Ideal & Real Solutions

Quasichemical models

Solutions

0. Ideal vs. Real Solutions
1. Colligative properties
2. Quasichemical Models

Ideal dilute Solutions

$[Solute] \to 0$ – Solvent obeys Raoult's law

$[Solvent] \to 1$ – Solute obeys Henry's law

$a_A = x_A \qquad a_B = \gamma_0 x_B$

See the table

Mixture of acetone (CH_3COCH_3) (A) and chloroform ($CHCl_3$) (C) at 35°C

x_C	0	0·2	0·4	0·6	0·8	1
p_C (kPa)	0	4·7	11	18·9	26·7	36·4
p_A (kPa)	46·3	33·3	23·3	12·3	4·9	0

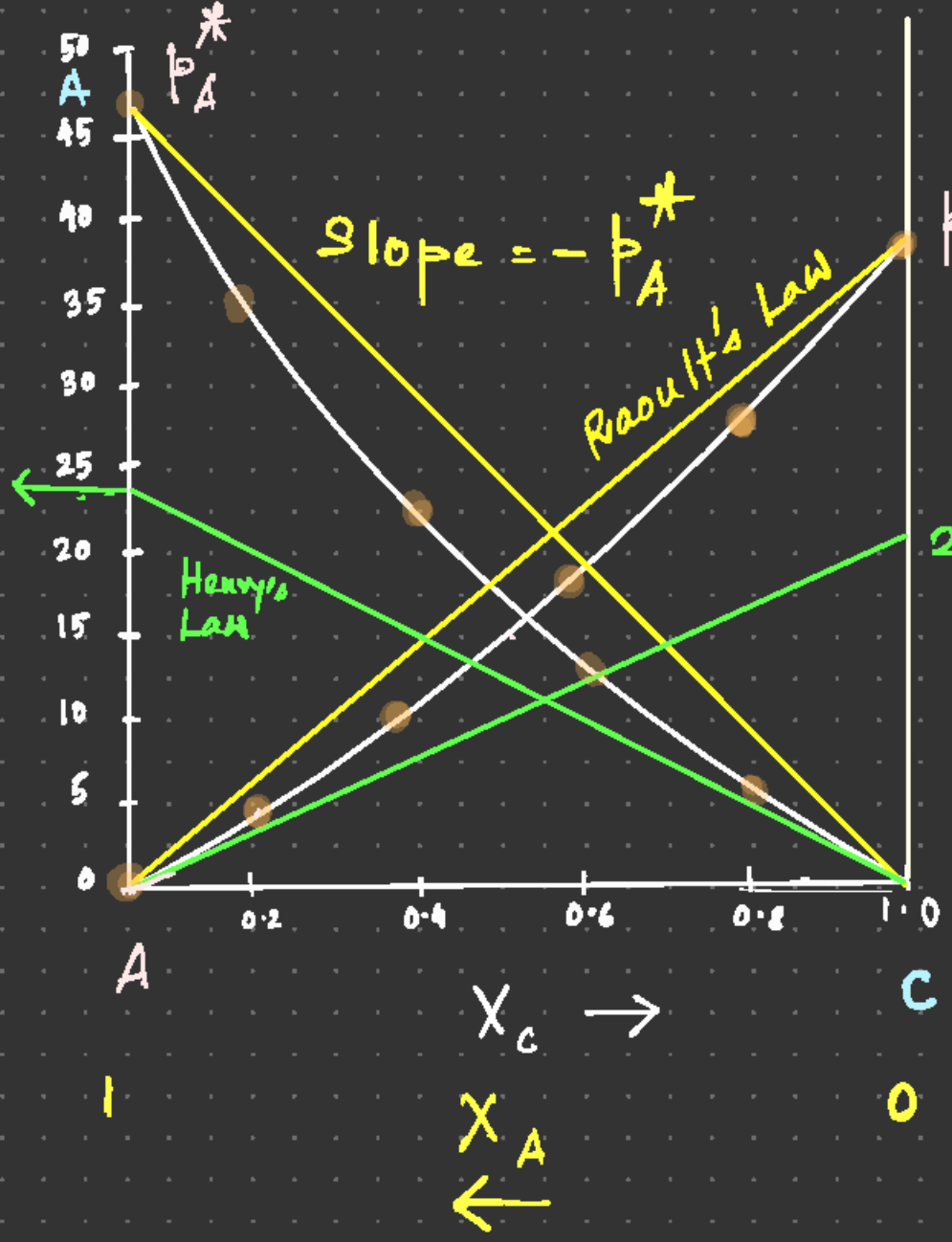
$p_C = \gamma_C^{\circ} x_C \quad \lim x_C \to 0$

Raoult's law

$p_A = p_A^* x_A$

$= p_A^* (1 - x_C)$

$p_C^* \quad p_C = p_C^* x_C$



$p \uparrow$

$\gamma_A^{\circ} = 23.3$

$22.0 = \gamma_C^{\circ}$

Partial pressure of oxygen in water (25°C)

$\rho_{H_2O} = 1\ kg/l$ $\qquad p_{O_2} = 21\ kPa$

Henry's Law contant (25°C or 298 K)

$p_B = k_B b_B \qquad k_{O_2} = 7.9 \times 10^4\ kPa\ kg\ mol^{-1}$

b_B (molality)

$$b_{O_2} = \frac{p_{O_2}}{k_{O_2}} = 2.9 \times 10^{-4}\ mol/kg$$

$$[O_2] = b_{O_2} \times \rho_{H_2O} = 0.29\ milli\ mol/l$$

Ideal Solutions

$a_A = \gamma_A X_A \qquad \gamma_A = 1$

Consider a binary solution

$\mu_A^* = \mu_A^\circ$ (Pure state = Standard state)

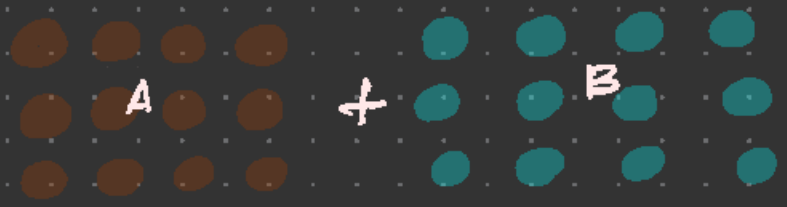
$\mu_B^* = \mu_B^\circ$ (Pure state = Standard State)

$$\overline{G}_A^* = \overline{G}_A^\circ = \mu_A^* = \mu_A^\circ$$

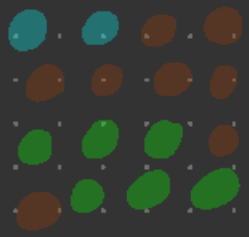
$$\overline{G}_B^* = \overline{G}_B^\circ = \mu_B^* = \mu_B^\circ$$

Before MIXING

At given T, P



$$G^i = n_A \mu_A^\circ + n_B \mu_B^\circ$$



After MIXING

$$G^f = n_A \mu_A + n_B \mu_B$$

$$\mu_A = \mu_A^\circ + RT \ln a_A$$

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

$$a_A = X_A \\ a_B = X_B \Big\} \text{ Ideal}$$

$$n_A = n X_A \\ n_B = n X_B$$

$$G^f = n_A \left[\mu_A^\circ + RT \ln X_A\right] + n_B \left[\mu_B^\circ + RT \ln X_B\right]$$

$$\Delta G_{mix} = G^f - G^i$$

$$n = n_A + n_B = n_A RT \ln X_A + n_B RT \ln X_B$$

↓ mole no. of A ; ↓ mole no. of B

$$= n X_A RT \ln X_A + n X_B RT \ln X_B$$

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

↓ total mole number of component A + B

$$\therefore \quad \Delta G_{m,mix} = \frac{\Delta G_{mix}}{n} = RT\left[x_A \ln x_A + x_B \ln x_B\right]$$

For a solution with c components

$$\Delta G_{m,mix} = RT\left[\sum_{i=1}^{c} x_i \ln x_i\right]$$

$$\Delta S_{m,mix} = -\left(\frac{\partial \Delta G_{m,mix}}{\partial T}\right)_{p,n}$$

$$= -R \sum_{i=1}^{c} x_i \ln x_i > 0$$

$$\Delta H_{m,mix} = \Delta G_{m,mix} + T \Delta S_{m,mix}$$

$$= RT \sum_{i=1}^{c} x_i \ln x_i - RT \sum_{i=1}^{c} x_i \ln x_i$$

$$= 0$$

$$\Delta V_{m,mix} = \left(\frac{\partial \Delta G_{m,mix}}{\partial p}\right)_{T,n} = 0$$

Real Solutions

$$G^f = n_A\left(\mu_A^\circ + RT\ln a_A\right) + n_B\left(\mu_B^\circ + RT\ln a_B\right)$$

$$a_A = \gamma_A X_A$$
$$a_B = \gamma_B X_B$$

$$\Delta G_{mix}^{Real} = nRT\left(X_A \ln a_A + X_B \ln a_B\right)$$

$$G^f - G^i = nRT\left(X_A \ln \gamma_A + X_A \ln X_A + X_B \ln \gamma_B + X_B \ln X_B\right)$$

$$= nRT\left(X_A \ln X_A + X_B \ln X_B\right) + nRT\left(X_A \ln \gamma_A + X_B \ln \gamma_B\right)$$

$$\Delta G^{real}_{m,mix} = \frac{\Delta G^{real}_{mix}}{n}$$

$$= RT\left(X_A \ln X_A + X_B \ln X_B\right) + RT\left(X_A \ln \gamma_A + X_B \ln \gamma_B\right)$$

$$= \Delta G^{ideal}_{m,mix} + \Delta G^{xs}_{m,mix}$$

$$\Delta G^{xs}_{m,mix} = \Delta G^{real}_{m,mix} - \Delta G^{ideal}_{m,mix}$$

$$\Delta S^{xs}_{m,mix} = \Delta S^{real}_{m,mix} - \Delta S^{ideal}_{m,mix}$$

$$\Delta H^{xs}_{m,mix} = \Delta H^{real}_{m,mix} - \Delta H^{ideal}_{m,mix}$$

A-A
B-B
C-C
A-C
B-C
A-B

$$= \Delta H^{real}_{m,mix} - 0$$

$$= \Delta H^{real}_{m,mix} = \Delta H^{observed}_{m,mix}$$

due to A-A, B-B, A-B interactions

$$\Delta S^{xs}_{m,mix} = \Delta S^{real}_{m,mix} - \Delta S^{ideal}_{m,mix}$$

$$= \Delta S^{real}_{m,mix} - \left(-R \sum_{i=1}^{c} x_i \ln x_i\right)$$

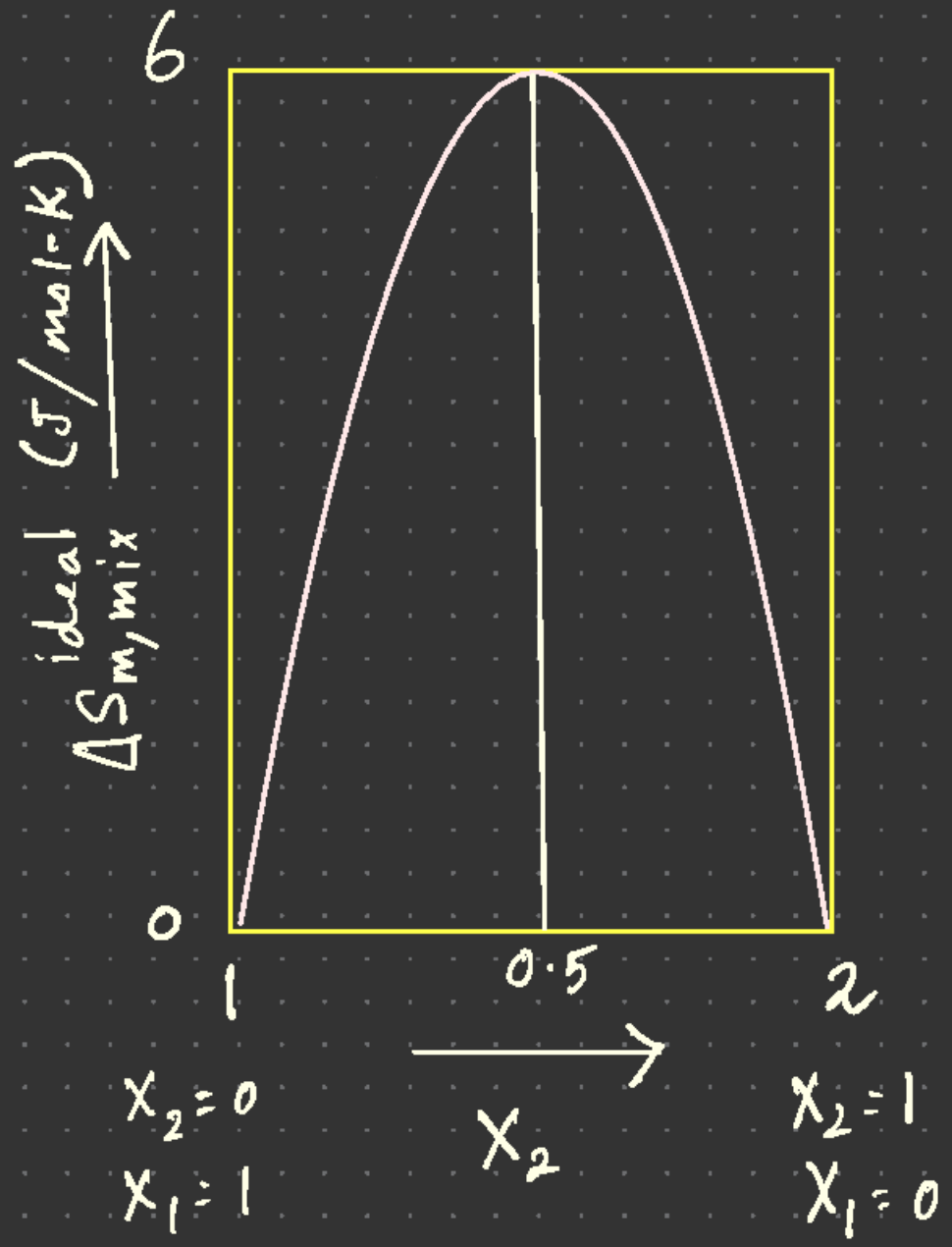
Assume $\Delta S^{real}_{m,mix} = \Delta S^{ideal}_{m,mix}$

$$= -R \sum_{i=1}^{c} X_i \ln X_i$$

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

$$\Delta S^{xs}_{m,mix} = 0$$

Regular Solution



At $X = 0.5$

$$\Delta S^{real}_{m,mix} = -R \ln \frac{1}{2}$$

$$= R \ln 2$$

$$\Delta H^{xs}_{m,mix} = h R T x_i x_j$$

h is a parameter

Ideal solution: $\Delta H^{xs}_{m,mix} = 0$

Binary Solution $A-B$

$$\Delta H^{real}_{m,mix} = \Delta H^{xs}_{m,mix} = h R T x_A x_B$$

$$\Delta S^{xs}_{m,mix} = 0$$

$$\Delta S^{real}_{m,mix} = \Delta S^{ideal}_{m,mix} = -R\left(x_A \ln x_A + x_B \ln x_B\right)$$

> 0

$A-A$ $\quad$ $A-B$ $\quad$ $B-B$

$A-B$ = $B-A$

Regular Solution – Model of a real solution

$$\Delta G_{m,mix} = \Delta H_{m,mix} - T\Delta S_{m,mix}$$

$$= \Delta H^{xs}_{m,mix} - T\Delta S^{ideal}_{m,mix}$$

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

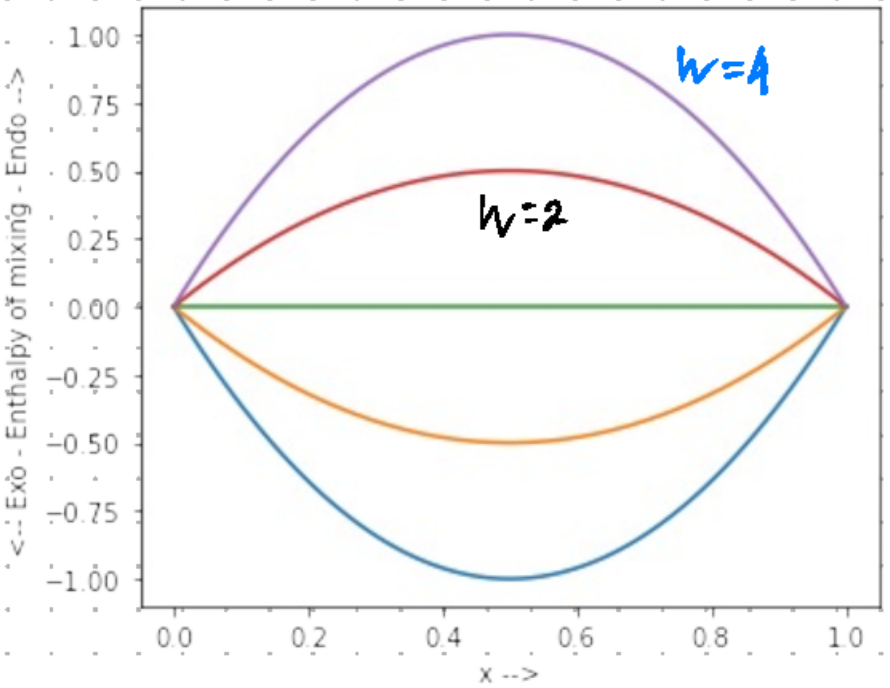
Normalize both sides with RT

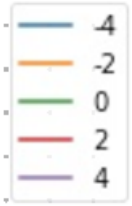
$$\frac{\Delta G^{regular}_{m,mix}}{RT} = h\,x_A x_B + \left(x_A \ln x_A + x_B \ln x_B\right)$$

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

Let $x = x_B$

$x_A = 1 - x$





$\Delta H_{m,mix} > 0$: Endothermic

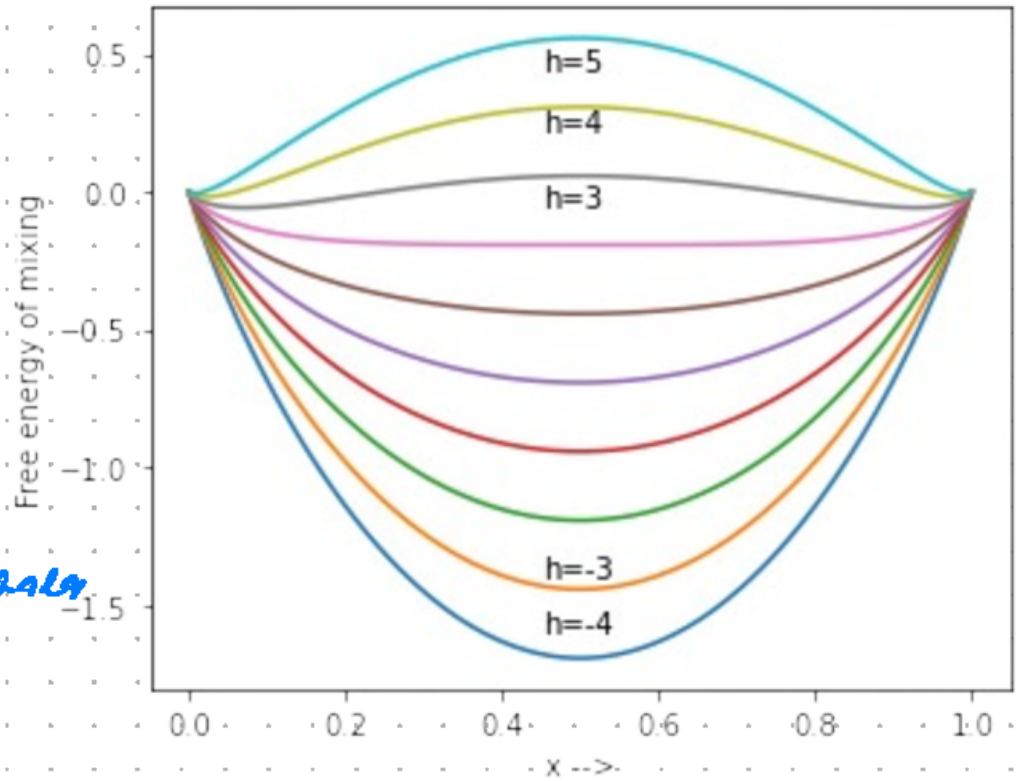
$\Delta H_{m,mix} < 0$: Exothermic

$\Delta G_{m,mix} > 0$

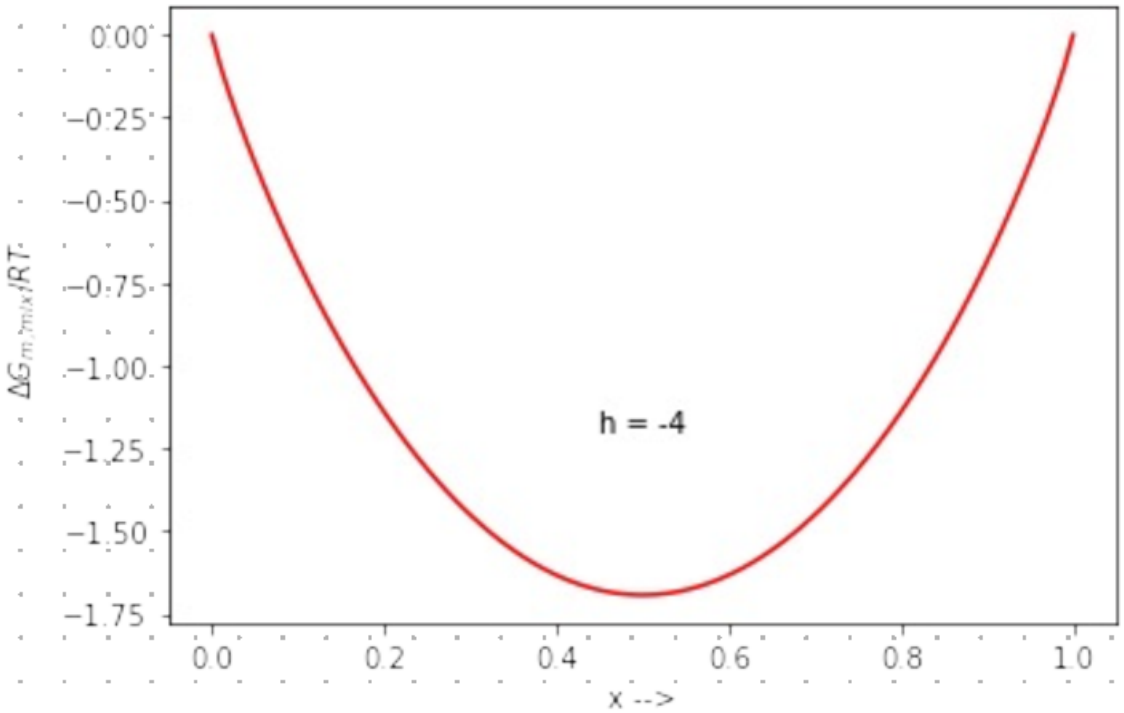
When $h > 2$,

System Separates

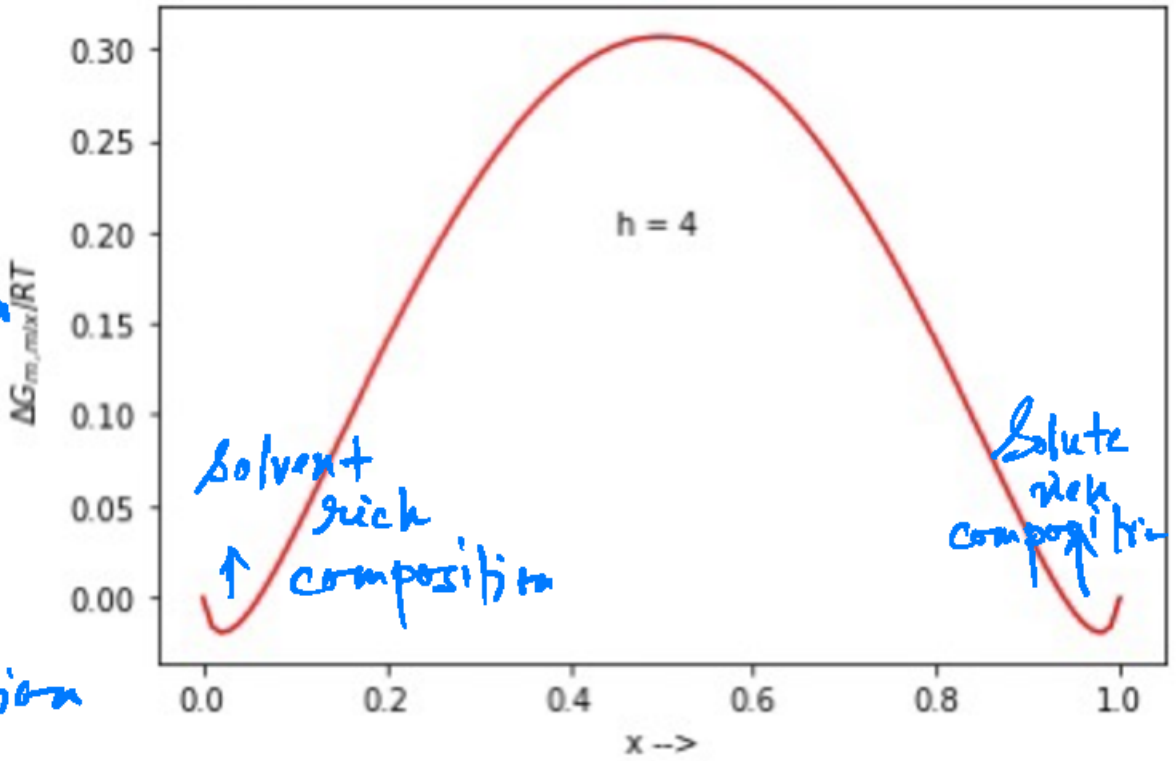
Spontaneously into two phases







Solute - Solute and
Solvent - Solvent interaction
are more
favorable than
solute - Solvent interaction



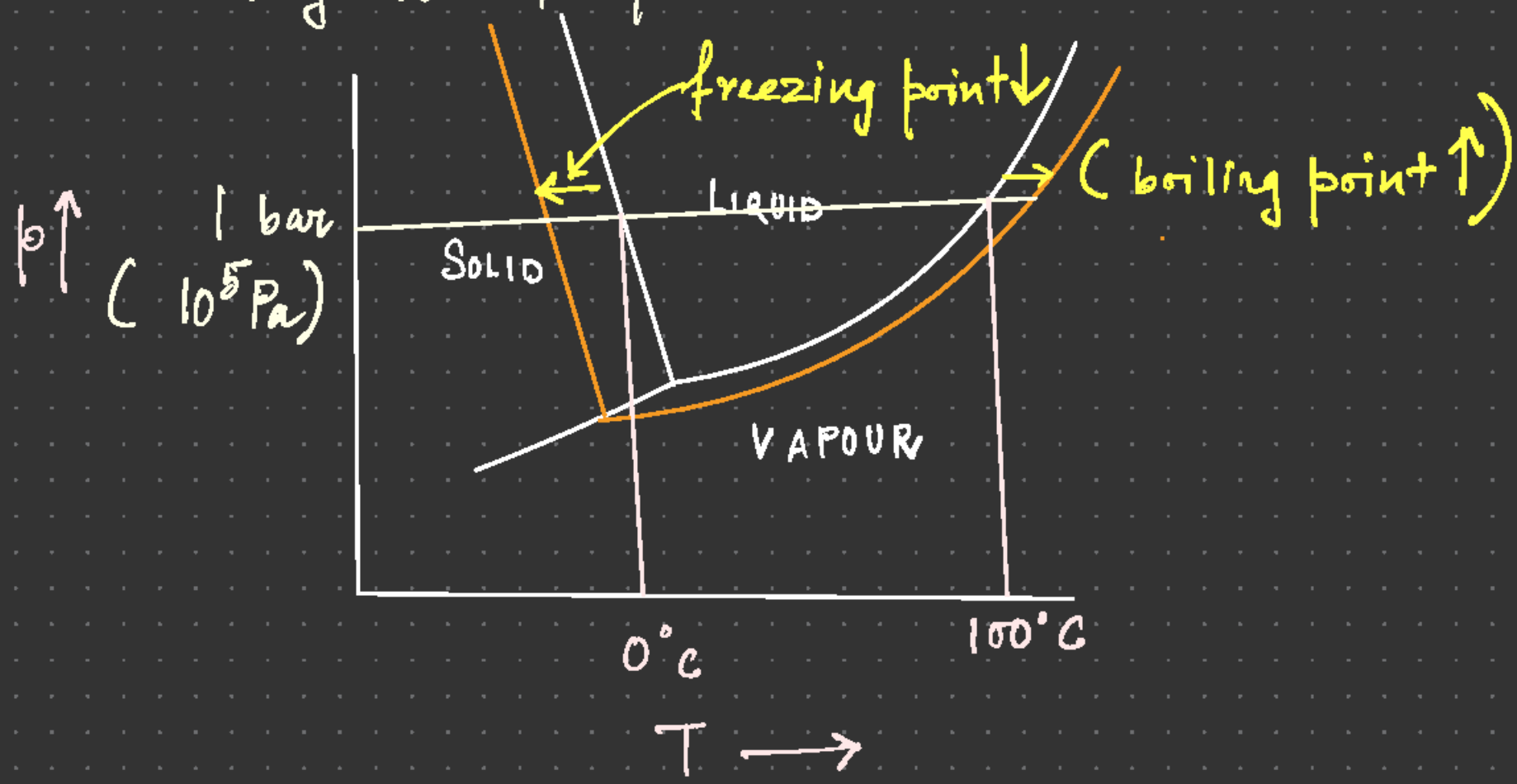
Colligative Properties

↓

"Collective"

- Depends on the number of solute particles present
- Does not depend on the identity of solute or solvent

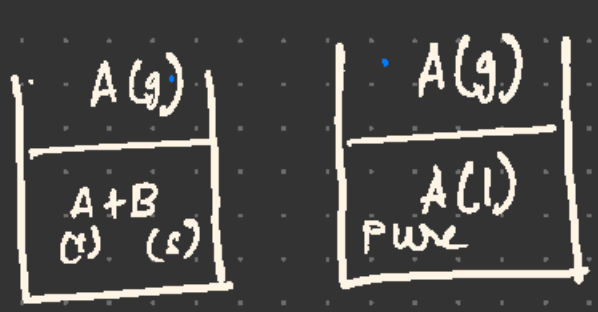
Colligative properties



$$p = x p^*$$

Elevation of boiling point

Solvent A + Solute B → Solution



Solution

$$\mu_A(g) = \mu_A(l) \Rightarrow \mu_A^*(g) = \mu_A^*(l) + RT \ln X_A$$

Pressure - 1 atm.

$$\mu_A(g) = \mu_A^*(g) \qquad T_b \rightarrow T_b^* + \Delta T$$

$$\Delta T = K_H X_B \qquad K_H = \frac{RT_b^*}{\Delta H^{vap}} = \frac{RT_b^*}{\Delta H^{l \rightarrow g}} = \frac{RT_b^*}{\Delta H^{vap}}$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln a_A \quad (\downarrow \text{ideal})$$

$$= \mu_A^*(l) + RT \ln X_A$$

T_b^* is boiling point of pure A liquid

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln X_A$$

$$\ln X_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta G^{vap}}{RT} = \frac{\Delta G^{l \to g}}{RT}$$

Gibbs-Helmholtz equation

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

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

$$\Delta G^{vap} = RT \ln X_A$$

$$\frac{\Delta G^{vap}}{T} = R \ln X_A$$

$$\left[\frac{\partial(\Delta G^{vap}/T)}{\partial T}\right]_P = \frac{d(\Delta G^{vap}/T)}{dT} = R\frac{d\ln X_A}{dT}$$

$$\frac{d \ln X_A}{dT} = \frac{1}{R} \frac{d\left(\Delta G^{vap}/T\right)}{dT} = -\frac{\Delta H^{vap}}{RT^2}$$

Pure A

$X_A = 1$

$\Downarrow$

$\ln X_A = 0$

$$\int_{X_A=1\,(Pure)}^{X_A} d \ln X_A = -\frac{1}{R} \int_{T_b^*}^{T_b} \frac{\Delta H^{vap}}{T^2} dT$$

$$\ln X_A = \ln\left(1 - X_B\right) = \frac{\Delta H^{vap}}{R}\left(\frac{1}{T_b} - \frac{1}{T_b^*}\right)$$

$$\ln(1-X_B) = \frac{\Delta H^{vap}}{R}\left(\frac{1}{T_b} - \frac{1}{T_b^*}\right)$$

$X_B \ll 1$ (Dilute solution)

or, $X_B \to 0$

$\ln(1-x) = -x - x^2/2 - \cdots$

$$\ln(1-X_B) \simeq -X_B$$

$$X_B \simeq \frac{\Delta H^{vap}}{R}\left(\frac{1}{T_b^*} - \frac{1}{T_b}\right)$$

$$\simeq \frac{\Delta H^{vap}}{R}\left(\frac{T_b - T_b^*}{T_b T_b^*}\right) \simeq \frac{\Delta H^{vap}}{R}\frac{\Delta T}{T_b^{*2}}$$

$$X_B = \frac{\Delta T}{K_H}$$

$$= \frac{\Delta H^{vap}}{R} \frac{\Delta T}{T_b^{*2}}$$

$$K_H = \frac{R T_b^{*2}}{\Delta H^{vap}}$$

$$\Delta T = K_H X_B$$

$$K_H = \frac{R T_b^{*2}}{\Delta H^{l \to g}}$$

T_b^* — boiling point of pure solvent

Depression of freezing point

$A(l)$

$H_2O(l) \xrightarrow{A(s)} H_2O(s)$

pure solid Solvent + A

liquid solution $A(l) + B$

Example

$A(s)$ = ice

$A(l) + B$

$H_2O(l) + \text{salt (solute)} \longrightarrow H_2O(s)$

$= \text{Water}(l) + NaCl(s)$

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} = \frac{\Delta G^{l \to s}}{RT}$$

$$= \frac{\Delta G^{\text{freezing}}}{RT}$$

$$\frac{d \ln X_A}{dT} = \frac{d}{dT}\left(\frac{\Delta G^{freezing}}{RT}\right)$$

$$= -\frac{\Delta H^{l \to s}}{RT^2} = -\frac{\Delta H^{freezing}}{RT^2}$$

$$\int_{X_A=1\ (pure)}^{X_A\ (soln)} d \ln X_A = -\int_{T^*_{freeze}}^{T\ (soln)} \frac{\Delta H^{freezing}}{RT^2}\, dT$$

$$\ln X_A = \ln(1 - X_B) = \frac{\Delta H^{freeze}}{R}\left(\frac{1}{T} - \frac{1}{T^*_{freeze}}\right)$$

$$= \frac{\Delta H^{freeze}}{R}\left(\frac{T^*_{fv} - T}{T\, T^*_{fv}}\right)$$

$$\ln(1-X_B) = \frac{\Delta H^{fr}}{R}\left(\frac{1}{T} - \frac{1}{T^*_{fr}}\right)$$

$X_B \ll 1$ (Dilute)

$$-X_B \simeq \frac{\Delta H^{fr}}{R}\left(\frac{T^*_{fr} - T}{T T^*_{fr}}\right)$$

$$X_B = \frac{\Delta H^{fr}}{R}\left(\frac{T - T^*_{fr}}{T T^*_{fr}}\right)$$

$$\Delta T = T - T^*_{fr} = \frac{R T^{*2}_{fr}}{\Delta H^{fr}} = \frac{R T^{*2}}{-\Delta H^{fusion}}$$

$\Delta H^{fusion} > 0 \qquad \Delta H^{fr} < 0$

$\therefore \Delta T < 0$ (depression in freezing point)

Solubility

$X_B = 1$ at $T = T_{fusion}$

$\mu_B^*(s) = \mu_B(l)$ (chemical potential of B in the liquid solution)

$= \mu_B^*(l) + RT \ln X_B$

$T = T_{fusion}$

$B(s) \longrightarrow B(l)$ $\quad s \to l$

$$\ln X_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT}$$

$\mu^*(l) - \mu^*(s) = \Delta\mu^{s\to l} = \Delta G^{fusion}$

$$= \frac{-\Delta G^{fusion}}{RT}$$

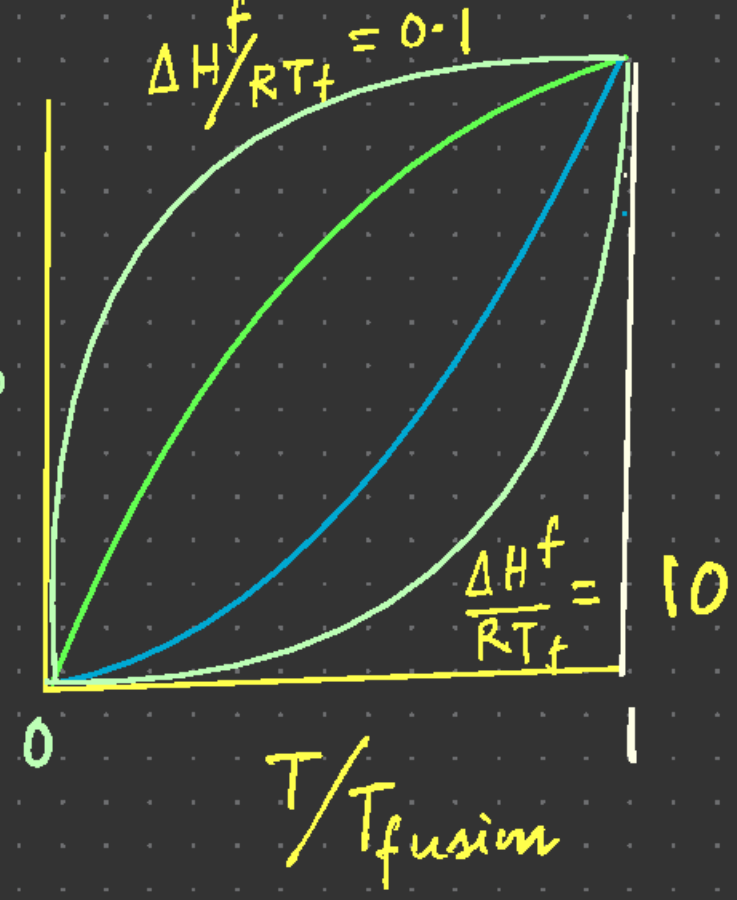
$$\int_{X_B = 1 \text{ (pure solute)}}^{X_B = X_B} d\ln X_B = -\frac{1}{R}\int_{T_f}^{T} \frac{\Delta H^{fusion}}{T^2} dT$$

$$\ln X_B = \frac{\Delta H^{fusion}}{R}\left(\frac{1}{T_{fusion}} - \frac{1}{T}\right)$$

$X_B = e$

T_f – melting point of pure B solute

No solvent property



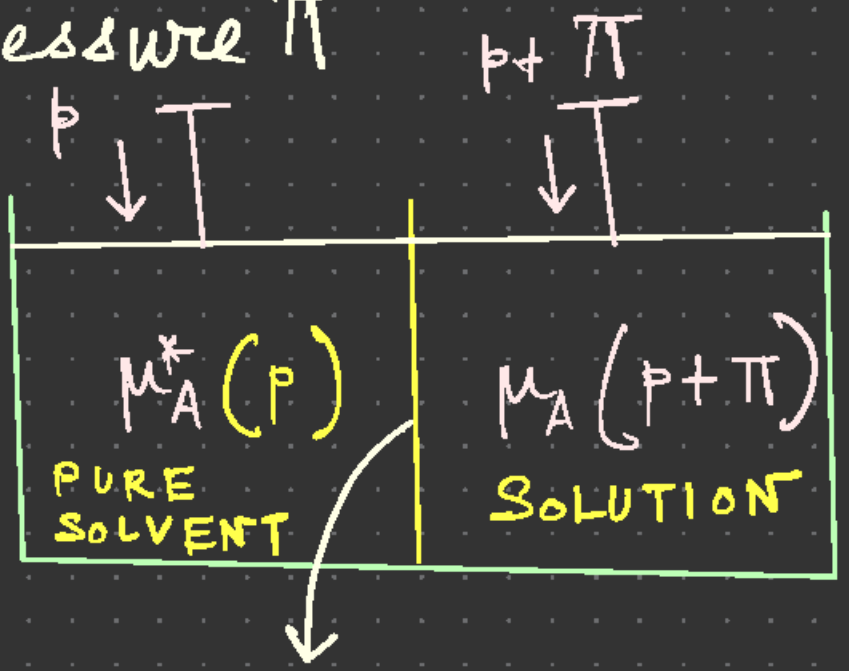
$T_{fusion}\ T$

$= T^2_{fusion}$

$T_{fusion} = T_f$

$$\ln X_B = \frac{\Delta H^f}{RT_f}\,\frac{T - T_f}{T_f} = \frac{\Delta H_f}{RT_f}\left(\frac{T}{T_f} - 1\right)$$

Osmotic pressure Π



Solute molecules cannot pass through the membrane

Semipermeable membrane (only allows solvent molecules to pass through the membrane)

$$\mu_A^*(P) = \mu_A(X_A, P+\Pi)$$

$$\mu_A(X_A, P+\Pi) = \mu_A^*(P+\Pi) + RT \ln X_A$$

$$\mu_A^* \longrightarrow \text{Pure A}$$

$$d\mu_A^* = dG_m^{\text{pure A}} = V_m\, dP$$

$$\therefore \int_{(P)}^{(P+\Pi)} d\mu_A^* = V_m \int_P^{P+\Pi} dP$$

$$\mu_A^*(P+\Pi) - \mu_A^*(P) = V_m(P+\Pi-P)$$

$$= V_m \Pi$$

$$\mu_A^*(p+\pi) = \mu_A^*(p) + V_m \pi$$

$$\mu_A(x_A, p+\pi) = \mu_A^*(p) + V_m \pi + RT \ln x_A$$

$$\| \quad \mu_A^*(p) = \mu_A^*(p) + V_m \pi + RT \ln x_A$$

$$\frac{x_B}{V_m} = \frac{N x_B}{V} = \frac{n_B}{V}$$

$$-RT \ln x_A = V_m \pi$$

$$V_m = \frac{V}{N}$$

$$\ln x_A = \ln(1 - x_B)$$

x_B = mole fraction of solute ($\ll 1$)

$$= -x_B \quad \because x_B \ll 1$$

$$RT x_B = V_m \pi$$

$$\therefore \pi = \frac{RT}{V_m} x_B = [B] RT$$

$$x_B / V_m = \frac{n_B}{V} = [B]$$

van't Hoff Equation

Van't Hoff Equation

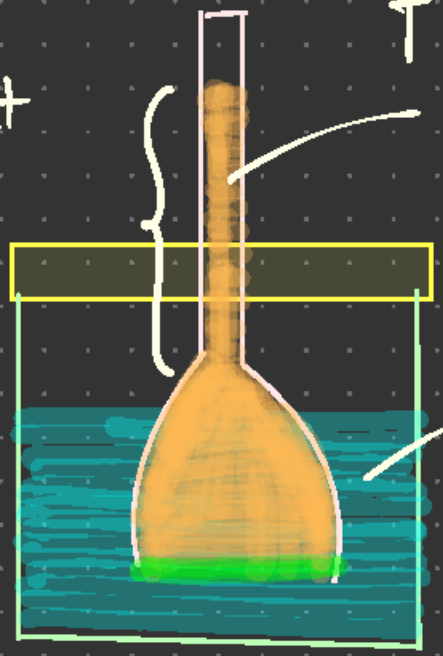
$$\frac{c}{M} RT = \rho g h$$

$$\Pi = [B] RT$$

$$M = \frac{cRT}{\rho g h}$$

ρ – density of solution

Used to measure molar masses of macromolecules

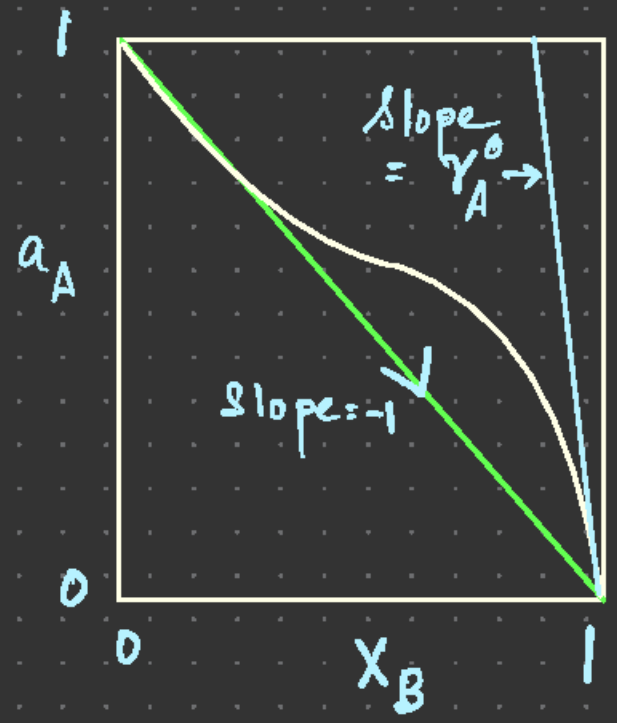


$$\Pi = \rho g h$$

$$[P] = \frac{c}{M} = \frac{\text{mass/volume}}{\text{mass/mole}}$$

$$\Pi = \rho g h = [P] RT = \frac{c}{M} RT$$

Deviation from ideality



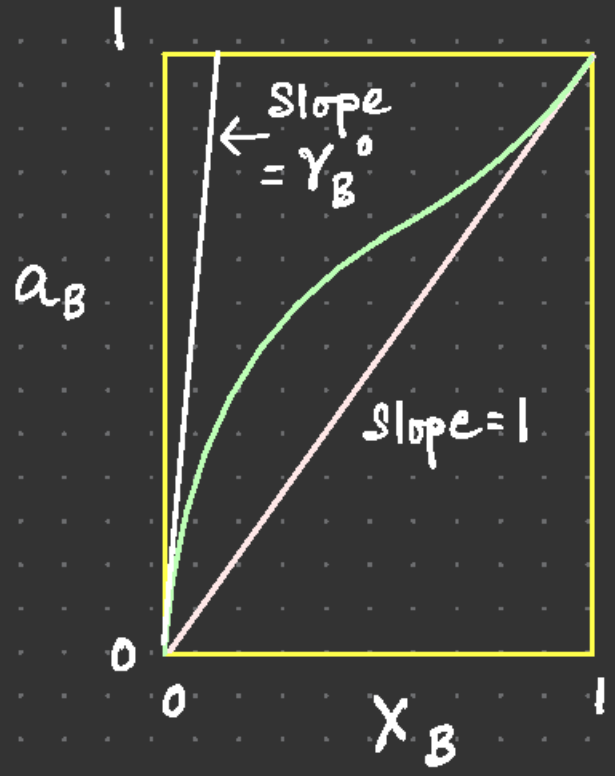
$$a_A = \gamma_A x_A$$

Raoult's law

$$a_A = x_A$$

Henry's law

$$\lim_{x_A \to 0} a_A = \gamma_A^0 x_A$$



Raoult' law

$a_B = X_B$

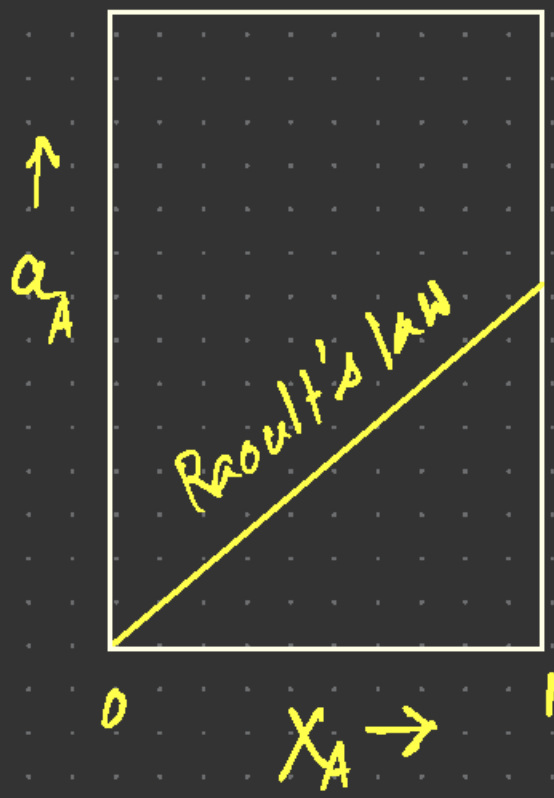
Henry's law

$\lim_{X_B \to 0} \quad a_B = \gamma_B^0 X_B$

$a_B = \gamma_B X_B$

$\gamma_B \neq 1$

A-B Solution

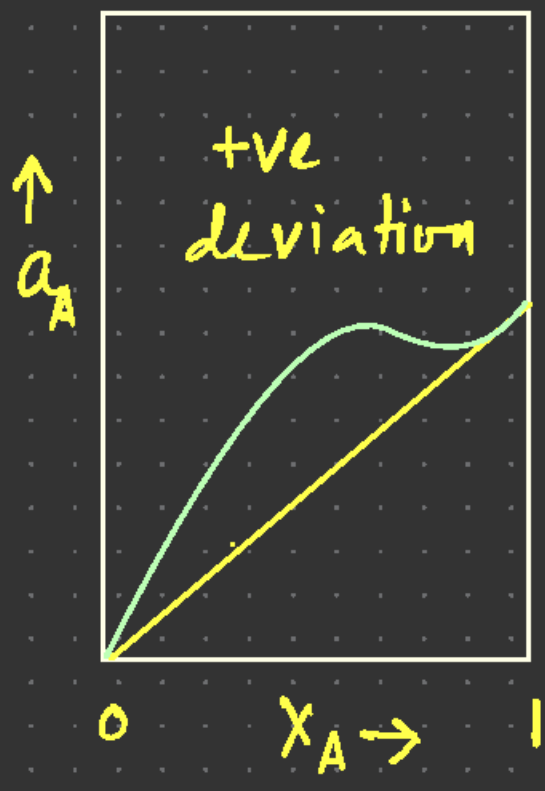


$A\text{-}B = \frac{1}{2}(A\text{-}A + B\text{-}B)$

Ideal

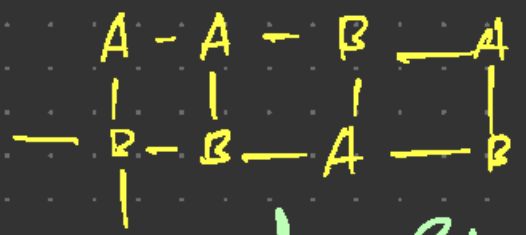


$A\text{-}B > \frac{1}{2}(A\text{-}A + B\text{-}B)$



$A\text{-}B < \frac{1}{2}(A\text{-}A + B\text{-}B)$

Regular Solution Model



Using quasichemical theory of solutions

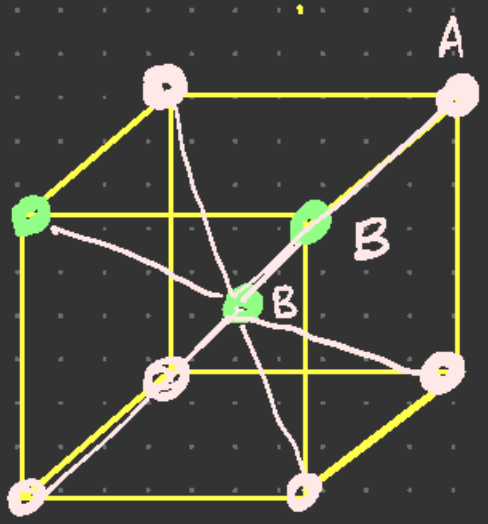
- Solution is like a large molecule
- Each pair of adjacent atoms are assumed to be connected by a chemical bond

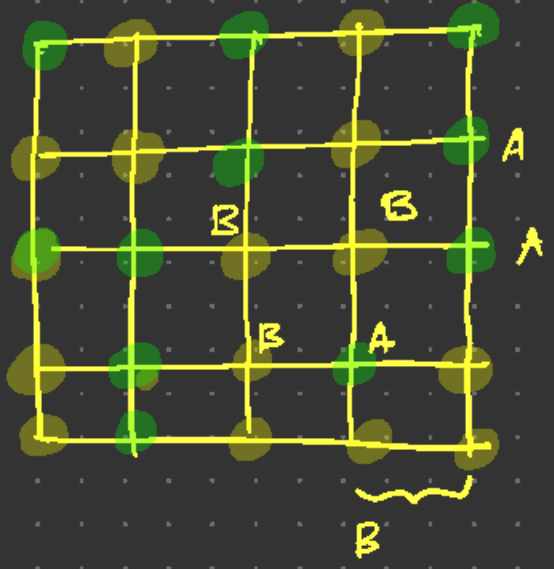
Binary solution — A and B are two kinds of atoms

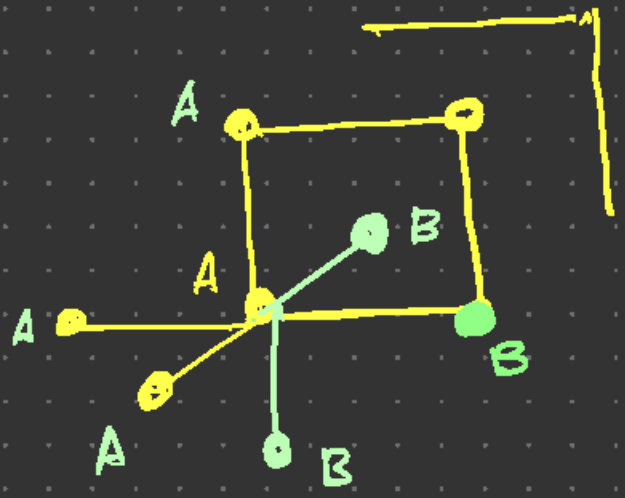
A-A, B-B, A-B bonds

— three nearest neighbour pairs

$$U \text{ or } E = E_{AA} N_{AA} + E_{BB} N_{BB} + E_{AB} N_{AB}$$







$Z = 6$

BCC $Z = 8$

FCC $Z = 12$

- Volumes of pure A and pure B are assumed to be equal
- Volumes of A and B do not change during mixing
- Interatomic distance and bond energy does not depend on composition

Regular Solution Model

Random alloy approximation:

Probability of finding an A atom

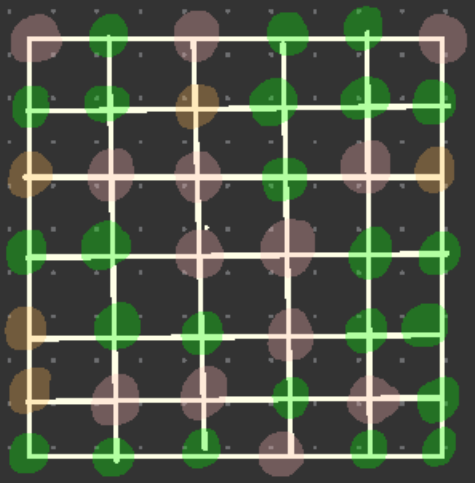
= mole fraction of A

Example:

$$p(A) = x_A \qquad p(A\text{-}B) = x_A x_B$$

$$p(B) = x_B$$

Rigid lattice



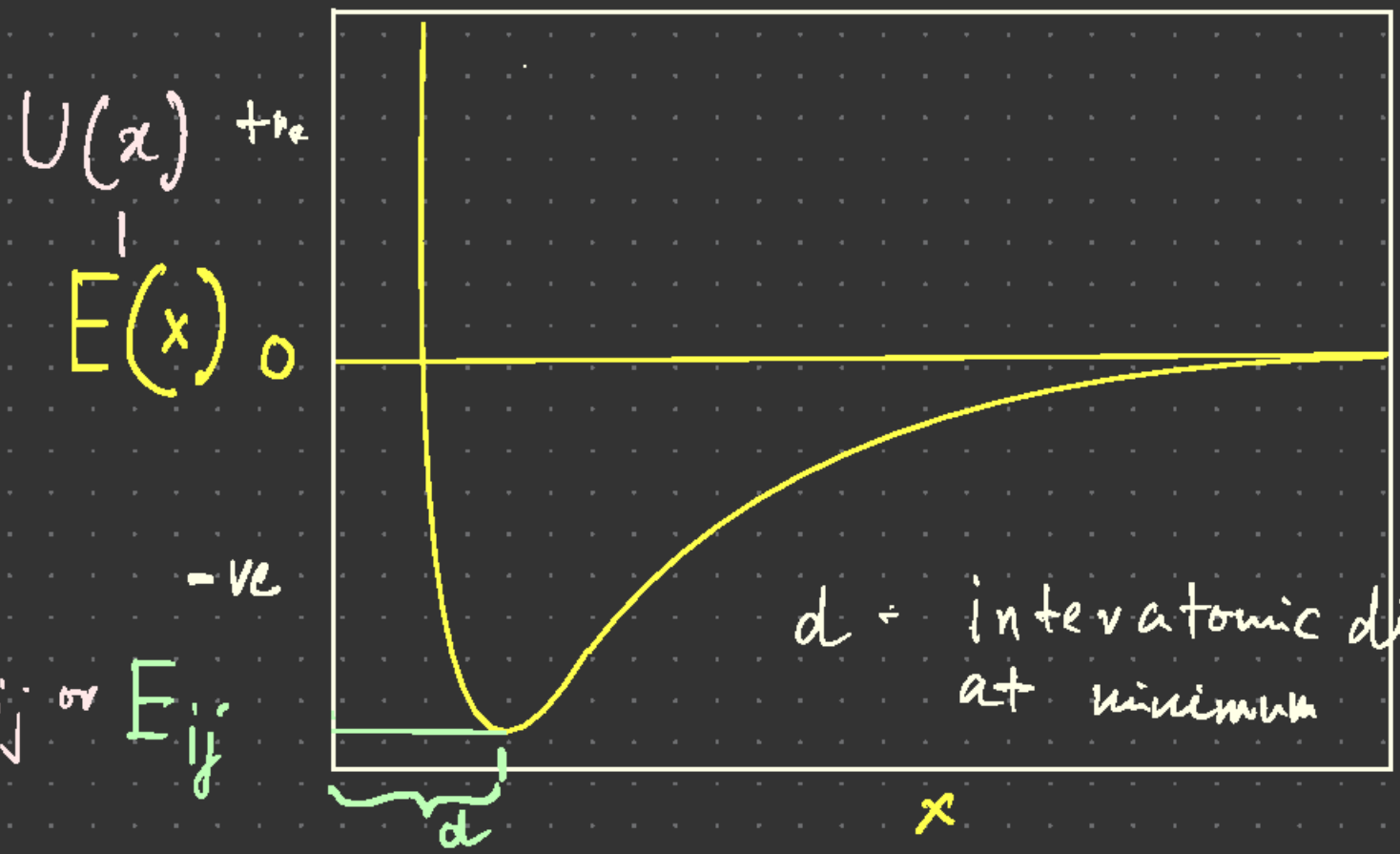
Atoms of different kinds strictly occupy lattice positions and lattice parameters are not allowed to change

- N_0 vacancies / interstitials

- Only pairwise interactions

E_{AA} E_{BB} E_{AB}





N_{AA} – number of A-A bonds

N_{BB} – number of B-B bonds

N_{AB} – number of A-B bonds

$$U_{soln} = N_{AA} E_{AA} + N_{BB} E_{BB} + N_{AB} E_{AB}$$

Total number of atoms $N_o = N_A + N_B$

N_o → total number

N_A → no. of A atom

N_B → no. of B atom

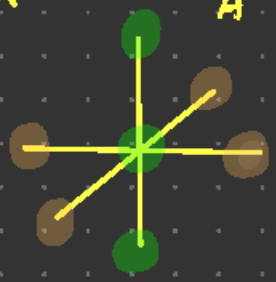
A B C

AA BB CC

AB BC AC

} ternary solution

$X_B = X$ $X_A = 1 - X$



$Z = 6$

cubic

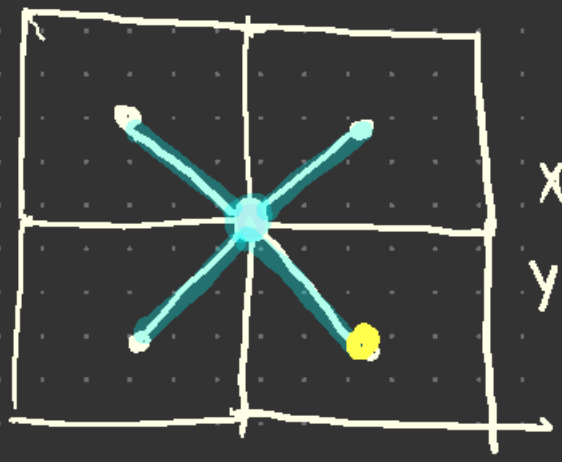
face centred cubic

$Z = 12$

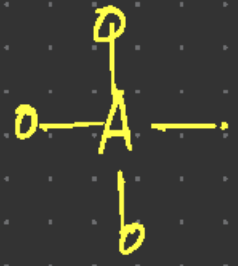
body centred cubic

$Z = 8$

Total number of bonds $N_T = \frac{1}{2} N_0 Z$



$N_{AA} = \frac{1}{2} N_A Z X_A$



$Z X_A$

$= \frac{1}{2} N_0 Z X_A^2$



$= \frac{1}{2} N_0 Z (1-X)^2$

$N_A = N_0 X_A$

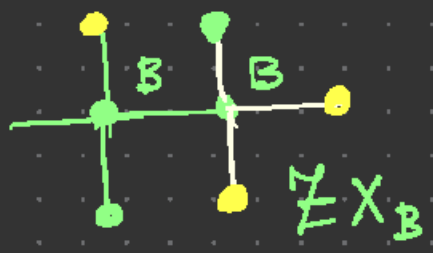
$X_B = X$

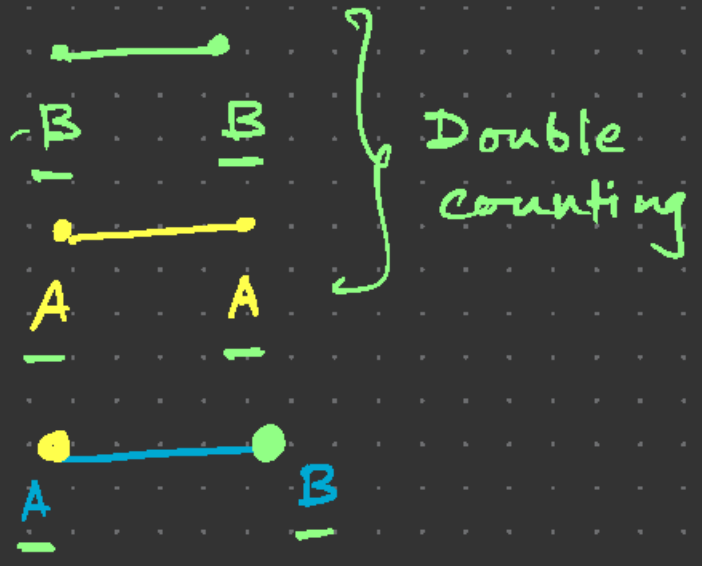
$X_A = 1 - X$

$$N_{BB} = \frac{1}{2} N_B z x_B$$

$$= \frac{1}{2} N_0 z x_B^2$$

$$= \frac{1}{2} N_0 z x^2$$





$$N_{AB} = N_A z x_B$$

$$= N_0 z x_A x_B$$

$$= N_0 z x (1-x)$$

$$U_{Soln} = \frac{N_0}{2} z (1-x)^2 E_{AA} + \frac{N_0}{2} z x^2 E_{BB}$$

$$+ N_0 z x(1-x) E_{AB}$$

$$(1-x)^2 = (1-x)(1-x) = (1-x) - x(1-x)$$

$$= \frac{N_0 z}{2} \left[(1-x)^2 E_{AA} + x^2 E_{BB} + 2x(1-x) E_{AB} \right]$$

$$x^2 = x \cdot x = x - x(1-x)$$

$$= \frac{N_0 z}{2} \left[2E_{AB} x(1-x) - E_{AA} x(1-x) - E_{BB} x(1-x) + (1-x) E_{AA} + x E_{BB} \right]$$

Regular soln parameter

$$U_{soln} = \frac{N_0 z}{2}\left(2E_{AB} - E_{AA} - E_{BB}\right) \underbrace{x(1-x)}_{x_B x_A}$$

$$+ \underbrace{\frac{N_0 z}{2}(1-x)}_{x_A} E_{AA} + \underbrace{\frac{N_0 z}{2} x}_{x_B} E_{BB}$$

$$S_{soln} = -R\left[x_A \ln x_A + x_B \ln x_B\right]$$

$$= -R\left[(1-x)\ln(1-x) + x \ln x\right]$$

$$G_{soln} = H_{soln} - TS_{soln}$$

$$H_{soln} = U_{soln} + PV_{soln} \approx U_{soln}$$

or, $$\Delta H_{mix} = \Delta U_{mix} + \underbrace{P\Delta V_{mix}}_{\text{negligible for condensed phases}} \approx \Delta U_{mix}$$

$$\therefore \quad G_{soln} = U_{soln} - TS_{soln}$$

$$= (1-x)G_A(T) + xG_B(T) + \omega_{AB}x(1-x) + RT\left[x\ln x + (1-x)\ln(1-x)\right]$$

$$(1-x)G_A(T) = (1-x)\frac{N_0 Z}{2}E_{AA}(T)$$

$$x\ G_B(T) = x\frac{N_0 Z}{2}E_{BB}(T) \qquad A\ B\ A\ B\ \cdots$$

$$\omega_{AB} = \frac{N_0 Z}{2}\left(2E_{AB} - E_{AA} - E_{BB}\right)$$

$\omega_{AB} = 0$ Ideal Soln. $E_{AB} = \frac{1}{2}(E_{AA} + E_{BB})$

-ve departure $\omega_{AB} < 0$ Increase in no. of A-B bonds, ordering

+ve departure $\omega_{AB} > 0$ Increase in no. of A-A and B-B bonds, clustering

A-A-A-B-B-B

$$\therefore \mu_i = G_m + \sum_{j=2}^{n} (\delta_{ij} - x_j) \frac{\partial G_m}{\partial x_j}$$ } Generalized formula

Binary system

$$\begin{cases} \mu_A = G_{soln} - x \dfrac{dG_{soln}}{dx} \\ \mu_B = G_{soln} + (1-x) \dfrac{dG_{soln}}{dx} \end{cases}$$

$x_1 + x_2 + x_3 = 1$

$\delta_{12} = 0$

$\delta_{22} = 1$

$$\mu_A = \mu_A^\circ + RT \ln \gamma_A + RT \ln x_A$$

$$\mu_B = \mu_B^\circ + RT \ln \gamma_B + RT \ln x_B$$

$$G_{soln} = x_A G_A + x_B G_B + \omega_{AB} x_A x_B + RT (x_A \ln x_A + x_B \ln x_B)$$

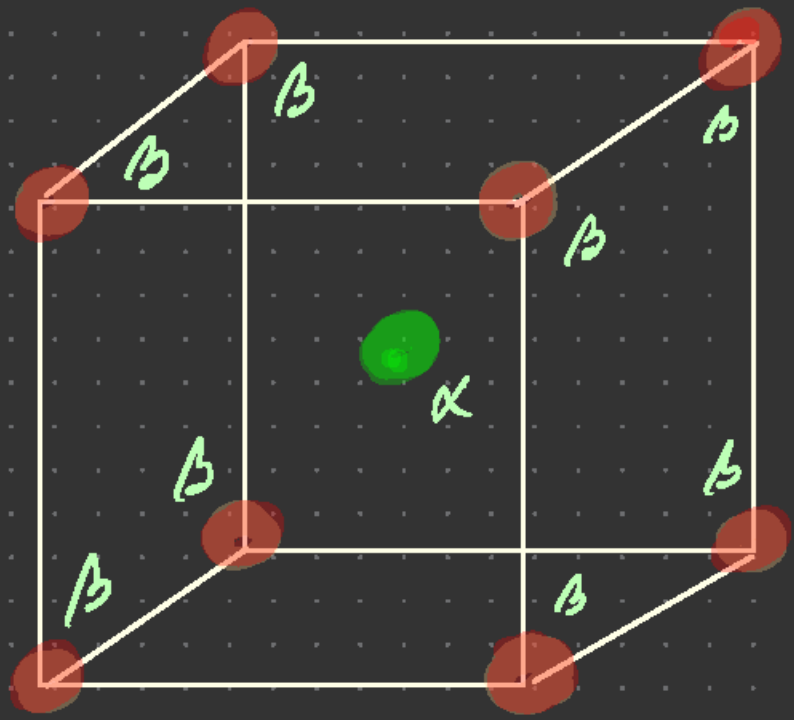
$$\Delta G_{mix} = \omega_{AB} X (1-X) + RT \left[(1-X) \ln (1-X) + X \ln X \right]$$

Prove that

$$\ln \gamma_A = \frac{(1-X_A)^2 \omega_{AB}}{RT}$$

$$\ln \gamma_B = \frac{(1-X_B)^2 \omega_{AB}}{RT}$$

Ordered phases or phases with ordered lattice

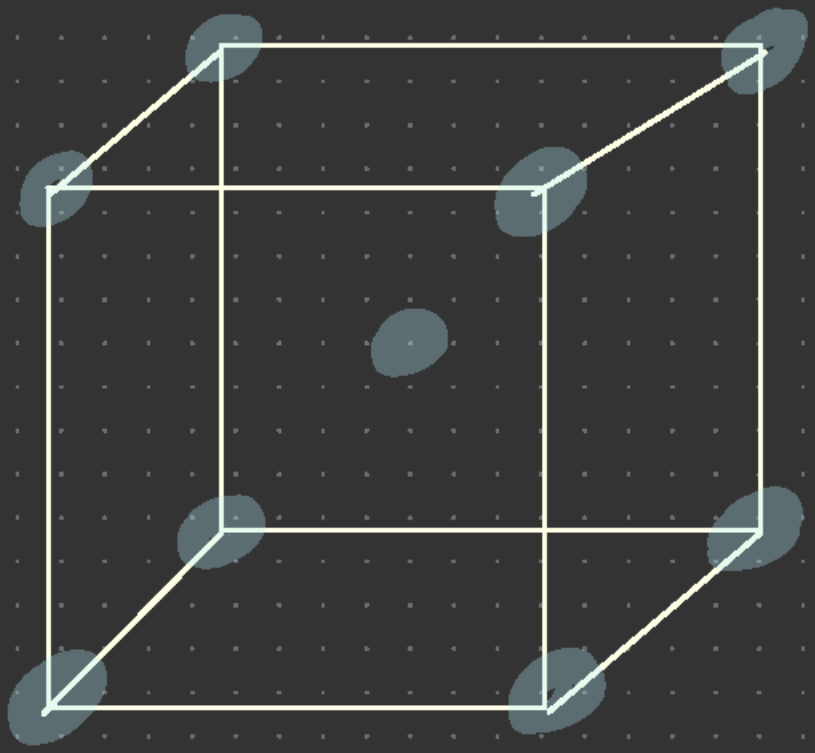


– B

– A

B2 crystal Structure

1 B site
1 α site
} 1 B2 unit cell



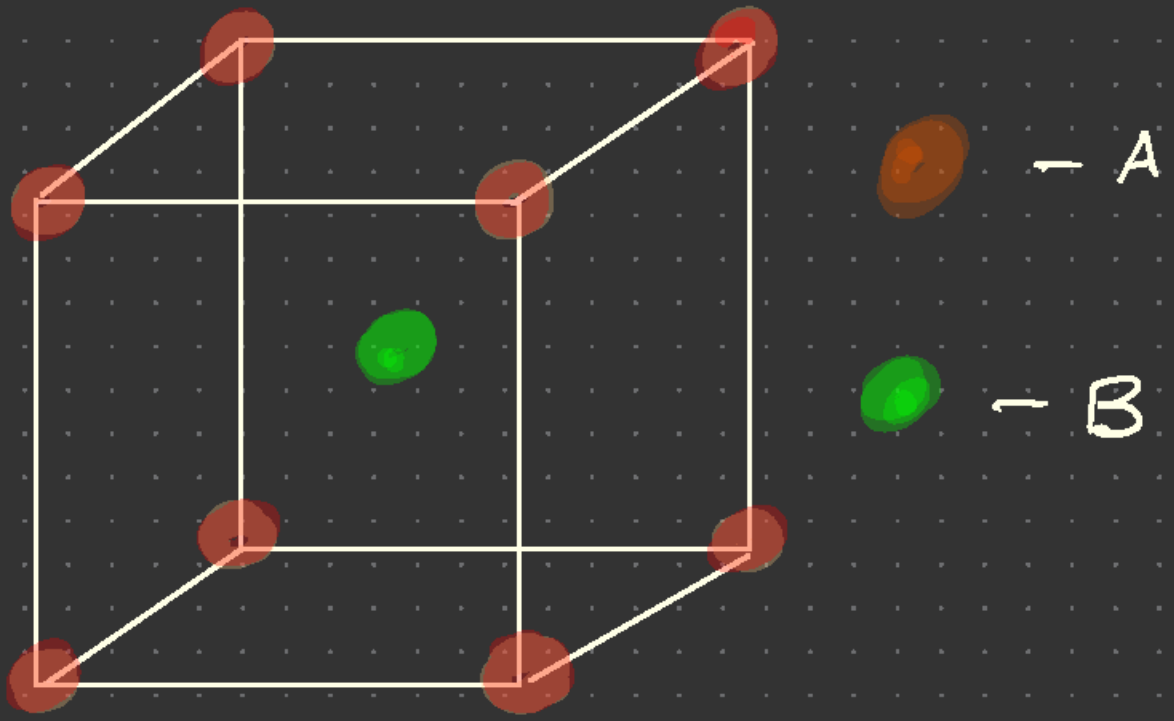
B1 Structure

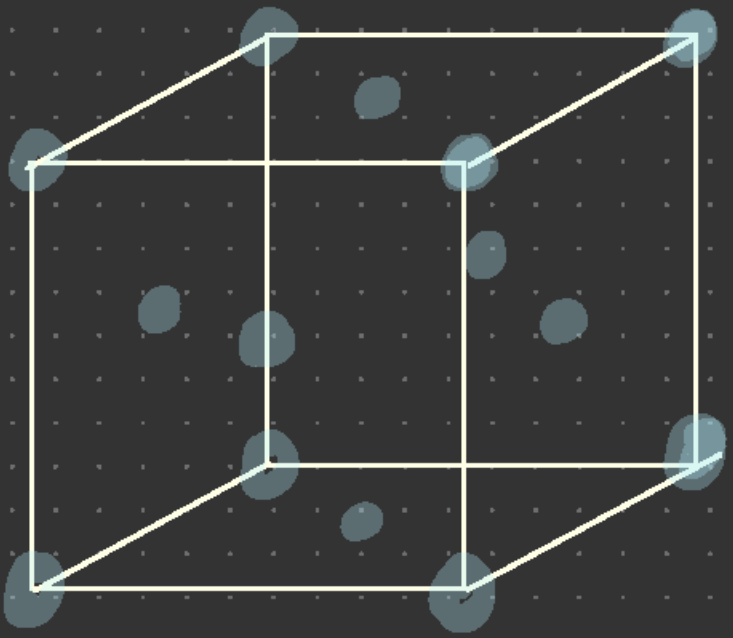
Disordered

Ordered

B2

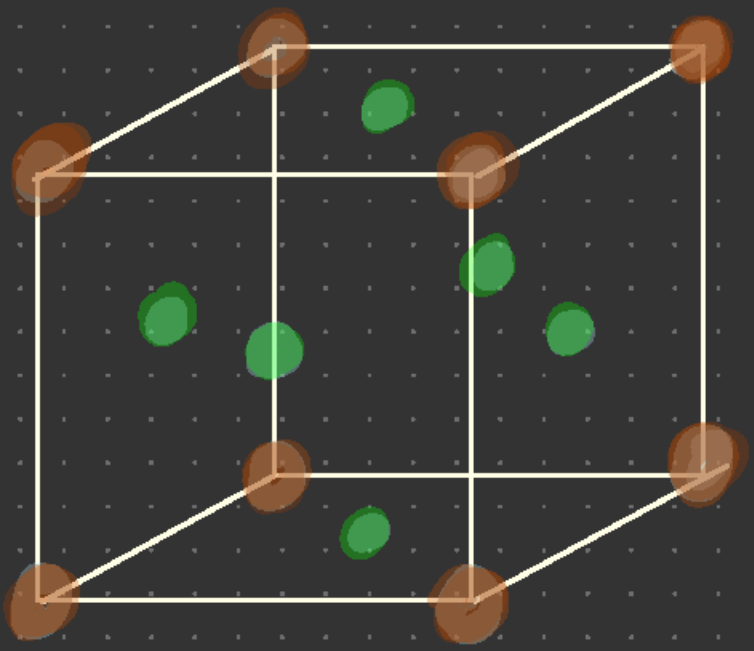
Structure





γ

Al



γ'

$L1_2$

Ordered lattices

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

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

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. $r_\alpha = X_A$

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 $0 \ll L \ll 1$, fraction of A on α- or A-site $= n_\alpha$

Total no. of sites N_s

Consider B2 structure

$\frac{N_s}{2}$ α sites

$\frac{N_s}{2}$ β sites

A atoms in α site $\quad \frac{N}{2} \eta_\alpha$

B atoms in β site $\quad \frac{N}{2} \eta_\beta$

Consider an alloy of composition

50% A, 50% B

undergoing disorder to order transition

$$x_A = x_B = 1/2$$

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

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

$\therefore$ A atoms on α-sites

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

B atoms on β-sites

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

Fraction of B atoms on α-site

$$= 1 - \eta_\alpha$$

No. of B atoms on α-site

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

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

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

No. of A atoms on B-site $= \left(\frac{1-L}{4}\right) N$

Now 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

Each α-site surrounded by $Z\beta$ sites

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

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

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

$Z = 8$ for BCC

$$\Gamma_{BB} = (1-L^2)\,\Gamma$$

$$\Gamma_{AB} = \sum_{\alpha\beta}\left[\pi_\alpha \pi_\beta + (1-\pi_\alpha)(1-\pi_\beta)\right]\frac{\Gamma}{2}$$

$$= \sum_{\alpha\beta}\left[\frac{(1+L)^2}{4} + \frac{(1-L)^2}{4}\right]\frac{\Gamma}{2}$$

$$= 2\,(1+L^2)\,\Gamma$$

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

$$S_{conf} = k \ln W$$

$$W = \frac{\left(\frac{N}{2}\right)!}{(\text{No. of A atoms on } K)!\,(\text{No. of B atoms on } K)!} \times \frac{\left(\frac{N}{2}\right)!}{(\text{No. of A atoms on } b)!\,(\text{No. of B atoms on } K)!}$$

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

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

$L = 1 \quad S_{conf} = 0$ (complete order)

$G = H - TS$

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

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

$+ N S_v^0$

S_v^0 – vibrational entropy per atom

$3N$ independent oscillators

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

Einstein model

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

Phase equilibrium in multiphase multicomponent non-reacting systems

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

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

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

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

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

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

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

$$\vdots$$

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

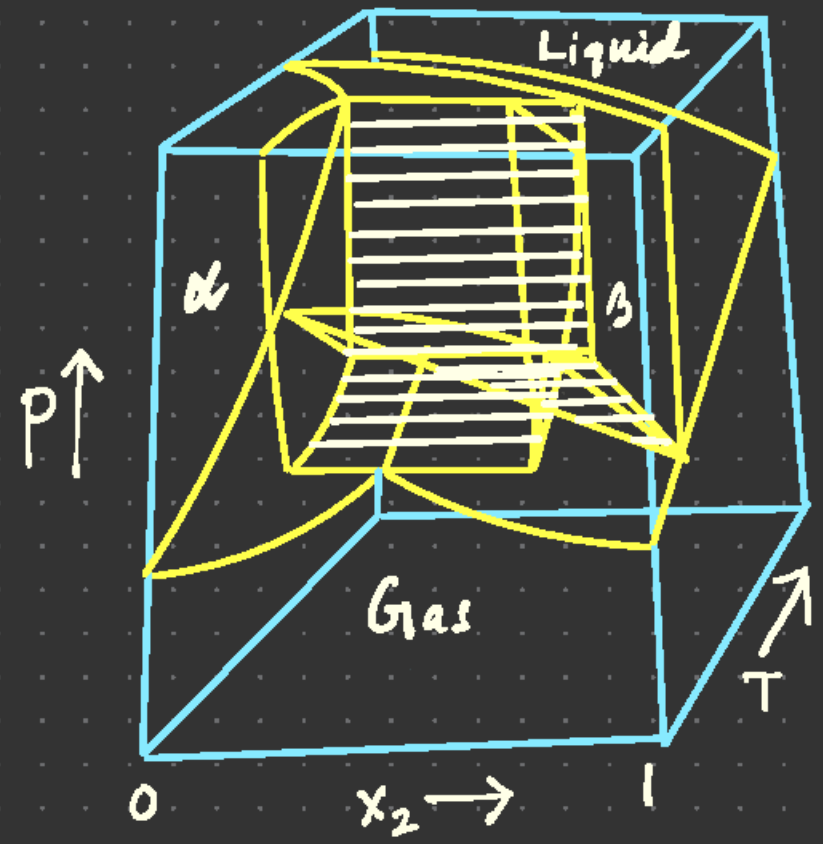
Gibbs phase rule

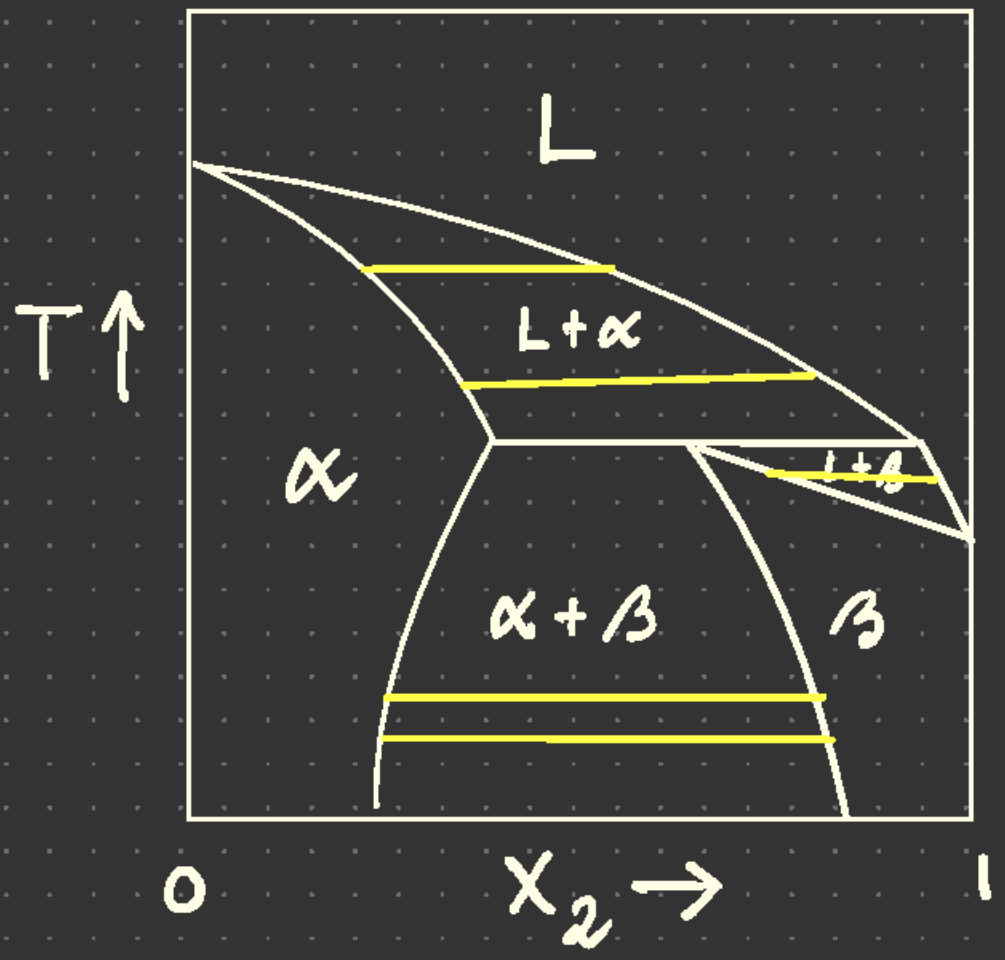
$$f = c - p + 2$$

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

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

P - T - X phase diagram





At a fixed pressure

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

$$a_A^L = X_A^L$$

$$a_B^L = X_B^L$$

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

Liquid to Solid transformation of pure A

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

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

Solution of A + B

$$\mu^{o}_{AS}\left(T^{o}_{A,\,freeze}\right) - \mu^{o}_{AL}\left(T^{o}_{A,\,freeze}\right) \neq 0$$

Solution of A + B :

Freezing point = T_{freeze}

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

$$= 0$$

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

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

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

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

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

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

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