Quasichemical models for ordered solutions with sublattices

Binary phase diagrams I

Solutions Quasichemical approach

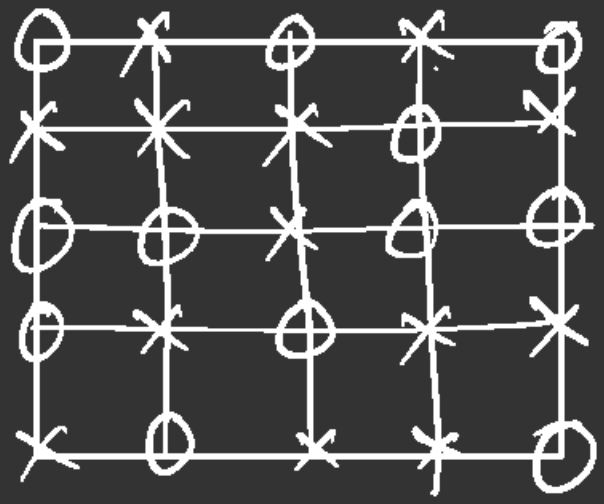
Regular Solution model

Ideal Solution Model

$$\Delta S^{id}_{m,mix} = -R\sum_{i=1}^{n_c} X_i \ln X_i$$

$\Delta V_{m,mix} = 0$ $\Delta H_{m,mix} = 0$ $E_{A-B} = \frac{1}{2}(E_{A-A} + E_{B-B})$

$$\Delta G_{m,mix} = RT\sum_{i=1}^{C} X_i \ln X_i$$



X – B

O – A

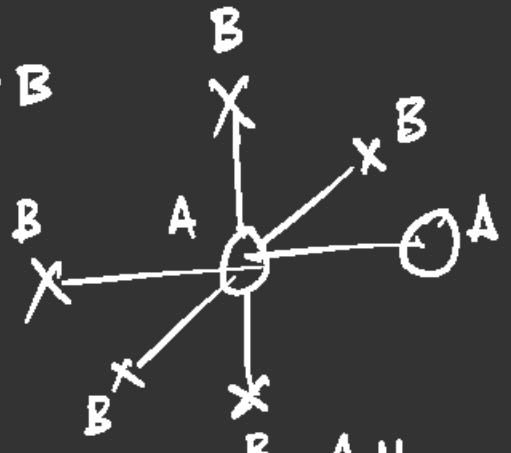
Regular Solution model - Random alloy approximation

- Interaction between atomic species

$$\Delta H_{m,mix} \neq 0 = \omega_{ij} X_i X_j$$

$$\omega_{ij} = \frac{N_0 Z}{2}\left\{2E_{ij} - (E_{ii} + E_{jj})\right\} \qquad i,j = A, B, C, D, \ldots$$

$\omega_{AB} X_A X_B$



$\omega_{ij} > 0$ Clustering

$\omega_{ij} < 0$ Ordering

more i-j bonds $i \neq j$

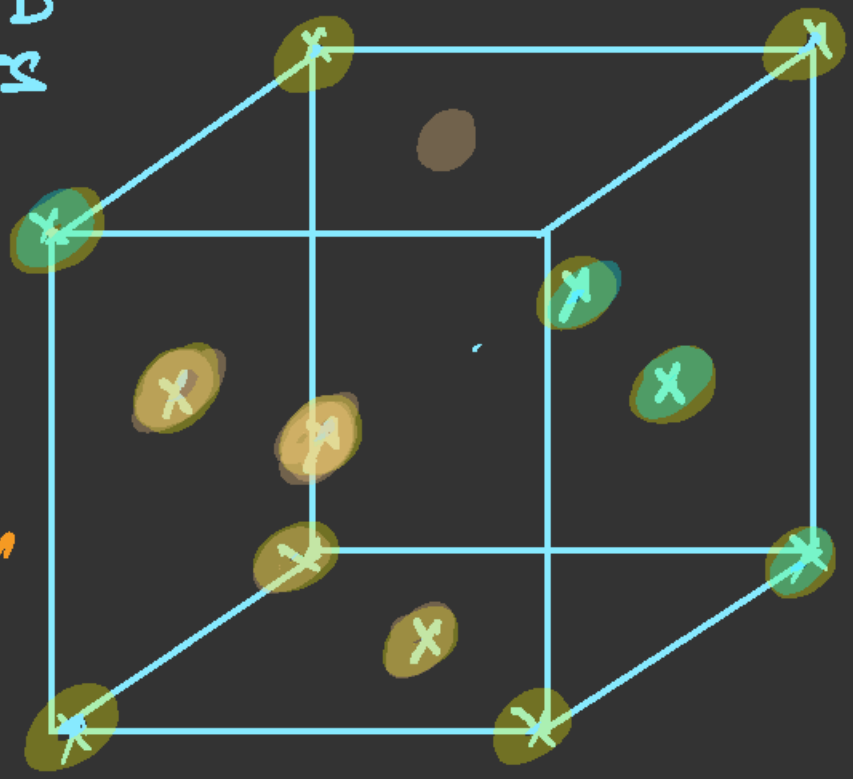
$$\Delta H_{m,mix} = \sum_{i=A,B,C,\ldots} \sum_{\substack{j=A,B,C,\ldots \\ j \neq i}} \omega_{ij} X_i X_j$$

DISORDERED SOLUTIONS

– A

– B

Lattice positions are randomly occupied by either A or B



Disordered phases

$P(A) = X_A$

$P(B) = X_B$

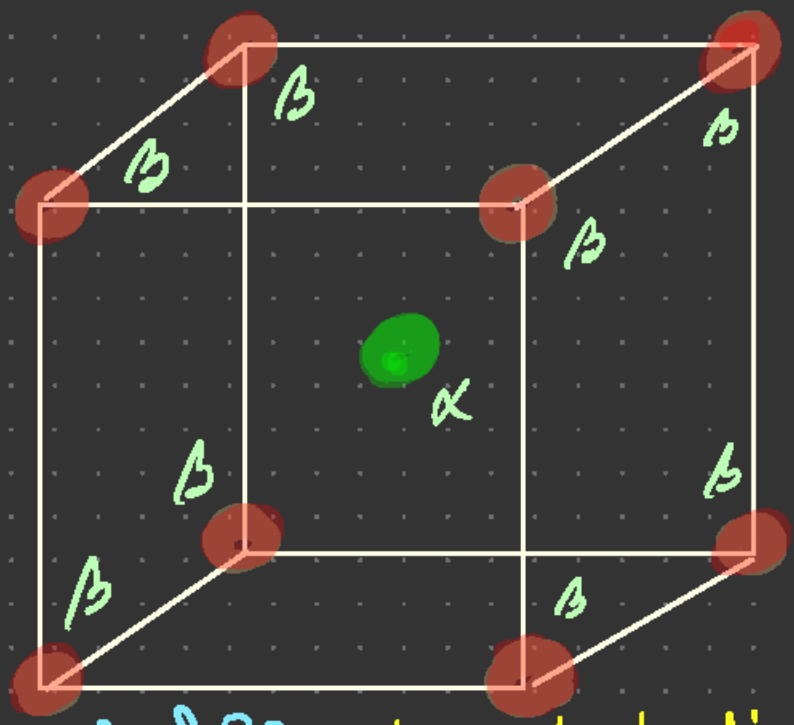
Disordered arrangement

Ordering – $\omega_{AB} < 0$ $\quad N_{AB} > N_{AA}, N_{BB}$

Clustering – $\omega_{AB} > 0$ $\quad N_{AA}, N_{BB} > N_{AB}$

clustering

Ordered phases or phases with ordered lattice



Ordered B2 – bcc derivative

| B site
| α site

α – A
B – B

AB ordered Crystal Structure

NiAl
Cs Cl

– B

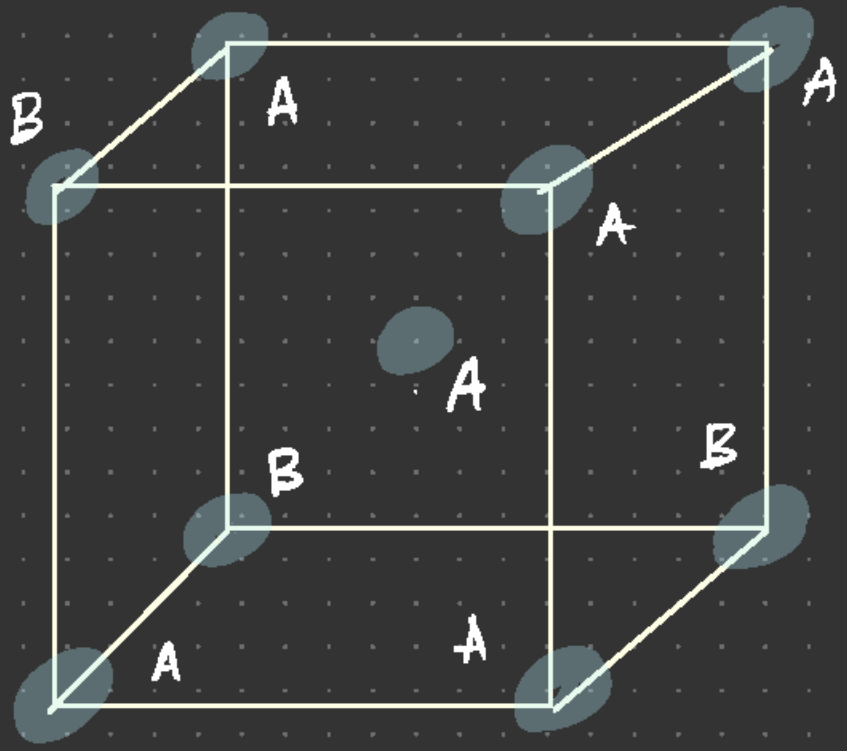
– A

AB phase NiAl

B2 cryotal Structure

| B site
| α site
} | B2 unit cell

Site fraction



Disorder $\rightleftarrows$ Order transformation

B1 Structure

|||

Disordered BCC

↑

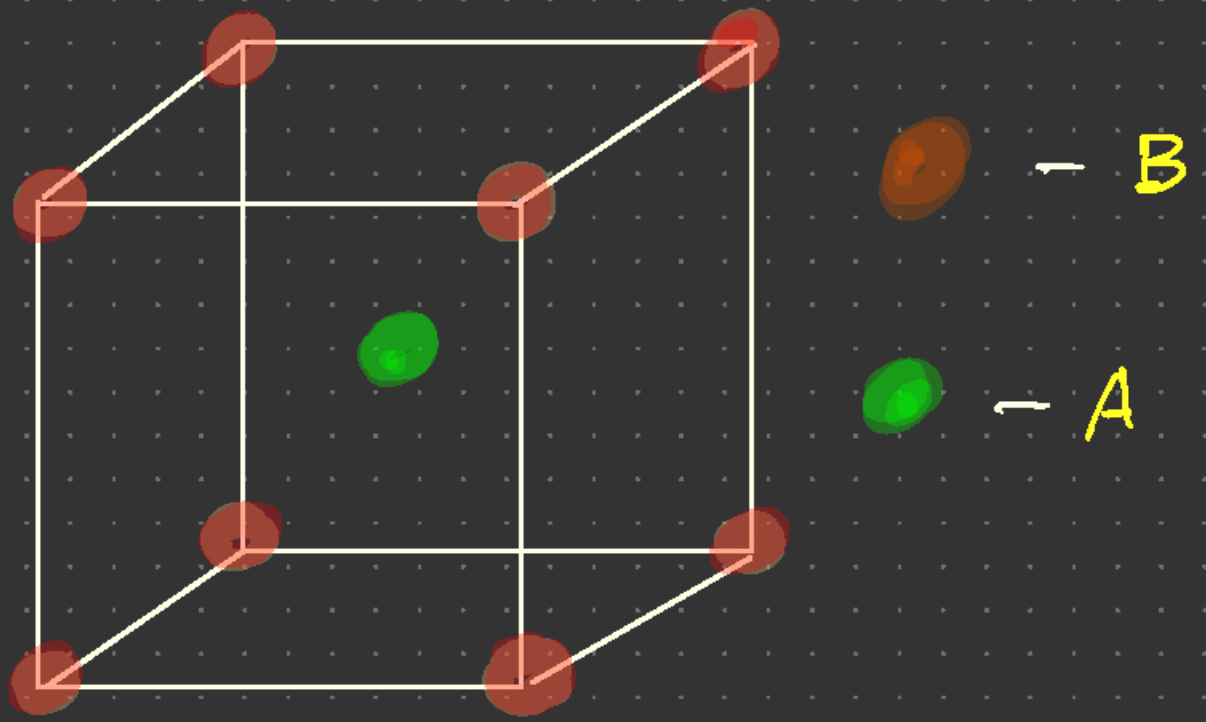
T_c – Phase transition temperature

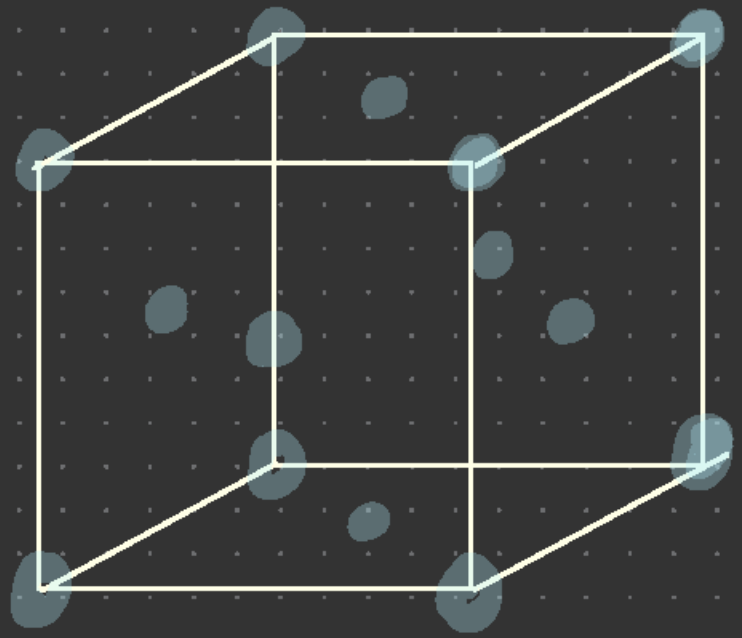
↓

Ordered

B2

Structure





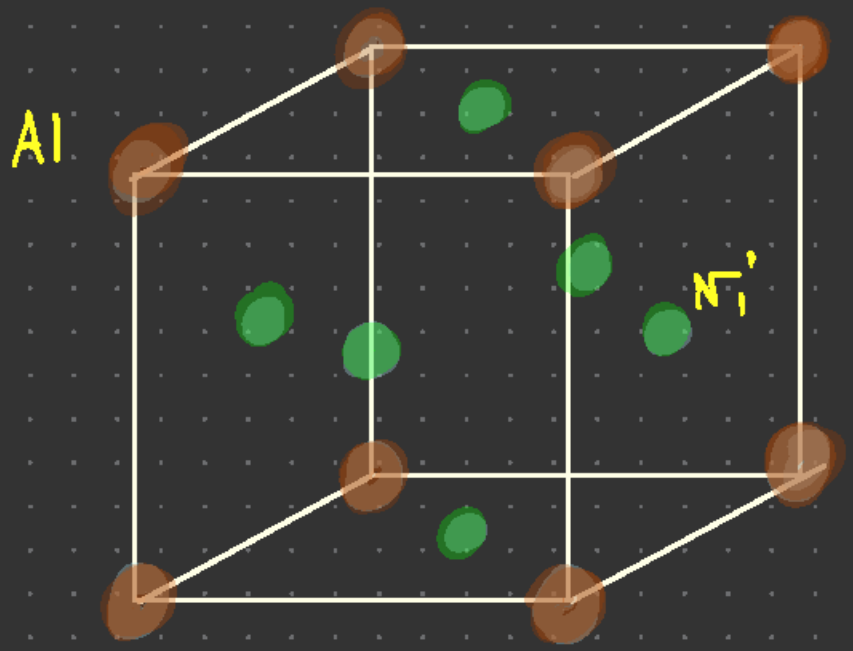
γ Ni
Al

disordered fcc

Random arrangement
of different kinds of atoms

3 Ni
1 Al

Site-fraction



γ'

$L1_2$

Ni_3Al

ordered fcc derivative

Ordered lattices B2 ordered structure or B2 phase

Denote x_α as the fraction of α sites occupied by right atoms (say, A)

α-site fraction of one kind of atomic species

x_α — fraction of α-sites occupied by A atoms

x_β as the fraction of β sites occupied by right atoms (say, B)

x_β — fraction of β sites occupied by B atoms

Fraction of α sites occupied by wrong (B) atoms

$$W_\alpha = 1 - r_\alpha$$

Fraction of β sites occupied by wrong (A) atoms

$$W_\beta = 1 - r_\beta$$

Complete order

$$r_\alpha = r_\beta = 1$$

Probability of an A-site (α-site) occupied by an A atom $= X_A$ for Complete disorder

i.e. $r_\alpha = X_A \qquad r_\beta = X_B$

Define long range order parameter

$$L = \frac{r_\alpha - X_A}{1 - X_A} = \frac{r_\beta - X_B}{1 - X_B}$$

When $r_\alpha = X_A$, $L = 0$ (complete disorder)

$r_\alpha = 1$, $L = 1$ (complete order)

For $0 \leq L \leq 1$, fraction of A on α- or A-site $= x_\alpha$

Total no. of sites N

Consider B2 structure $\underset{\text{site}}{\alpha} : \underset{\text{site}}{\beta}$

$\equiv$ A-site : B-site

$= 1 : 1$

$\frac{N}{2}$ α sites

$\frac{N}{2}$ β sites

# of A atoms in α site $\frac{N}{2} n_\alpha$

# of B atoms in β site $\frac{N}{2} n_\beta$

Consider an alloy of composition

50 at% A, 50 at% B $\Rightarrow$ $X_A = X_B = \frac{1}{2}$

undergoing disorder to order transition

$$X_A = X_B = 1/2$$

$$L = \frac{n_\alpha - X_A}{1 - X_A} = \frac{n_\alpha - 1/2}{1 - 1/2} = 2n_\alpha - 1$$

$L = 1$ when $n_\alpha = 1$

$L =$

Put $X_A = \frac{1}{2}$ in the definition of L

$$n_\alpha = \frac{1+L}{2} \qquad n_\beta = \frac{1+L}{2}$$

No. of A atoms on α-sites

$$= \frac{N}{2} n_\alpha = \left(\frac{1+L}{4}\right) N$$

No. of B atoms on β-sites

$$= \frac{N}{2} n_\beta = \left(\frac{1+L}{4}\right) N$$

Fraction of B atoms on α-site

$$n_\alpha = 1 - x_\alpha$$

No. of B atoms on α-site

$$= \left(1 - x_\alpha\right) \frac{N}{2}$$

$$= \left(1 - \frac{1+L}{2}\right) \frac{N}{2}$$

$$= \left(\frac{1-L}{4}\right) N$$

r_α fraction of α sites occupied by A — X_A

r_β – fraction of β sites occupied by — X_B

$$X_A = \frac{1}{2} \qquad X_B = \frac{1}{2}$$

B2 lattice NiAl

$$L = \frac{r_\alpha - X_A}{1 - X_A} = \frac{r_\beta - X_B}{1 - X_B}$$

$$L = \frac{r_\alpha - 1/2}{1 - 1/2}$$

$$L = 2 r_\alpha - 1$$

$$\text{or, } r_\alpha = \frac{1+L}{2}$$

If $r_\alpha = 1 = r_\beta$

$L = 1$ (complete order)

If $r_\alpha = X_A$ or $r_\beta = X_B$

$L = 0$ (complete disorder)

$$r_\alpha = \frac{1+L}{2}$$

$$r_\beta = \frac{1+L}{2}$$

N — total

$\frac{N}{2}$ α sites

$\frac{N}{2}$ β sites

$$w_\alpha = 1 - r_\alpha = 1 - \frac{1+L}{2} = \frac{1-L}{2}$$

$$w_\beta = 1 - r_\beta = \frac{1-L}{2}$$

$r_\alpha \cdot \frac{N}{2}$ = # of A atoms in α sites

$\frac{1+L}{2} \cdot \frac{N}{2} = \frac{1+L}{4} \cdot N$

$w_\alpha \cdot \frac{N}{2}$ = # of B atom in α-sites

$\frac{1-L}{4} N$

# of A atoms on α-site $= \left(\frac{1+L}{4}\right) N$

# of A atoms on β-site $= \left(\frac{1-L}{4}\right) N$

# of B atoms on β-site $= \left(\frac{1+L}{4}\right) N$

# of B atom on α site $= \left(\frac{1-L}{4}\right) N$

$x_\alpha(L)$

$x_\beta(L)$

Evaluate N_{AA}, N_{BB}, N_{AB}

$$P(A \text{ on } \alpha\text{-site}) = x_\alpha$$

$$P(A \text{ on } \beta\text{-site}) = 1 - x_\beta = N_\beta$$

Z is coordination number of sites

body centre

Each α-site surrounded by Z_β sites
8 B (B2 unit cell)

$$P\left(\underset{\text{pair}}{A-A}\right) = Z\, x_\alpha (1 - x_\beta) = \frac{Z(1+L)(1-L)}{4}$$

$$= \frac{Z(1-L^2)}{4}$$

$$\therefore N_{AA} = \frac{Z(1-L^2)}{4}\,\frac{N}{2} = (1-L^2)\,N$$

$$\therefore Z = 8 \text{ for B2}$$

$$\sum \pi_\beta (1-\pi_\alpha) = P(B-B)$$

$$N_{BB} = (1-L^2)N \qquad A-B$$

$$N_{AB} = \sum \left[\pi_\alpha \pi_\beta + (1-\pi_\alpha)(1-\pi_\beta) \right] \frac{N}{2}$$

$$= \sum \left[\frac{(1+L)^2}{4} + \frac{(1-L)^2}{4} \right] \frac{N}{2}$$

$$= 2(1+L^2)N$$

$P(A \text{ on } \alpha)(B \text{ on } \beta)$

$= \sum \pi_\alpha \pi_\beta$

$P(B \text{ on } \alpha)(A \text{ on } \beta)$

$= \sum w_\alpha w_\beta$

$= \sum (1-\pi_\alpha)(1-\pi_\beta)$

β	α
A	B
B	A

Enthalpy of mixing

$$H_{ord} = N(1-L^2)(E_{AA}+E_{BB}) + 2N(1+L^2)E_{AB}$$

$$N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB}$$

$$S_{conf} = k \ln W \quad \text{– Boltzmann's law}$$

$$W = \left\{ \frac{\left(\frac{N}{2}\right)!}{(\text{No. of A atoms on } \alpha)!\,(\text{No. of B atoms on } \alpha)!} \right\} \leftarrow \alpha\text{-sublattice}$$

$$\times \left\{ \frac{\left(\frac{N}{2}\right)!}{(\text{No. of A atoms on } \beta)!\,(\text{No. of B atoms on } \beta)!} \right\} \leftarrow \beta \text{ sublattice}$$

$$\ln W = \ln\left\{ \frac{(Nr/2)!}{\left(\frac{1+L}{4}\right)Nr!\left(\frac{1-L}{4}\right)Nr!} \times \frac{(Nr/2)!}{\left(\frac{1+L}{4}\right)Nr!\left(\frac{1-L}{4}\right)Nr!} \right\}$$

$$= 2\ln(Nr/2)! - 2\ln\left(\frac{1+L}{4}\right)Nr! - 2\ln\left(\frac{1-L}{4}\right)Nr!$$

$$= 2\frac{Nr}{2}\ln\frac{Nr}{2} - 2\frac{Nr}{2} - 2\left(\frac{1+L}{4}\right)Nr\ln\left(\frac{1+L}{4}\right)Nr$$

$$+ 2\left(\frac{1+L}{4}\right)Nr - 2\left(\frac{1-L}{4}\right)Nr\ln\left(\frac{1-L}{4}\right)Nr$$

$$+ 2\left(\frac{1-L}{4}\right)Nr$$

$$= N \ln \frac{N}{2} - \left(\frac{1+L}{2}\right) N \ln\left(\frac{1+L}{4}\right) N$$

$$- \left(\frac{1-L}{2}\right) N \ln\left(\frac{1-L}{4}\right) N$$

$$= N \ln N - N \ln 2 - \left(\frac{1+L}{2}\right) N \ln\left(\frac{1+L}{4}\right)$$

$$- \left(\frac{1+L}{2}\right) N \ln N$$

$$- \left(\frac{1-L}{2}\right) N \ln N - \left(\frac{1-L}{2}\right) N \ln\left(\frac{1-L}{4}\right)$$

$$= \ln N \left\{ N - \left(\frac{1+L}{2}\right) N - \left(\frac{1-L}{2}\right) N \right\} + \cdots$$

$$= \ln N(0) - N\left\{ \ln 2 + \left(\frac{1+L}{2}\right)\ln\left(\frac{1+L}{4}\right) + \left(\frac{1-L}{2}\right)\ln\left(\frac{1-L}{4}\right)\right\}$$

$$= -N\left\{ \ln 2 + \left(\frac{1+L}{2}\right)\ln(1+L) - \left(\frac{1+L}{2}\right)\ln 4 + \left(\frac{1-L}{2}\right)\ln(1-L) - \left(\frac{1-L}{2}\right)\ln 4\right\}$$

$$= -N\left\{ \ln 2 - (1+L)\ln 2 - (1-L)\ln 2 + \frac{1}{2}\left[(1+L)\ln(1+L) + (1-L)\ln(1-L)\right]\right\}$$

$$= N\left[\ln 2 - \frac{1}{2}\left\{(1+L)\ln(1+L) + (1-L)\ln(1-L)\right\}\right]$$

$$R = kN$$

$$S_{conf} = R\left[\ln 2 - \frac{1}{2}\left\{(1+L)\ln(1+L) + (1-L)\ln(1-L)\right\}\right]$$

$$L = 0 \qquad S_{conf} = R\ln 2$$

In the limit of $L = 1$ $\qquad S_{conf} = 0$ (complete order)

$$G = H_{ord} - TS$$

$$= N(1-L^2)(E_{AA} + E_{BB}) + 2N(1+L^2)E_{AB}$$

$$+ RT\left\{\ln 2 - \frac{1}{2}\left[(1+L)\ln(1+L) + (1-L)\ln(1-L)\right]\right\}$$

$$+ N S_v^0$$

S_v^0 – vibrational entropy per atom

$3N$ independent oscillators

$$S_v = k_B \sum_{i=1}^{3N} \left[-\ln\left(1 - e^{\beta \epsilon_i}\right) + \frac{\beta \epsilon_i}{e^{\beta \epsilon_i} - 1} \right]$$

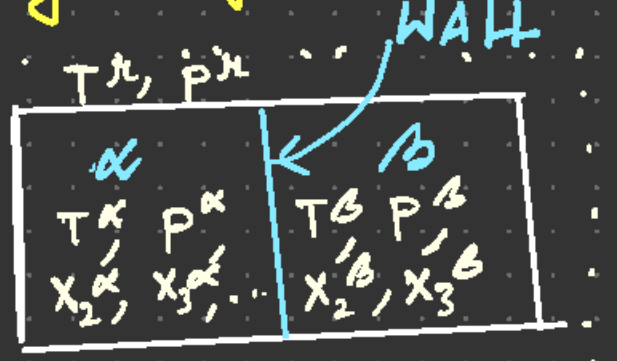
$$\beta = \left(k_B T\right)^{-1} = \frac{1}{k_B T}$$

Phase equilibrium in multiphase, multicomponent, non-reacting systems

$dG_1 = 0$
$d^2G_1 > 0$

$G_m^{\alpha}(T^{\alpha}, P^{\alpha}, x_2^{\alpha}, x_3^{\alpha}, \ldots)$ — α — β — $G_m^{\beta}(T^{\beta}, P^{\beta}, x_2^{\beta}, x_3^{\beta}, \ldots)$

$G_m^{\alpha}(T, P, x_2^{\alpha}, x_3^{\alpha})$



At equilibrium

$$T^{\alpha} = T^{\beta}, \quad P^{\alpha} = P^{\beta}, \quad \mu_1^{\alpha} = \mu_1^{\beta}, \quad \mu_2^{\alpha} = \mu_2^{\beta}$$
$$\mu_3^{\alpha} = \mu_3^{\beta}, \ldots$$

$T^{\alpha} = T^{\beta}$ (Thermal equilibrium)

$P^{\alpha} = P^{\beta}$ (Mechanical Equilibrium)

$\left.\begin{aligned} \mu_1^{\alpha} &= \mu_1^{\beta} \\ \mu_2^{\alpha} &= \mu_2^{\beta} \\ &\vdots \\ \mu_c^{\alpha} &= \mu_c^{\beta} \end{aligned}\right\}$ Chemical Equilibrium

$\alpha, \beta, \gamma, \cdots, \rho$

$$T^{\alpha} = T^{\beta} = T^{\gamma} = \cdots = T^{\rho} \left(= T^{e} \right)$$

$$p^{\alpha} = p^{\beta} = p^{\gamma} = \cdots = p^{\rho} \left(= p^{e} \right)$$

$$\mu_1^{\alpha} = \mu_1^{\beta} = \mu_1^{\gamma} = \cdots = \mu_1^{\rho}$$

$$\mu_2^{\alpha} = \mu_2^{\beta} = \mu_2^{\gamma} = \cdots = \mu_2^{\rho}$$

$$\vdots$$

$$\mu_c^{\alpha} = \mu_c^{\beta} = \mu_c^{\gamma} = \cdots = \mu_c^{\rho}$$

$T^{\alpha}, T^{\beta}, \cdots$

$p^{\alpha}, p^{\beta}, \cdots$

$x_2^{\alpha}, x_3^{\alpha}, x_4^{\alpha}, \cdots$

$x_2^{\beta}, x_3^{\beta}, x_4^{\beta}, \cdots$

$$x_1^{\alpha} + x_2^{\alpha} + \cdots x_c^{\alpha} = 1$$

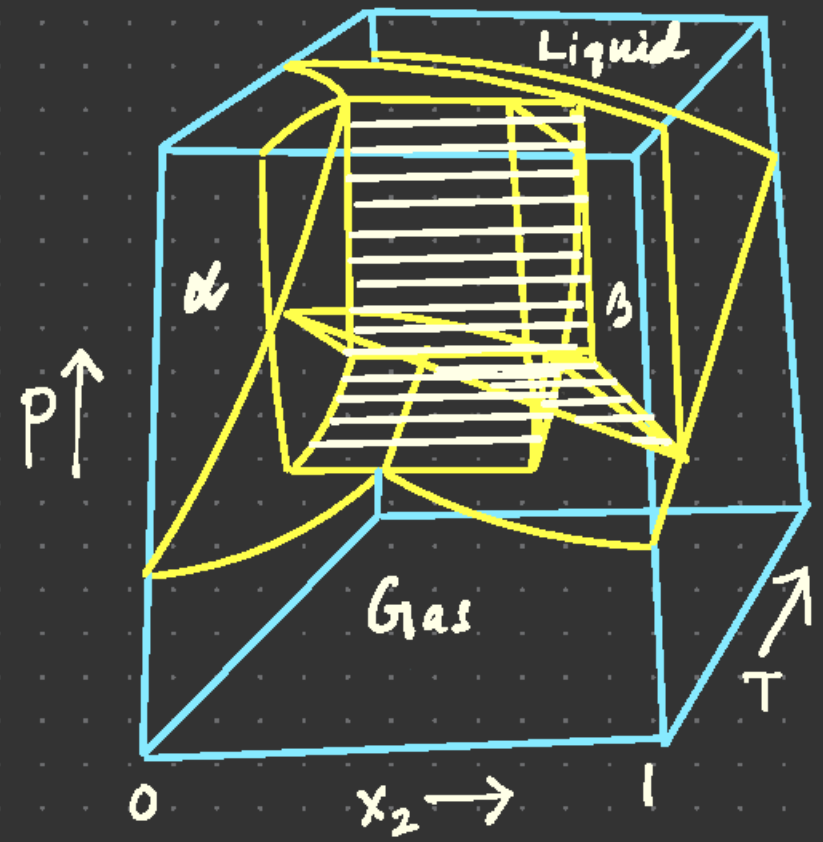
Gibbs phase rule

$$f = c - p + 2$$

Condensed phases: $f = c - p + 1$

pressure p is assumed to have a fixed value for the entire system

P - T - X phase diagram



2 as the independent component in each phase

$$x_1^{\alpha} + x_2^{\alpha} = 1$$

x_1^{α} ↓ dependent

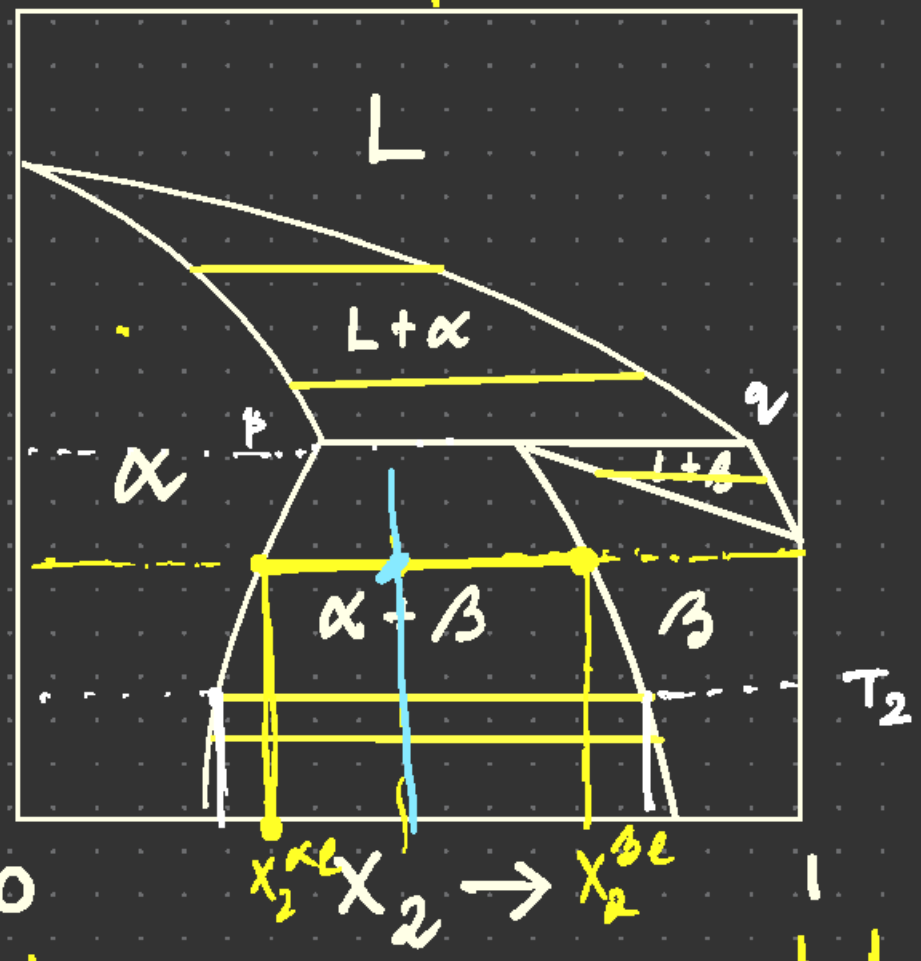
x_2^{α} ↓ independent

Binary phase diagram

At T_P

$f = 2 - 3 + 1$

$= 0$



At a fixed pressure

T-X maps

phase diagrams

$f = C - P + 1$

$= 2 - 1 + 1$

$= 2$

$f = 2 - 2 + 1$

$= 1$

$\mu_2^{\alpha} = \mu_2^{\beta}$

$\mu_1^{\alpha} = \mu_1^{\beta}$

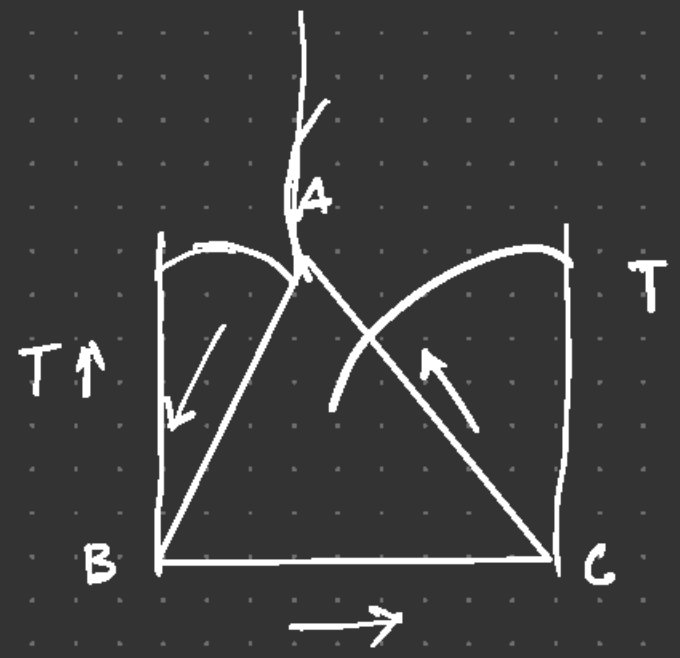
$x_2^{\alpha,e}(\alpha/\beta)$ $x_2^{\beta,e}(\beta/\alpha)$ $x_1^{\alpha,e}$

$= 1 - x_2^{\alpha,e}$

Ternary phase diagrams

Alan Prince Alloy Phase Equilibria

p is fixed



$$x_A + x_B + x_C = 1$$

Isothermal projection

Vertical section

I. Binary alloy A-B

Components have infinite solubility in liquid state

Zero solubility in the solid state

Model the liquid phase L as an ideal solution

$$a_A^L = X_A^L$$

$$a_B^L = X_B^L$$

$$\mu_A = \mu_A^0 + RT \ln X_A$$

$$\Delta\mu_A = \mu_A - \mu_A^0$$

$$= RT \ln X_A$$

Liquid to Solid transformation of pure A

$T^{\circ}_{A,\,freeze}$ – freezing point of pure A

Solvent

$$\Delta\mu^{\circ}_{A}\left(T^{\circ}_{A,\,freeze}\right) = 0 = \mu^{\circ}_{AS}\left(T^{\circ}_{A,\,freeze}\right)$$

$$\mu^{\circ}_{A(s)} = \mu^{\circ}_{A(l)} - \mu^{\circ}_{AL}\left(T^{\circ}_{A,\,freeze}\right)$$

at $T = T^{\circ}_{A,\,freeze}$

Solution of A + B (Freezing point $\neq T^{\circ}_{A,\,freeze}$)

$$\mu_{AS}\left(T^{\circ}_{A,\,freeze}\right) - \mu_{AL}\left(T^{\circ}_{A,\,freeze}\right)$$

$$\neq 0$$

Solution of A + B :

Freezing point = T_{freeze}

$$\Delta\mu_A\left(T_{freeze}\right) = \mu_{As}\left(T_{freeze}\right) - \mu_{AL}\left(T_{freeze}\right)$$

$$= 0 \quad \text{At } T_{freeze},$$

$$\mu_{A(s)} = \mu_{A(L)}$$

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

Gibbs - Helmholtz equation

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

Ideal Dilute Liquid Solution

$$\left[\frac{\partial(\mu_{AL}/T)}{\partial T}\right]_{p,x_i} = -\frac{\bar{H}_{AL}}{T^2} = -\frac{H^{\circ}_{AL}}{T^2}$$

$$\therefore \Delta\bar{H}_{AL} = \bar{H}_{AL} - H^{\circ}_{AL}$$

$$= 0$$

Solid Solution

$$\left[\frac{\partial(\mu_{AS}/T)}{\partial T}\right]_{p,x_i} = -\frac{\bar{H}_{AS}}{T^2} = -\frac{H^{\circ}_{AS}}{T^2}$$

$L \rightarrow S$

Exothermic

$$\Delta H^{\circ}_{freeze\ (L\rightarrow S)} = -\Delta H^{\circ}_{melt}$$

$-ve$

$$= \underbrace{H^{\circ}_{AS}}_{final} - \underbrace{H^{\circ}_{AL}}_{initial}$$

$$\therefore \left[\frac{\partial\left(\Delta\mu_A^{L\rightarrow S}/T\right)}{\partial T}\right]_{P,x_i}$$

$$= \left[\frac{\partial\left(\mu_{AS}/T\right)}{\partial T}\right]_{P,x_i} - \left[\frac{\partial\left(\mu_{AL}/T\right)}{\partial T}\right]_{P,x_i}$$

$$= -\frac{H^{\circ}_{AS} - H^{\circ}_{AL}}{T^2} = -\frac{\Delta H^{\circ}_{freeze\ (A)}}{T^2}$$

$$\int_{\Delta\mu_A(T^0_{freeze})/T^0_{freeze}}^{\Delta\mu_A(T_{freeze})/T_{freeze}} d\left(\frac{\Delta\mu_A}{T}\right)$$

$$\Delta\mu_A = \mu_{A(s)} - \mu_{A(l)}$$
$$= \mu_{As} - \mu_{AL}$$

$$= -\Delta H^0_{freeze} \int_{T^0_{freeze}}^{T_{freeze}} \frac{dT}{T^2}$$

$$\frac{\Delta\mu_A(T_{freeze})}{T_{freeze}} - \frac{\Delta\mu_A(T^0_{freeze})}{T^0_{freeze}} = \Delta H^0_{freeze}\left(\frac{1}{T_{freeze}} - \frac{1}{T^0_{freeze}}\right)$$

$$\underbrace{\Delta\mu_A(T_{freeze})}_{T_{freeze}} - \underbrace{\Delta\mu_A(T^\circ_{freeze})}_{T^\circ_{freeze}}$$

$T^\circ_{freeze} = T^\circ_{A,freeze}$

At T_{freeze}

$\mu_{As} = \mu_{AL}$

or, $\Delta\mu_A = 0$

$$= \Delta H^\circ_{freeze}\left(\frac{1}{T_{freeze}} - \frac{1}{T^\circ_{freeze}}\right)$$

$\therefore \Delta\mu_A(T_{freeze}) = 0$

$$-\frac{\Delta\mu_A(T^\circ_{freeze})}{T^\circ_{freeze}} = \Delta H^\circ_{freeze}\left(\frac{1}{T_{freeze}} - \frac{1}{T^\circ_{freeze}}\right)$$

$$T^{\circ}_{freeze} - T_{freeze} = \Delta T_{fr}$$

$$\Delta \mu_A \left(T^{\circ}_{freeze}\right) \neq 0$$

$$\Delta \mu_A \left(T^{\circ}_{freeze}\right) = \mu_{AS}\left(T^{\circ}_{freeze}\right) - \mu_{AL}\left(T^{\circ}_{freeze}\right)$$

$$= \mu^{\circ}_{AS}\left(T^{\circ}_{freeze}\right) + RT^{\circ}_{freeze} \ln X_{AS} - \mu^{\circ}_{AL}\left(T^{\circ}_{freeze}\right) - RT^{\circ}_{freeze} \ln X_{Al}$$

$$\mu_{AS}\left(T^{\circ}_{freeze}\right) = \mu^{\circ}_{AS}\left(T^{\circ}_{freeze}\right) + RT^{\circ}_{freeze} \ln X_{AS}$$

$$\mu_{AL}\left(T^{\circ}_{freeze}\right) = \mu^{\circ}_{Al}\left(T^{\circ}_{freeze}\right) + RT^{\circ}_{freeze} \ln X_{AL}$$

$$\frac{-R T^{\circ}_{freeze} \ln\left(\frac{X_{AS}}{X_{AI}}\right)}{T^{\circ}_{freeze}} = \Delta H^{\circ}_{freeze}\left(\frac{1}{T_{freeze}} - \frac{1}{T^{\circ}_{freeze}}\right)$$

$$\therefore \ln \frac{X_{AS}}{X_{AI}} = -\frac{\Delta H^{\circ}_{freeze}}{R}\left(\frac{1}{T_{freeze}} - \frac{1}{T^{\circ}_{freeze}}\right)$$

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

$$\ln\left(\frac{X_{AS}}{X_{AL}}\right) = \ln\left(\frac{1-X_{BS}}{1-X_{BL}}\right)$$

$$= \ln\left(1-X_{BS}\right) - \ln\left(1-X_{BL}\right)$$

$$= -X_{BS} + X_{BL}$$

$$= X_{BL}\left(1 - \frac{X_{BS}}{X_{BL}}\right)$$

$$= X_{BL}\left(1-L\right)$$

$L = \frac{X_{BS}}{X_{BL}}$ is partition coefficient of solute between solid and liquid solutions

$$X_{BL}(1-L) = \frac{\Delta H^{\circ}_{melt}}{R}\left(\frac{1}{T_{freeze}} - \frac{1}{T^{\circ}_{freeze}}\right)$$

$$\Delta T_{fr} = T^{\circ}_{freeze} - T_{freeze}$$

$$X_{BL}(1-L) = \frac{\Delta H^{\circ}_{melt}}{R}\left(\frac{\Delta T_{fr}}{T^{\circ}_{freeze}\, T_{freeze}}\right)$$

$$T_{freeze} \sim T^{\circ}_{freeze}$$

$$\therefore \quad \Delta T_{fr} = \frac{R\left(T^{\circ}_{freeze}\right)^{2}\left(1-L\right) X_{BL}}{\Delta H^{\circ}_{melt}}$$

When $L < 1$ or, $X_{BS} < X_{BL}$

$$\Delta T_{fr} > 0 \quad \text{or,} \quad T_{freeze} < T^{\circ}_{freeze}$$

Depression of freezing point

When $L > 1$ or, $X_{BS} > X_{BL}$

$$\Delta T_{fr} < 0 \quad \text{or,} \quad T_{freeze} > T^{\circ}_{freeze}$$

Elevation of freezing point

If q° is the specific heat of pure solvent A in J/g

$$\Delta H^\circ_{melt} = 1000\, q^\circ$$

Molality m_{BL} = no. of moles of B in 1000 g. of A

1000 gm. of A = $\frac{1000}{M_A}$ moles of A

For dilute solutions $\rightarrow$ $X_B = \frac{N_B}{N_A + N_B} \approx \frac{N_B}{N_A}$

$X_{BL} \approx m_{BL} \cdot \left(\frac{M_A}{1000}\right)$

$$X_{BL} \simeq \frac{M_A}{1000} m_{BL}$$

$\frac{\text{gm}}{\text{mole}}$ $\quad$ $\frac{\text{moles}}{1000\ \text{gm}}$

$$\therefore \quad \Delta T_{fr} = K_f (1 - L) m_{BL}$$

$$K_f = \frac{R (T^0_{freezing})^2}{1000\ q^0}$$

If $X_{BS} = 0$ (no solubility of B in solid solution)

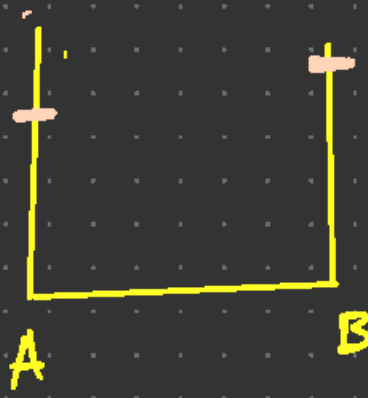
$$L = 0$$

$$\Delta T_{fr} = K_f m_{BL}$$

Phase equilibrium - Composition range from pure A to pure B

A + B completely soluble in liquid

no solubility in solid



$$\ln\left(\frac{X_{AS}}{X_{AL}}\right) = \frac{\Delta H^{\circ}_{A,melt}}{R}\left(\frac{1}{T_{A,freeze}} - \frac{1}{T^{\circ}_{A,freeze}}\right)$$

$$\ln\left(\frac{X_{BS}}{X_{BL}}\right) = \frac{\Delta H^{\circ}_{B,melt}}{R}\left(\frac{1}{T_{B,freeze}} - \frac{1}{T^{\circ}_{B,freeze}}\right)$$

No solubility of A in B

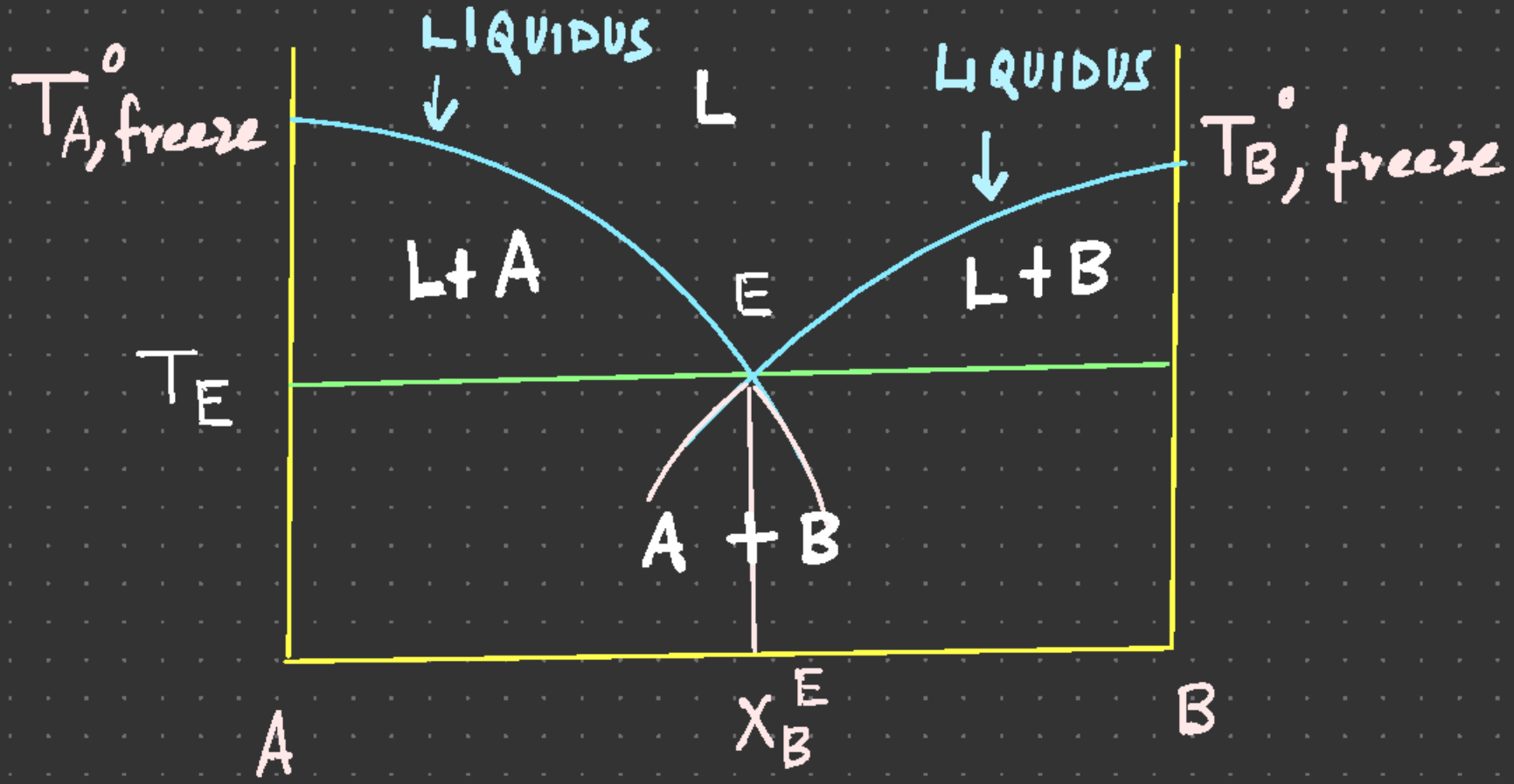
or, B in A

in solid solution

$$\Rightarrow X_{AS} = 1 \qquad X_{BS} = 1$$

$$\therefore \ln X_{AL} = \frac{\Delta H^{\circ}_{A,\,melt}}{R}\left(\frac{1}{T^{\circ}_{A,\,freeze}} - \frac{1}{T_{A,\,freeze}}\right)$$

$$\ln X_{BL} = \frac{\Delta H^{\circ}_{B,\,melt}}{R}\left(\frac{1}{T^{\circ}_{B,\,freeze}} - \frac{1}{T_{B,\,freeze}}\right)$$



$X_B \longrightarrow$

At E, $T_{A,\,freeze}^{(X_A)} = T_{B,\,freeze}^{(X_B)} = T_E$

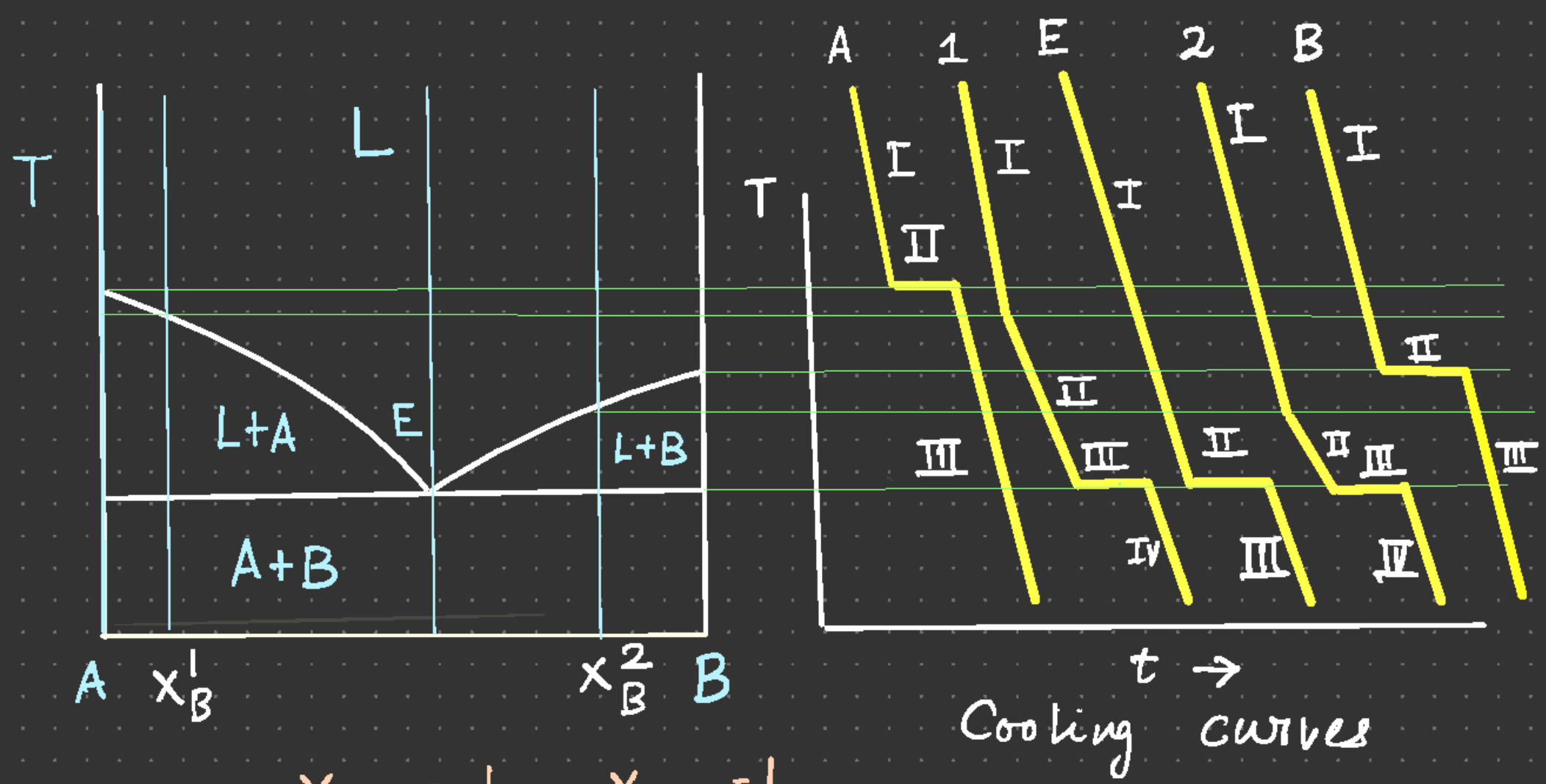
$X_A = 1 - X_B^E \qquad X_B = X_B^E$

At $T = T_E$, $L \rightarrow A + B$

Eutectic Reaction

T_E – Eutectic Temperature

X_B^E – Eutectic Composition



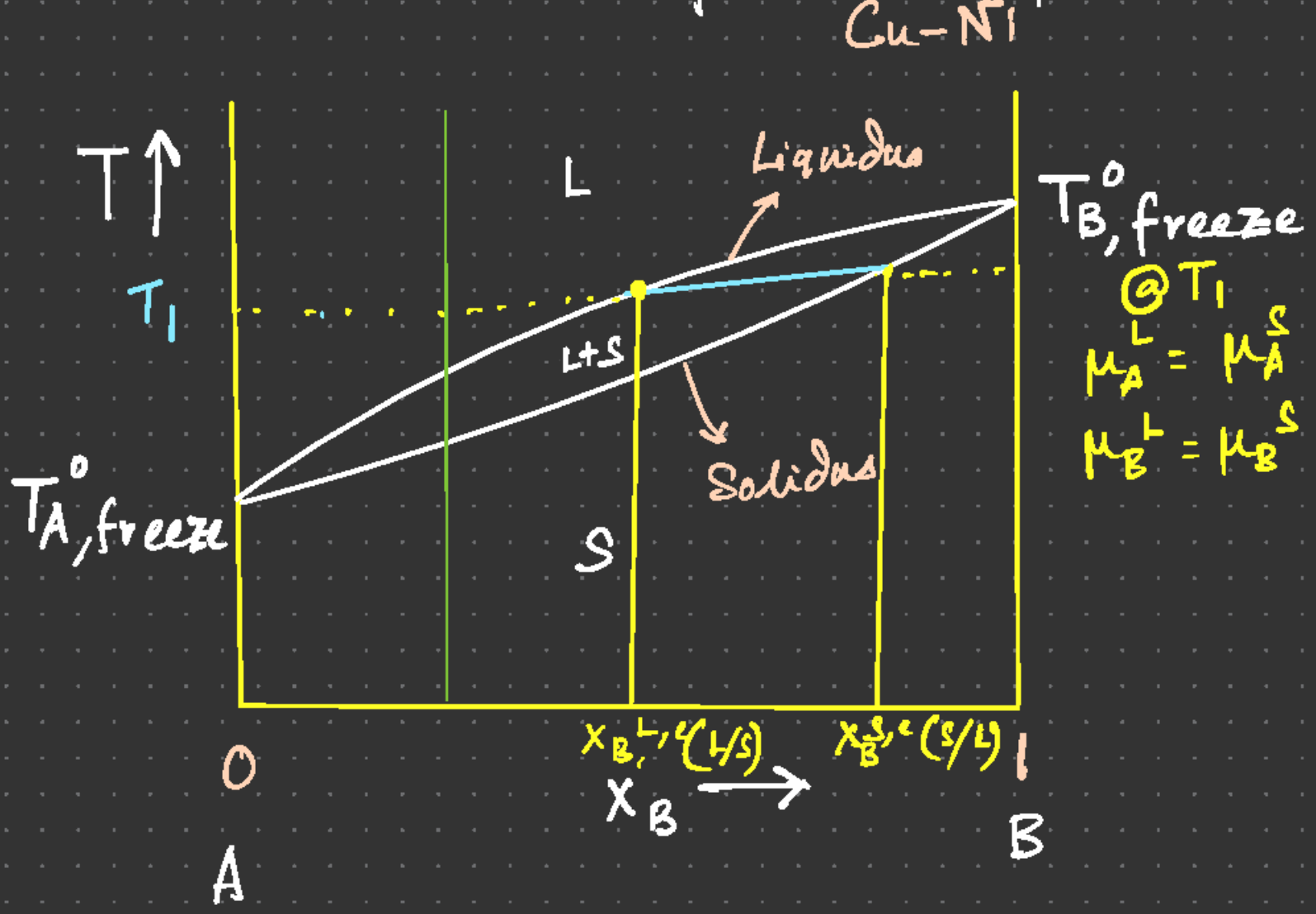
Cooling curves

$X_{AS} = 1 \quad X_{BS} = 1$

$\frac{dT}{dt}$: Slope of cooling curve

II A-B alloy

Infinite solubilities in both liquid and solid state - Isomorphous components



Ideal Solid Solution + Ideal liquid Solution

$$\ln\left(\frac{X_{AS}}{X_{AL}}\right) = \frac{\Delta H^{\circ}_{A,melt}}{R}\left(\frac{1}{T_{A,freeze}} - \frac{1}{T^{\circ}_{A,freeze}}\right) \quad -(1)$$

$$\ln\left(\frac{X_{BS}}{X_{BL}}\right) = \frac{\Delta H^{\circ}_{B,melt}}{R}\left(\frac{1}{T_{B,freeze}} - \frac{1}{T^{\circ}_{B,freeze}}\right) \quad -(2)$$

$$X_{AS} + X_{BS} = 1 \quad -(3)$$

S – Solid phase

$$X_{AL} + X_{BL} = 1 \quad -(4)$$

L – Liquid phase

Solve to get $X_{BS}(T)$, $X_{BL}(T)$

$X_{BS}(T)$ → Solidus

$X_{BL}(T)$ → Liquidus

Non-ideal Solutions

$$a_{AS} = \gamma_{AS} X_{AS}$$

Replace X_{AS} by a_{AS}

X_{AL} by a_{AL}

X_{BS} by a_{BS}

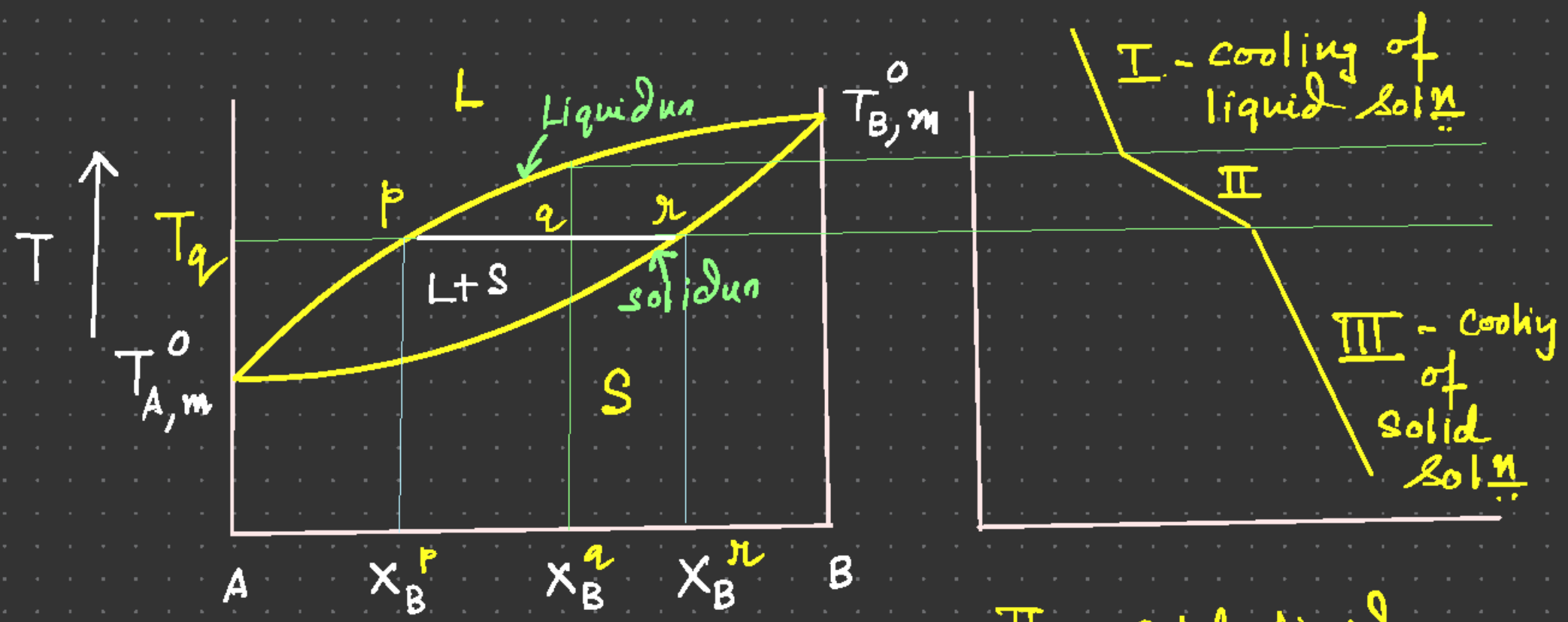
X_{BL} by a_{BL}

$$X_{AS} + X_{BS} = 1$$

$$a_{AS} + a_{BS} \neq 1$$

$$X_{AS}\left(\frac{\partial \ln a_{AS}}{\partial X_{AS}}\right)_{P,T} = X_{BS}\left(\frac{\partial \ln a_{BS}}{\partial \ln X_{BS}}\right)_{P,T}$$

$$X_{AL}\left(\frac{\partial \ln a_{AL}}{\partial \ln X_{AL}}\right)_{P,T} = X_{BL}\left(\frac{\partial \ln a_{BL}}{\partial \ln X_{BL}}\right)_{P,T}$$



II - Solid-liquid coexistence

Line pr - Tie Line at T_q

X_B^q is alloy composition

Amount of phases L, S: $\phi_L = \frac{qr}{pr}$ $\phi_S = \frac{pq}{pr}$

Lever Rule

$n_{A(L)} + n_{B(L)} = n^L$

$n_{A(S)} + n_{B(S)} = n^S$

n^T total no. of moles of components A + B

n_A no. of moles of A $= n_{A(L)} + n_{A(S)}$

n_B no. of moles of B $= n_{B(L)} + n_{B(S)}$

n^L no. of moles of Liquid phase

n^S no. of moles of solid phase

Overall alloy composition X_B^q (Composition of two-phase mixture)

$\therefore$ number of moles of B in the alloy $n_B = n^T X_B^q$

Moles of B in alloy : $n^T x_B^q$

Moles of B in liquid phase L : $n^L x_B^p$

Moles of B in solid phase S : $n^S x_B^r$

Conservation of component B:

Moles of B in (L + S) mixture

= Moles of B in L

+

Moles of B in S

$$n^T x_B^q = n^L x_B^p + n^S x_B^r \quad -(1)$$

Divide both sides of Eq (1) by n^T

$$X_B^q = \frac{n^L}{n^T} X_B^P + \frac{n^S}{n^T} X_B^R$$

phase fraction $\phi_L = \frac{n^L}{n^T}$

phase fraction $\phi_S = \frac{n^S}{n^T}$

$\phi_L + \phi_S = 1$

$$X_B^q = \phi_L X_B^P + \phi_S X_B^R$$

$$= \phi_L X_B^P + (1 - \phi_L) X_B^R$$

$$= X_B^R + \phi_L (X_B^P - X_B^R)$$

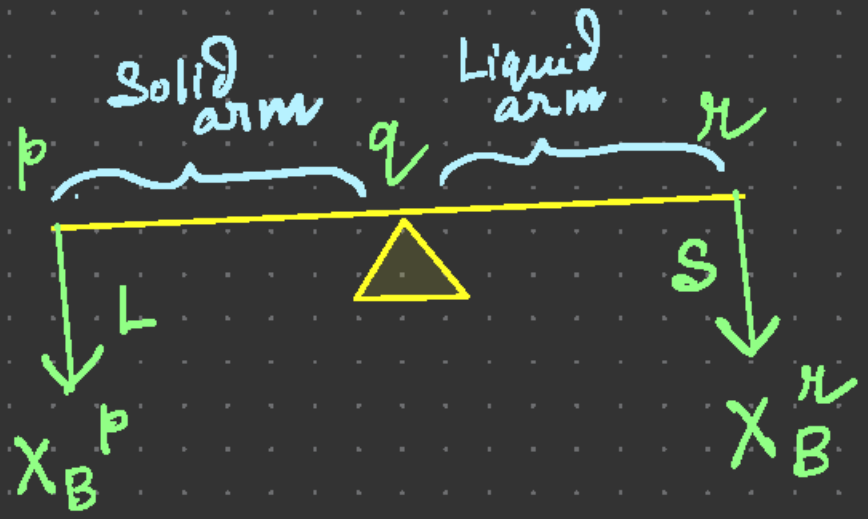
$$\therefore \quad \phi_L \left(X_B^{\,p} - X_B^{\,n} \right) = X_B^{\,q} - X_B^{\,n}$$

$$\text{or,} \quad \phi_L = \frac{X_B^{\,q} - X_B^{\,n}}{X_B^{\,p} - X_B^{\,n}} = \frac{X_B^{\,n} - X_B^{\,q}}{X_B^{\,n} - X_B^{\,p}} = \frac{qn}{pn}$$

$$\therefore \quad \phi_S = 1 - \phi_L = 1 - \frac{X_B^{\,n} - X_B^{\,q}}{X_B^{\,n} - X_B^{\,p}}$$

$$= \frac{X_B^{\,n} - X_B^{\,p} - X_B^{\,n} + X_B^{\,q}}{X_B^{\,n} - X_B^{\,p}}$$

$$= \frac{X_B^{\,q} - X_B^{\,p}}{X_B^{\,n} - X_B^{\,p}} = \frac{pq}{pn}$$



$$\phi_L = \frac{qr}{pr}, \quad \phi_S = \frac{pq}{pr}$$

moves

$q \to r$: A small amount of L balances a large amount of S

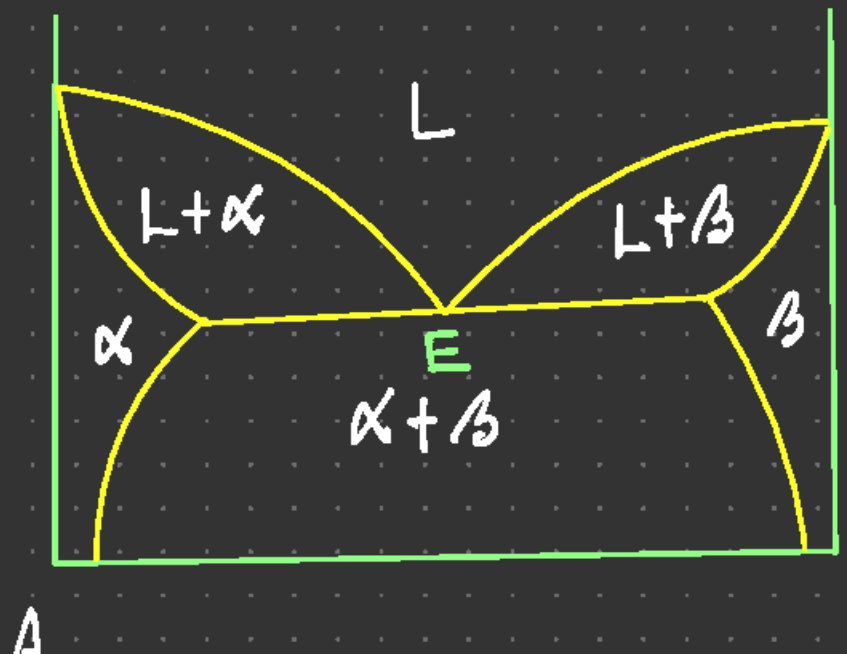
$q \to p$: A small amount of S balances a large amount L

III

A-B alloy

Solubility of A+B in liquid is infinite

Solubility of A+B in solid is limited



Eutectic phase diagram

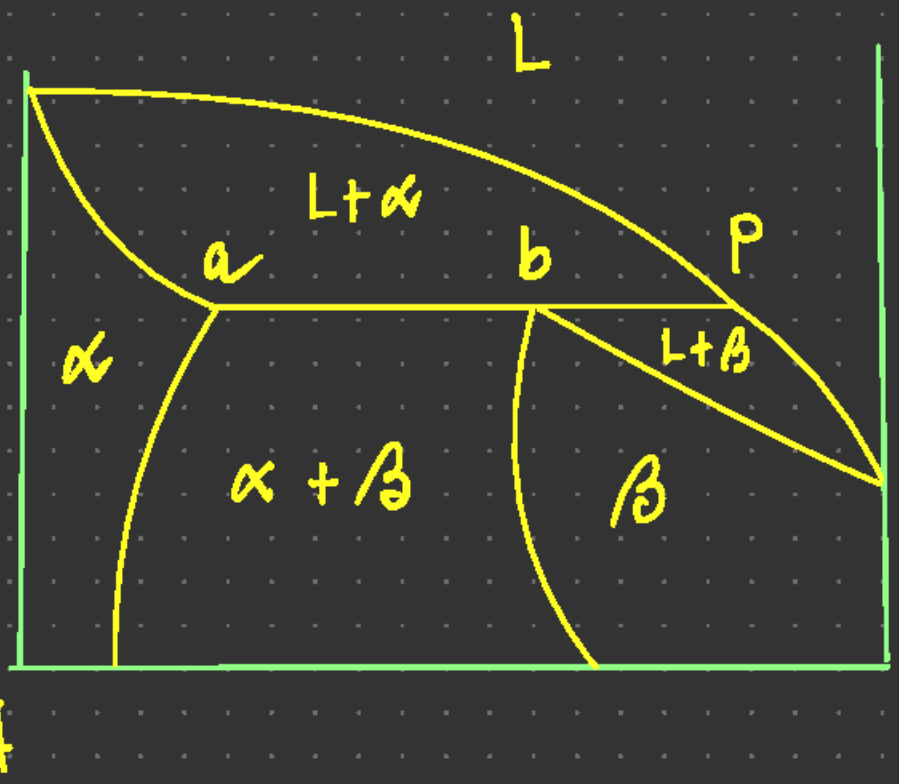
At E: $f = c - p + 1$

$= 2 - 3 + 1$

$= 0$

$L \rightarrow \alpha + \beta$

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



Peritectic phase diagram

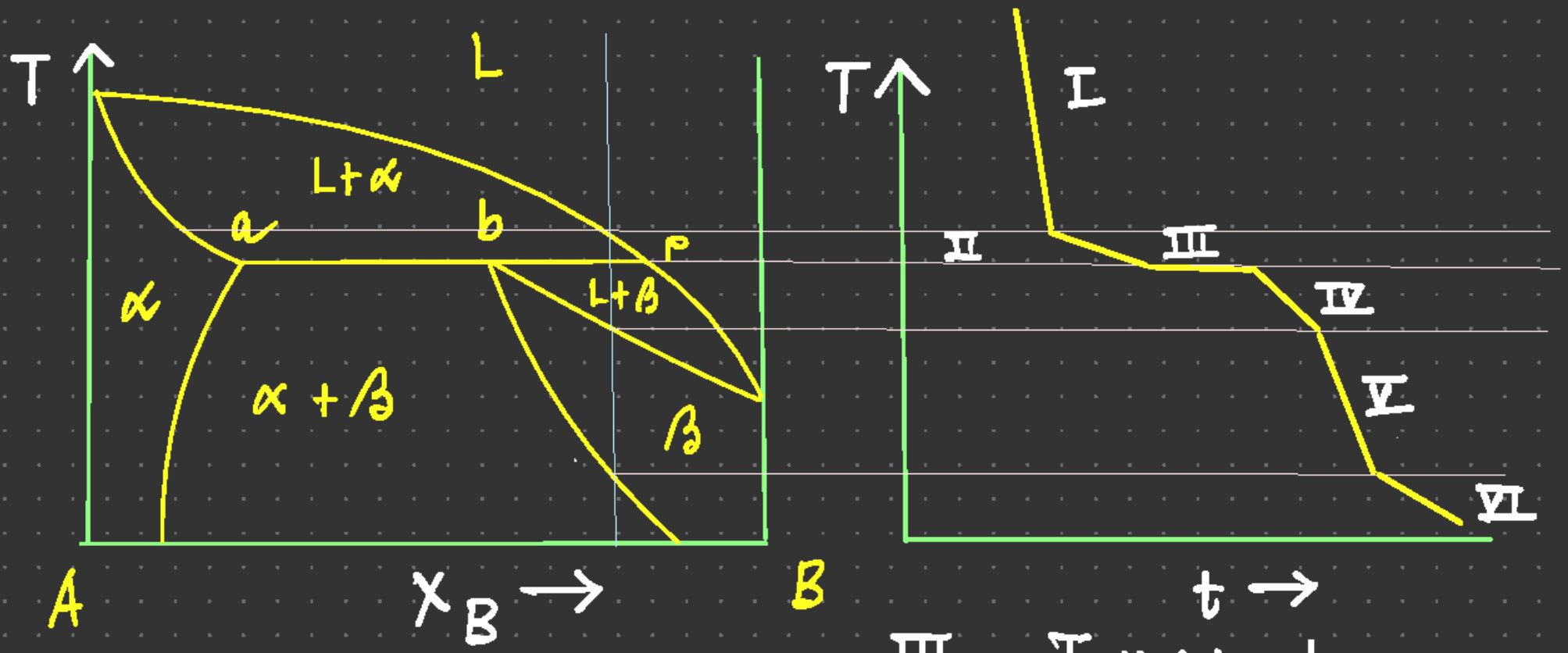
Invariant reaction at P: $L + \alpha \rightarrow \beta$

(peritectic reaction)

a b P : peritectic reaction

P – Liquid composition, a – α composition

b – β composition



III – Invariant peritectic reaction (horizontal segment)

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

Stoichiometric

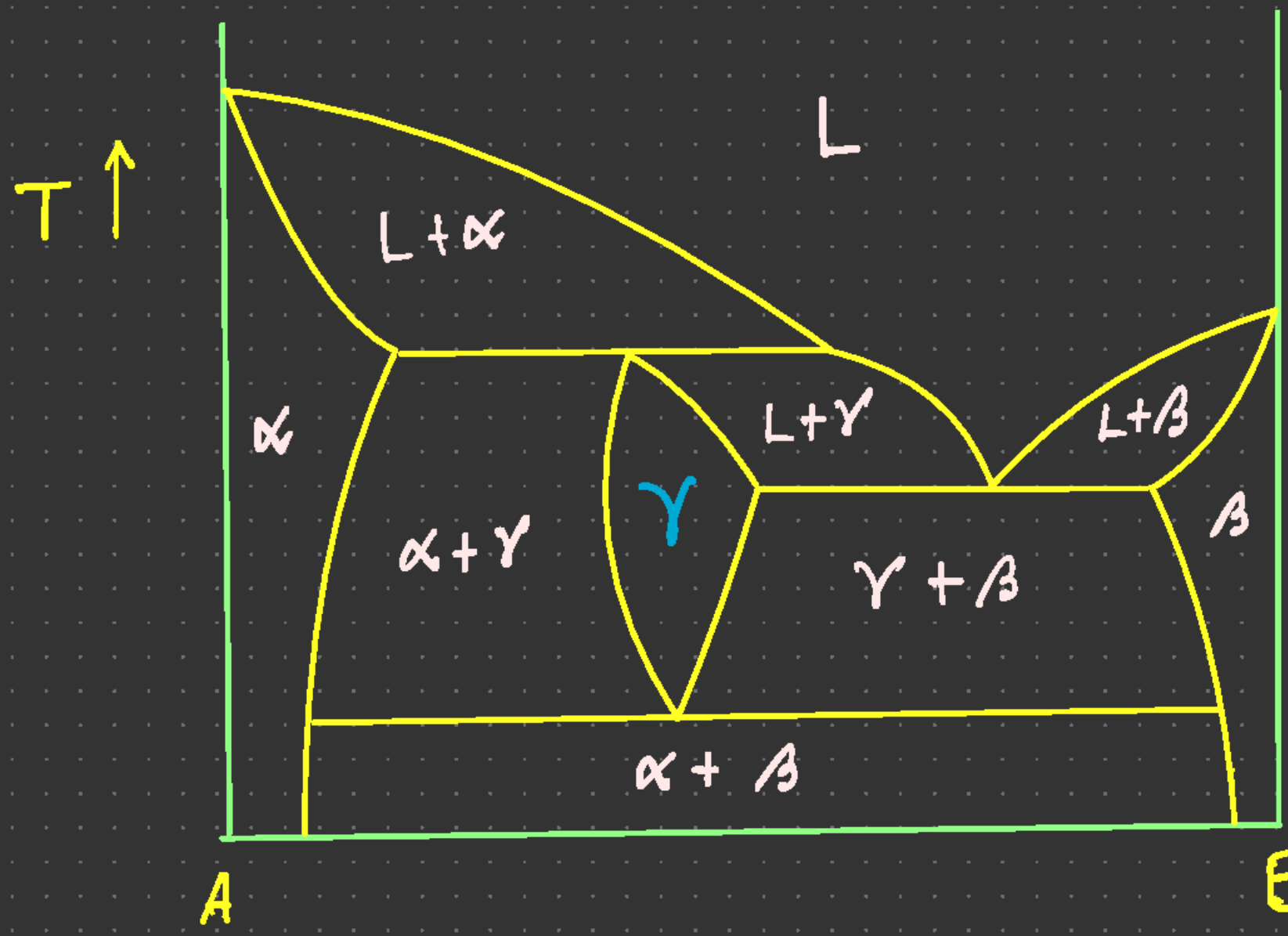
— Well defined composition

Eg. AB, A_2B, AB_3, ...

Non-Stoichiometric

— phase with a new crystalline arrangement but with variable composition

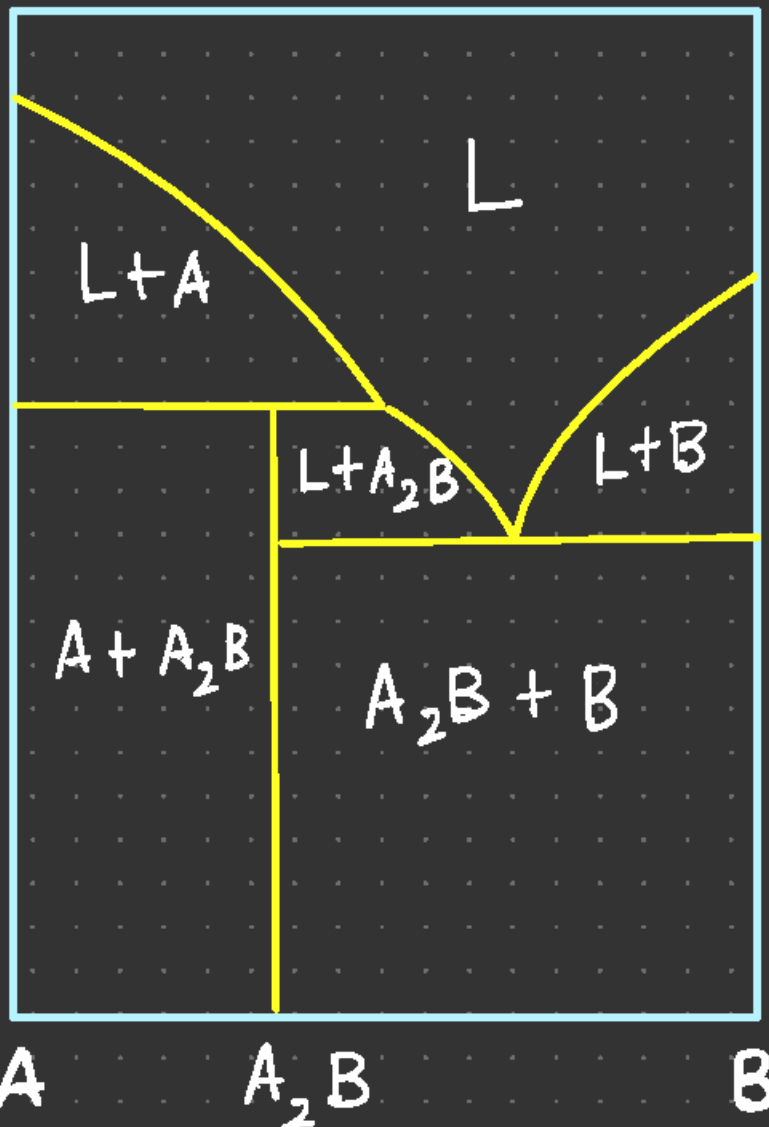
Eg. $A_{55-60}B_{45-40}$



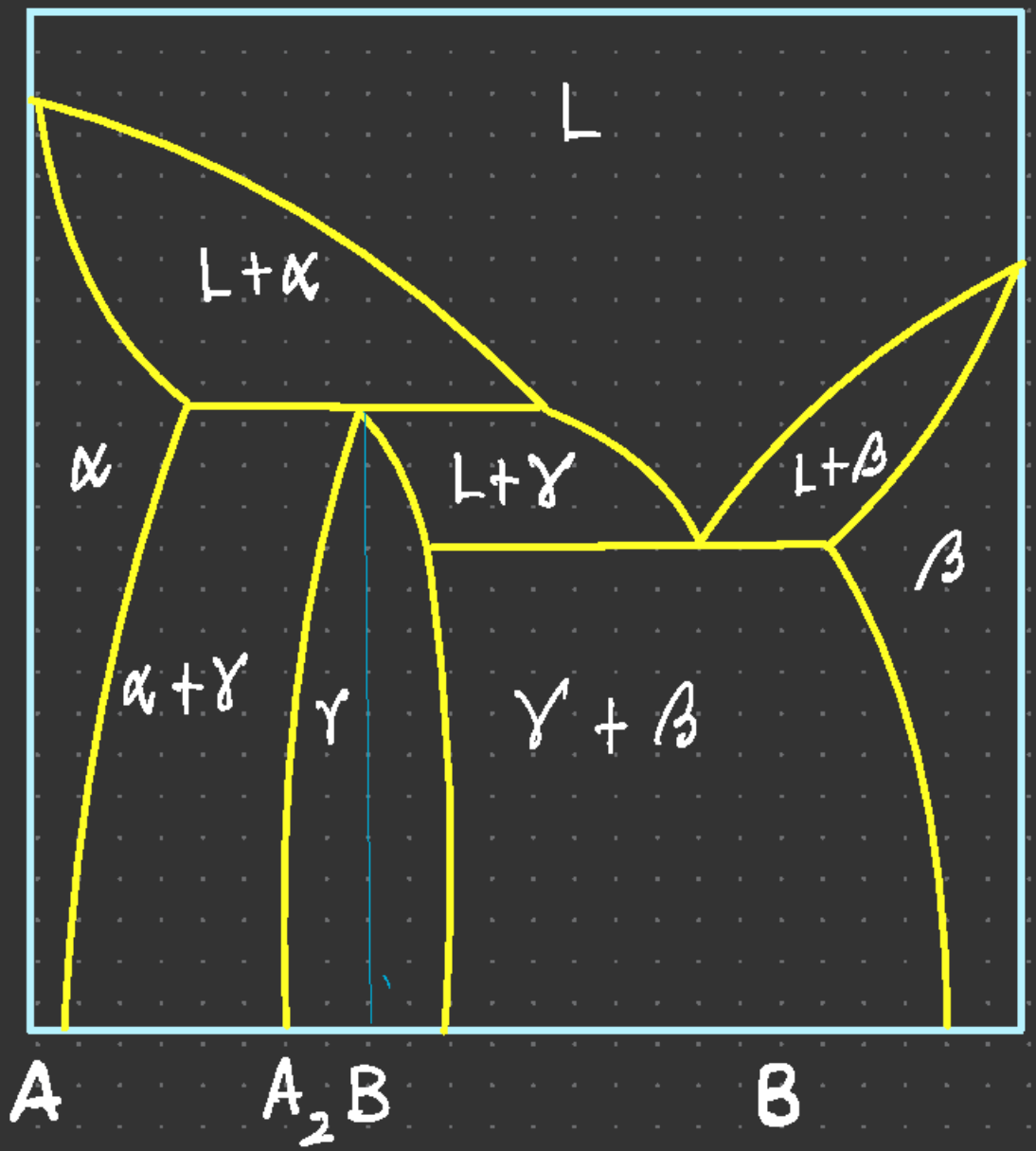
γ – Unstable at low and high temperatures

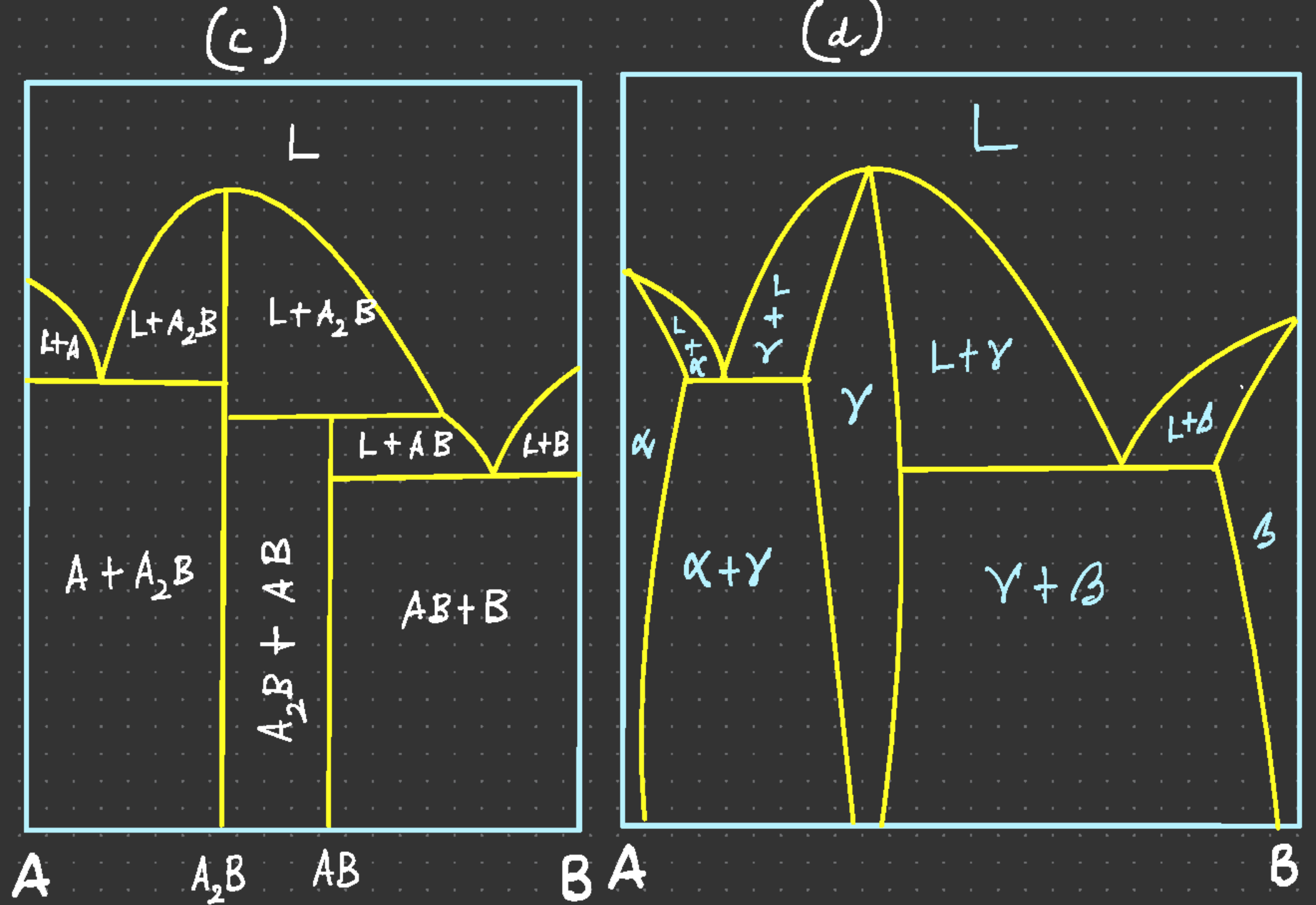
V. Presence of stable, Stoichiometric / non-Stoichiometric compounds

(a)

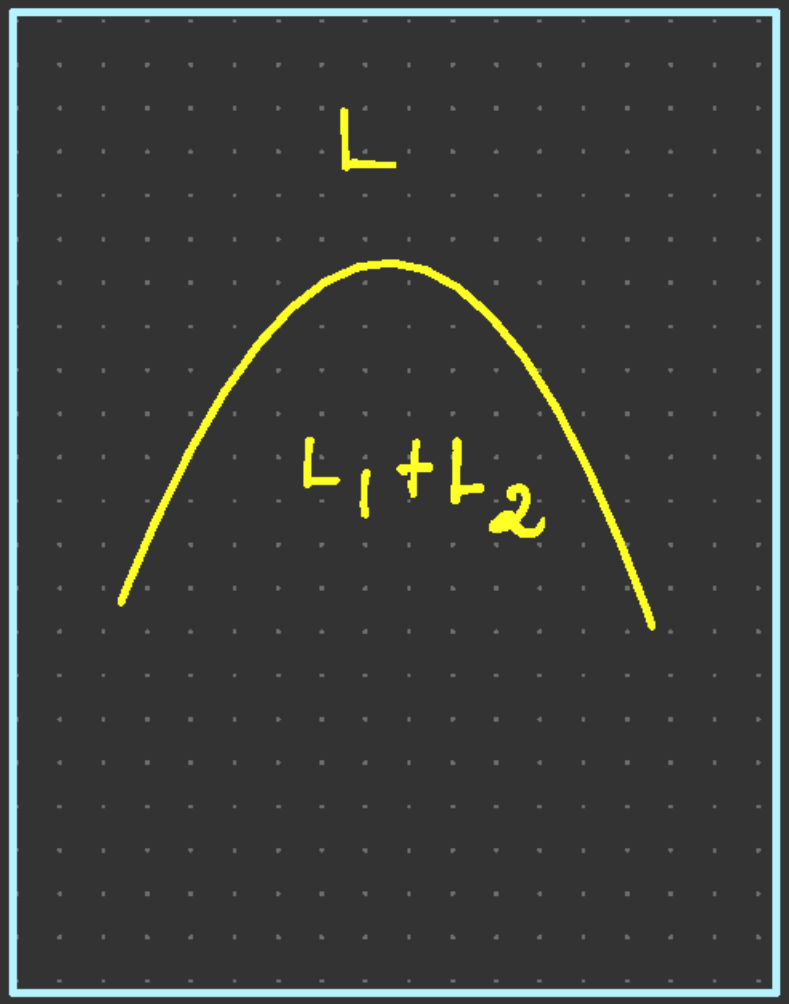


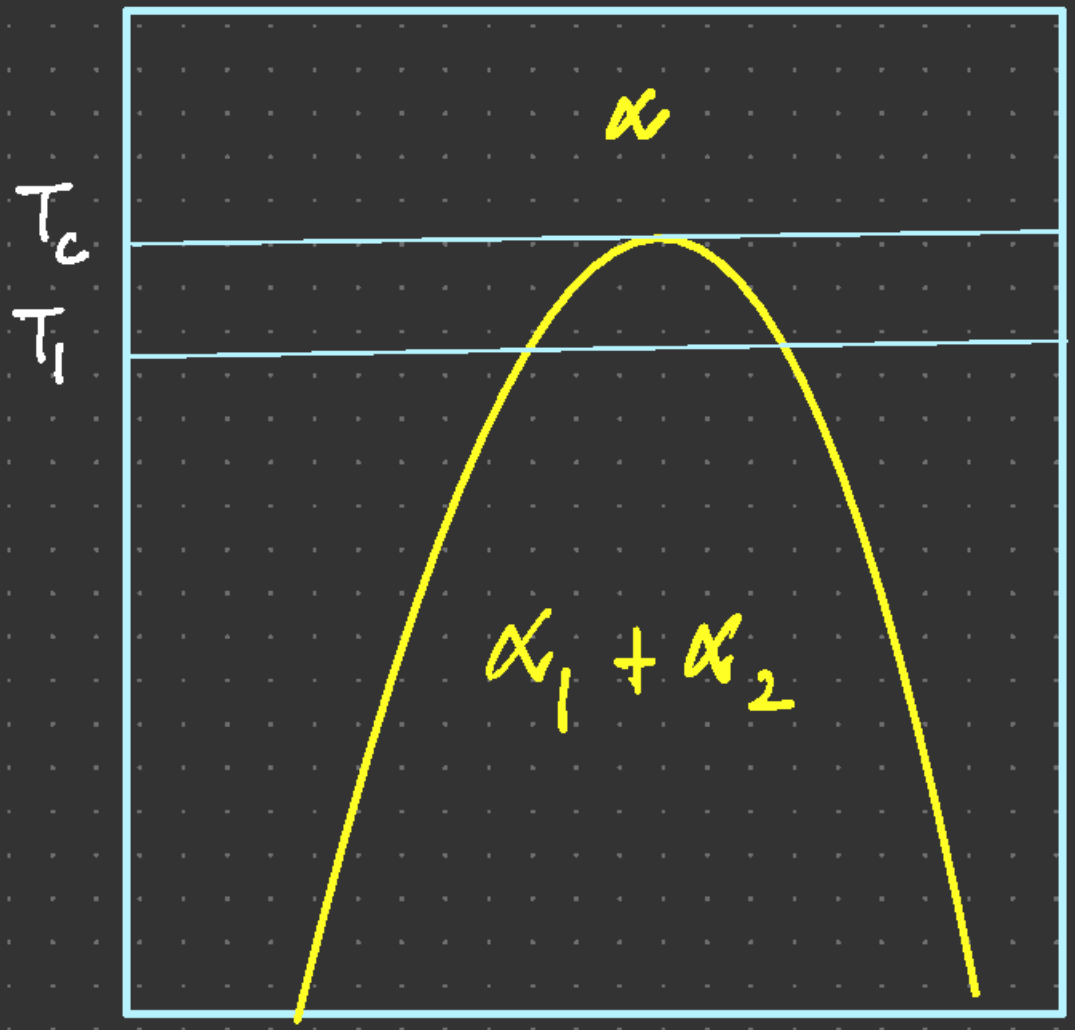
(b)

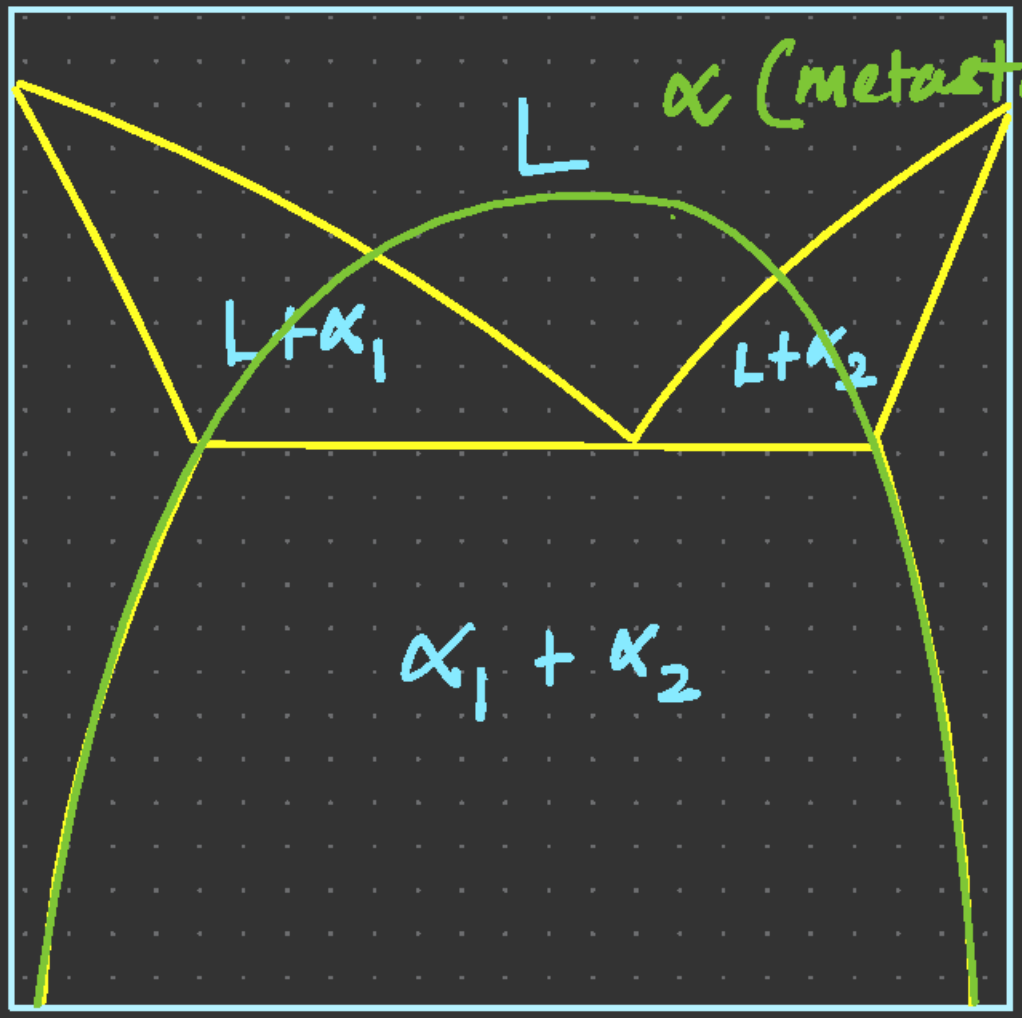



(c)
L
L+A
L+A2B
L+A2B
L+AB
L+B
A+A2B
A2B+AB
AB+B
A
A2B
AB
B
(d)
L
L+α
L+γ
γ
L+γ
L+β
α
α+γ
γ+β
β
A
B

VI. Phase separation – Miscibility gap







Metastable miscibility gap

Free Energy - Composition Diagrams

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

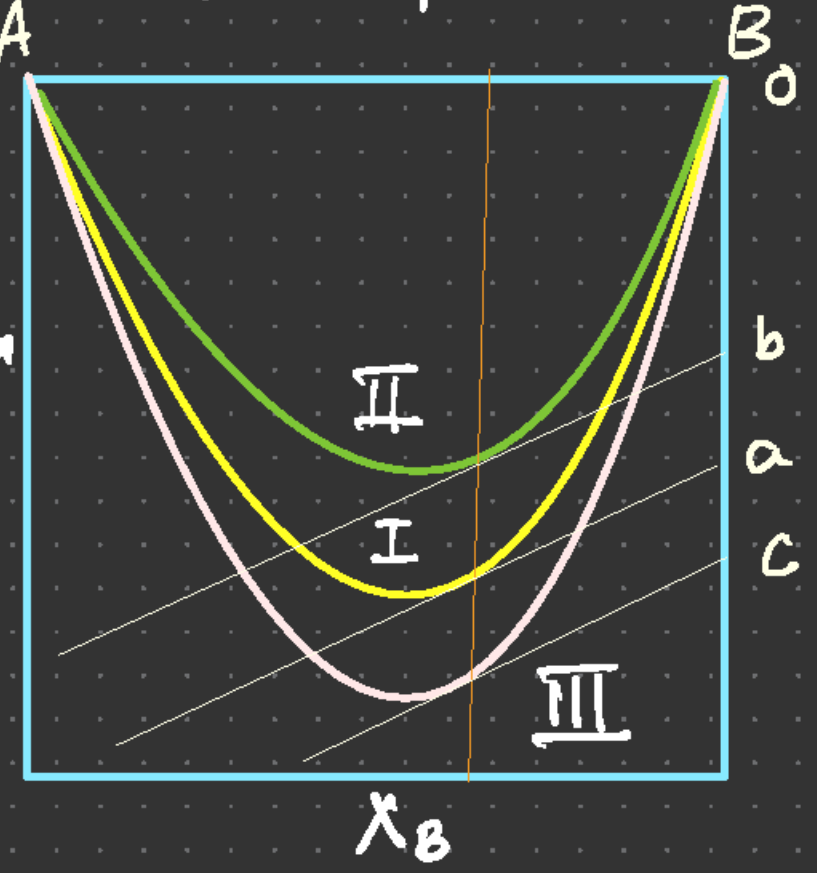
Non-ideal

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

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

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

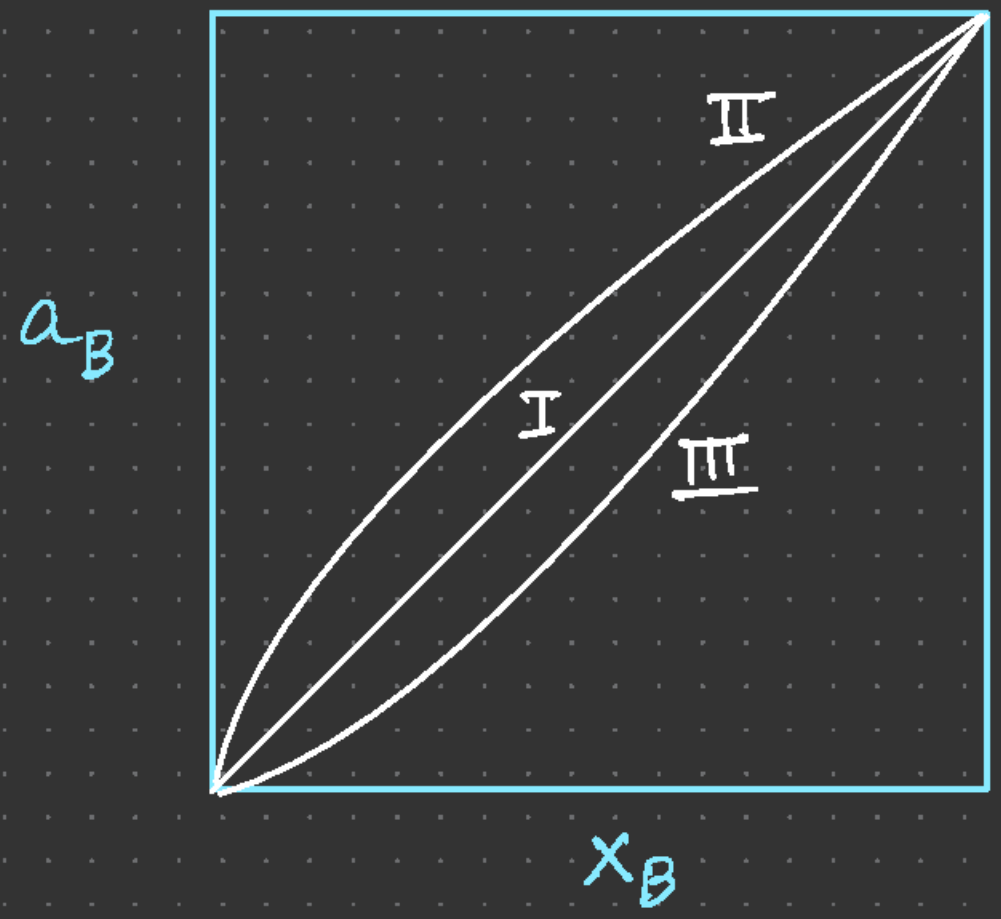
I $\gamma_i = 1$ $a_i = x_i$

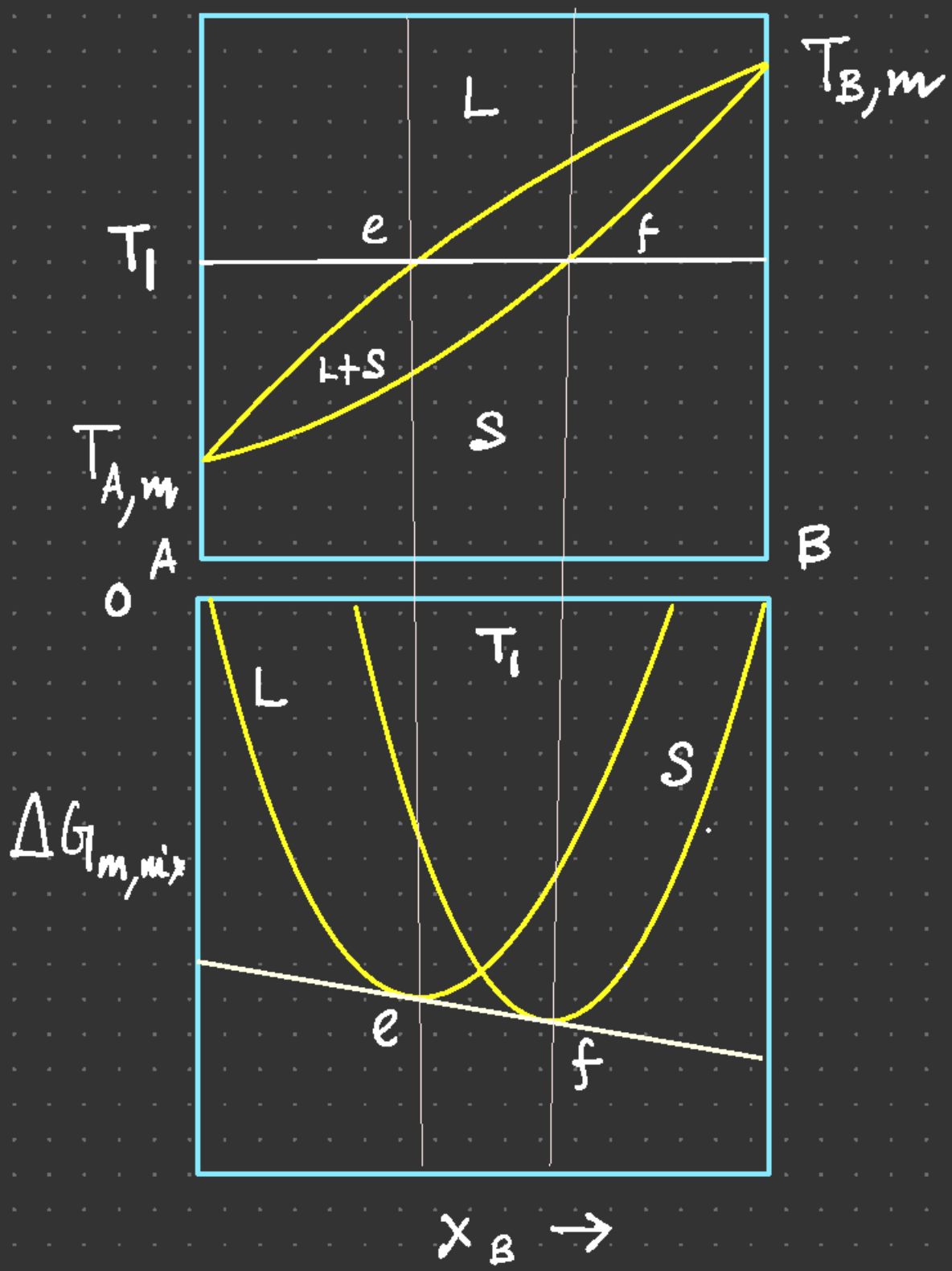


$$\left| B_b = \Delta\bar{G}_B = RT \ln a_B \ (II) \right|$$

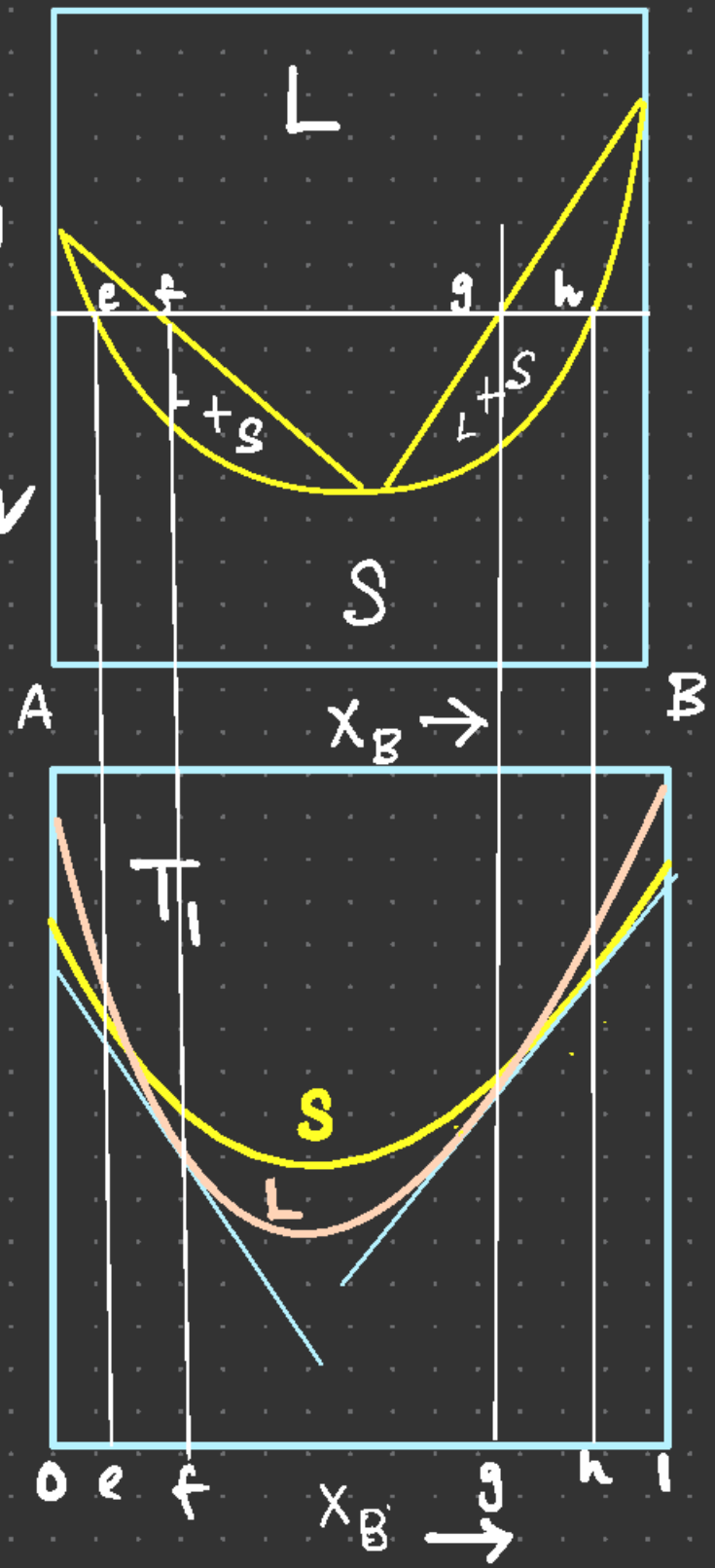
$$< \left| B_a = \Delta\bar{G}_B = RT \ln X_B \ (I) \right|$$

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



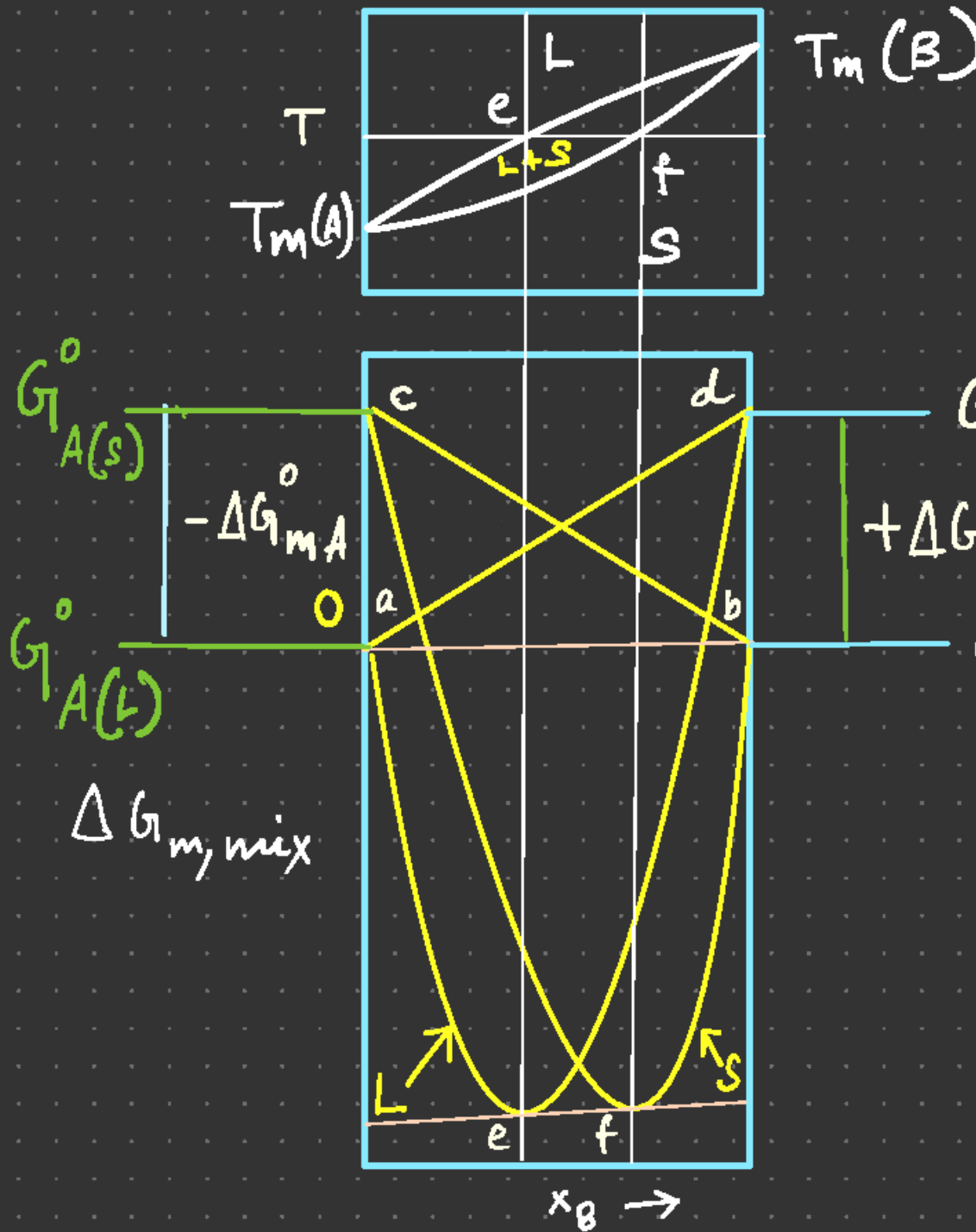

L
$T_{B,m}$
T_l
e
f
L+S
S
$T_{A,m}$
A
B
O
L
T_l
S
$\Delta G_{m,mix}$
e
f
$x_B \rightarrow$

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



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

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

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

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

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

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

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

$T < T_{mB}$

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

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 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

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

— 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

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

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

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

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

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

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

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

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

Now,

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

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

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

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

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)

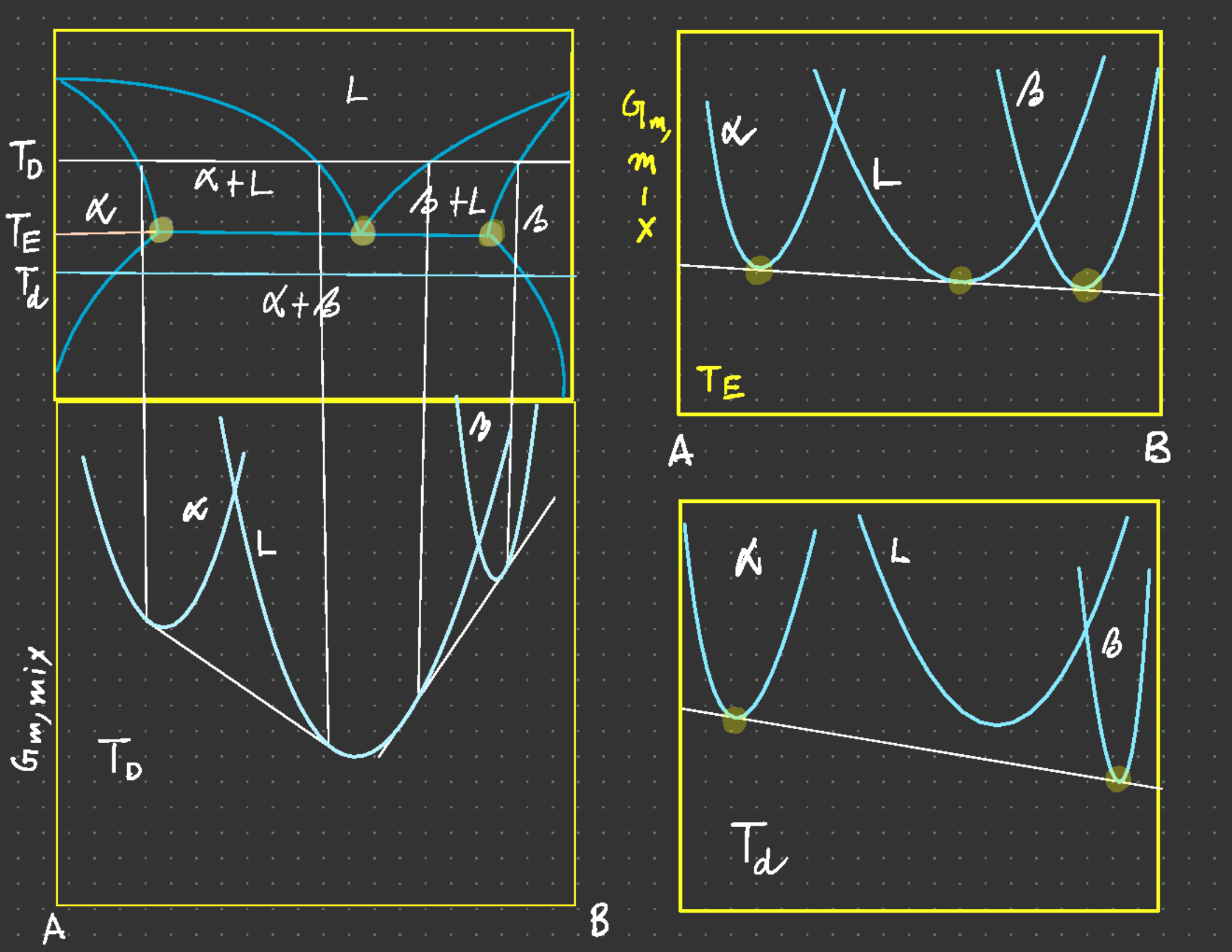
$$1 - X_{AL} = (1 - X_{AS}) \exp\left(\frac{-\Delta G^{\circ}_{m_B}}{RT}\right)$$

— (4)

From (3) and (4)

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

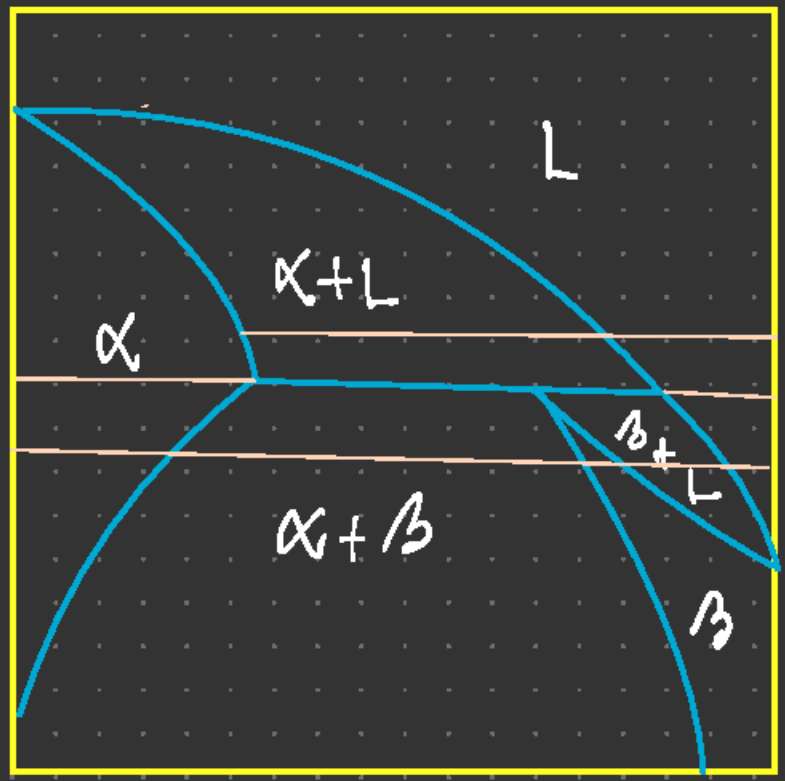
$$X_{AL} = \frac{\left[1 - \exp\left(-\frac{\Delta G_{mB}^{\circ}}{RT}\right)\right] \exp\left(-\frac{\Delta G_{mA}^{\circ}}{RT}\right)}{\exp\left(-\frac{\Delta G_{mA}^{\circ}}{RT}\right) - \exp\left(-\frac{\Delta G_{mB}^{\circ}}{RT}\right)}$$


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

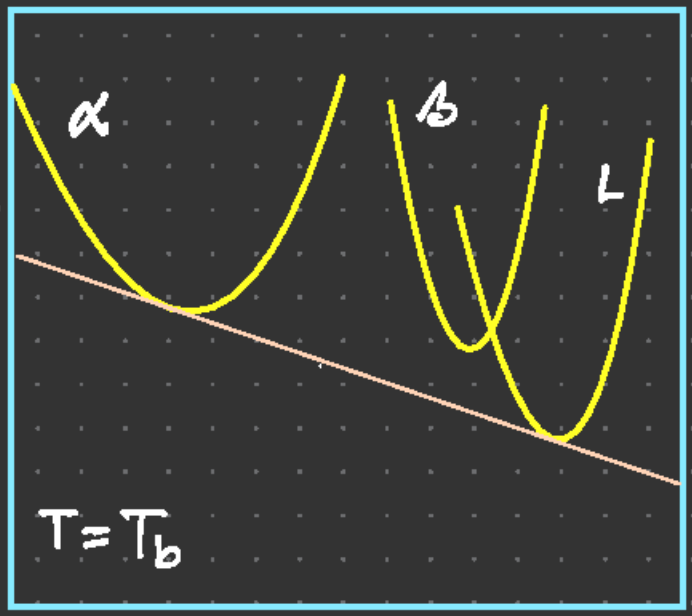
Ab T_E,

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

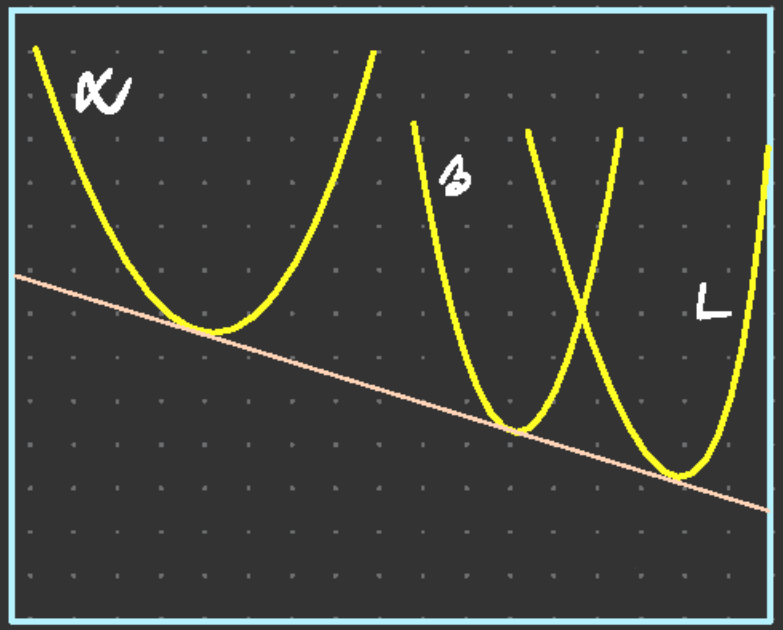
$$\mu_B^L = \mu_B^\alpha = \mu_B^\beta$$



$\Delta G_{m,mix}$



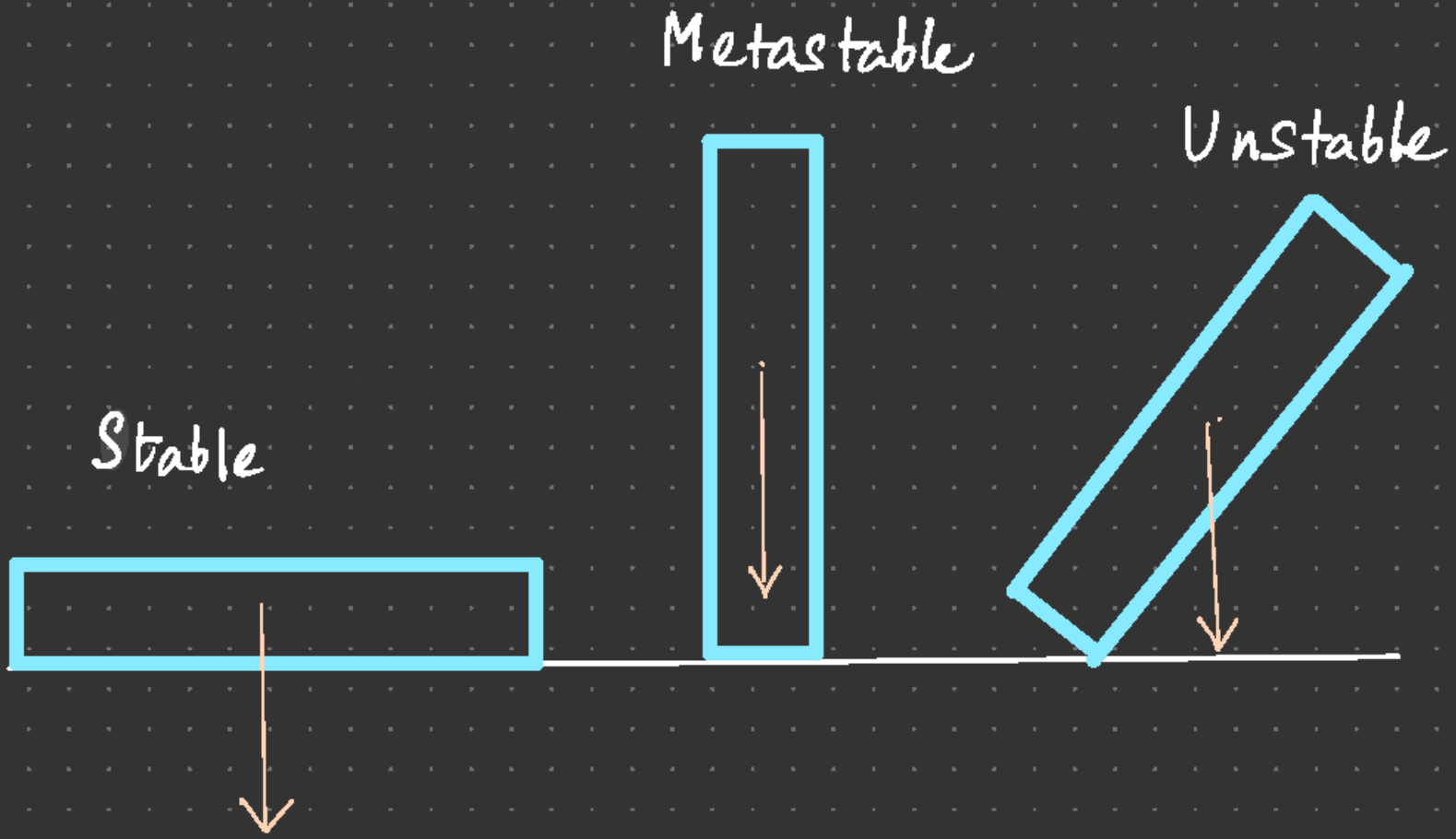
$\Delta G_{m,mix}$

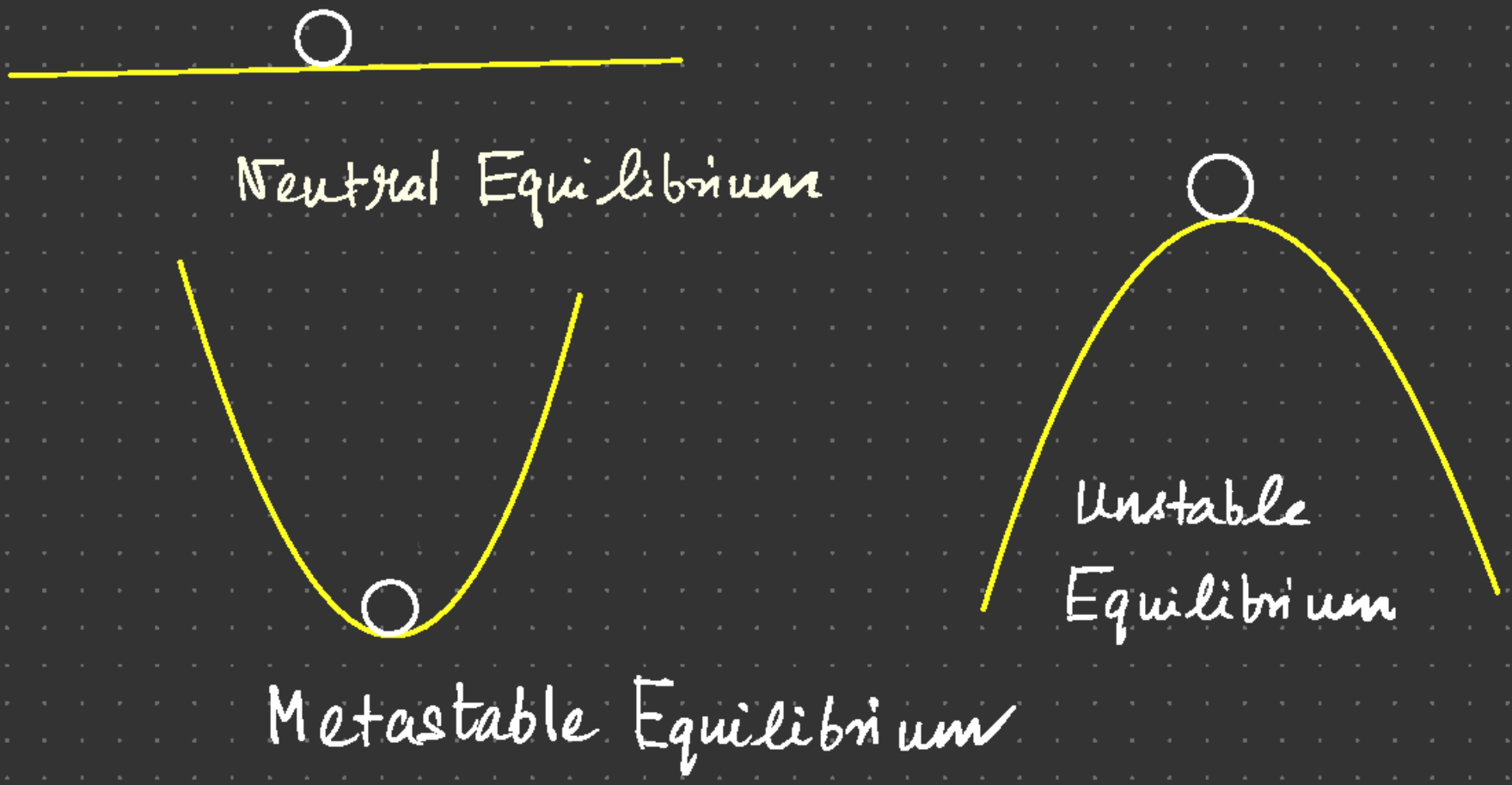


L+α → β

Criteria for phase stability

Mechanical Analogue




Neutral Equilibrium
Unstable Equilibrium
Metastable Equilibrium

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

$x_A + x_B = 1$

$(1-x) \quad x$

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

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

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

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

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

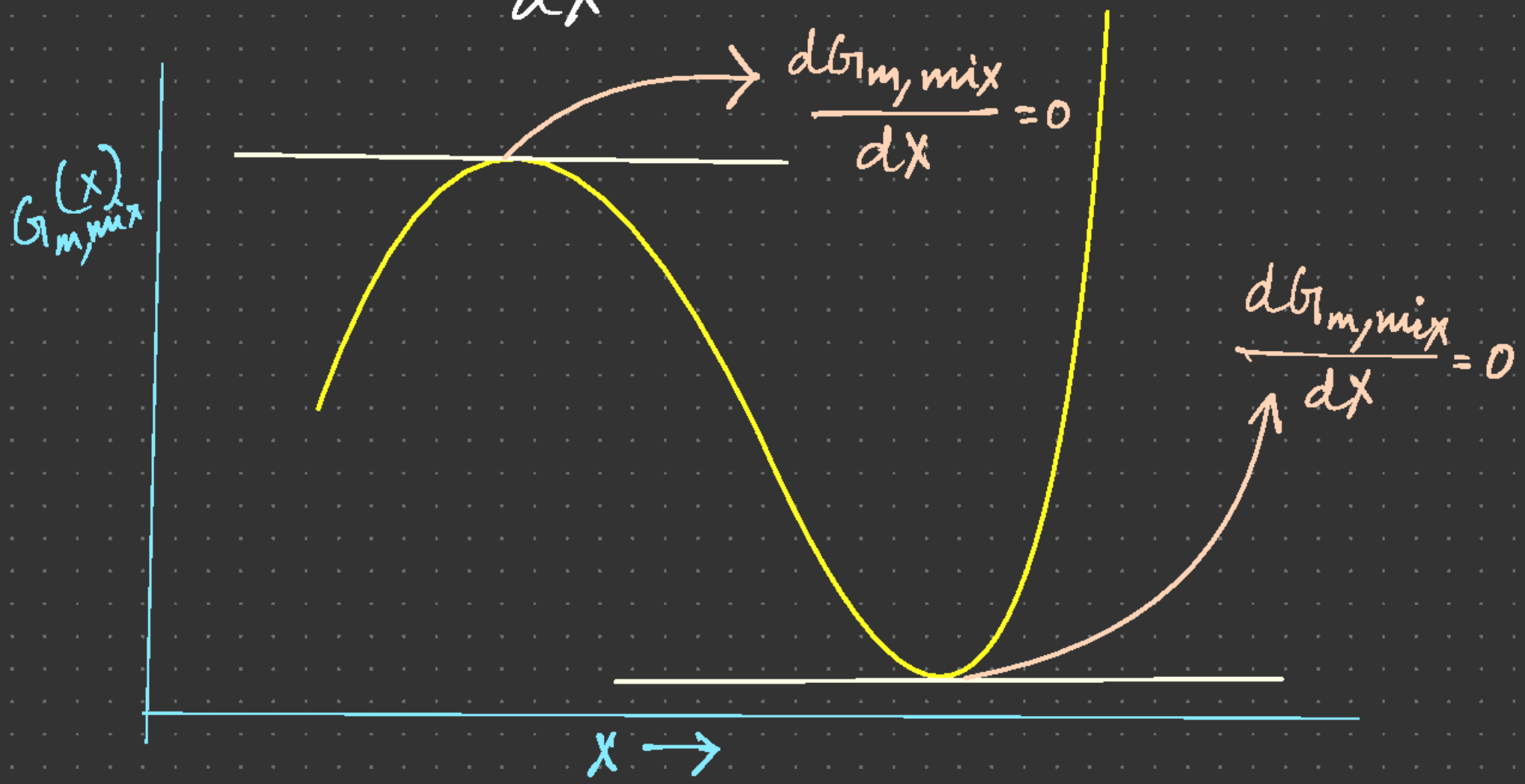
$$\frac{d^2G_{m,mix}}{dX^2} = RT\left\{\frac{1}{X} + \frac{1}{1-X}\right\} - 2\omega$$

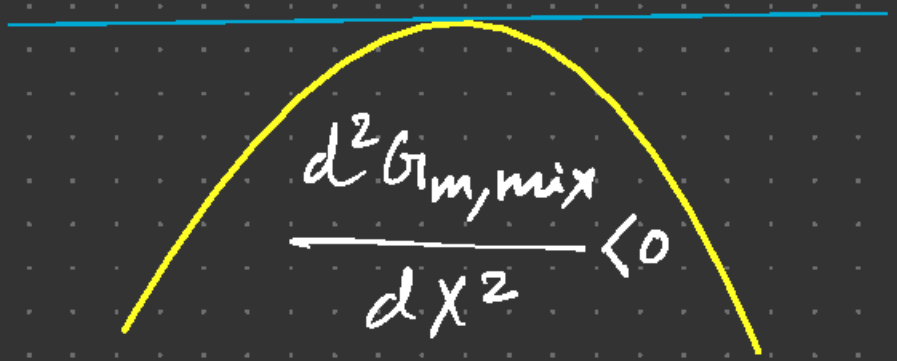
$$\frac{d^3G_{m,mix}}{dX^3} = RT\left\{\frac{1}{(1-X)^2} - \frac{1}{X^2}\right\}$$

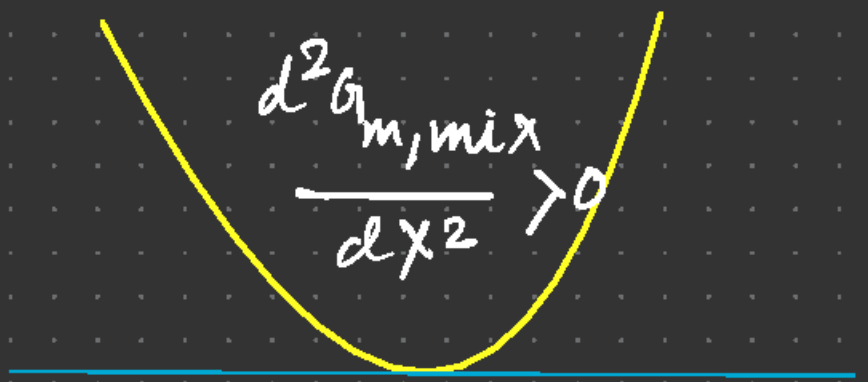
When $X = 0.5$

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

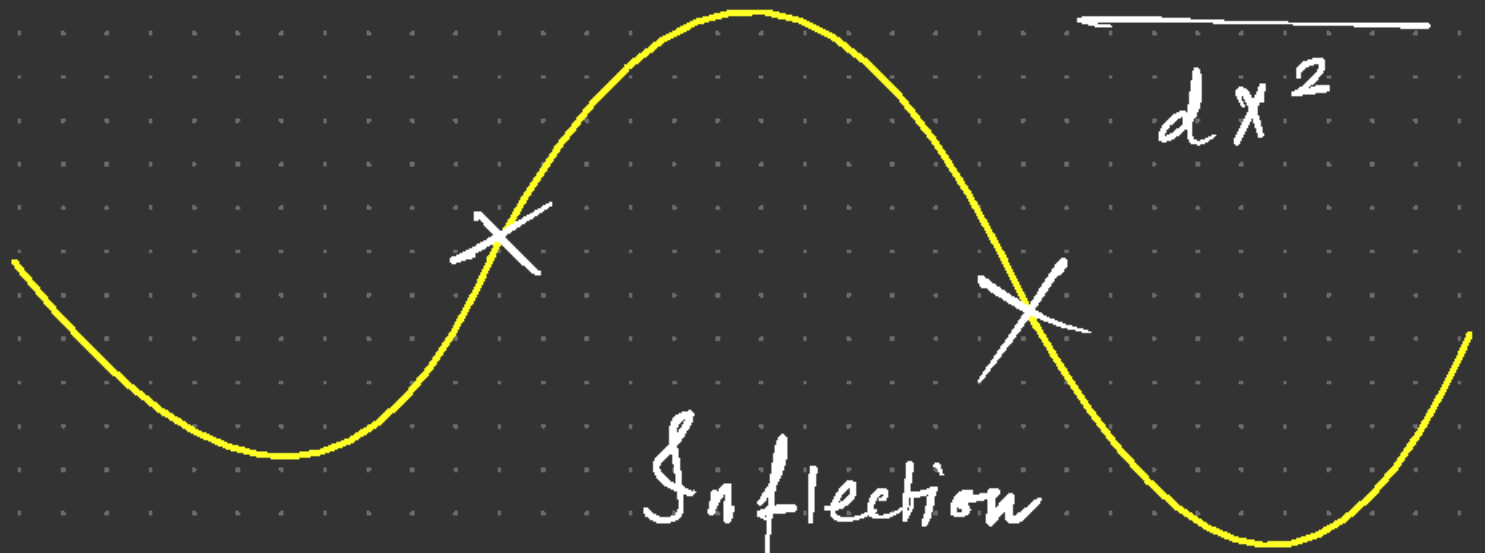
$$\frac{d^3 G_{m,mix}}{dX^3} = 0$$







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 $X = 0.5$

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

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

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

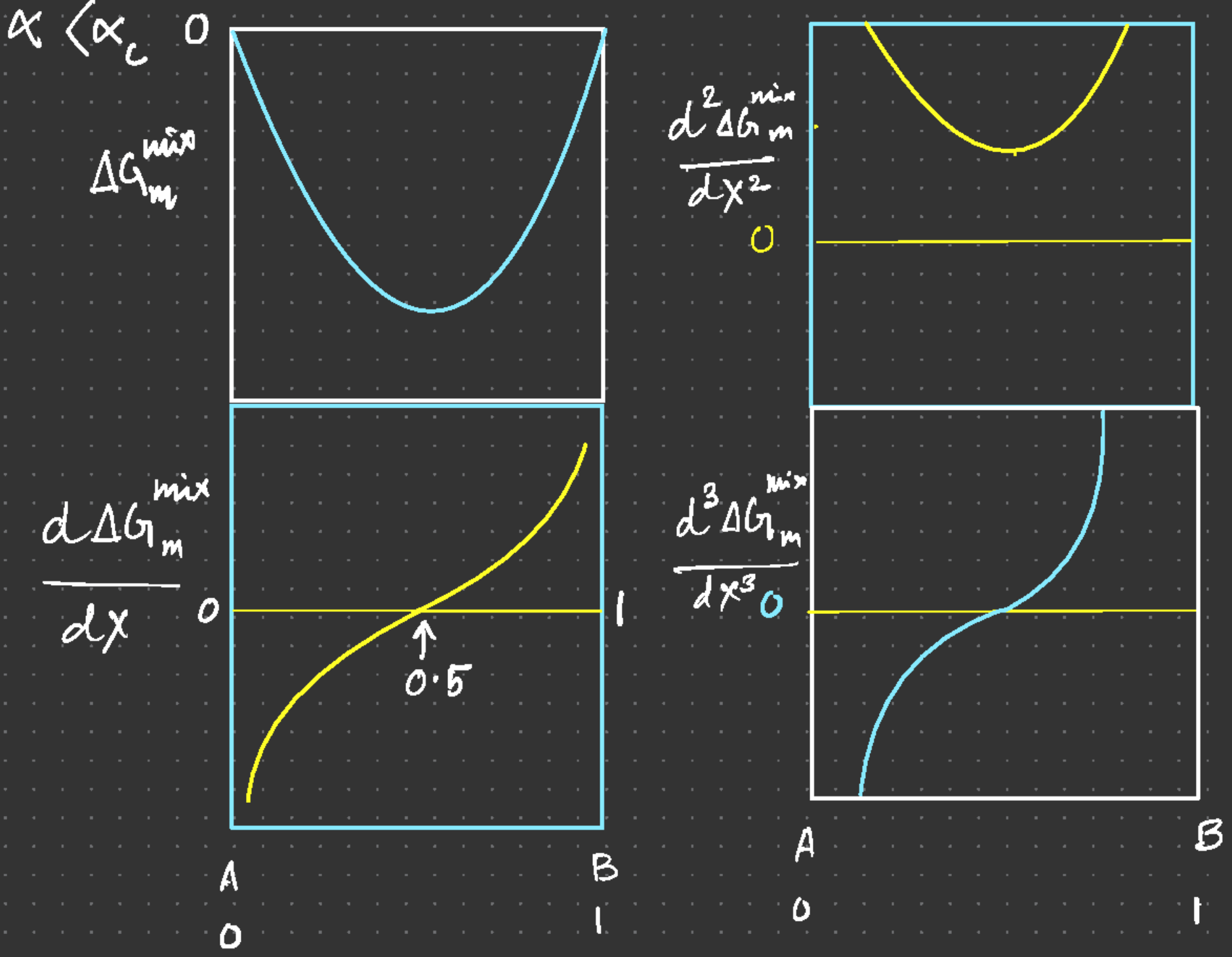
$$T_c = \frac{\omega}{2R}$$

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

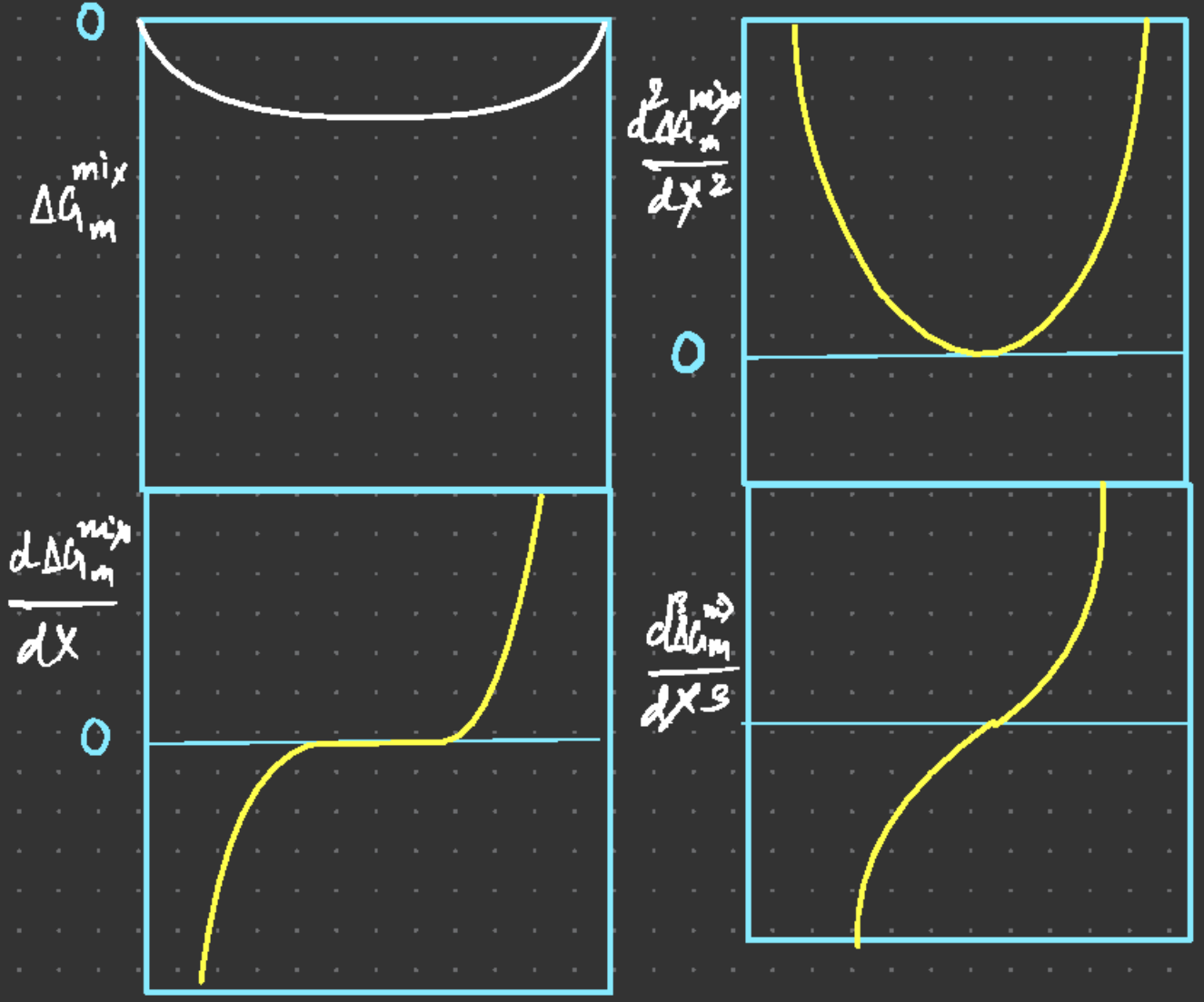
$\alpha > \alpha_c$ phase separation

$\alpha = \alpha_c$ Critical

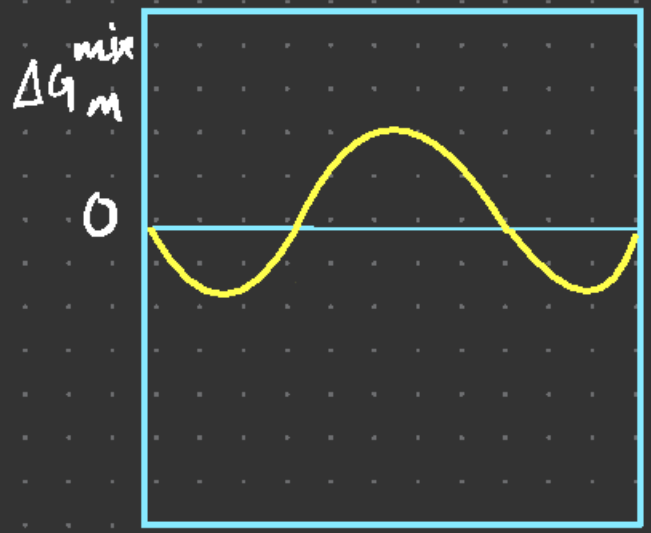
$\alpha < \alpha_c$ Homogeneous single phase

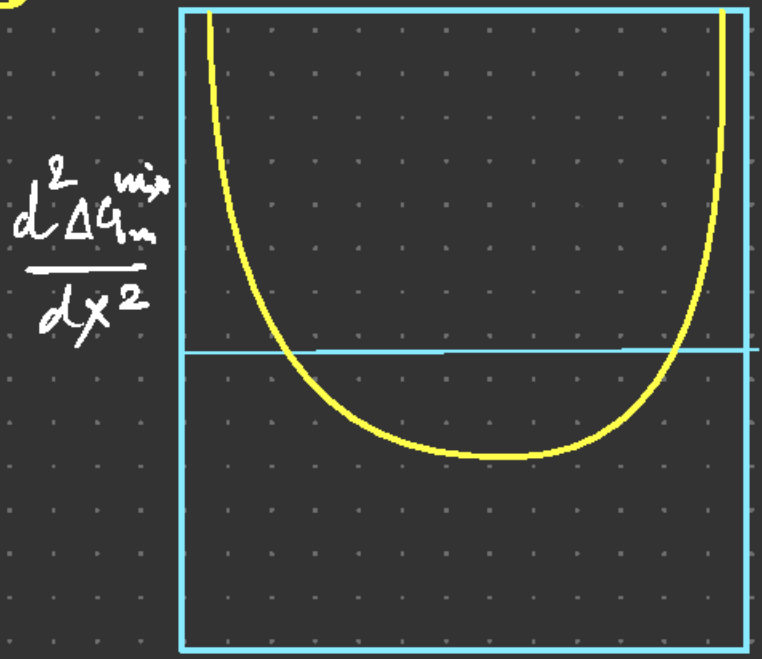

$\alpha < \alpha_c$
0
ΔG_m^{mix}
$\frac{d\Delta G_m^{mix}}{dx}$
0
0·5
1
A
B
0
1
$\frac{d^2\Delta G_m^{mix}}{dx^2}$
0
$\frac{d^3\Delta G_m^{mix}}{dx^3}$
0
A
B
0
1

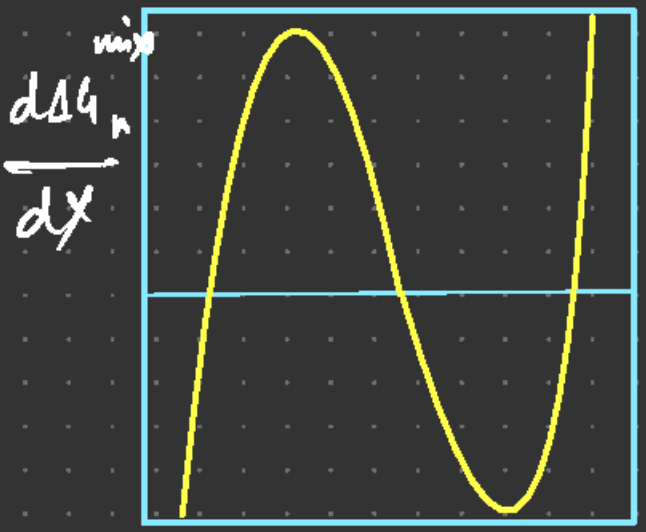
$\alpha = \alpha_c$

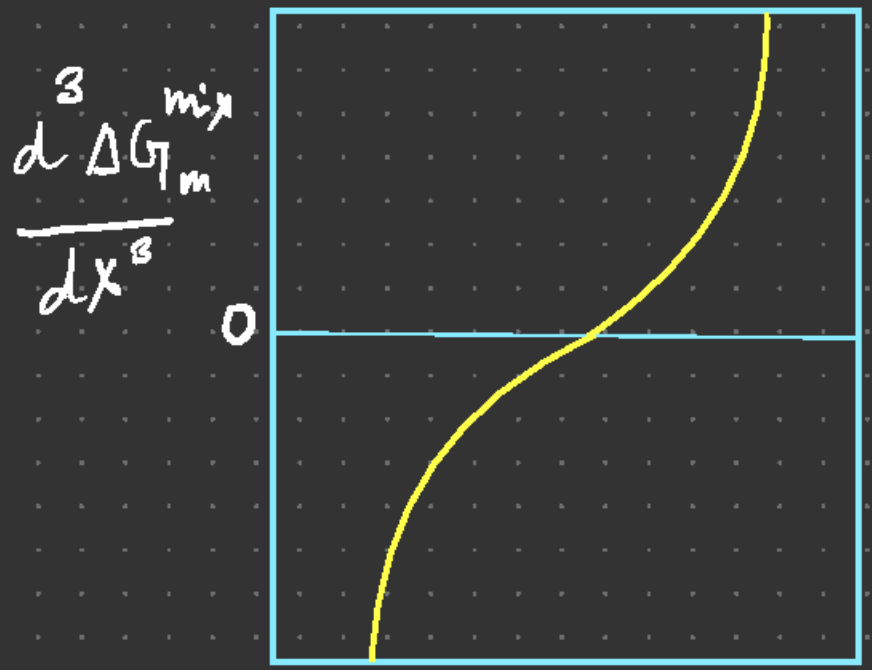


$\alpha > \alpha_c$









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

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

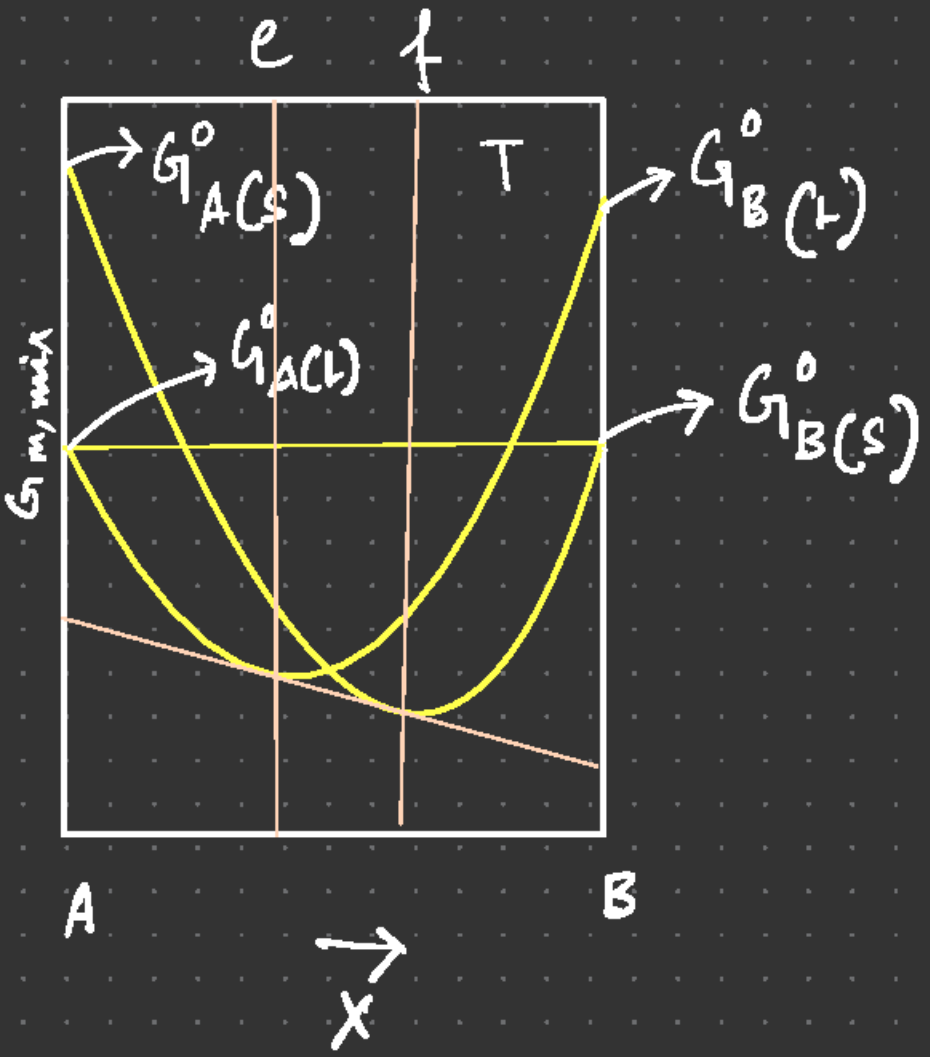
$$\frac{d\Delta\bar{G}_B^{mix}}{dx_B} = x_A\frac{d^2\Delta G_m^{mix}}{dx_B^2} = \frac{RT}{a_B}\frac{da_B}{dx_B}$$

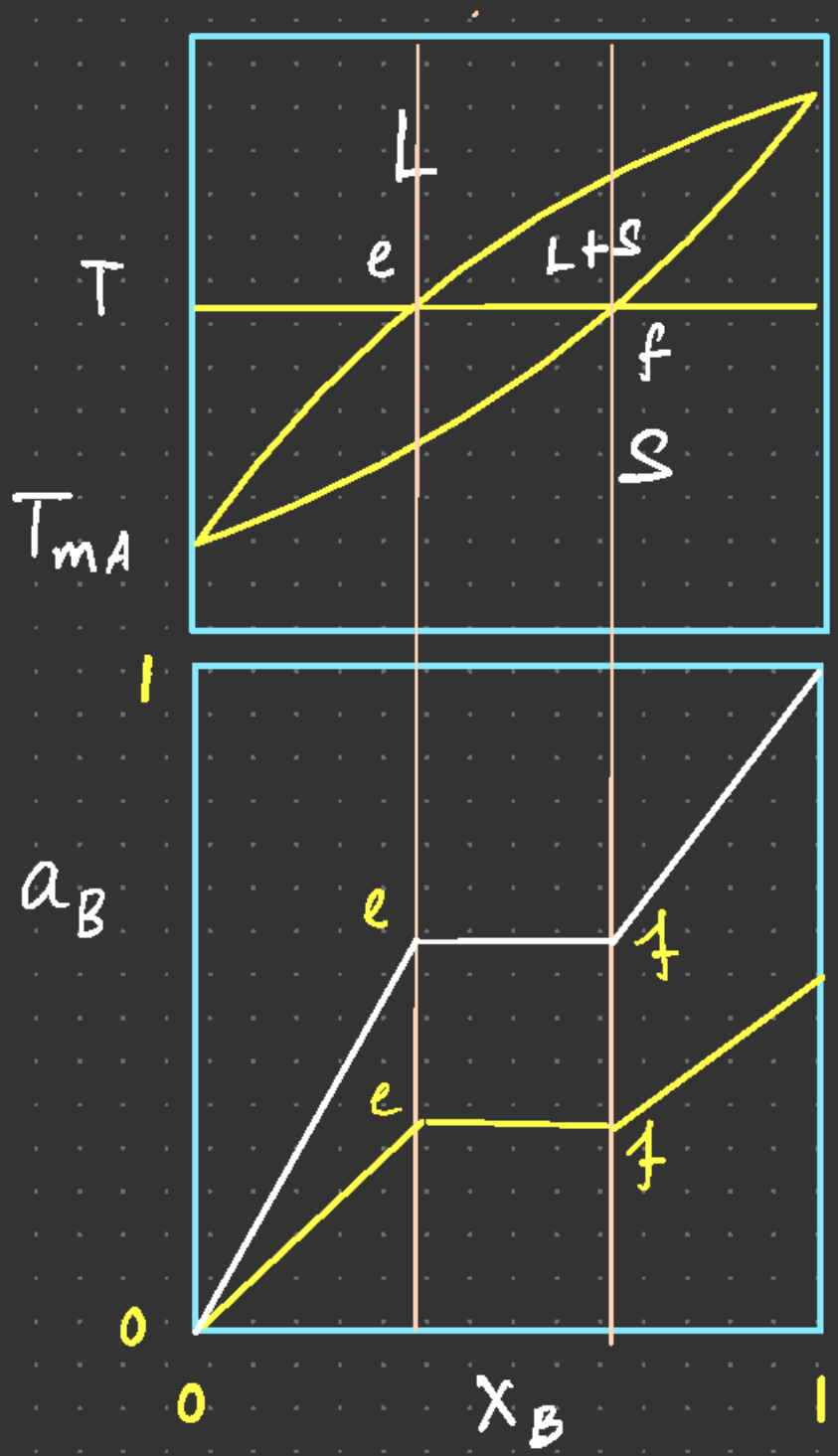
$$\mu_B^L = \mu^{\circ}_{B(L)} + RT \ln a_{B(L)}$$

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

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

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





(Solid as standard state)

(Liquid as standard state)