sat)}^{\beta} = \ln X_{B(sat)}^{\alpha} + \ln \gamma_B^{\circ}$$

$$\gamma_B^{\circ} = \frac{X_B^{\beta}(sat)}{X_B^{\alpha}(sat)}$$

Nickel and an element A are related by a Type III eutectic phase diagram. At 1000 K, A dissolves 4 at %. Ni and Ni dissolves 6 at % A. Calculate the oxygen partial pressure at which Ni dissolved in A to the extent of 1 at %. will begin to oxidize to NiO. A is more stable and does not oxidize.

Thermodynamics of Reactions

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

$$a\,A(s) + b\,B(s) \rightleftharpoons c\,C(s) + d\,D(s)$$

ΔG°

Each component in equilibrium with its own vapour phase

$$a\,A\,(g, p_A^\circ) = a\,A(s)$$

$$b\,B\,(g, p_B^\circ) = b\,B(s)$$

$$c\,C(s) = c\,C\,(g, p_c^\circ)$$

$$d\,D(s) = d\,D\,(g, p_d^\circ)$$

$$a\,A(s) + b\,B(s) = c\,C(s) + d\,D(s) \quad \Delta G_1$$

$$a\,A(g, p_A^\circ) = a\,A(s) \quad \Delta G_2 = 0$$

$$b\,B(g, p_B^\circ) = b\,B(s) \quad \Delta G_3 = 0$$

$$c\,C(s) = c\,C(g, p_C^\circ) \quad \Delta G_4 = 0$$

$$d\,D(s) = d\,D(g, p_D^\circ) \quad \Delta G_5 = 0$$

$+$

$$a\,A(g, p_A^\circ) + b\,B(g, p_B^\circ) = c\,C(g, p_C^\circ) + d\,D(g, p_D^\circ)$$

$$\Delta G_6 = \Delta G_1^\circ$$

At equilibrium (1 atm. pressure)

$$a\,A(g, p_A^e) + b\,B(g, p_B^e) = c\,C(g, p_C^e) + d\,D(g, p_D^e)$$

Total pressure = 1 atm.

$$\Delta G_T = 0$$

$$p_i^0 \rightarrow p_i^e$$

$$dG = V dP - S dT$$

T constant, $dT = 0$

$$dG = RT \, d \ln p$$

$$\Delta G_i = RT \ln \frac{p_i^e}{p_i^o}$$

$$a\,A(g, p_A^0) + b\,B(g, p_B^0) = c\,C(g, p_C^0) + d\,D(g, p_D^0)$$

$$\Delta G_6 = \Delta G_1^0$$

$$a\,A(g, p_A^e) = a\,A(g, p_A^0) \qquad \Delta G_2 = aRT \ln \frac{p_A^0}{p_A^e}$$

$$b\,B(g, p_B^e) = b\,B(g, p_B^0) \qquad \Delta G_3 = bRT \ln \frac{p_B^0}{p_B^e}$$

$$c\,C(g, p_C^0) = c\,C(g, p_C^e) \qquad \Delta G_4 = cRT \ln \frac{p_C^e}{p_C^0}$$

$$d\,D(g, p_D^0) = d\,D(g, p_D^e) \qquad \Delta G_5 = dRT \ln \frac{p_D^e}{p_D^0}$$

$$\therefore\ aA\left(g, p_A^{\,e}\right) + bB\left(g, p_B^{\,e}\right) = cC\left(g, p_C^{\,e}\right) + dD\left(g, p_D^{\,e}\right)$$

$$\Delta G_T = 0$$

$$\Delta G_T = 0 = \Delta G_0 + \sum_i \Delta G_i$$

$$\ln \frac{p_B^{\,e}}{p_B^{\,e}} = -\ln\left(\frac{p_B^{\,e}}{p_B^{\,0}}\right) = \Delta G_1^{\,0} + RT \ln\left[\frac{\left(p_C^{\,e}/p_C^{\,0}\right)\left(p_D^{\,e}/p_D^{\,0}\right)}{\left(p_A^{\,e}/p_A^{\,0}\right)\left(p_B^{\,e}/p_B^{\,0}\right)}\right]$$

$$\therefore\ \Delta G_1^{\,0} = -RT \ln(k)$$

$$a_C = p_C^{\,e}/p_C^{\,0}, \quad \cdots \quad a_i = \frac{p_i^{\,e}}{p_i^{\,0}} = \frac{p_i}{p_i^{\,0}}$$

$$dG_i = RT\, d\ln a_i$$

$$G_i - G_i^{\circ} = RT \ln \frac{a_i}{a_i^{\circ}}$$

$$NiO(s) \rightleftarrows \frac{1}{2} O_2 (g, 1\,atm.) + Ni(s)$$

$$\Delta G^{\circ} = 146000\ J = -RT \ln K$$

$$K = 2.34 \times 10^{-8} = \frac{a_{Ni} \cdot p_{O_2}^{1/2}}{a_{NiO}}$$

$$a(NiO) = 1 \qquad a(Ni_{pure}) = 1$$

Activity of Ni in a 1 at% solution?

(solvent)

Ni-rich soln, Ni follows Raoult's Law

$X_A = 0.06$ $X_{Ni} = 0.94$

A-rich solution Ni is solute $X_{Ni} = 0.04$

$$X_{Ni} = 0.94 \longrightarrow a_{Ni} = 0.94$$

This phase is in equilibrium with A-rich phase with $X_{Ni} = 0.04$

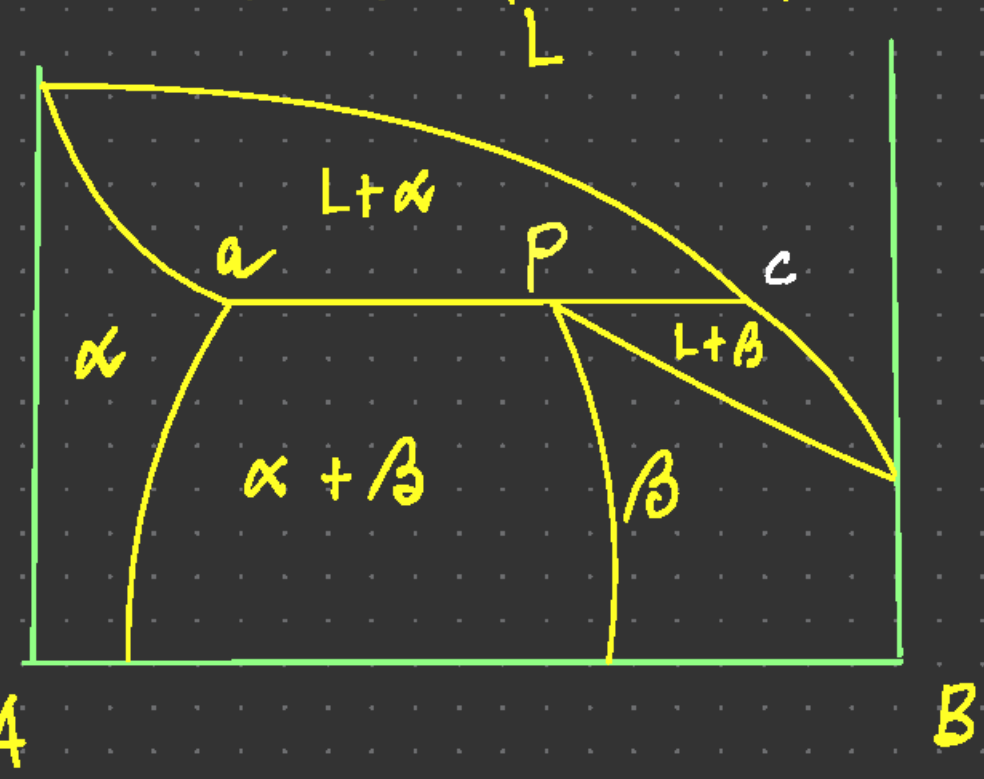
A-rich soln, Ni follows Henry's law

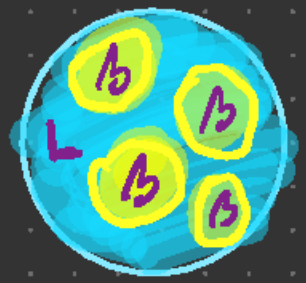
$$a_{Ni} = \gamma^{\circ}_{Ni} X_{Ni} \qquad \gamma^{\circ}_{Ni} = \frac{0.94}{0.04} = 23.5$$

$$a_{Ni}\left(1\text{at\% solid solution}\right) = 0.01 \times 23.5 = 0.235$$

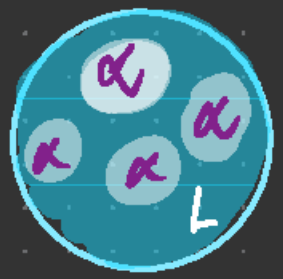
$$\therefore p_{O_2} = 9.6 \times 10^{-10} \text{ Pa}$$

Peritectic Reaction







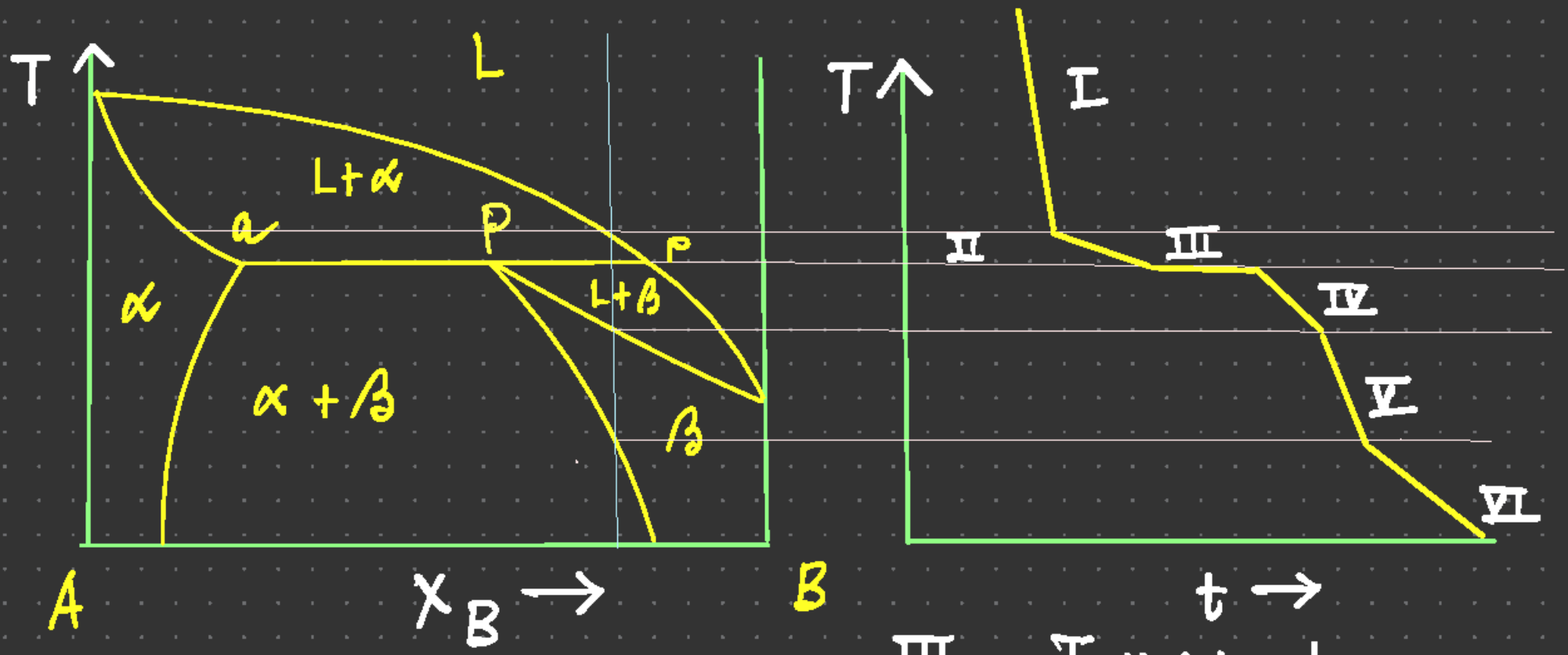




Peritectic phase diagram

Invariant reaction at P : $L + \alpha \rightarrow \beta$
(peritectic reaction)

aPc : peritectic reaction
c – Liquid composition, a – α composition
b – β composition





III – Invariant peritectic reaction (horizontal segment)

Type II - phase diagram

$\Delta H_m^{mix}(\alpha) = 0$

$\Delta H_m^{mix}(L) = 0$

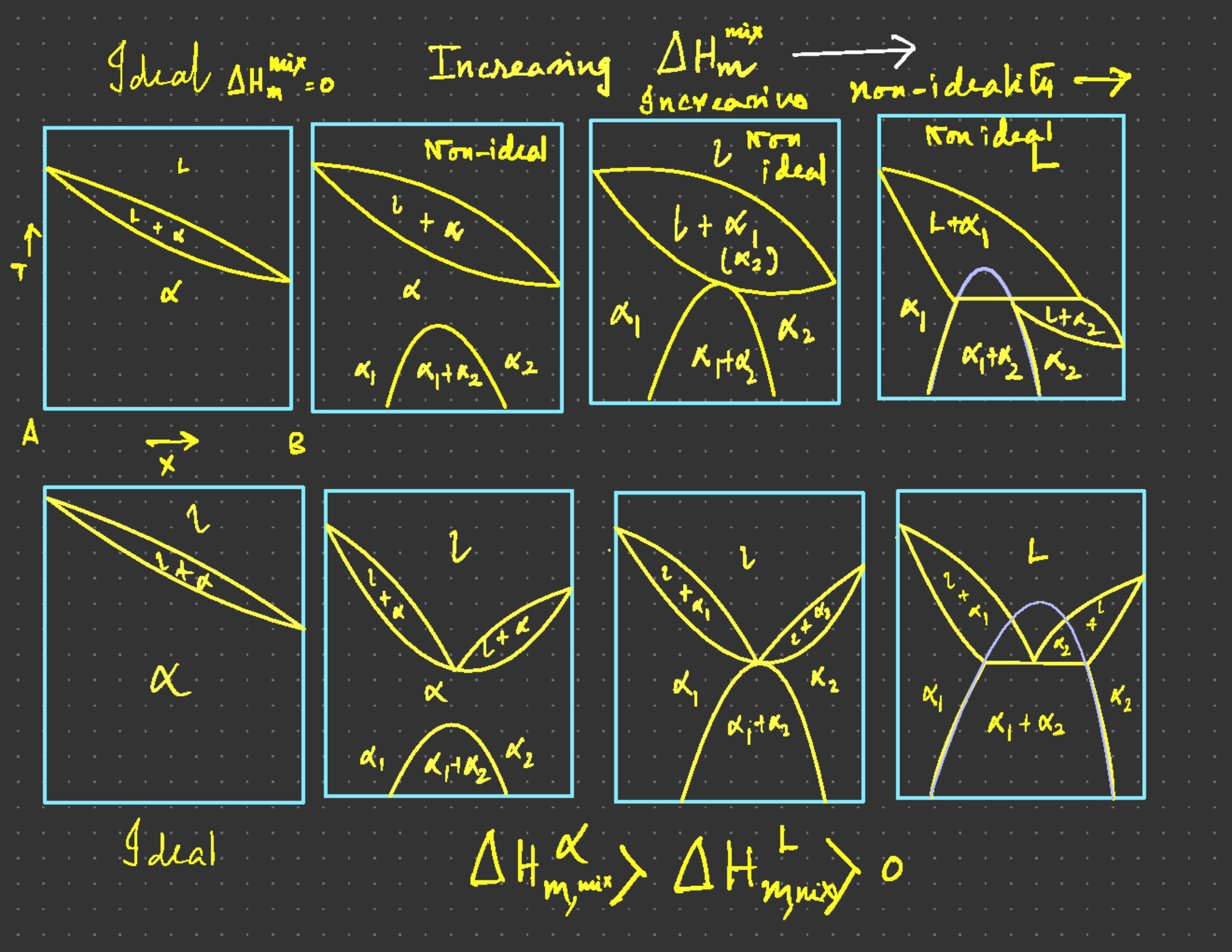
} complete solubility in liquid and solid solutions.

Lens-shaped two phase region

$\Delta H_m^{mix}(\alpha) > 0$

$\Delta H_m^{mix}(L) > 0$

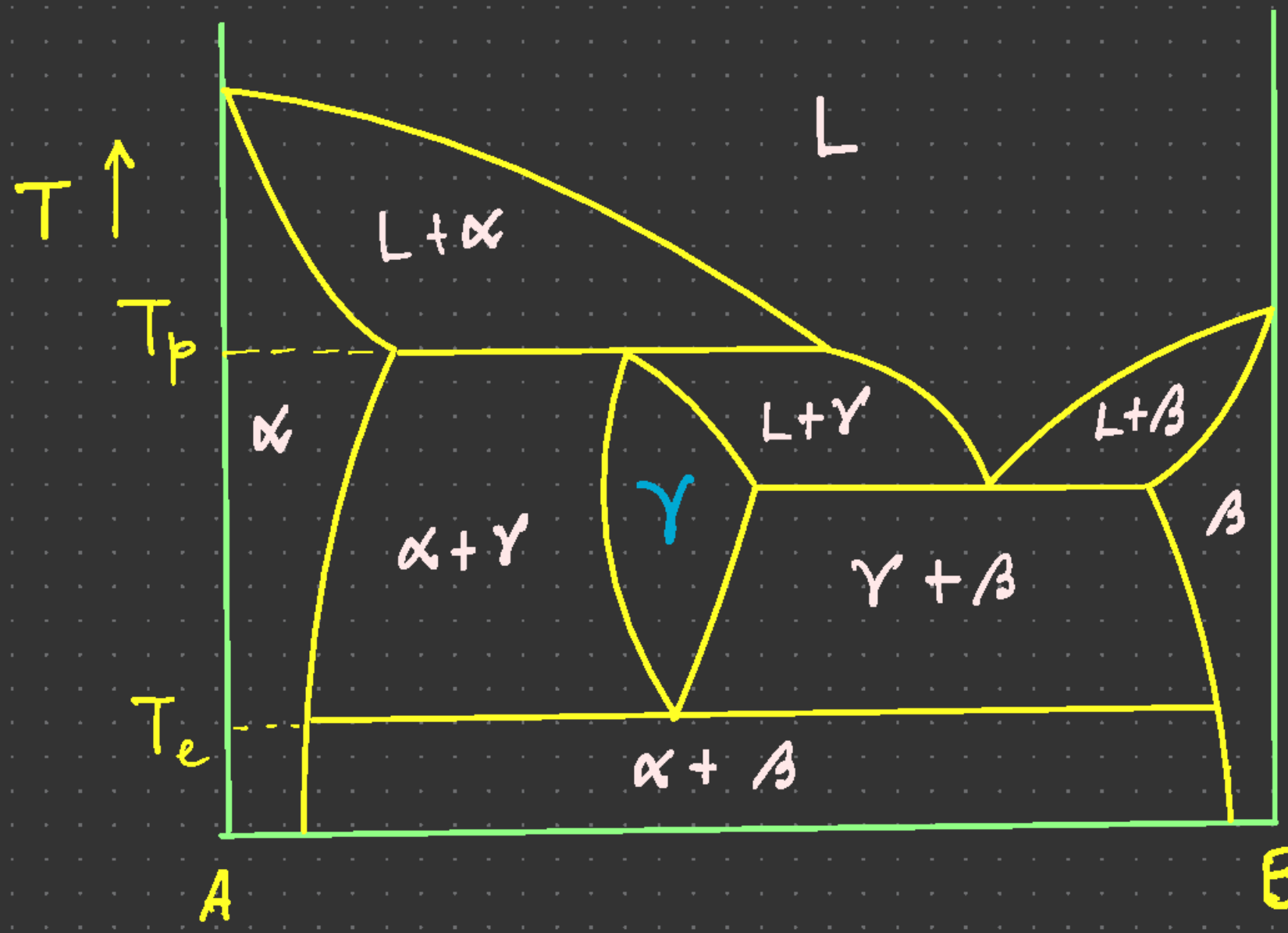
$\Delta H_n^{mix}(\alpha) > \Delta H_m^{mix}(L)$


Ideal $\Delta H_m^{mix} = 0$
Increasing ΔH_m^{mix} increasing
non-ideality
Non-ideal
Non ideal
Non ideal
T
A
B
x
Ideal
$\Delta H^{\alpha}_{m,mix} > \Delta H^{L}_{m,mix} > 0$

IV. Presence of unstable (Stoichiometric or non-Stoichiometric compounds)

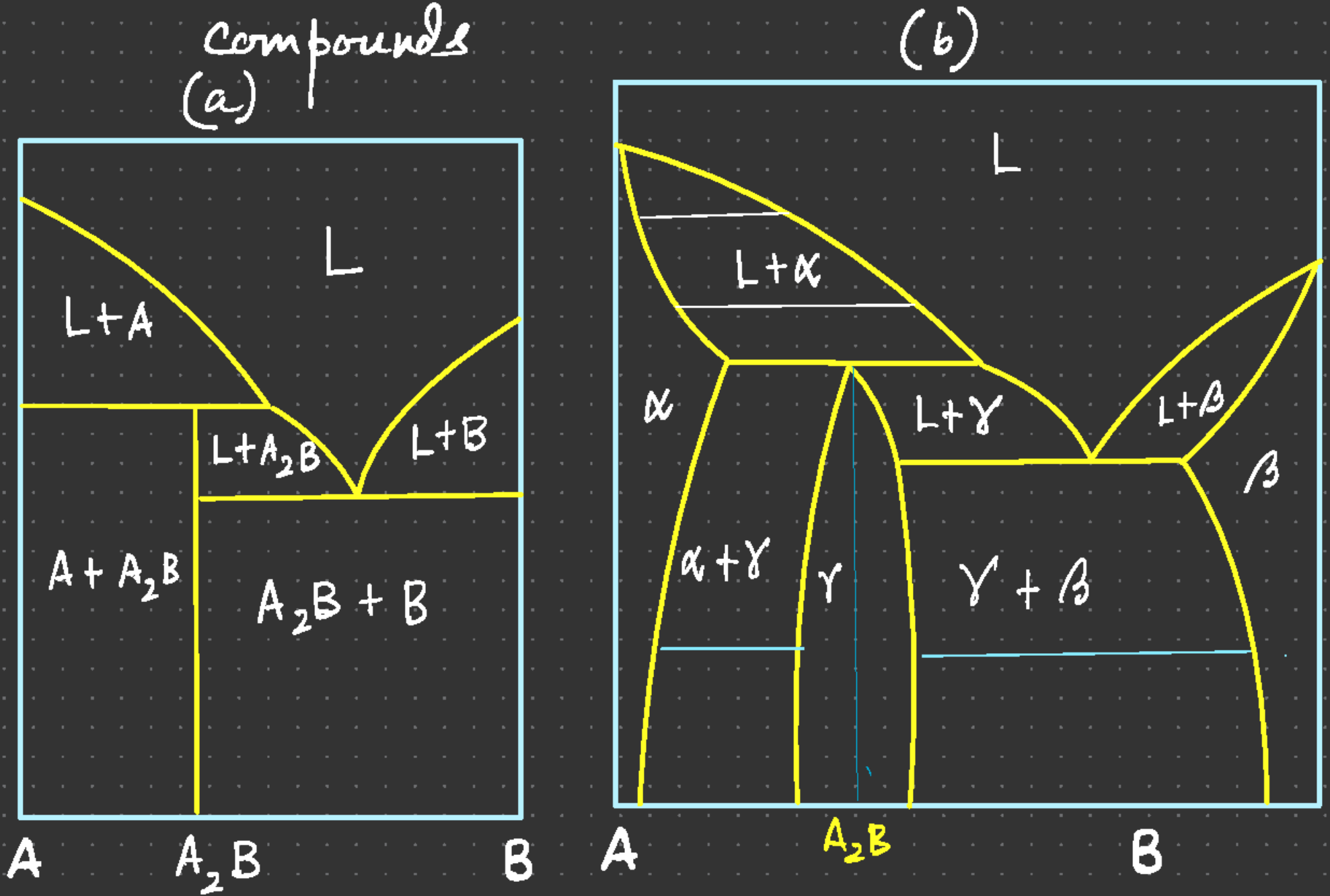
Stoichiometric
— Well defined composition
Eg. AB, A_2B, AB_3, ...
line compound

Non-Stoichiometric
— phase with a new crystalline arrangement but with variable composition
Eg. $A_{55-60}B_{45-40}$
Area or Region

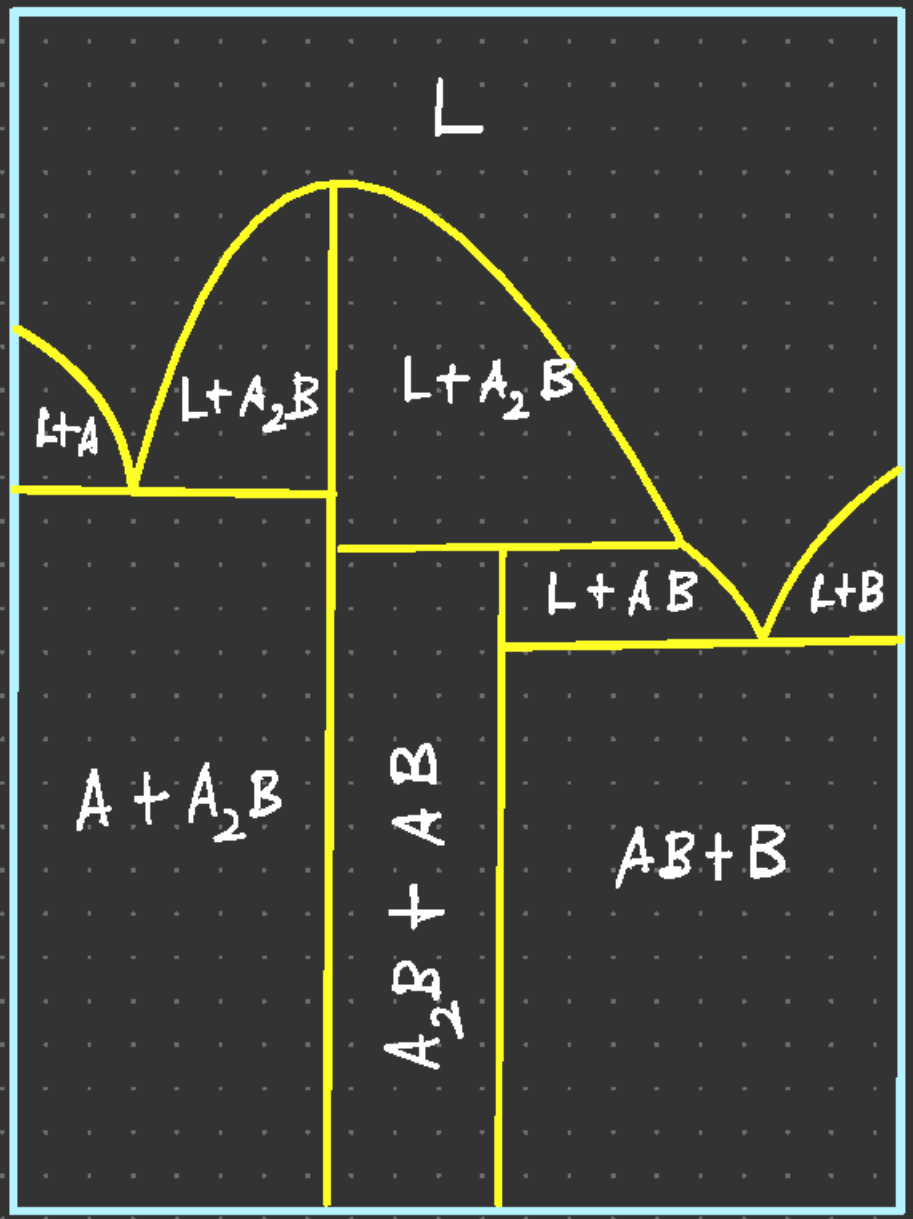


γ – Unstable at low and high temperatures

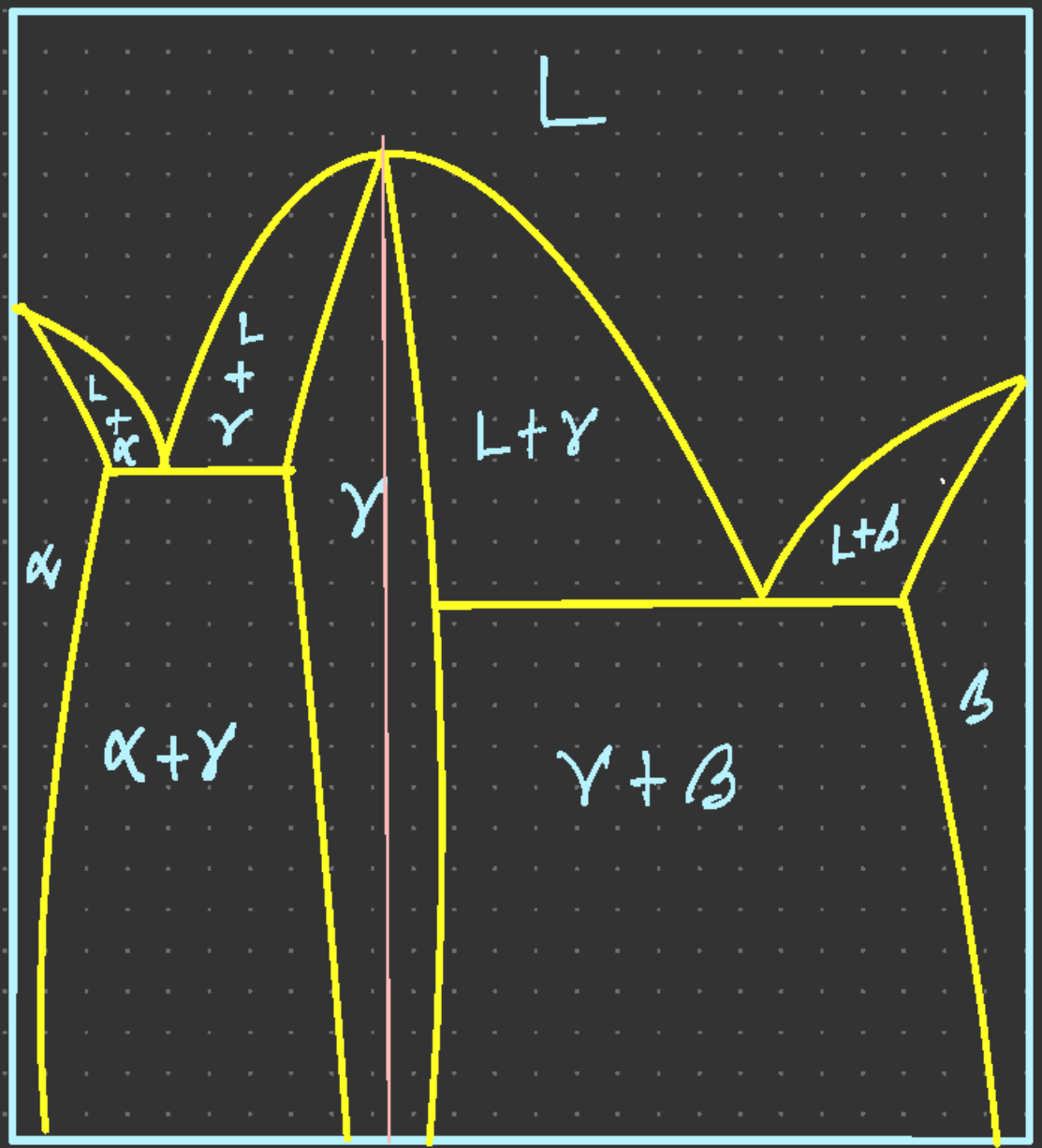
V. Presence of stable, Stoichiometric / non-Stoichiometric compounds



(c)

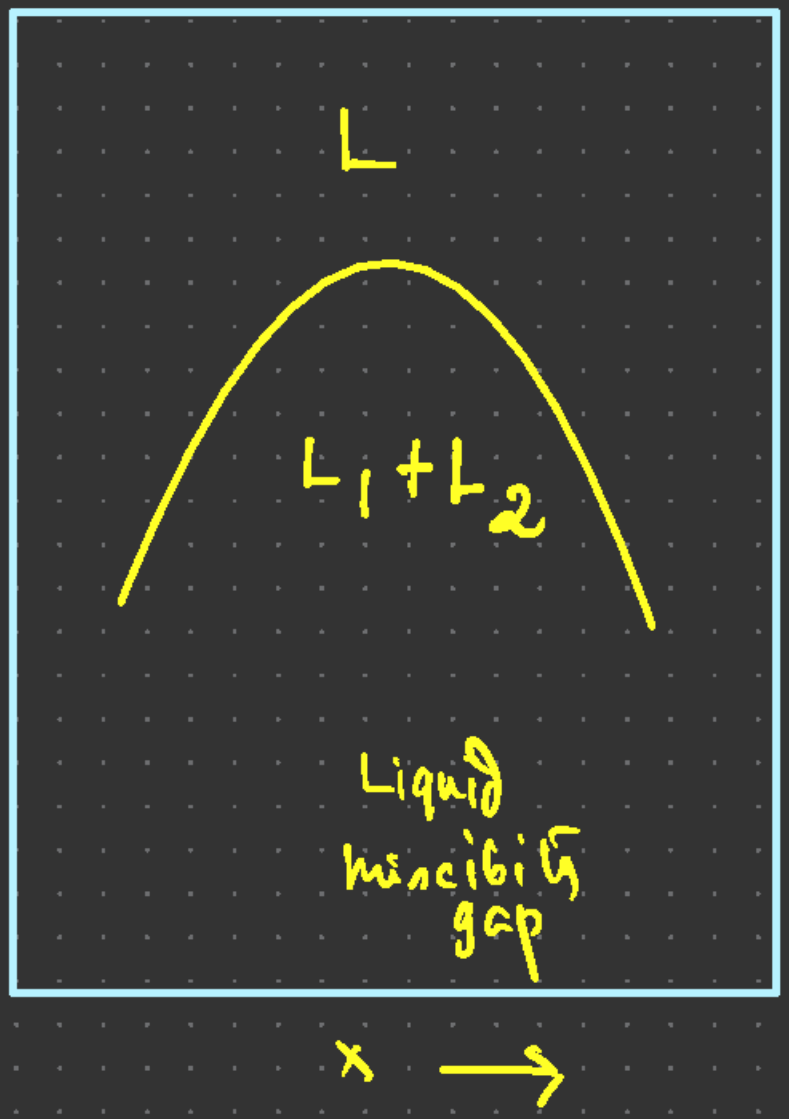

L
L+A
L+A2B
L+A2B
L+AB
L+B
A+A2B
A2B+AB
AB+B
A
A2B
AB
B

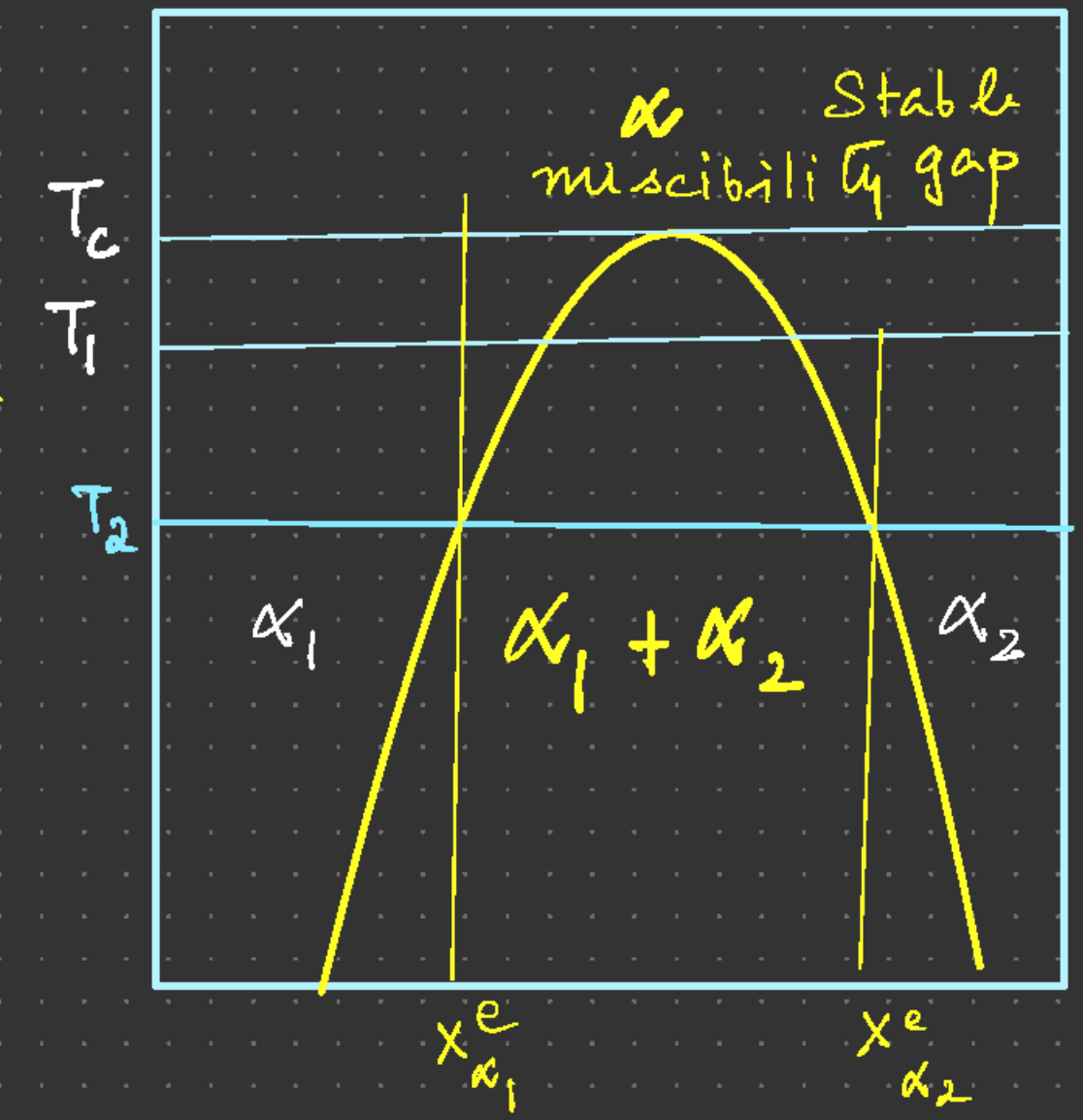
(d)

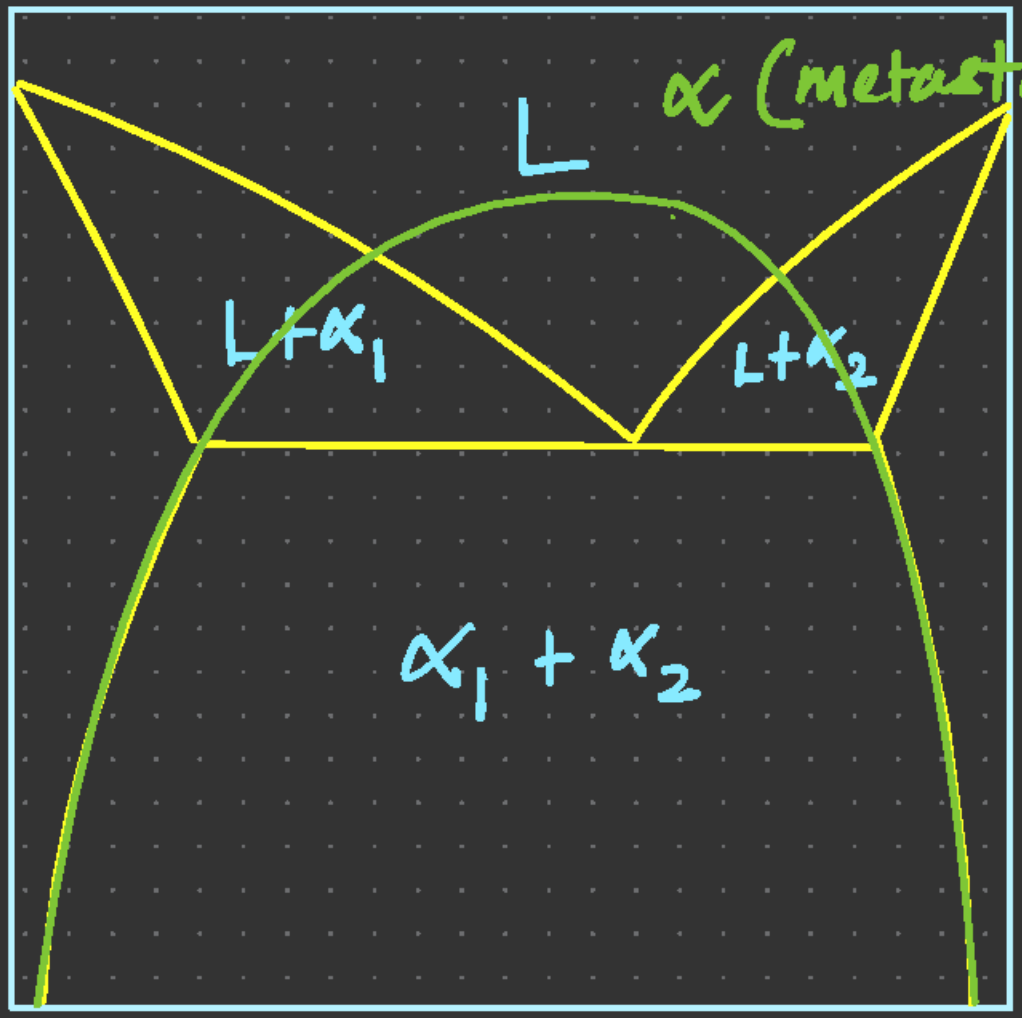

L
L+α
L+γ
L+γ
α
γ
L+B
B
α+γ
γ+B
A
A2B
B

VI. Phase separation – Miscibility gap

Solutions are non ideal







Metastable miscibility gap

Free Energy - Composition Diagrams

$$\Delta G^{id}_{m,mix} = RT(x_A \ln x_A + x_B \ln x_B)$$

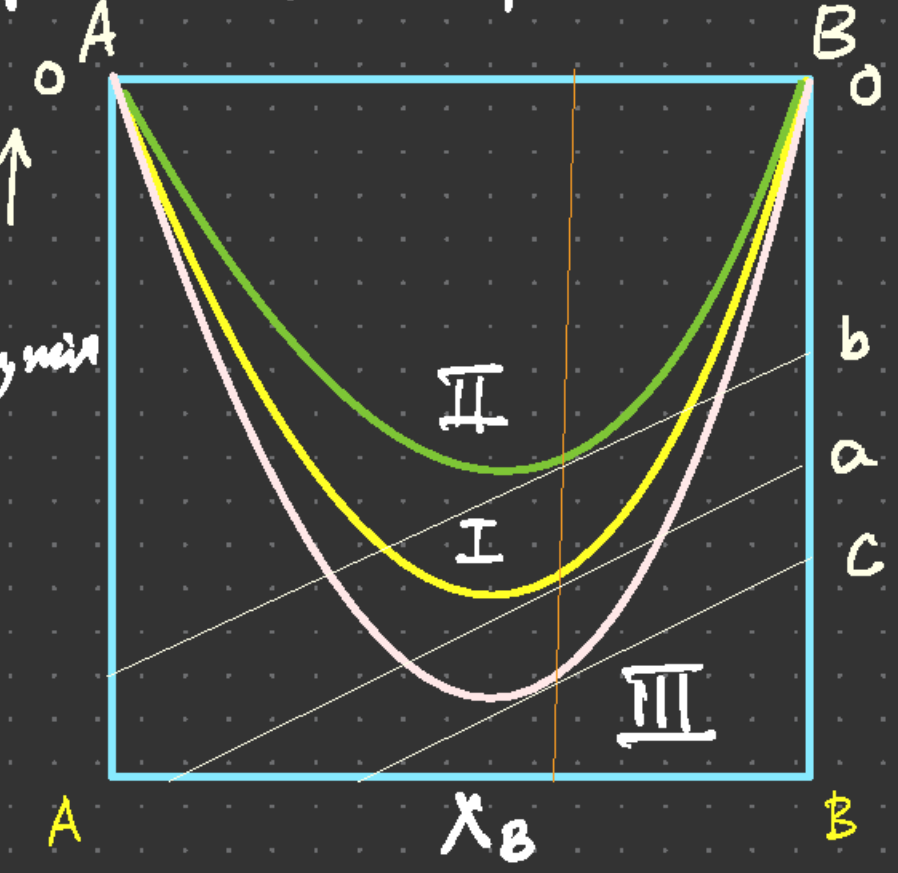
Non-ideal

$$a_i \neq x_i \qquad a_i = \gamma_i x_i$$

II $\gamma_i > 1$ $a_i > x_i$

III $\gamma_i < 1$ $a_i < x_i$

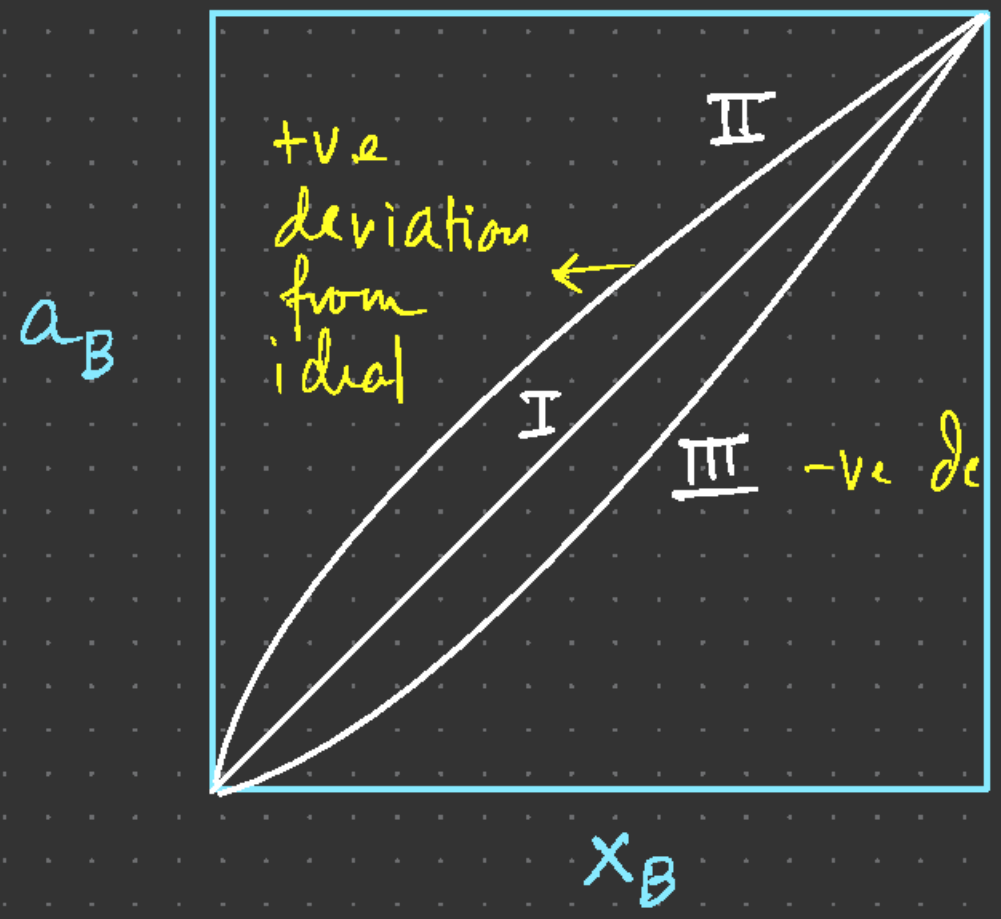
I $\gamma_i = 1$ $a_i = x_i$



$$\left| B_b = \Delta \bar{G}_B = RT \ln a_B \ (\mathrm{II}) \right|$$

$$\left\langle \left| B_a = \Delta \bar{G}_B = RT \ln X_B \ (\mathrm{I}) \right| \right.$$

$$\left\langle \left| B_c = \Delta \bar{G}_B = RT \ln a_B \ (\mathrm{III}) \right| \right.$$



For I

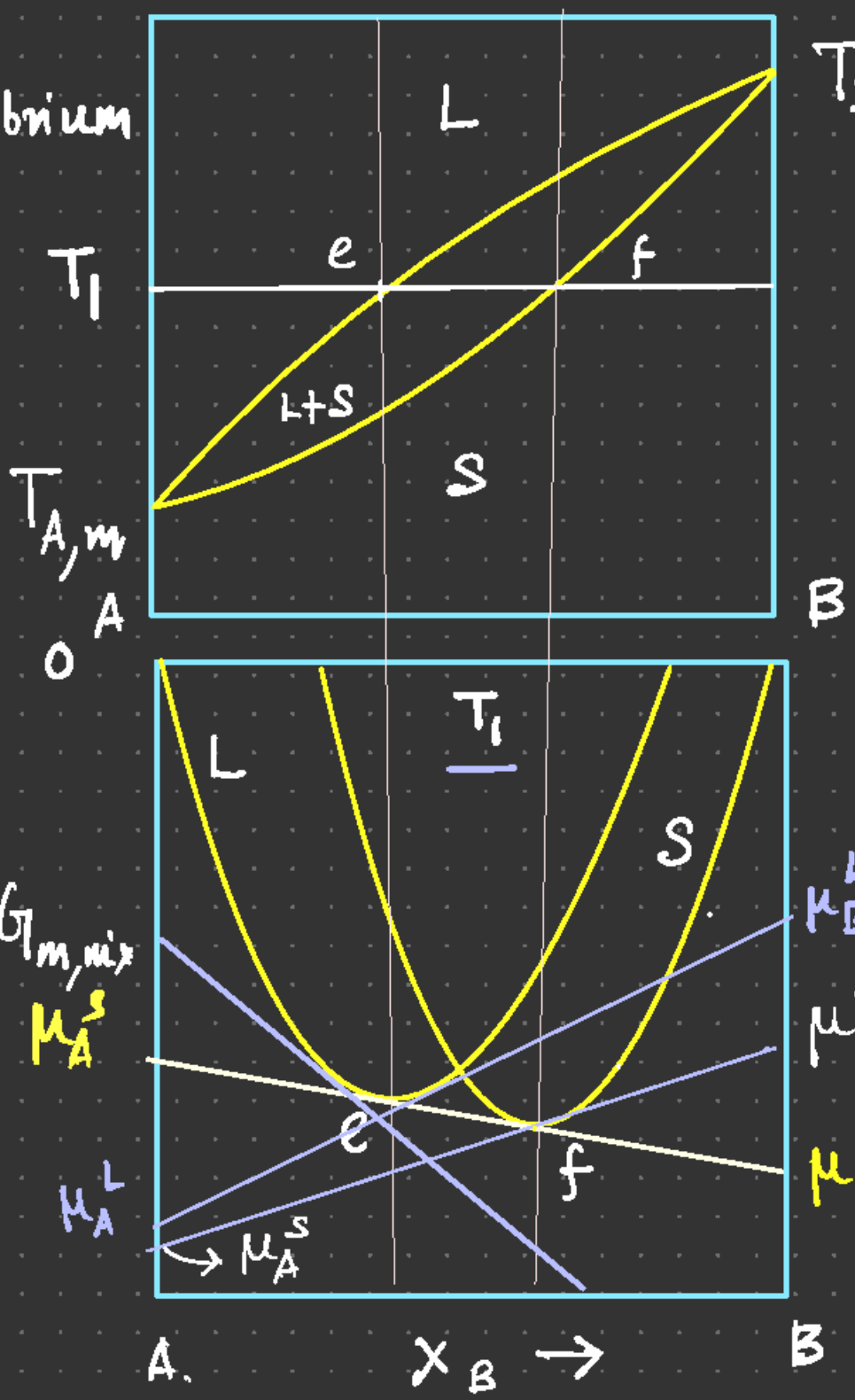
$a_B = X_B$

-ve deviation from ideal

Chemical Equilibrium

$\mu_A^S = \mu_A^L$

$\mu_B^S = \mu_B^L$



Common tangent construction

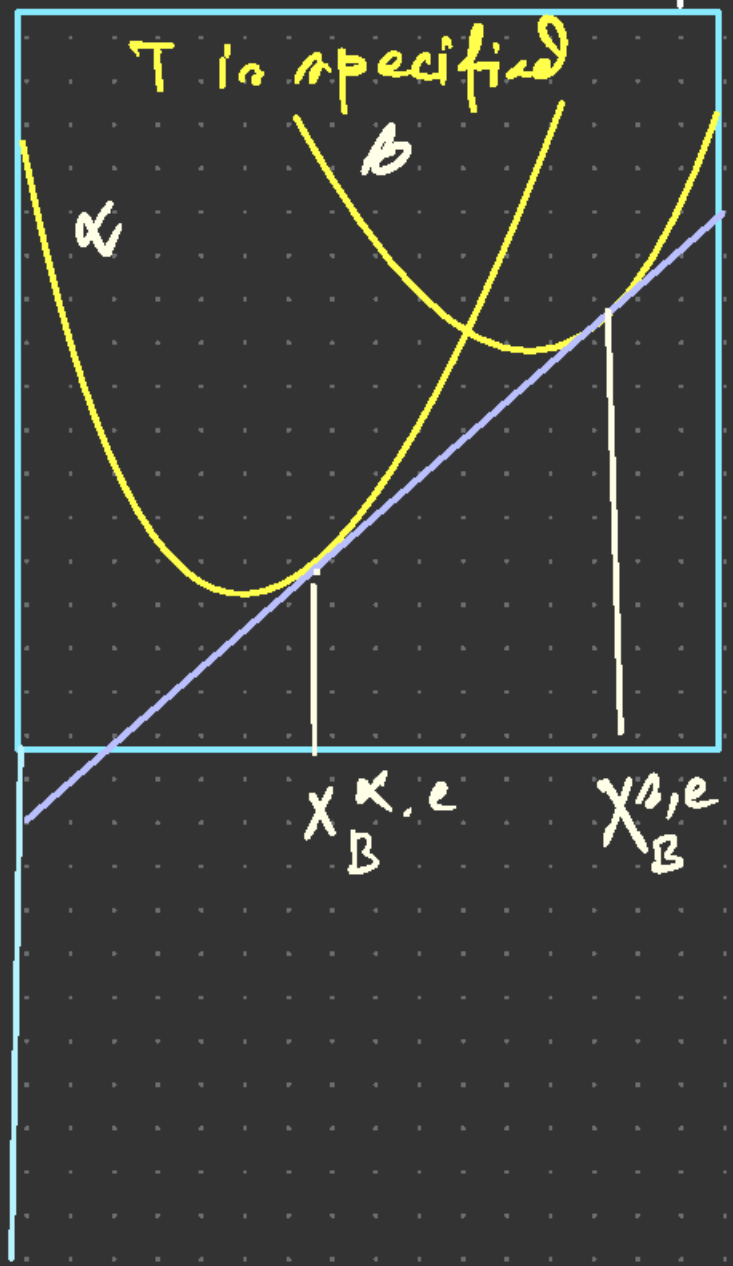
Note that common tangent need not pass through the minima of the free energy curves

G-x diagram

$$\left\{ \begin{aligned} \mu_A^{\alpha} &= \mu_A^{\beta} \\ \mu_B^{\alpha} &= \mu_B^{\beta} \end{aligned} \right\}$$

↓

Common tangent construction



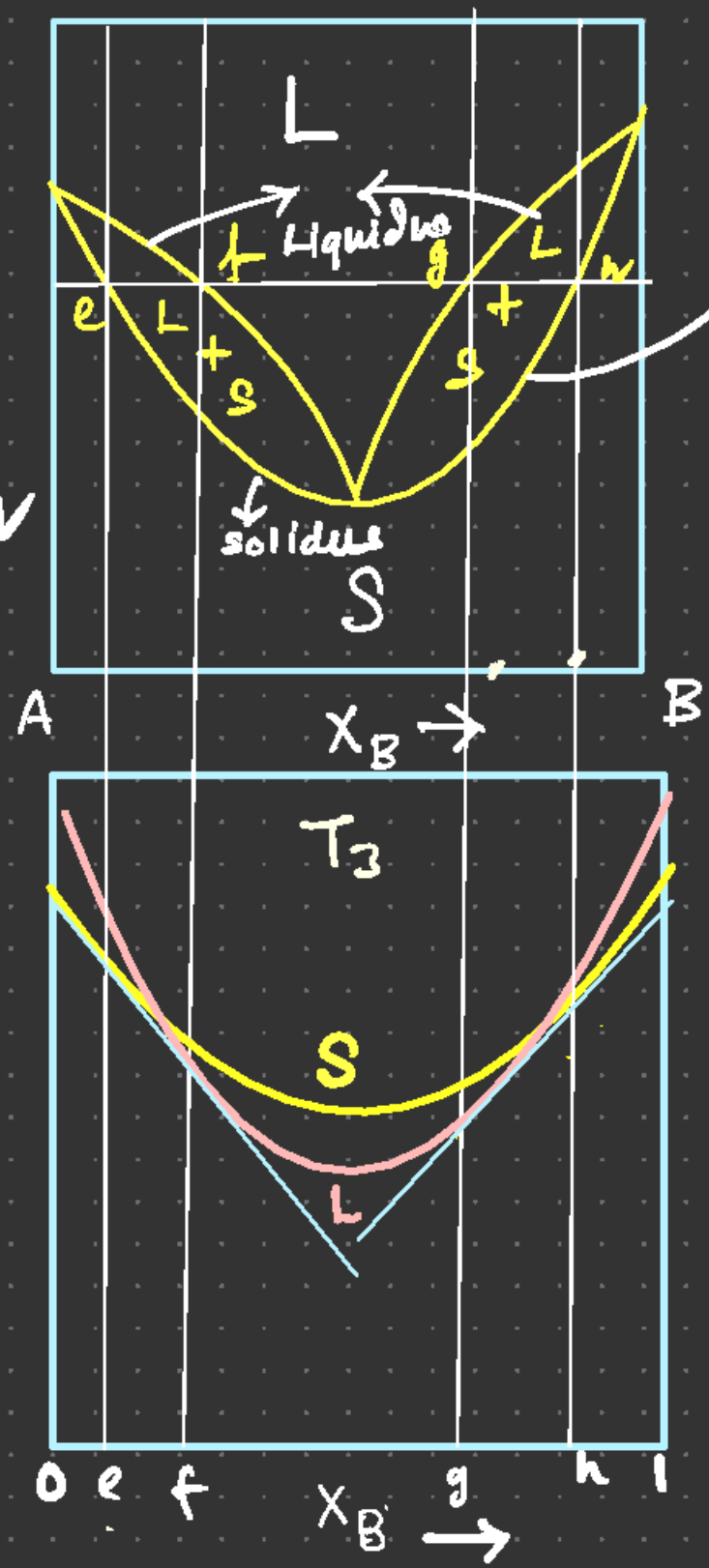
$\mu_B^{\alpha} = \mu_B^{\beta}$

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

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

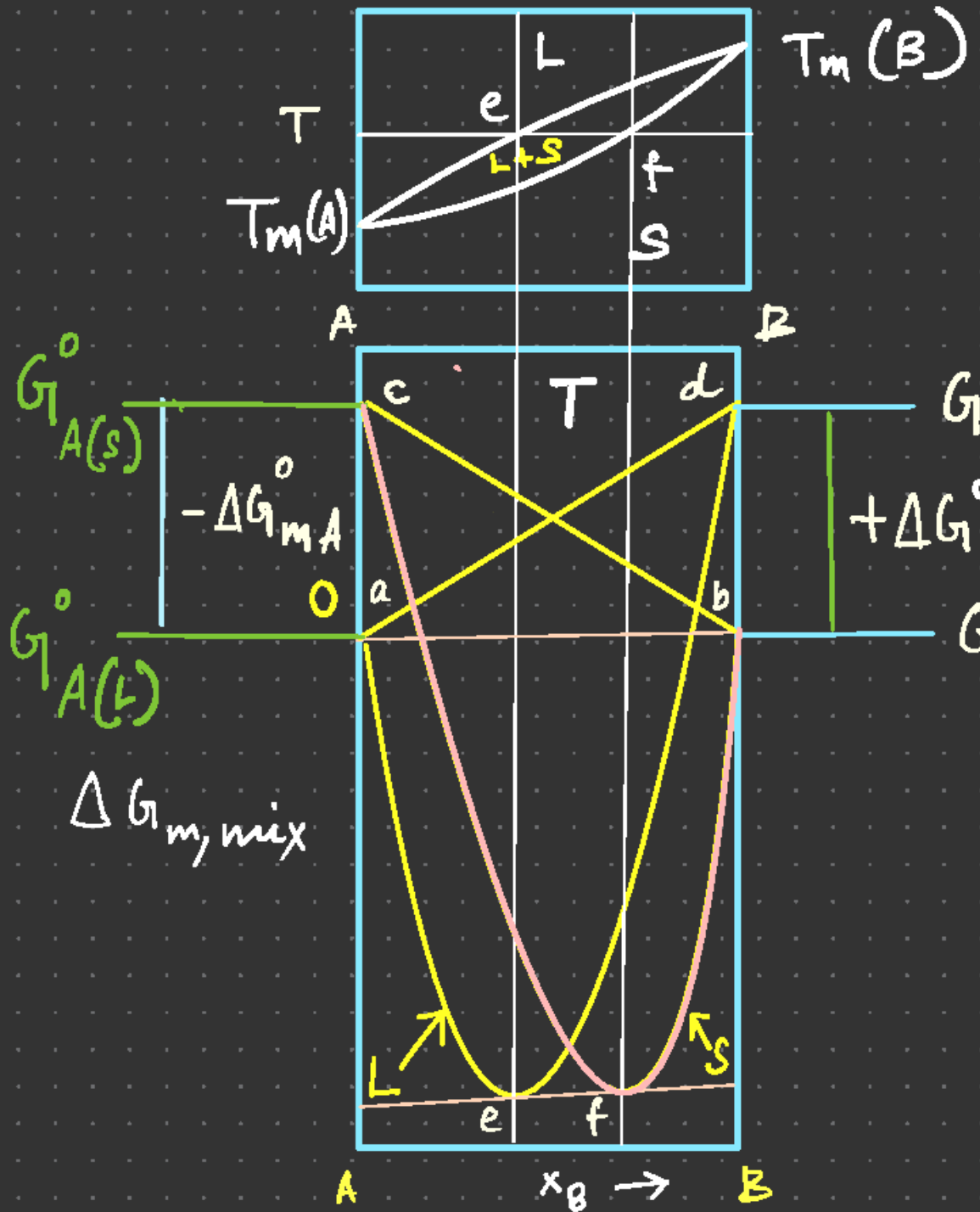
. . .

L and S are regular solutions with unequal enthalpies of mixing



$$\Delta H^{L}_{m,mix} \neq \Delta H^{S}_{m,mix} \neq 0$$

Liquid and Solid standard states



$$\Delta G^{S\to L}_{m,A} = G^\circ_{A(L)} - G^\circ_{A(S)}$$

$$\Delta G^{S\to L}_{m,B} = G^\circ_{B(L)} - G^\circ_{B(S)}$$

$$G^{\circ}_{A(s)} - G^{\circ}_{A(L)} = -\Delta G^{s\to L}_{mA} = -\Delta G^{\circ}_{mA}$$

$L \to S$ transformation

$$= -\left(\Delta H^{\circ}_{mA} - T\Delta S^{\circ}_{mA}\right)$$

$$\Delta G^{\circ}_{mA} = 0 \quad \text{at} \quad T = T_{mA}$$

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

$$\Delta S^{\circ}_{mA} = \frac{\Delta H^{\circ}_{mA}}{T_{mA}}$$

$$\Delta G^{\circ}_{mA} = \Delta H^{\circ}_{mA} - T\Delta S^{\circ}_{mA}$$

$$= \Delta H^{\circ}_{mA} - T\frac{\Delta H^{\circ}_{mA}}{T_{mA}}$$

$$= \Delta H^{\circ}_{mA}\left(1 - \frac{T}{T_{mA}}\right)$$

$$\Delta G^{\circ}_{mA} = \Delta H^{\circ}_{mA}\left(\frac{T_{mA} - T}{T_{mA}}\right)$$

$$= \Delta H^{\circ}_{mA}\left(\frac{T_{mA} - T}{T_{ma}}\right)$$

$T < T_{mB}$

$$G^{\circ}_{B(l)} - G^{\circ}_{B(s)} = \Delta G^{\circ}_{mB}$$

a, d — Gibbs free energies of unmixed liquid A and liquid B

c, b — Gibbs free energies of unmixed solid A and solid b

Standard state — unmixed liquid A and unmixed solid B

Line cb

$$\Delta G_m = -X_A \Delta G^{\circ}_{m_A}$$

Line ad

$$\Delta G_m = X_B \Delta G^{\circ}_{m_B}$$

Formation of a homogeneous liquid solution from pure liquid A and pure solid B at any composition is a two-step process

I Melting of x_B moles of B

$$\Delta G^{I} = x_B \Delta G^{o}_{mB}$$

II Mixing of x_B moles of liquid B with x_A moles of liquid A to form an ideal liquid solution

$$\Delta G^{II} = \Delta G^{id}_{m,mix}$$

$$= RT\left(x_A \ln x_A + x_B \ln x_B\right)$$

Molar Gibbs free energy of formation of an ideal liquid solution $\quad X_B = 1 - X_A$

$$\Delta G^{L}_{m,mix} = X_B \Delta G^{\circ}_{mB} + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

— Curve marked as L

Similarly, the formation of an ideal solid solution from liquid A and solid B is

$$\Delta G^{S}_{m,mix} = -X_A \Delta G^{\circ}_{mA} + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

- Curve marked as S

Equilibrium between L and S at a temperature T

$$\Delta \bar{G}_A^S = \Delta \bar{G}_A^L \quad \text{or,} \quad \mu_A^S = \mu_A^L$$

$$\Delta \bar{G}_B^S = \Delta \bar{G}_B^L \quad \text{or,} \quad \mu_B^S = \mu_B^L$$

$$\frac{d \Delta G_{m,mix}^L}{d X_{AL}} = RT \left(\ln X_{AL} - \ln X_{BL} \right) - \Delta G_{mB}^o$$

$$X_{BL} \frac{d \Delta G_{m,mix}^L}{d X_{AL}} = RT \left(X_{BL} \ln X_{AL} - X_{BL} \ln X_{BL} \right) - X_{BL} \Delta G_{mB}^o$$

$$\mu_A^L = \bar{\Delta G}_A^L = \Delta G_{m,mix}^L + X_{BL} \frac{d\Delta G_{m,mix}^L}{dX_{AL}}$$

$$= X_{BL} \Delta G_{mB}^{\circ} + RT\left(X_{AL} \ln X_{AL} + X_{BL} \ln X_{BL}\right)$$

$$+ RT\left(X_{BL} \ln X_{AL} - X_{BL} \ln X_{BL}\right) - X_{BL} \Delta G_{mB}^{\circ}$$

$$= RT \ln X_{AL}$$

Now,

$$\frac{d\Delta G_{m,mix}^S}{dX_{AS}} = RT\left(\ln X_{AS} - \ln X_{BS}\right) - \Delta G_{mA}^{\circ}$$

$$X_{BS} \frac{\Delta G_{m,mix}^S}{X_{AS}} = RT\left(X_{BS} \ln X_{AS} - X_{BS} \ln X_{BS}\right) - \Delta G_{mA}^{\circ}$$

$$\therefore \quad \Delta\bar{G}_A^S = \mu_A^S = RT \ln X_{AS} - \Delta G^\circ_{mA}$$

$$\therefore \quad RT \ln X_{AL} = RT \ln X_{AS} - \Delta G^\circ_{mA} \quad \text{— (1)}$$

Similarly

$$\mu_B^L = \Delta\bar{G}_B^L = RT \ln X_{BL} + \Delta G^\circ_{mB}$$

$$\mu_B^S = \Delta\bar{G}_B^S = RT \ln X_{BS}$$

$$\therefore \quad RT \ln X_{BL} + \Delta G^\circ_{mB} = RT \ln X_{BS} \quad \text{— (2)}$$

From (1)

$$X_{AL} = X_{AS} \exp\left(\frac{-\Delta G^{\circ}_{m_A}}{RT}\right) \quad \text{— (3)}$$

From (2)

$$1 - X_{AL} = (1 - X_{AS}) \exp\left(\frac{-\Delta G^{\circ}_{m_B}}{RT}\right)$$

— (4)

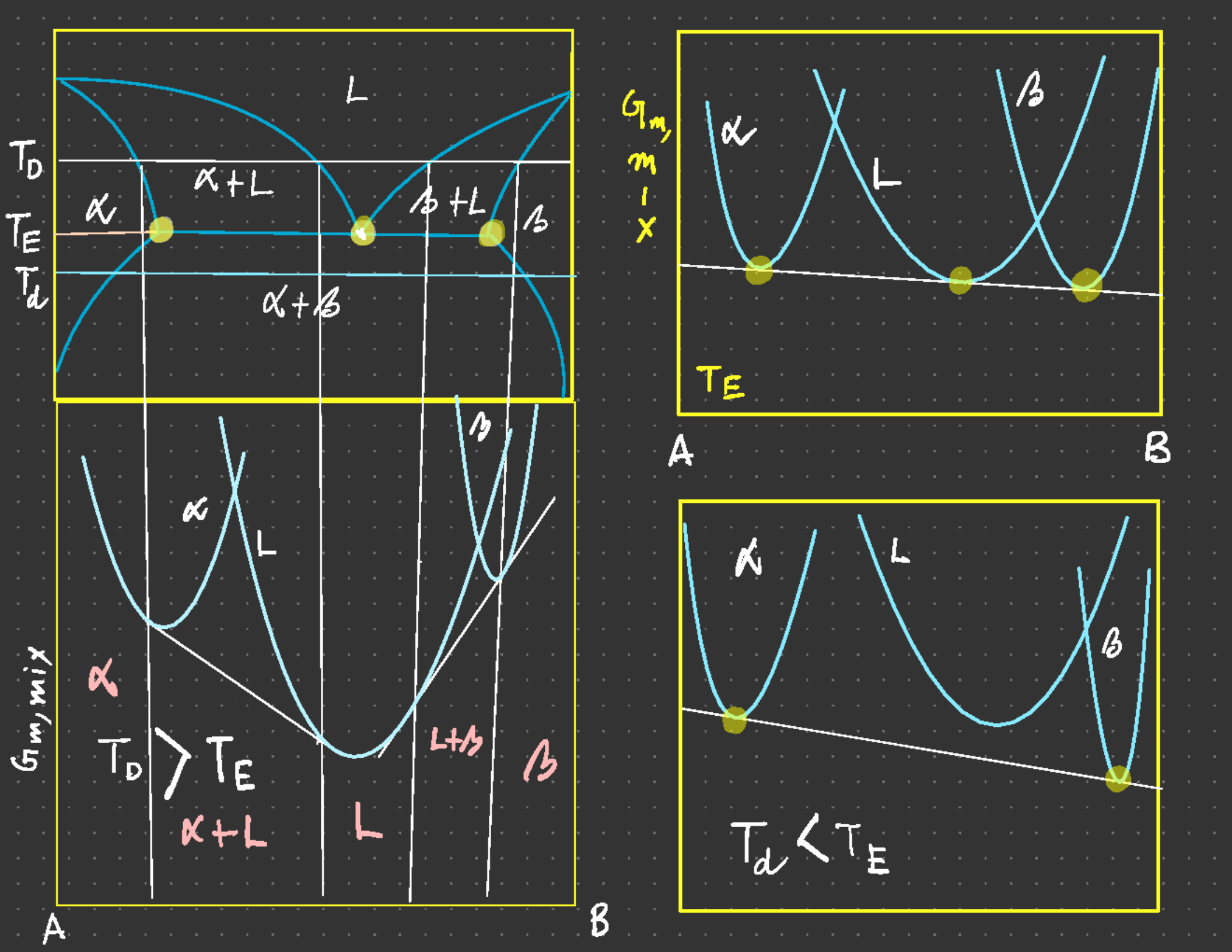
From (3) and (4)

$$X_{AS} = \frac{1 - \exp\left(-\frac{\Delta G_{mB}^{\circ}}{RT}\right)}{\exp\left(-\frac{\Delta G_{mA}^{\circ}}{RT}\right) - \exp\left(-\frac{\Delta G_{mB}^{\circ}}{RT}\right)}$$

solidus

$$X_{AL} = \frac{\left[1 - \exp\left(-\frac{\Delta G_{mB}^{\circ}}{RT}\right)\right] \exp\left(-\frac{\Delta G_{mA}^{\circ}}{RT}\right)}{\exp\left(-\frac{\Delta G_{mA}^{\circ}}{RT}\right) - \exp\left(-\frac{\Delta G_{mB}^{\circ}}{RT}\right)}$$

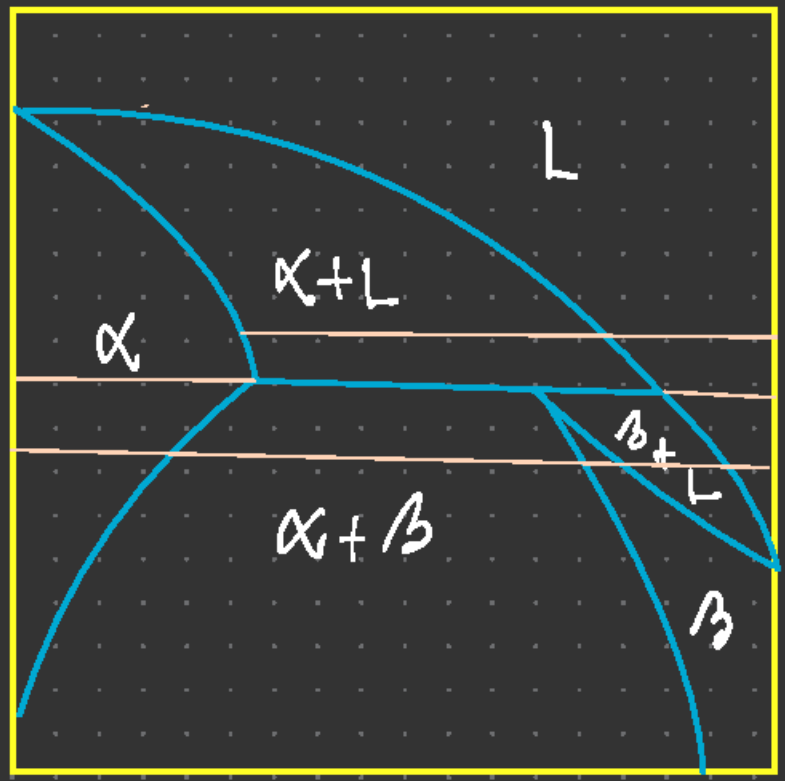
liquidus


L
T_D
α+L
α
β+L
β
T_E
T_d
α+β
$G_{m,mix}$
α
L
β
T_E
A
B
α
L
β
$G_{m,mix}$
α
$T_D > T_E$
α+L
L
L+β
β
A
B
α
L
β
$T_d < T_E$

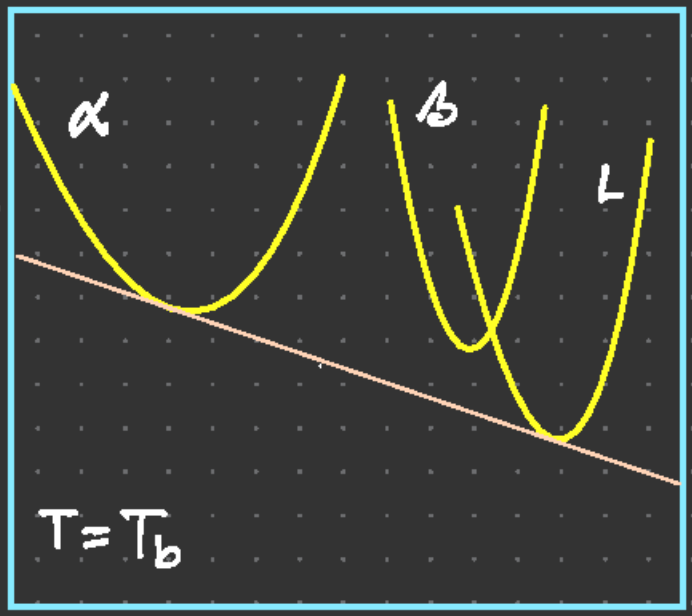
At T_E,

$$\mu_A^L = \mu_A^\alpha = \mu_A^\beta$$

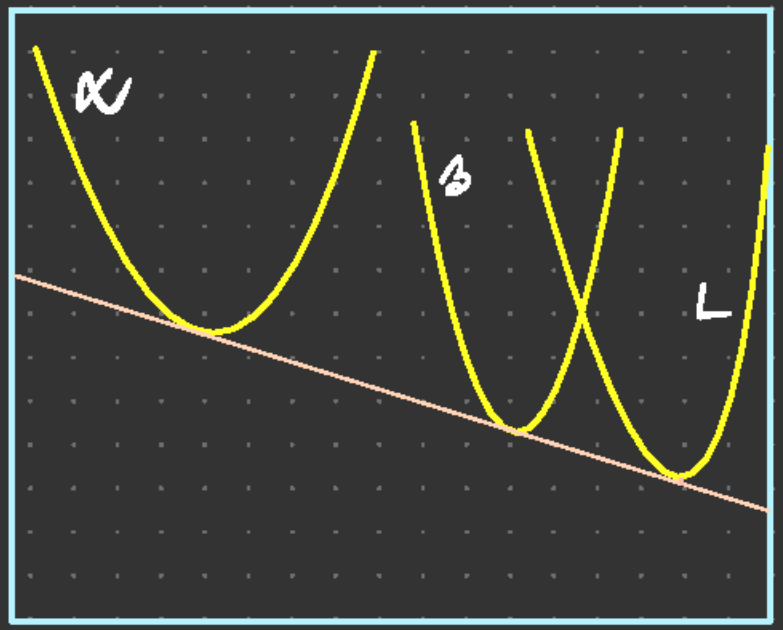
$$\mu_B^L = \mu_B^\alpha = \mu_B^\beta$$



$\Delta G_{m,mix}$



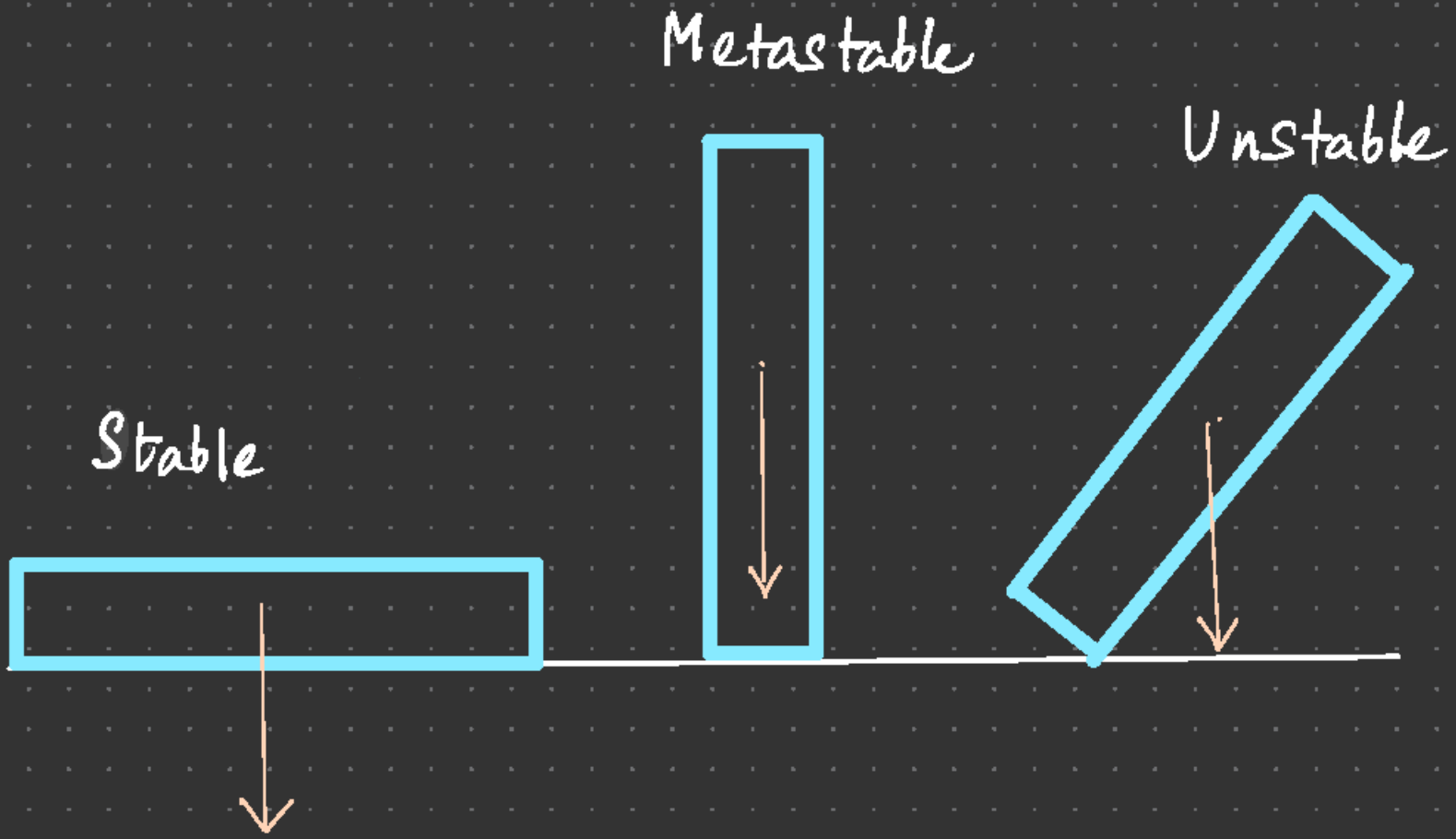
$\Delta G_{m,mix}$

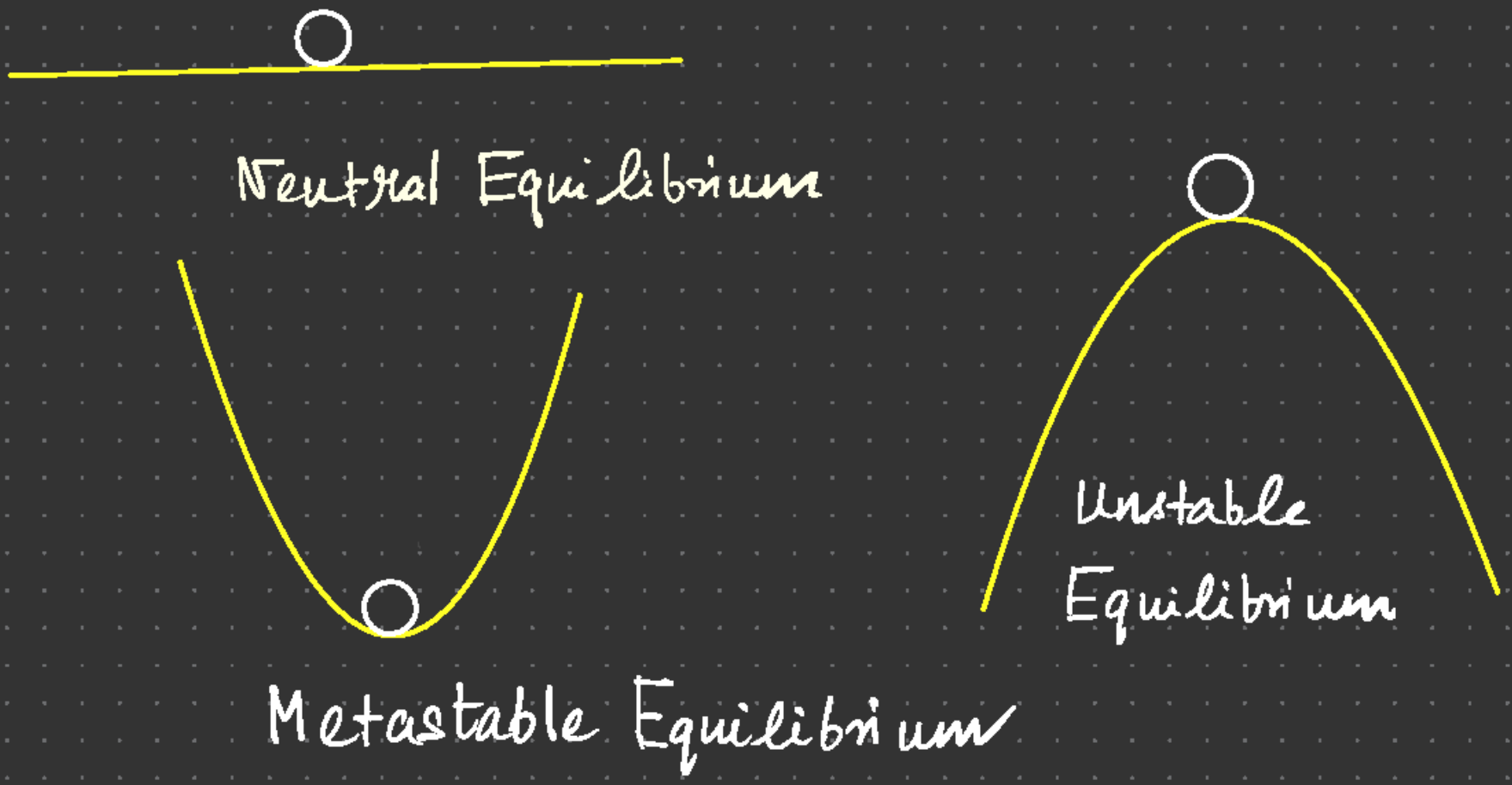


L+α → β

Criteria for phase stability

Mechanical Analogue




Neutral Equilibrium
Unstable Equilibrium
Metastable Equilibrium

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

$x_A + x_B = 1$

$(1-x) \quad x$

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

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

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

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

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

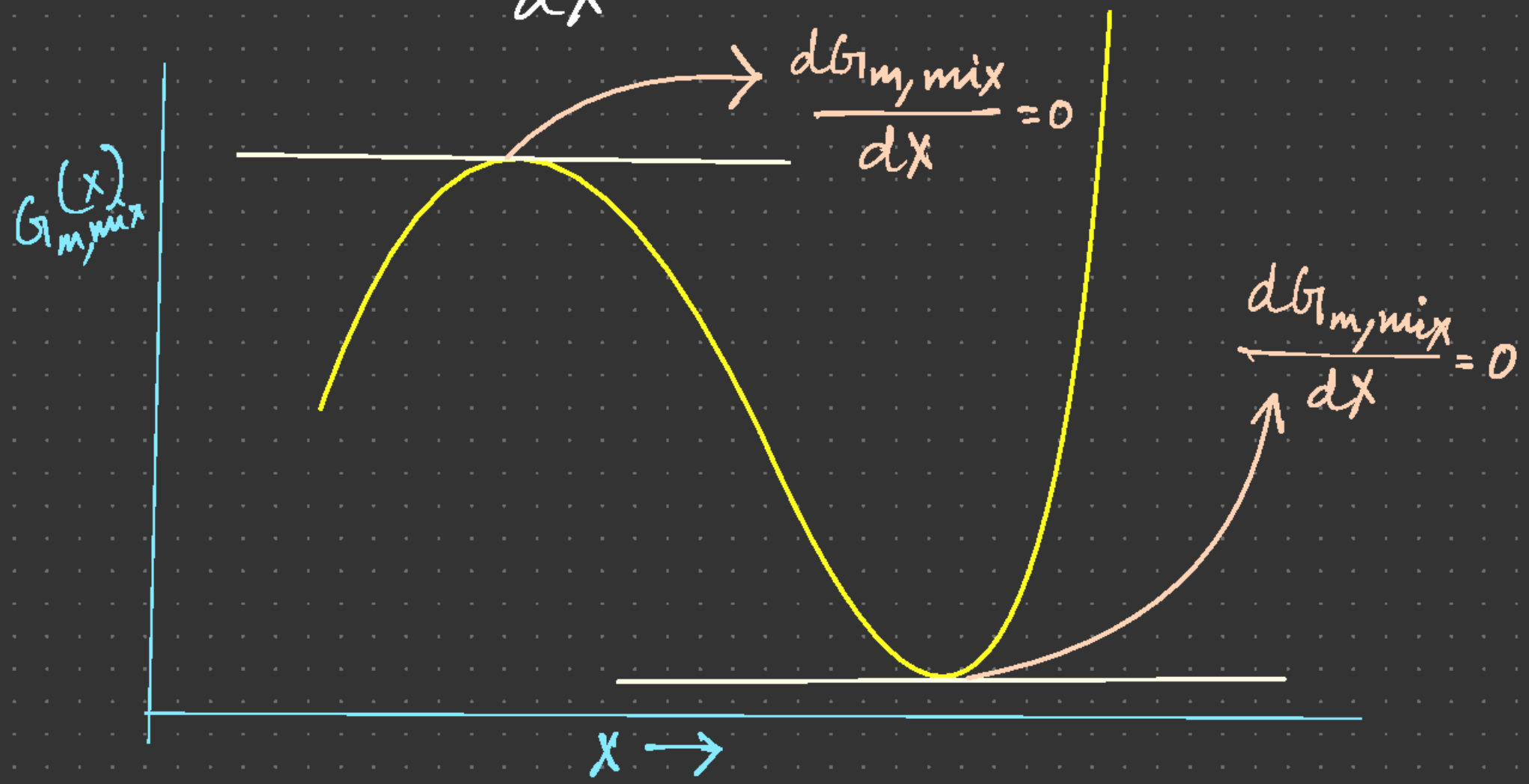
$$\frac{d^2G_{m,mix}}{dX^2} = RT\left\{\frac{1}{X} + \frac{1}{1-X}\right\} - 2\omega$$

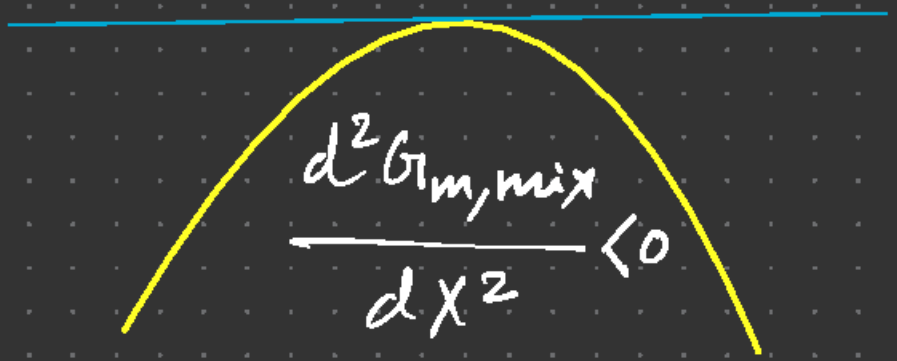
$$\frac{d^3G_{m,mix}}{dX^3} = RT\left\{\frac{1}{(1-X)^2} - \frac{1}{X^2}\right\}$$

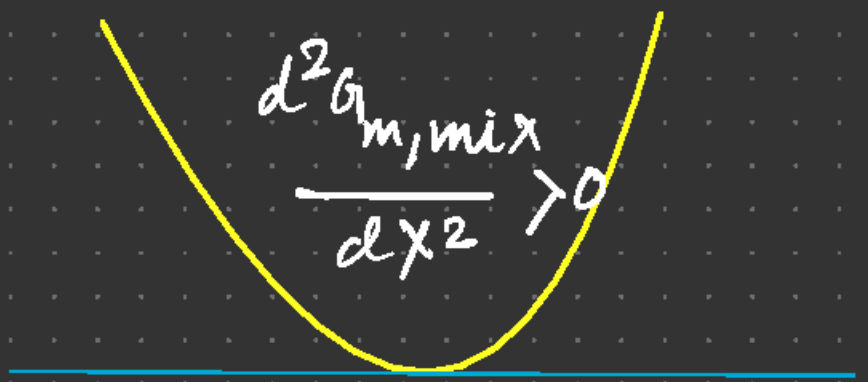
When $X = 0.5$

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

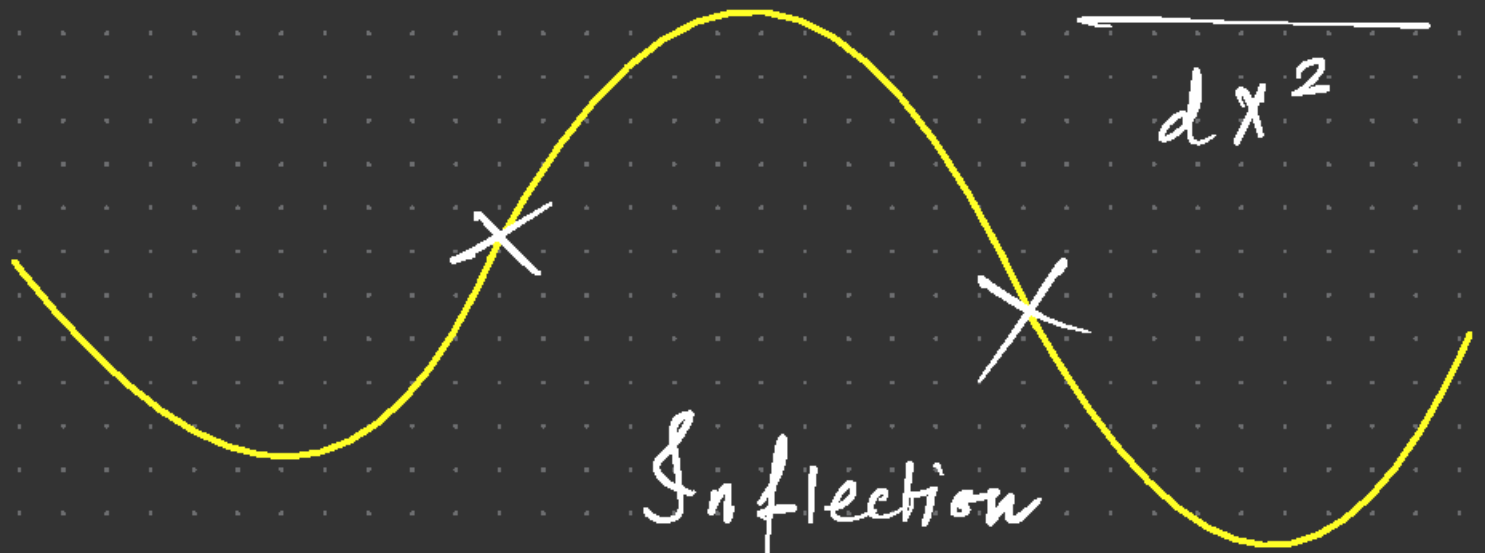
$$\frac{d^3 G_{m,mix}}{dX^3} = 0$$







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



Inflection point

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

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

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

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

When $X = 0.5$

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

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

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

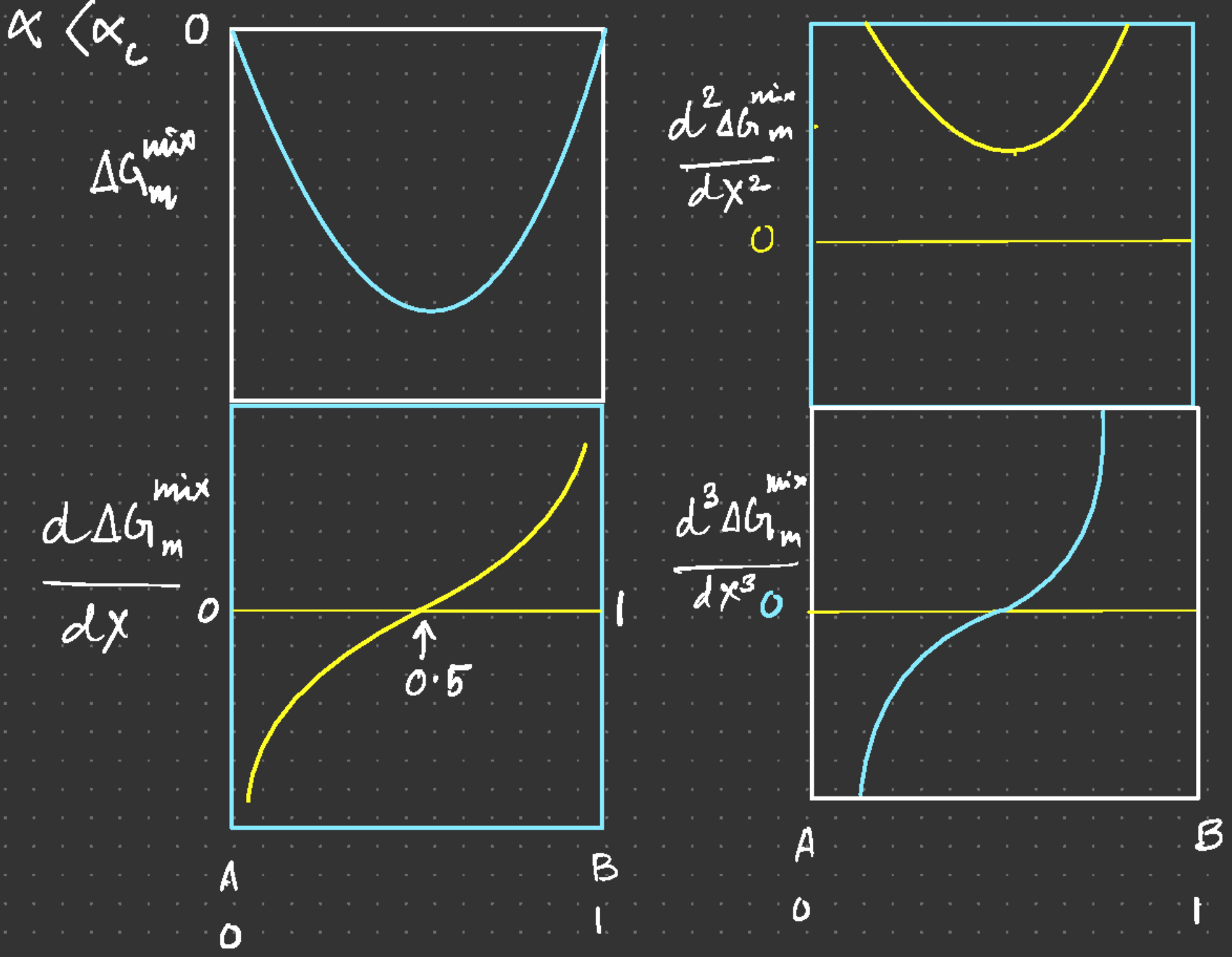
$$T_c = \frac{\omega}{2R}$$

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

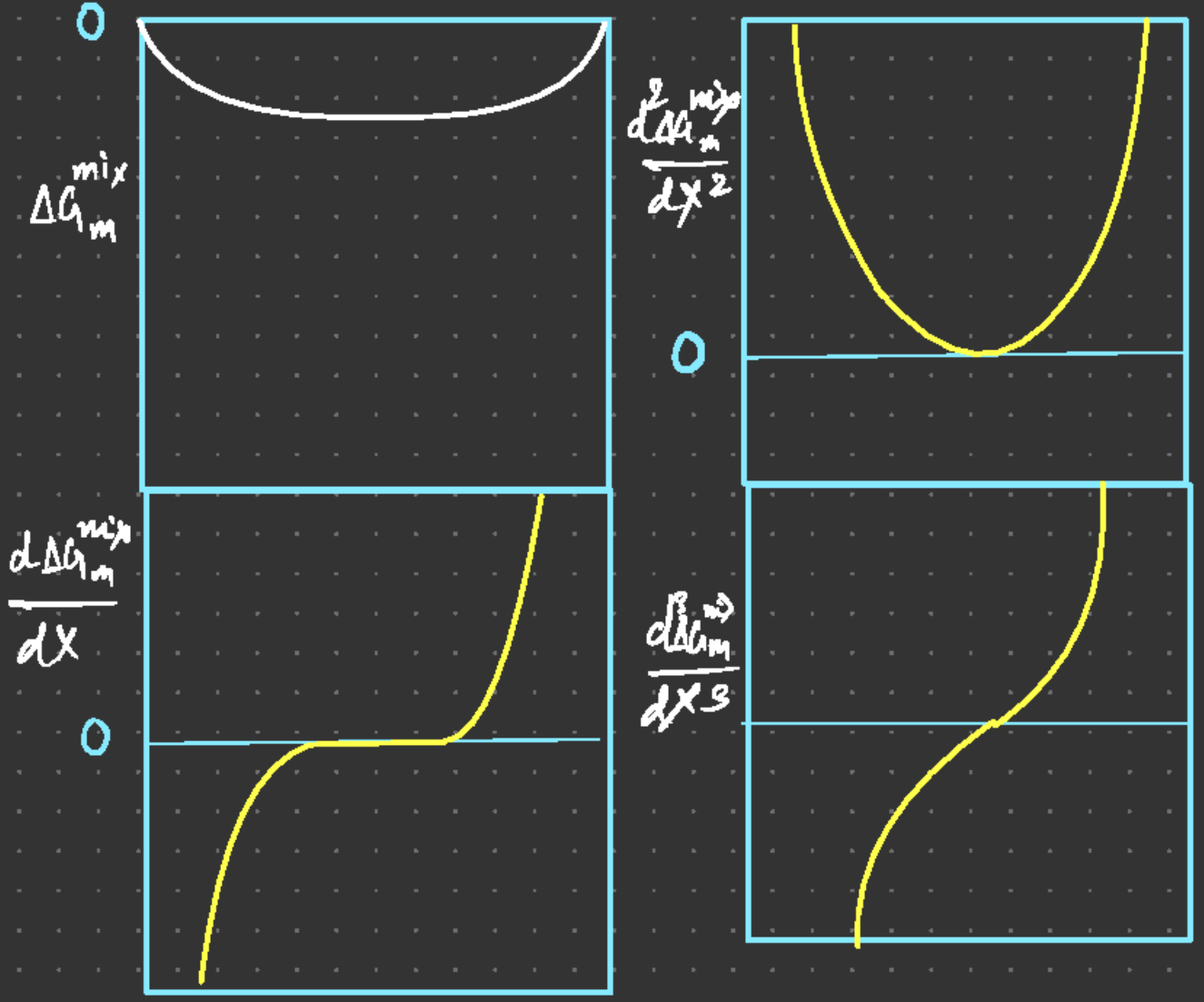
$\alpha > \alpha_c$ phase separation

$\alpha = \alpha_c$ Critical

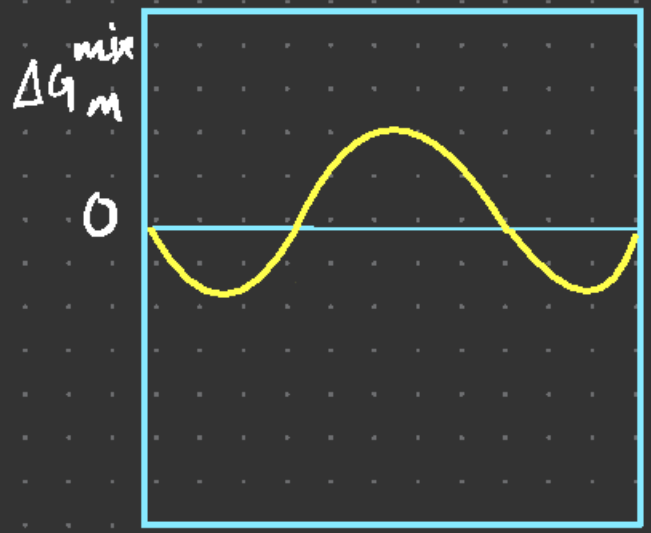
$\alpha < \alpha_c$ Homogeneous single phase

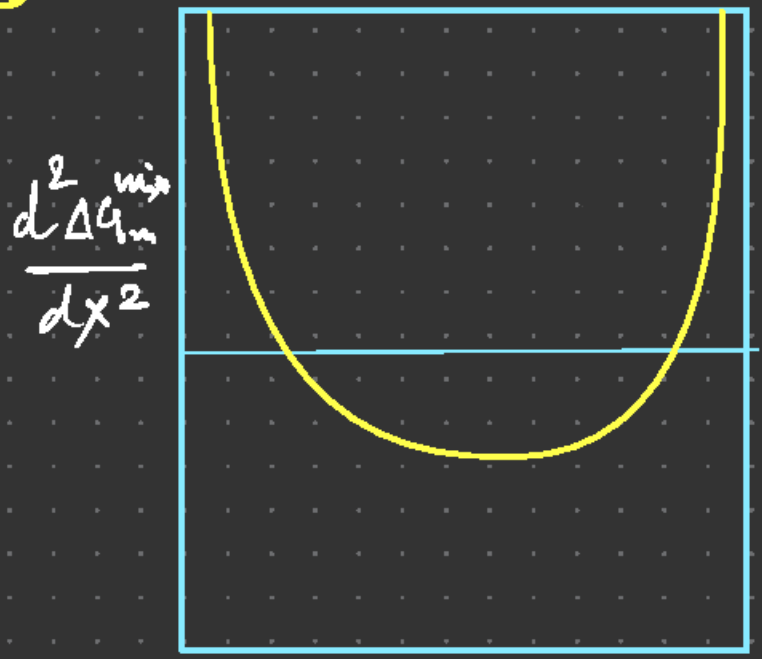

$\alpha < \alpha_c$
0
ΔG_m^{mix}
$\frac{d\Delta G_m^{mix}}{dx}$
0
0·5
1
A
B
0
1
$\frac{d^2\Delta G_m^{mix}}{dx^2}$
0
$\frac{d^3\Delta G_m^{mix}}{dx^3}$
0
A
B
0
1

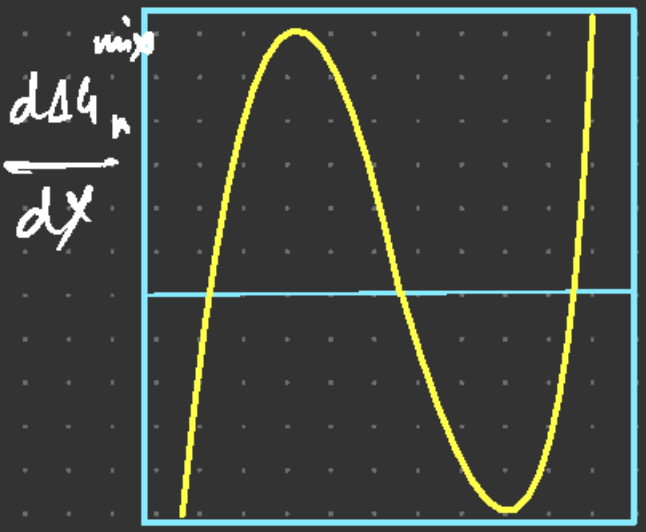
$\alpha = \alpha_c$

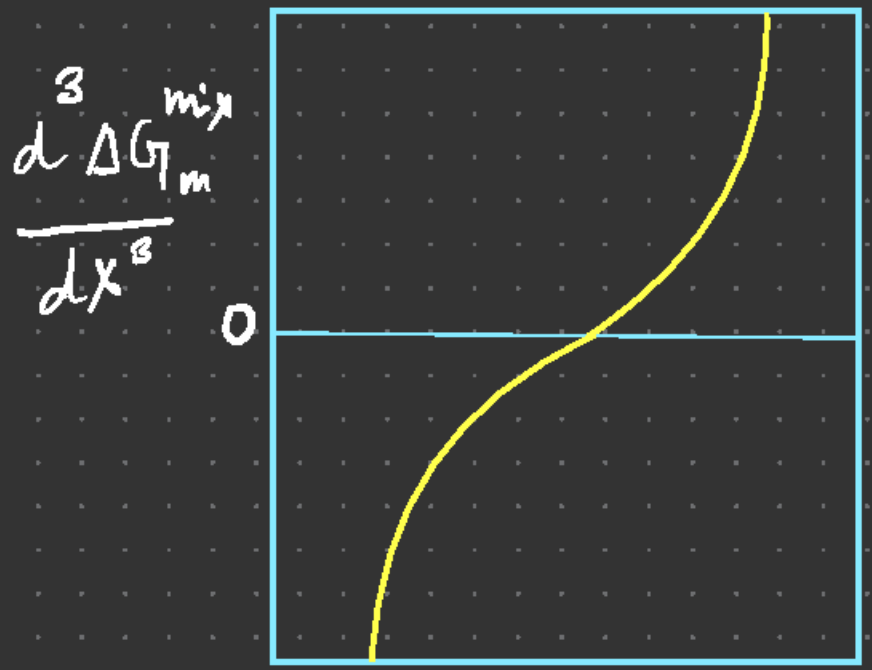


$\alpha > \alpha_c$









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

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

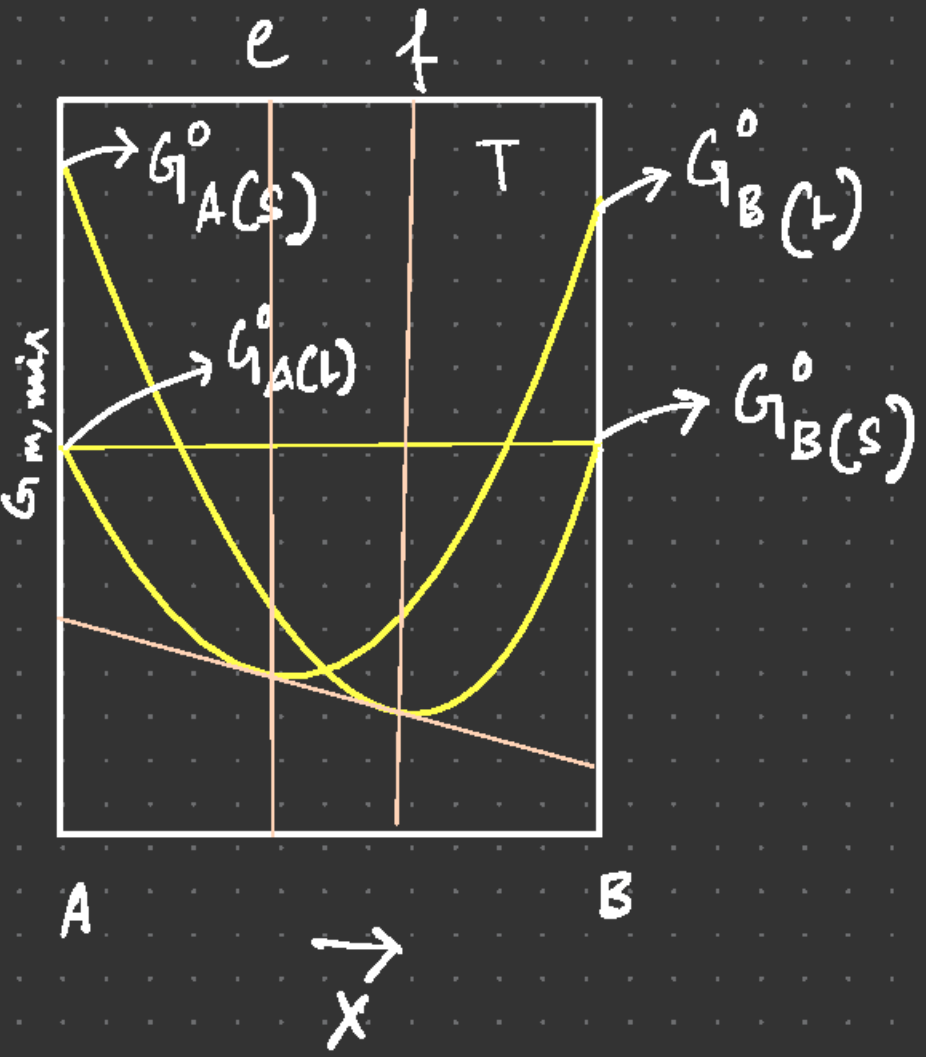
$$\frac{d\Delta\bar{G}_B^{mix}}{dx_B} = x_A\frac{d^2\Delta G_m^{mix}}{dx_B^2} = \frac{RT}{a_B}\frac{da_B}{dx_B}$$

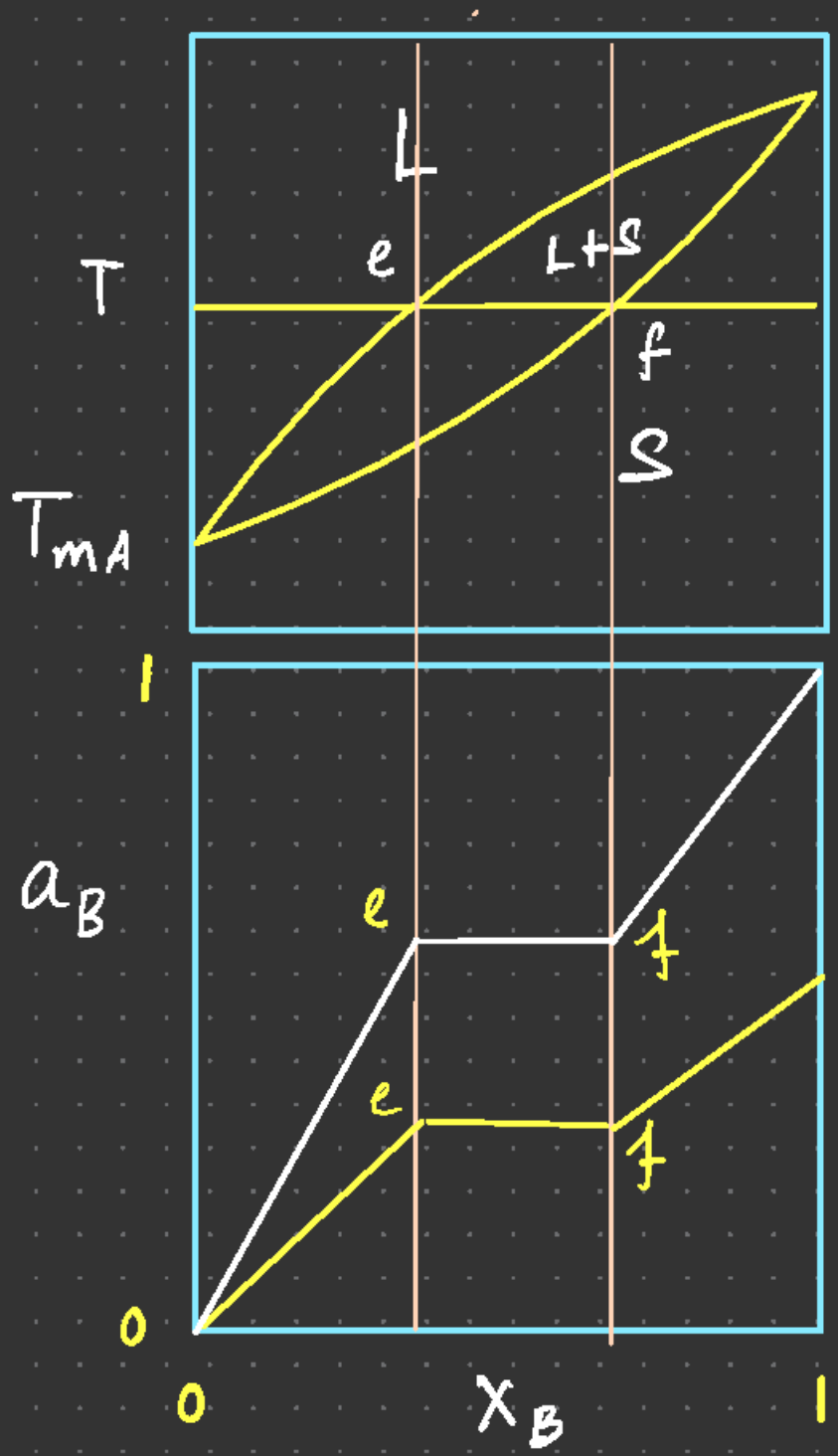
$$\mu_B^L = \mu^{\circ}_{B(l)} + RT \ln a_{B(l)}$$

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

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

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





(Solid as standard state)

(Liquid as standard state)

$T_{mA} = 800\ K$

$T_{mB} = 1200\ K$

$G^{\circ}_{mA} = 800 - 10T$

$G^{\circ}_{mB} = 12000 - 10T$

$\omega_L = -20000\ J$ (Liquid)

$\omega_s = 0$ (Solid)

$$G_{m}(\text{solid}) = X_A G^{\circ}_{m_A} + RT\left(X_A \ln X_A + X_B \ln X_B\right) + \omega_S X_A X_B$$

$$G_{m}(\text{liquid}) = X_A G^{\circ}_{m_B} + RT\left(X_A \ln X_A + X_B \ln X_B\right) + \omega_L X_A X_B$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Reacting systems.

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 relations among intensive variables of individual phases other than thermal, mechanical, chemical equilibri

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

$s = 3$

$p = 3$

$\mathcal{R} = 1$

$f = 3 - 3 - 1 + 2$

$= 1$

Reaction equilibria

$\nu_i > 0$ for products
$\nu_i < 0$ for reactants

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

$\nu_i = 0$ for inert species

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

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

- 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

$$dU = 0$$

$$dV = 0$$

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

$dn_K \neq 0$ Reacting system

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

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

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

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

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

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

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

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

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

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

$N_{a,i}^{0}$ = 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)

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

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

$C + O_2 = CO_2$ — (1)

$2C + O_2 = 2CO$ — (2)

$C + CO_2 = 2CO$ — (3)

$S = C, O_2, CO_2, CO$

$e = C, O$

$r = S - e = 4 - 2 = 2$

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

S p r

$CO_2 = C + O_2$ — (1·1)

(3) = (2) − (1)

(3) = (1·1) + (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

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

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

$$l\,L + m\,M = r\,R + s\,S$$

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

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

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

$$A = \left[\left(r\,G_R^{\circ} + s\,G_S^{\circ}\right) - \left(l\,G_L^{\circ} + m\,G_M^{\circ}\right)\right]$$

$$RT \ln \left[\frac{a_R^{r}\; a_S^{s}}{a_L^{l}\; a_M^{m}}\right]$$

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

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

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

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

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,

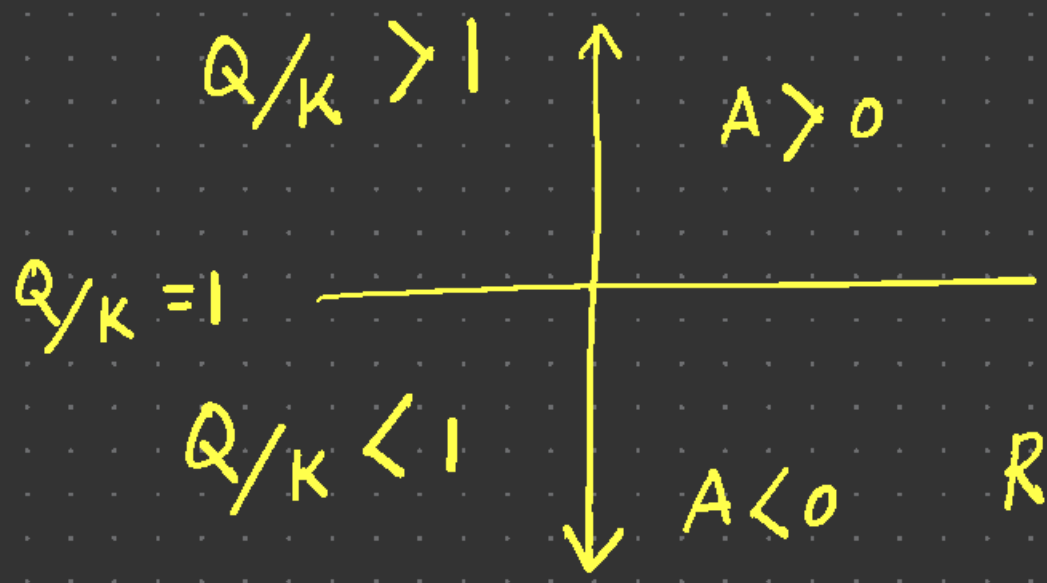
$$Q = \frac{a^2_{H_2O}}{a^2_{H_2}\, a_{O_2}} = \frac{X^2_{H_2O}}{X^2_{H_2}\, X_{O_2}} = \frac{(0.96)^2}{(0.01)^2\, 0.03}$$

$$= 3.1 \times 10^5$$

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

$$\ll 1$$

Strong tendency for products to form



Decomposition
Products → Reactants

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

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

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

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

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

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

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

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

$$p_i V = n_i RT$$

$$p_i = c_i RT$$

Heterogeneous Reaction

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

Gas

$$\mu_i = \mu_i^{\circ} + RT \ln f_i$$
$$= G_i^{\circ} + RT \ln f_i$$

Solid/liquid

$$\mu_i \approx \mu_i^{\circ} = G_i^{\circ}$$

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

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

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

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

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

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

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

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

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

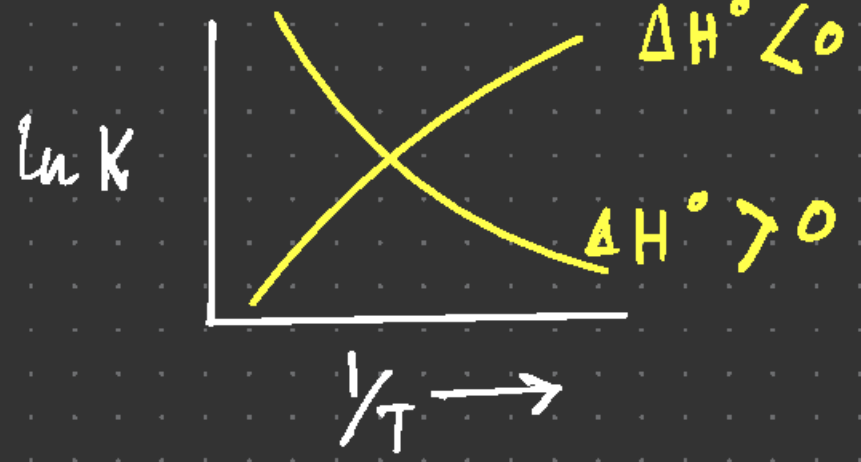
$$\nu_j \, dH_j^\circ = \nu_j \, C_{Pj}^\circ \, dT$$

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

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

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

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



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

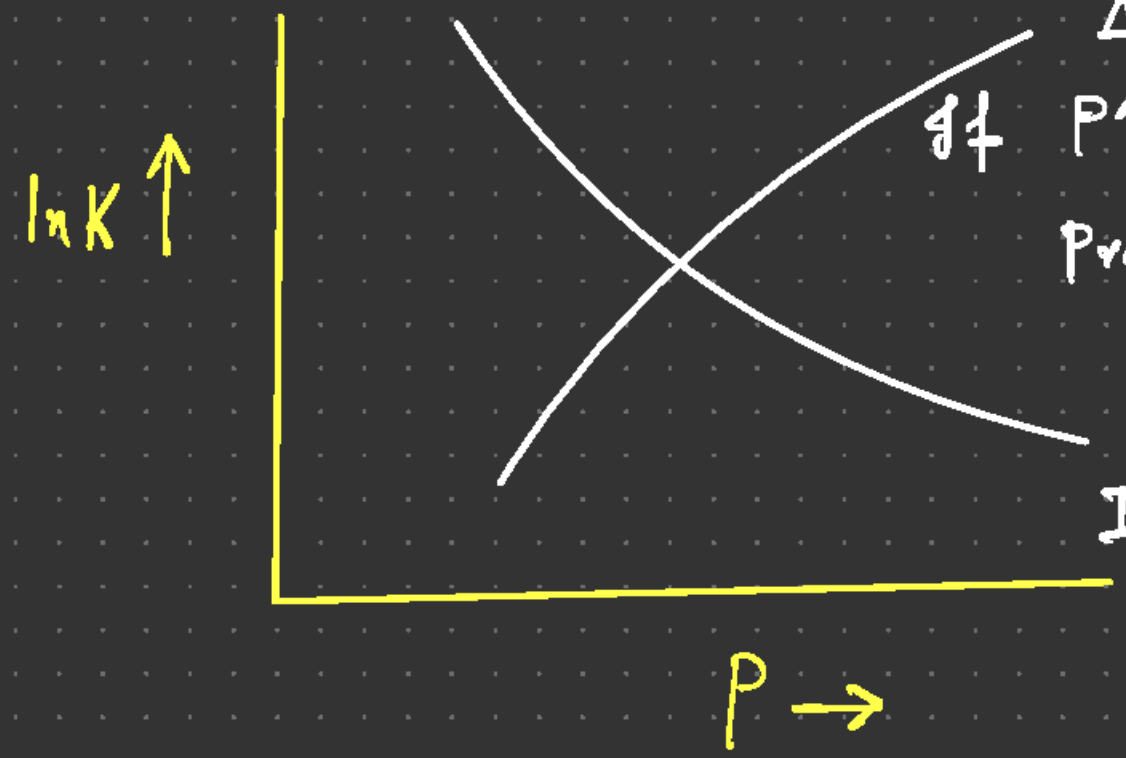
then $\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = 0$

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

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

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

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



$\Delta V^\circ < 0$

If P↑, K↑

Products are favored

$\Delta V^\circ > 0$

If P↑, K↓

Reactants are favored

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

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

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

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

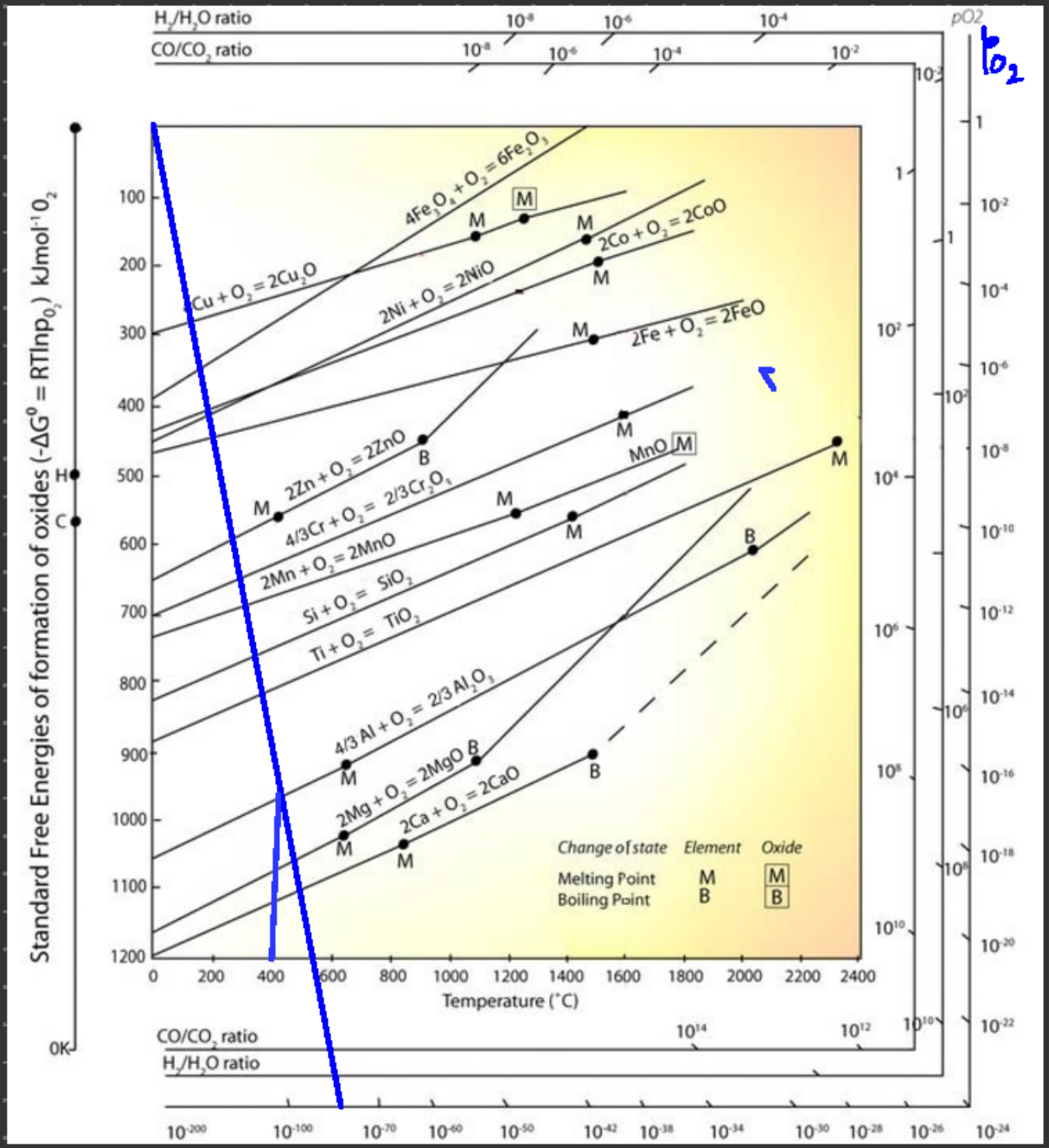
$$\left. \Delta G^\circ \right|_{0K} = \Delta H^\circ$$

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

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)



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

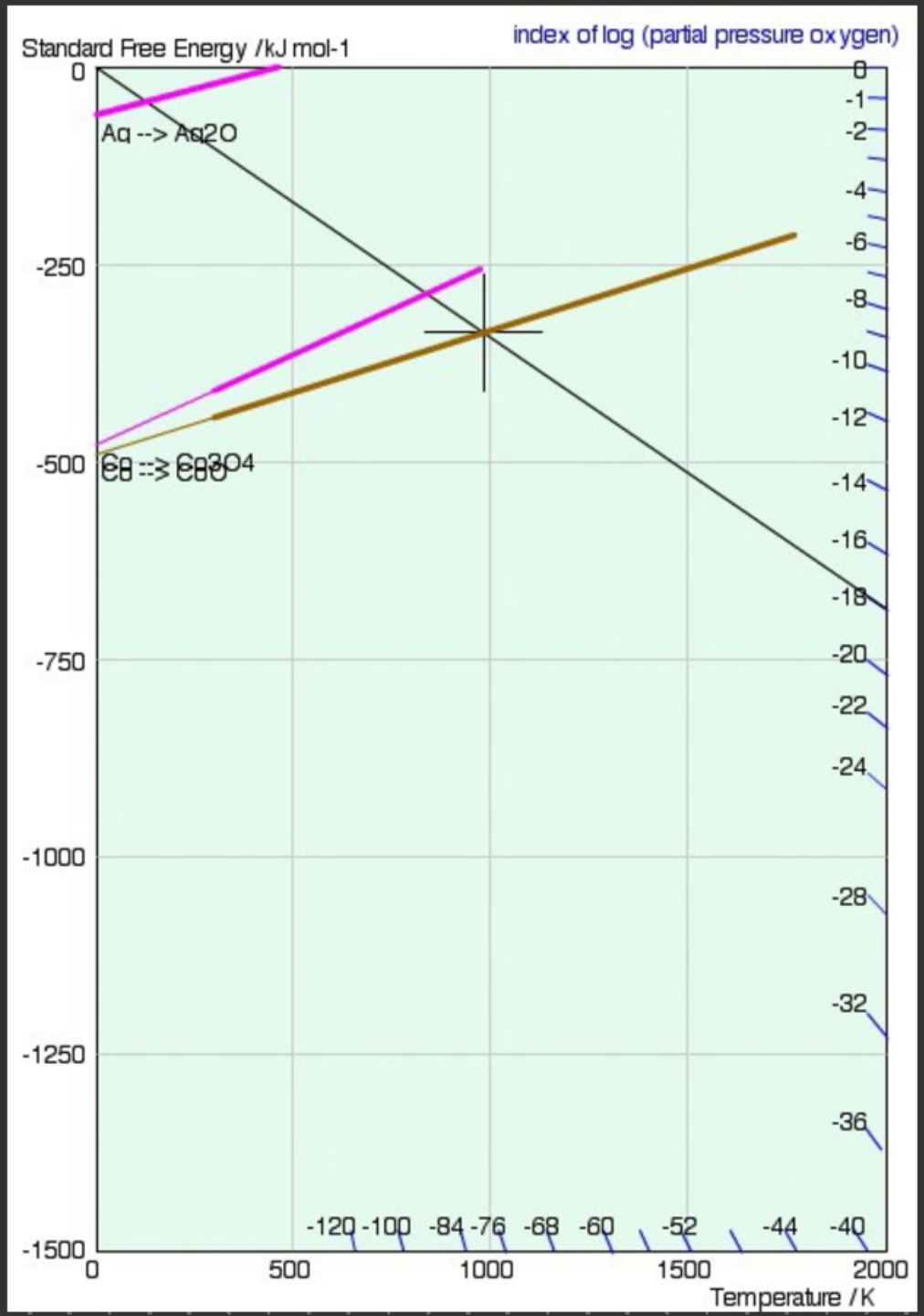
$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ$$

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

$\Delta G = RT \ln P$

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

Equilibrium partial pressure

— pressure at which driving force for oxidation drops to zero

equilibrium

If $p_{O_2} > p_{O_2}$

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

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

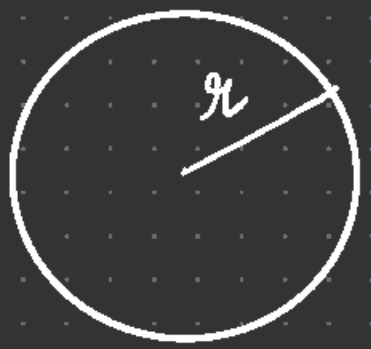
$$2M + O_2 \rightarrow 2MO$$

$\Delta G < 0$ 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

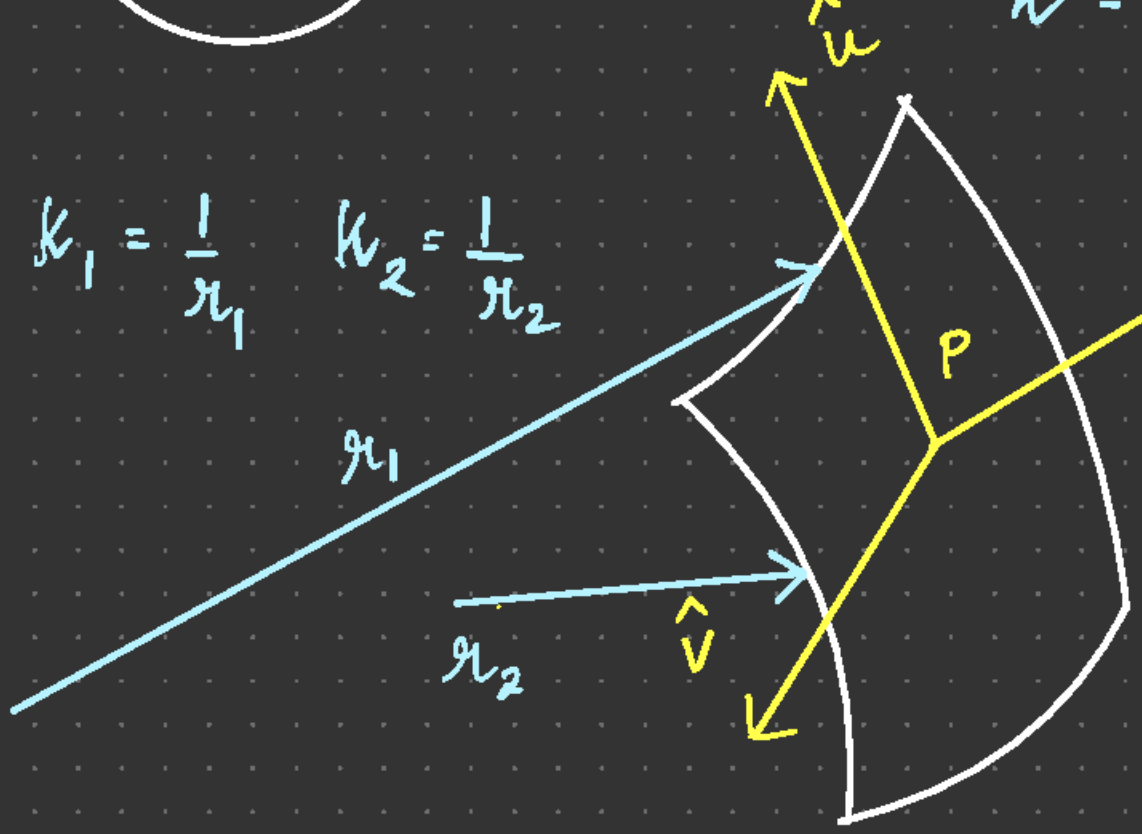


R - Radius of curvature

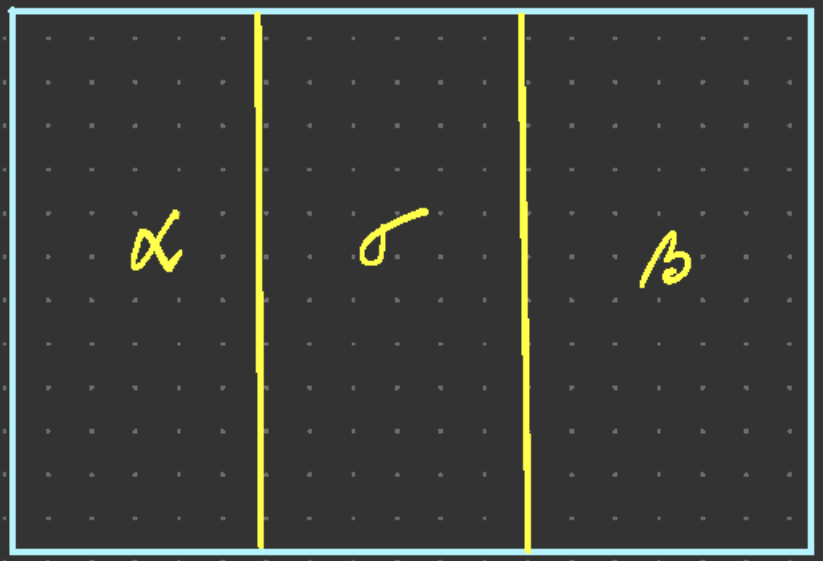
$k = \frac{1}{R}$ curvature

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

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



$\delta A = 2h\delta V$

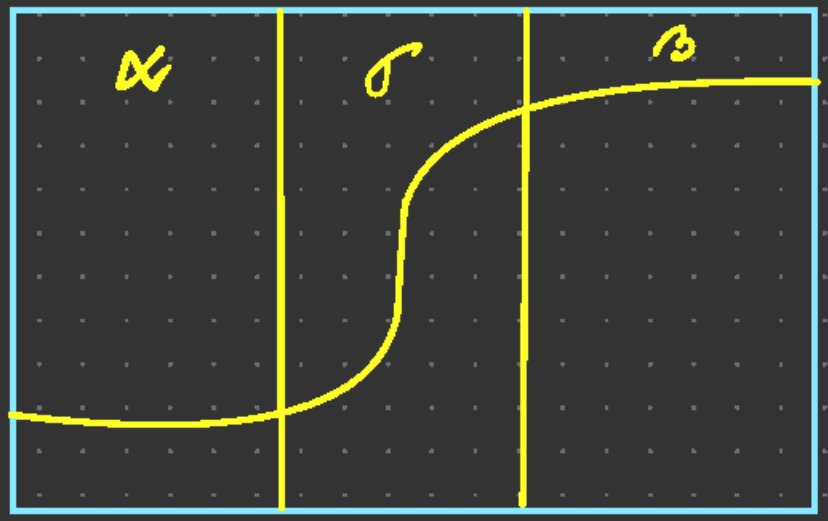


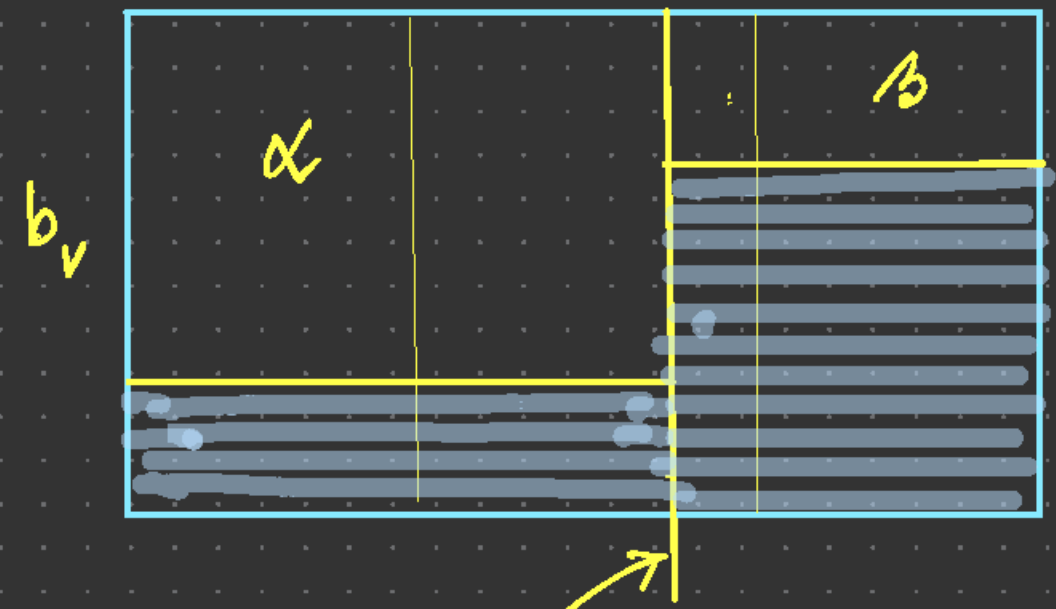
Physical Surface of discontinuity

$B \rightarrow$ extensive property

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

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





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

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

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

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

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

$$+ S^{s} dA$$

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)

$dT = 0$

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

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

$$-\frac{RT}{p}\,dp + 2\gamma V^l\,dh = 0$$

λ_v – capillarity length

$$d\ln p = \frac{2\gamma V^l}{RT}\,dh$$

$$\int_{p(h=0)}^{p(h)} d\ln p = \int_{h=0}^{h} \frac{2\gamma V^l}{RT}\,dH$$

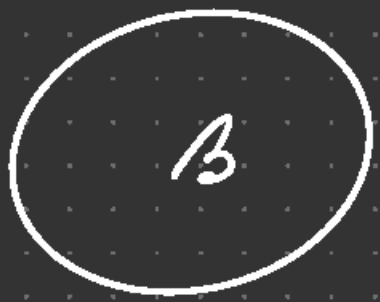
$$p(h) = p(h=0)\exp\left(\frac{2\gamma V^l h}{RT}\right)$$

$$p_H = p_0 e^{\lambda_v h} \qquad \lambda_v = \frac{2\gamma V^l}{RT}$$

Vapour pressure in liquid droplets is higher

Melting

β – solid
α – liquid



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

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

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

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

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

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

$T_0 = T_m(H=0)$

$T_0 \Delta S = \Delta H$

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

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

Chemical potential in unary system

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

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

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

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

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

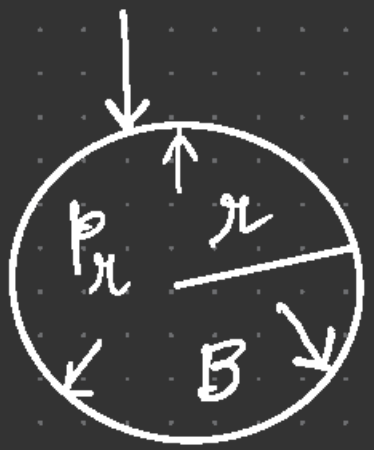
$$d\mu^{\alpha} = V^{\alpha} dP^{\alpha} = V^{\alpha} \frac{2\gamma V^{\beta}}{V^{\alpha} - V^{\beta}} dh$$

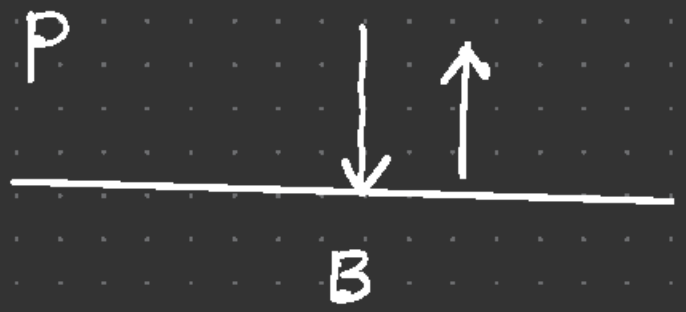
$$\mu_h^\alpha = \mu_{h=0}^\alpha + \frac{2\gamma v^\kappa v^\beta}{v^\alpha - v^\beta} h$$

Spherical particle of B immersed in A-rich α matrix

γ is the interfacial free energy between particle and matrix

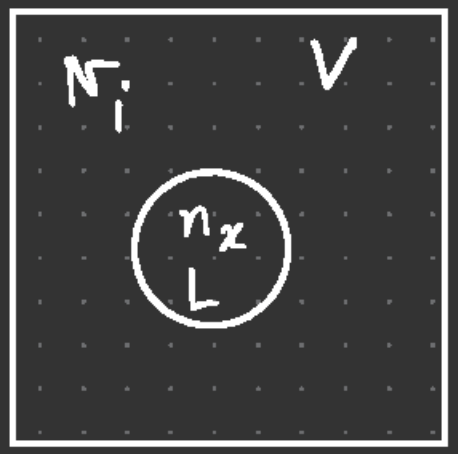
Find the vapour pressure of B as a function of its radius of curvature





$$G = U + pV - TS$$

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



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

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

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

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

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

$$v_v \gg v_l$$

$$dg = -v_v\, dP$$

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

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

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

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

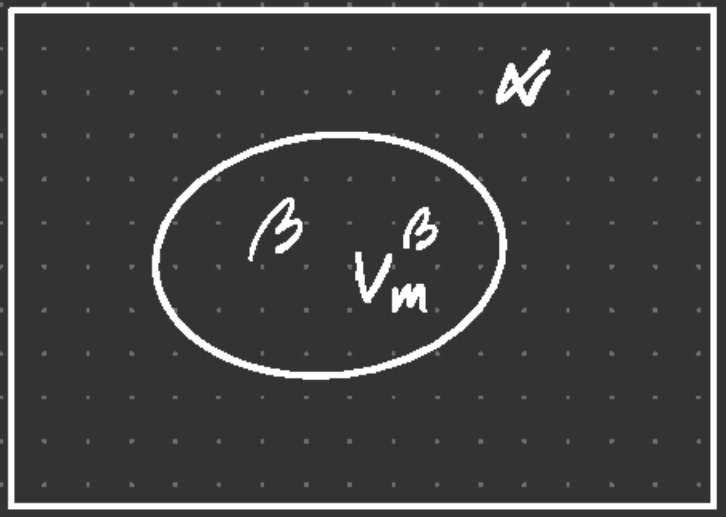
$$\frac{\partial \Delta G}{\partial r} = 0 \Rightarrow \ln\left(\frac{P}{P_\infty}\right) = \frac{2 v_L \gamma}{r k_B T}$$

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

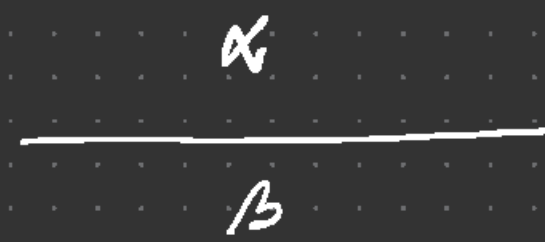
Ostwald - Freundlich equation

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

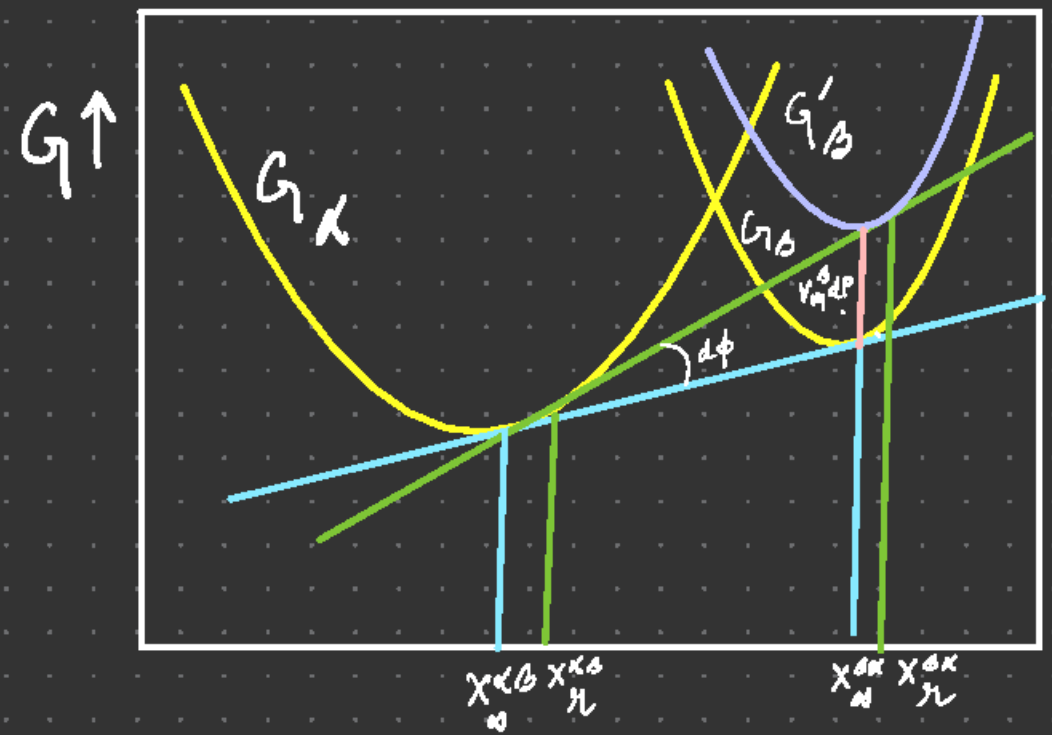
$$R_{critical} = \frac{2\gamma v_a}{k_B T}$$



ΔP



$$dG = V\,dP$$



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

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

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

$$dx^{\kappa\beta} = x^{\kappa\beta}_{n} - x^{\kappa\beta}_{\alpha}$$

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

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

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

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

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

Thermodynamics of irreversible process

Flux $\leftrightarrow$ driving force

Onsager's postulates

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

L_{ik} — kinetic coefficients

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

At steady state

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

j → steady state velocity

F = drag force

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

δW → 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 $\rightarrow$ $\frac{\partial c_i}{\partial t} + \nabla \cdot j_i = 0$

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

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

$$j_i = -D_i \nabla c_i$$

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

$$\nabla \mu_i = RT\, m \nabla c_i$$

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

$$M_i = L_{ii} RT$$

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

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