Thermodynamics of Solutions
- multicomponent non reacting phases

Thermodynamics of Solutions

Multicomponent homogeneous non reacting systems

Z – An extensive thermodynamic property $Z(T, P, n_1, n_2, \ldots, n_c)$

Total no of moles $n = \sum_{i=1}^{c} n_i$

Z_m – molar thermodynamic property $\quad Z_m = Z/n$

partial molar property of component k $\quad \bar{Z}_k = \left(\frac{\partial Z}{\partial n_k}\right)_{T, P, n_{j \neq k}}$

partial molar property of component k

$$Z = \sum_{k=1}^{C} \bar{Z}_k n_k$$ at a given temperature T and at a given pressure p

$$\sum_{k=1}^{C} n_k \, d\bar{Z}_k = 0$$ Gibbs-Duhem relation

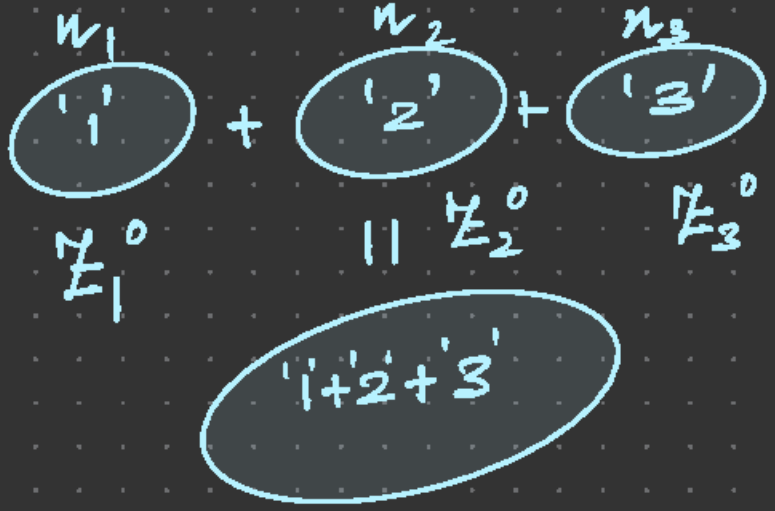
$$dZ = n_1 d\bar{Z}_1 + n_2 d\bar{Z}_2 + \cdots + \bar{Z}_1 dn_1 + \bar{Z}_2 dn_2 + \cdots \bar{Z}_C dn_C$$

$$= \sum_{k=1}^{C} n_k d\bar{Z}_k + \sum_{k=1}^{C} \bar{Z}_k dn_k$$ ($\sum_{k=1}^{C} n_k d\bar{Z}_k = 0$)

$$Z = n_1 \bar{Z}_1 + n_2 \bar{Z}_2 + \cdots + n_k \bar{Z}_k$$

Euler relation $= \sum_{k=1}^{C} n_k \bar{Z}_k$

Before mixing



$$Z^\circ = Z_1^\circ + Z_2^\circ + Z_3^\circ$$

$$Z^\circ = \sum_{k=1}^{C} n_k Z_k^\circ$$

Z_1° – molar property of component '1' before mixing (pure)

Z_k° – property of component k per mole before mixing (in the pure or reference state)

$$\Delta Z_{mix} = Z_{solution} - Z^\circ$$

change in Z due to mixing = Z after mixing − Z before mixing

$$Z^\circ = \sum_{k=1}^{C} n_k Z_k^\circ$$

$$Z_{solution} = \sum_{k=1}^{C} n_k \bar{Z}_k = Z$$

$$\Delta Z_{mix} = \sum_{k=1}^{c} \left(\bar{Z}_k - Z_k^{\circ}\right) n_k$$

For component 'k'

$$\Delta \bar{Z}_k = \bar{Z}_k - Z_k^{\circ} \quad \text{(pure/standard)}$$

Relative partial molar property of 'k'

$$\Delta Z_{mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k \, n_k$$

$$d\Delta Z_{mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k \, dn_k$$

$$\sum_{k=1}^{c} n_k \, d\Delta \bar{Z}_k = 0$$

$\therefore n_k d\Delta \bar{Z}_k = 0$

(Gibbs-Duhem equation)

$Z_m = Z/n$ $\quad$ n is the total no. of moles $= N_1 + N_2 + \cdots + N_c$

$dZ = \bar{Z}_1 dn_1 + \bar{Z}_2 dn_2 + \cdots$

$dZ_m = d(Z/n)$

$= \bar{Z}_1 d(n_1/n) + \cdots$

$= \bar{Z}_1 dx_1 + \cdots$

$$dZ_m = \sum_{i=1}^{c} \bar{Z}_i \, dx_i \qquad x_i = \frac{n_i}{n}$$

$$\sum_{i=1}^{c} n_i \, d\bar{Z}_i = 0$$

$$\sum_{i=1}^{c} x_i \, d\bar{Z}_i = 0$$

Gibbs-Duhem equation

$$Z_m = \sum_{k=1}^{c} \bar{Z}_k x_k \qquad x_k = \frac{n_k}{n}$$

$n_1 + n_2 = n$

$Z = \bar{Z}_1 n_1 + \bar{Z}_2 n_2$

$Z_m = \frac{Z}{n} = \bar{Z}_1 x_1 + \bar{Z}_2 x_2$

$$d\Delta Z_{m,mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k \, dX_k$$

$$\Delta Z_{m,mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k \, X_k$$

$$\sum_{k=1}^{c} X_k \, d\Delta \bar{Z}_k = 0 \quad \text{(Gibbs-Duhem)}$$

ΔZ_m
:
change in molar property due to mixing

ΔZ
change in the extensive property due to mixing

$$\Delta Z_{m,mix} = \Delta Z_m$$

$$\Delta \bar{Z}_1 = \left(\frac{\partial \Delta Z}{\partial N_1}\right)_{T,P,N_{k\neq 1}}$$

$$\Delta Z = n \Delta Z_m$$

$$= \Delta Z_m + (1 - x_1) \frac{d \Delta Z_m}{d x_1}$$

$$\Delta \bar{Z}_2 = \Delta Z_m + (1 - x_2) \frac{d \Delta Z_m}{d x_2}$$

$$\frac{d \Delta Z_m}{d x_2} = - \frac{d \Delta Z_m}{d x_1} \quad \left[\because x_1 + x_2 = 1 \right.$$

$$\left. \text{or, } dx_2 = -dx_1 \right]$$

$$\bar{H}_k = \bar{U}_k + P\bar{V}_k$$

$$\bar{F}_k = \bar{U}_k - T\bar{S}_k$$

$$\bar{G}_k = \mu_k = \bar{H}_k - T\bar{S}_k$$

Maxwell Relation

$$-\left(\frac{\partial \bar{S}_k}{\partial P}\right)_{T, N_k} = \left(\frac{\partial \bar{V}_k}{\partial T}\right)_{P, N_k}$$

We do not directly determine chemical potential.

We determine activity.

$$\mu_k = \mu_k^{\circ} + RT \ln X_k$$

$$\mu_k - \mu_k^{\circ} = \Delta\mu_k = RT \ln a_k$$

a_k – activity of component k in the solution

a_k – apparent concⁿ. of component k in the solution

$$a_k = \gamma_k X_k$$

γ_k: activity coefficient of component k

When $\gamma_k = 1$

$a_k = x_k$

Activity of component k = Apparent Concentration of component k in the solution

$$a_k = \gamma_k X_k$$

$$\mu_k = \mu_k^0 + RT \ln a_k$$

$$= \mu_k^0 + RT \ln \gamma_k X_k$$

$$= \mu_k^0 + RT \ln X_k + \underbrace{RT \ln \gamma_k}$$

$\gamma_k > 1$ $\quad a_k > X_k$

Component 'k' behaves as if its Concentration is more than its actual Concentration X_k

$\gamma_k < 1$

$a_k < x_k$

Component k — apparent concentration of k less than its actual concentration

Mixture of Pure Components

$$\mu^{\circ}(T, P, x_1, x_2, \cdots, x_c)$$

$$= x_1 \mu_1^{\circ}(T,P) + x_2 \mu_2^{\circ}(T,P) + \cdots + x_c \mu_c^{\circ}(T,P)$$

μ_i° – Chemical potential of pure Component i at T and P

↓

molar Gibbs free energy of Component i

Condensed mixture of pure components

$p = 1$ bar or 1 atmosphere (fixed)

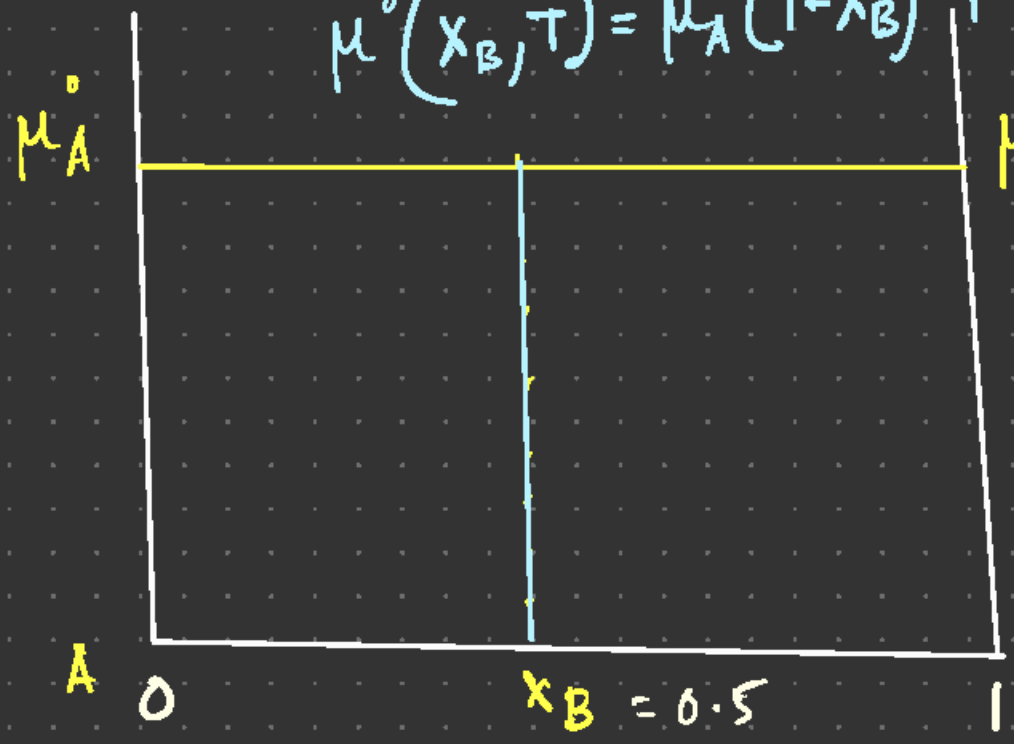
Two components A & B

Binary mixture or Solution of A and B

Prior to mixing

$$G_m(T, x_B) = \mu^\circ(T, x_B) = x_A \mu_A^\circ(T) + x_B \mu_B^\circ(T)$$

$$\mu^\circ(x_B, T) = \mu_A^\circ(1 - x_B) + \mu_B^\circ x_B$$



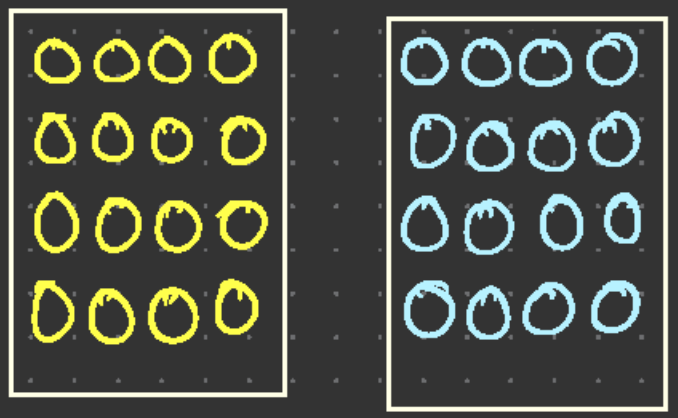
$x_A + x_B = 1$

Before mixing

$n = n_A + n_B$

T, P

50 at% A | 50 at% B



A $x_A = 0.5$ + B $x_B = 0.5$

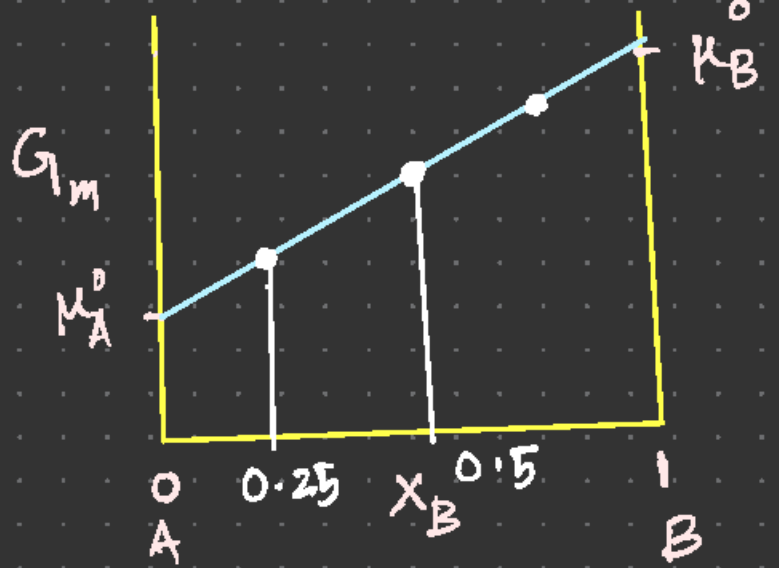
$G = n_A \mu_A^\circ + n_B \mu_B^\circ$

$G_m = x_A \mu_A^\circ + x_B \mu_B^\circ$ (before mixing)

G_m (before mixing) $= x_A \mu_A^\circ + x_B \mu_B^\circ$

μ_A° (free energy per mole of A in the pure or reference state)

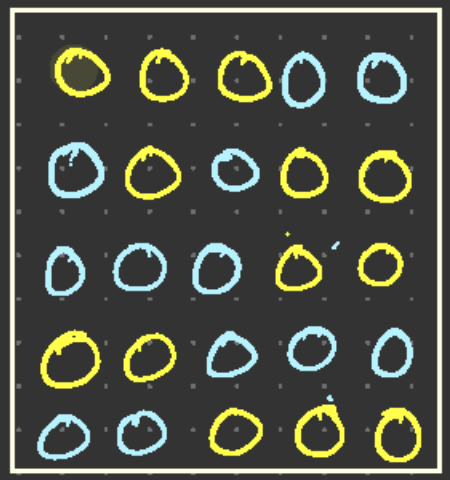
μ_B° (free energy per mole of pure B in the pure or reference state)



After mixing

(T, x_B)

$x_A + x_B = 1$



Random Solution

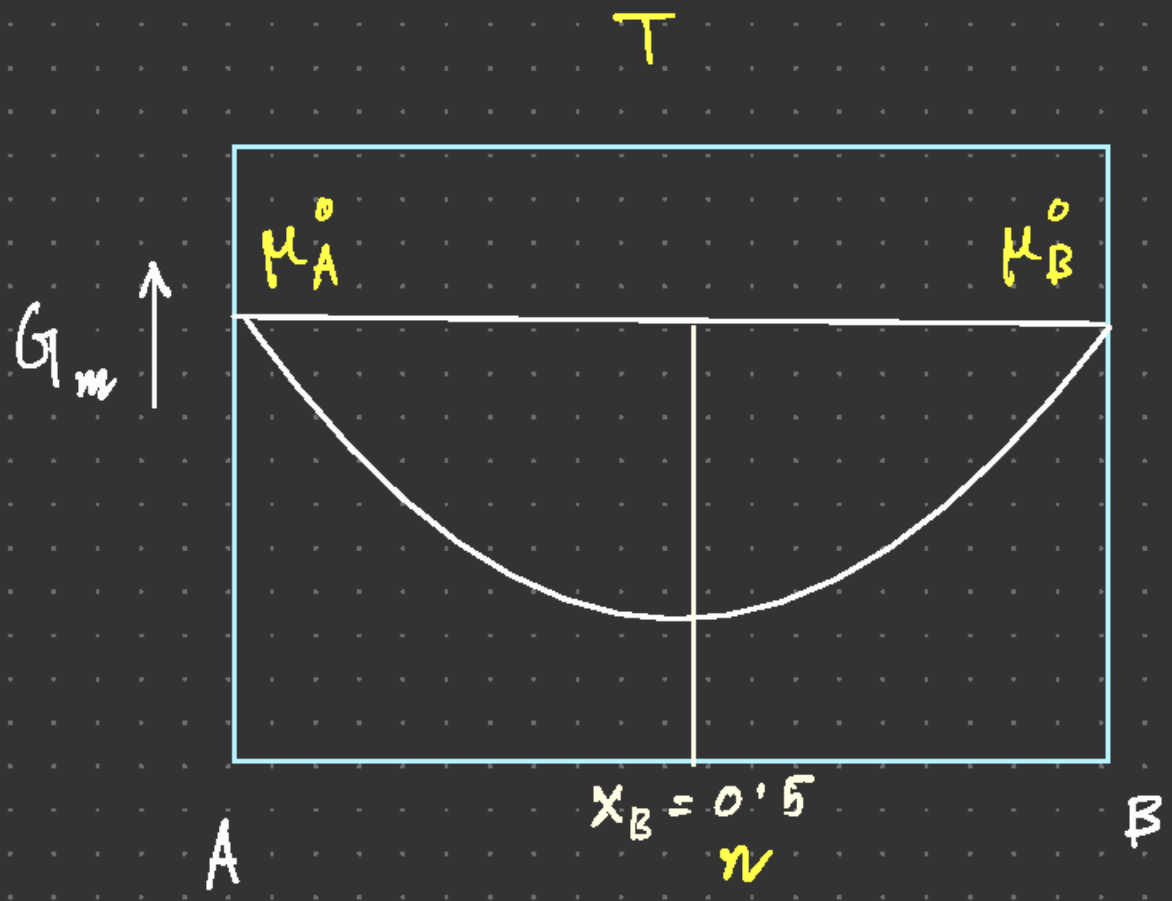
$G = H - TS$

$G_m = H_m - TS_m$

G_m (after mixing) $< G_m$ (before mixing)

$$G_m = \underbrace{\mu_A^\circ x_A + \mu_B^\circ x_B}_{G_m(\text{pure})\ \text{before mixing}} + \Delta G_{m,mix}$$

$$= G_m(\text{pure}) + \Delta G_{m,mix}$$



$$G_m^{\text{solution}} = x_A \mu_A^\circ + x_B \mu_B^\circ + \Delta G_m^{\text{mix}}$$

$$G_m^{\text{solution}} < G_m^{\text{before mixing}}$$

μ_A, μ_B

$$G_m = \sum_{j=1}^{n} x_j \mu_j$$

(After mixing)

(T, P)

$$G_m = \mu_A x_A + \mu_B x_B$$

$$\mu_j = \mu_j^\circ + RT \ln a_j$$

$$a_j = \gamma_j x_j$$

$$\mu_j = \mu_j^{\circ} + \underbrace{RT \ln \gamma_j}_{\text{due to interactions or formation of chemical bonds}} + \underbrace{RT \ln X_j}_{\text{due to random mixing}}$$

A-B solution

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

$$\mu_A = \mu_A^{\circ} + RT \ln \gamma_A + RT \ln X_A$$

Due to random mixing

$$G_m = \sum_{j=1}^{c} \mu_j x_j$$

$$dG_m = \sum_{j=1}^{c} \mu_j \, dx_j$$

$$\sum_{j=1}^{n} x_j = 1$$

$$x_i = 1 - \sum_{j=1, j\neq i}^{c} x_j$$

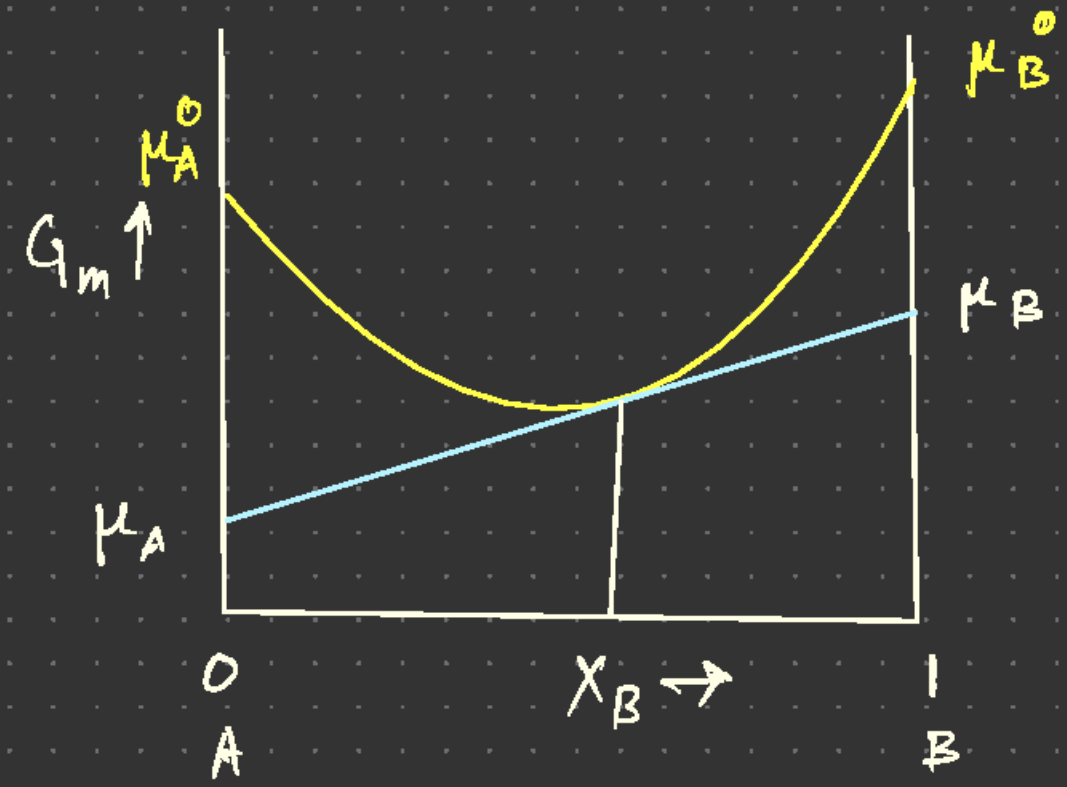
$$G_m = \mu_i + \sum_{j=1, j\neq i}^{c} x_j (\mu_j - \mu_i)$$

$$\left(\frac{dG_m}{dx_j}\right)_{j\neq i} = \mu_j - \mu_i$$

$$\Delta G_{m,mix} = x_A (\mu_A - \mu_A^\circ) + x_B (\mu_B - \mu_B^\circ)$$

$$\sum_{i=1}^{n} dx_i = 0$$

$$dx_i = -\sum_{\substack{j=1 \\ j\neq i}}^{n} dx_j$$



$$\frac{dG_m}{dx_B} = \frac{\mu_B - \mu_A}{1 - 0}$$

$$= \mu_B - \mu_A$$

$$G = n G_m$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left[\frac{\partial (n G_m)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$$

$$\frac{n_i}{n} = \frac{n_i}{\sum_i n_i} = x_i$$

$$n_1, n_2, n_3, \ldots, n_n$$

$$\rightarrow n, x_1, x_2, x_3, \ldots, x_n$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_k} = \left(\frac{\partial n}{\partial n_i}\right)_{n_k} G_m + n\left(\frac{\partial G_m}{\partial n_i}\right)_{n_k} \qquad G = n\,G_m$$

$$= G_m + n\left(\frac{\partial G_m}{\partial n}\right)_{x_i}\left(\frac{\partial n}{\partial n_i}\right)_{n_k} + n\sum_{j=2}^{n}\left(\frac{\partial G_m}{\partial x_j}\right)_{n, x_k}\left(\frac{\partial x_j}{\partial n_i}\right)_{n_k}$$

$$\frac{\partial G_m}{\partial \eta} = 0, \qquad \left(\frac{\partial n}{\partial n_i}\right)_{n_k} = 1$$

$$\left(\frac{\partial x_j}{\partial n_i}\right)_{n_k} = \frac{\delta_{ij} - x_j}{n}$$

Kronecker's delta

$\delta_{ij} = 1$ when $i = j$

$= 0$ $i \neq j$

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

Binary system

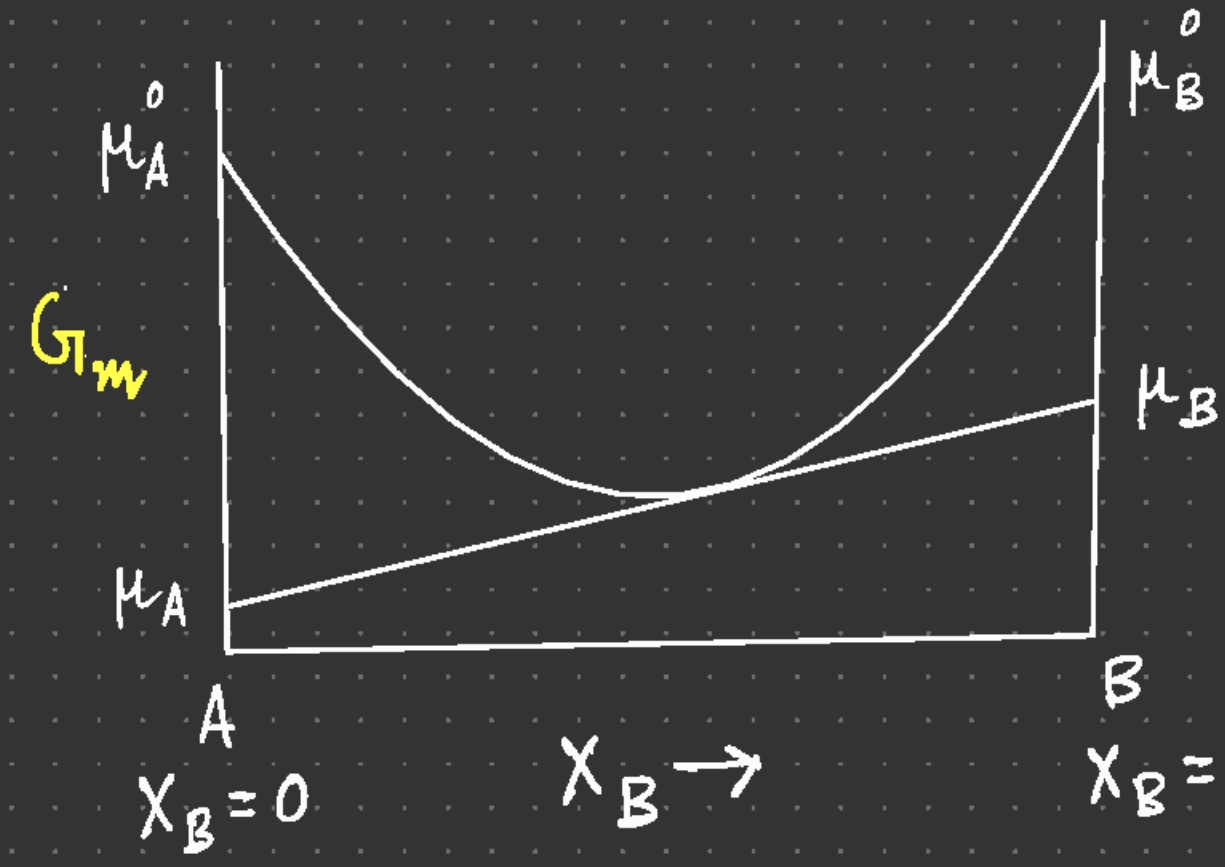
$$\begin{cases} \mu_1 = G_m - x_2 \dfrac{dG_m}{dx_2} \\ \mu_2 = G_m + (1 - x_2) \dfrac{dG_m}{dx_2} \end{cases}$$

$x_1 + x_2 = 1$

$x_1 + x_2 + x_3 = 1$

$\delta_{12} = 0$

$\delta_{22} = 1$



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

$$\frac{dG_m}{dX_B} = \frac{\mu_B - \mu_A}{1 - 0}$$

$$= \mu_B - \mu_A$$

$n = 3$

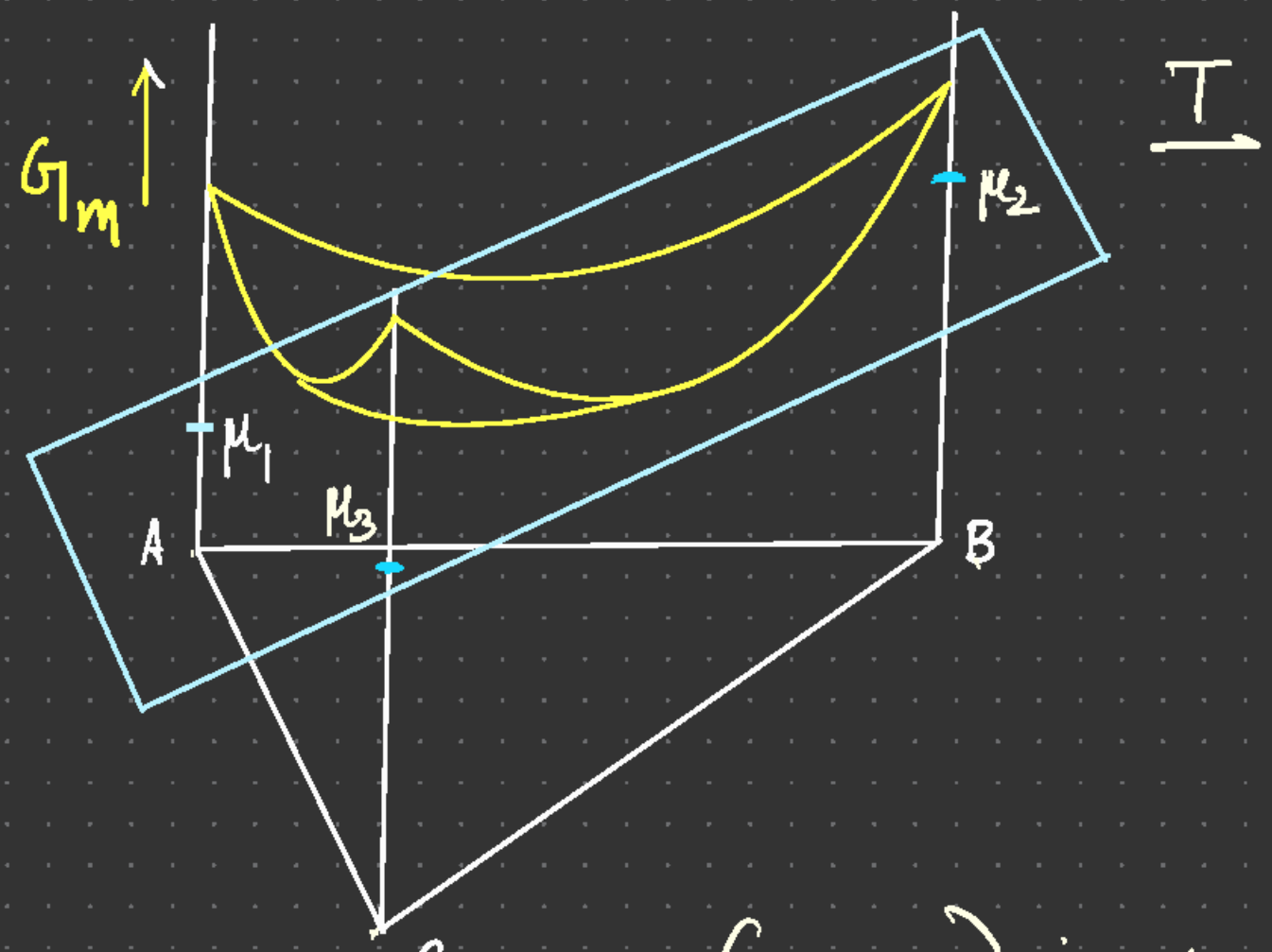
$x_1 + x_2 + x_3 = 1$

Assume x_1 is dependent variable

$$\mu_1 = G_m - x_2 \frac{\partial G_m}{\partial x_2} - x_3 \frac{\partial G_m}{\partial x_3}$$

$$\mu_2 = G_m + (1 - x_2) \frac{\partial G_m}{\partial x_2} - x_3 \frac{\partial G_m}{\partial x_3}$$

$$\mu_3 = G_m - x_2 \frac{\partial G_m}{\partial x_2} + (1 - x_3) \frac{\partial G_m}{\partial x_3}$$



Any given T, $G_m(x_2, x_3)$ in a surface

Ideal Gas Mixtures

Mixing process occurs at a given temperature T

Note: No interaction between particles in an ideal gas

Each component of ideal gas in the mixed state behaves "as if" it occupies the entire volume

Dalton's laws of partial pressure

$$p_k = X_k P \qquad P = \text{Total pressure}$$

$$P = \sum_{k=1}^{c} p_k = \sum_{k=1}^{c} X_k P = P \sum_{k=1}^{c} X_k = P$$

$$d\bar{G}_k = d\mu_k = -\bar{S}_k dT + \bar{V}_k dP$$

$dG = -SdT + VdP$

$dT = 0$

$$= \bar{V}_k dP$$

(: mixing process is isothermal)

Ideal Gas

$\mu_k^0 \leftrightarrow P$

$\mu_k \leftrightarrow p_k$

$$V = n\frac{RT}{P} = \frac{RT}{P}\sum_{k=1}^{C} n_k$$

$$\bar{V}_k = \left(\frac{\partial V}{\partial n_k}\right)_{T,P,n_{j\neq k}} = \frac{RT}{P}\left(\frac{\partial n}{\partial n_k}\right)_{n_{j\neq k}} = \frac{RT}{P}$$

$$\therefore \int_{\mu_k^0}^{\mu_k} d\mu_k = \bar{V}_k\, dP$$

$$\mu_k - \mu_k^0 = \int_P^{P_k} \bar{V}_k\, dP$$

$$= RT \ln \frac{p_k}{P}$$

$$\int \sqrt{\frac{RT}{P}}\, dP = RT \int \frac{dP}{P}$$

$$= RT \ln P + K_1$$

$$\mu_k - \mu_k^o = RT \ln \frac{p_k}{p}$$

$$p_k = x_k P \Rightarrow p_{k/p} = x_k$$

$$\Delta\mu_k = \mu_k - \mu_k^o = \Delta\bar{G}_k = RT \ln x_k$$

change in chemical potential of component 'k' due to mixing

relative partial molar free energy

$$\Delta\mu_k = \Delta\bar{G}_k = RT \ln X_k$$

$$\left(\frac{\partial \Delta\mu_k}{\partial T}\right)_{P,n_k} = \left(\frac{\partial \Delta\bar{G}_k}{\partial T}\right)_{P,n_k} = R \ln X_k$$

$$\left(\frac{\partial \Delta\mu_k}{\partial P}\right)_{T,n_k} = \left(\frac{\partial \Delta\bar{G}_k}{\partial P}\right)_{T,n_k} = 0$$

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

$$\Delta\bar{S}_k = -\left(\frac{\partial \Delta\bar{G}_k}{\partial T}\right)_{P,n} = -\left(\frac{\partial \Delta\mu_k}{\partial T}\right) = -R \ln X_k$$

$$\Delta\mu_k = RT \ln X_k = \Delta\bar{G}_k$$

relative partial molar free energy of component k due to mixing

$$\left(\frac{\partial \Delta\mu_k}{\partial T}\right)_{P,n_k} = R \ln X_k$$

$$\Delta\bar{S}_k = -\left(\frac{\partial \Delta\mu_k}{\partial T}\right)_{P,n_k} = -\left(\frac{\partial \Delta\bar{G}_k}{\partial T}\right)_{P,n_k}$$

$$= -R \ln X_k$$

$$0 < X_k < 1 \qquad > 0$$

$$\Delta \bar{V}_k = \left(\frac{\partial \Delta \mu_k}{\partial P}\right)_{T, n_k} = \left(\frac{\partial \Delta \bar{G}_k}{\partial P}\right)_{T, n_k} = 0$$

$$\Delta \mu_k = \Delta \bar{G}_k = \Delta \bar{H}_k - T \Delta \bar{S}_k$$

$$RT \ln X_k = \Delta \bar{H}_k - T\left(-R \ln X_k\right)$$

$$= \Delta \bar{H}_k + RT \ln X_k$$

$$\therefore \quad \Delta \bar{H}_k = 0$$

$$\Delta \bar{H}_k = \Delta \mu_k + T \Delta \bar{S}_k$$

$$= \Delta \mu_k - T\left(\frac{\partial \Delta \mu_k}{\partial T}\right)_{P, n_k}$$

$$\therefore \quad \Delta\bar{\mu}_k = T\left(\frac{\partial \Delta\mu_k}{\partial T}\right)_{P,\, n_k} = RT \ln X_k$$

$$\therefore \quad \Delta\bar{H}_k = 0$$

$$H = U + PV$$

$$\Delta\bar{H}_k = \Delta\bar{U}_k + P\Delta\bar{V}_k$$

$$\Delta\bar{U}_k = \Delta\bar{H}_k - P\Delta\bar{V}_k = 0$$

$$\Delta\bar{F}_k = \Delta\bar{U}_k - T\Delta\bar{S}_k$$

Relative partial molar Helmholtz free energy of component k

$$= RT \ln X_k = \Delta\bar{G}_k = \Delta\mu_k$$

$$\bar{\Delta S}_k = -R \ln X_k$$

$$\Delta S_{mix} = \sum_{k=1}^{c} n_k \bar{\Delta S}_k = -R \sum_{k=1}^{c} n_k \ln X_k$$

Extensive

$$\bar{Z} = \sum_{k=1}^{c} n_k \bar{Z}_k$$

$$X_k = \frac{n_k}{n}$$

$$\sum_{k=1}^{c} n_k = n$$

$$\frac{n_k}{n} = X_k$$

$$\therefore \Delta S_{m,mix} = \frac{\Delta S_{mix}}{n}$$

Molar entropy of mixing

$$= -R \sum_{k=1}^{c} X_k \ln X_k$$

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

$$\therefore \quad S = k_B \ln \Omega \qquad \text{Boltzmann's law}$$

$$= k_B \ln \frac{N!}{N_A!\, N_B!}$$

$$n! = n(n-1)(n-2)\cdots 3 \cdot 2 \cdot 1$$

$$\ln n! = \ln n + \ln(n-1) + \cdots + \ln 3 + \ln 2 + \ln 1$$

$$= \sum_{i=1}^{n} \ln i$$

When n is large

$$\sum_{i=1}^{n} \ln n = \int_1^n \ln x \, dx =$$

Let $z = \ln x$

$$dz = \frac{1}{x} dx$$

Integration by parts

$$\ln x \int_1^n dx - \int \left\{ \frac{d \ln x}{dx} \int dx \right\} dx$$

$$\int \ln x \, dx$$

$$= \ln x \int dx - \int \left\{ \frac{d \ln x}{dx} \int dx \right\} dx$$

$$= x \ln x - \int dx$$

$$\therefore \int_1^n \ln x \, dx$$

$$= \Big[x \ln x - x \Big]_1^n = n \ln n - n$$

$$- \ln 1 + 1$$

$$= n \ln n - n + 1$$

If n is very large,

$n \to \infty$

$$\ln(n!) = n\ln n - n + 1$$

$$\approx n\ln n - n \quad \because -n+1 \approx -n$$

$$\ln(n!) = n\ln n - n$$

— Stirling's approximation

$$\therefore \quad \ln \Omega = \ln \frac{N!}{N_A! N_B!}$$

$$X_A = \frac{N_A}{N} \qquad X_B = \frac{N_B}{N}$$

$$X_A + X_B = 1$$

$$N = N_A + N_B$$

$$= \ln(N!) - \ln(N_A!) - \ln(N_B!)$$

$$= N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B$$

$$= N \ln N - N_A \ln N_A - N_B \ln N_B + (N_A + N_B - N)$$

$$= N \ln N - N_A \ln N_A - N_B \ln N_B$$

$$= N \left(\ln N - X_A \ln N_A - X_B \ln N_B \right)$$

$$= -N \left(X_A \ln X_A + X_B \ln X_B \right)$$

$$\ln \Omega = N \ln N - N_A \ln N_A - N_B \ln N_B$$

$$N_A + N_B = N$$

$$X_A + X_B = 1$$

$$= -N \left(X_A \ln N_A - (X_A + X_B) \ln N + X_B \ln N_B \right)$$

$$= -N \left(X_A \ln \left(\frac{N_A}{N} \right) + X_B \ln \left(\frac{N_B}{N} \right) \right)$$

$$= -N \left(X_A \ln X_A + X_B \ln X_B \right)$$

$$\ln \Gamma = x_A \ln \Gamma + x_B \ln \Gamma \qquad \because x_A + x_B = 1$$

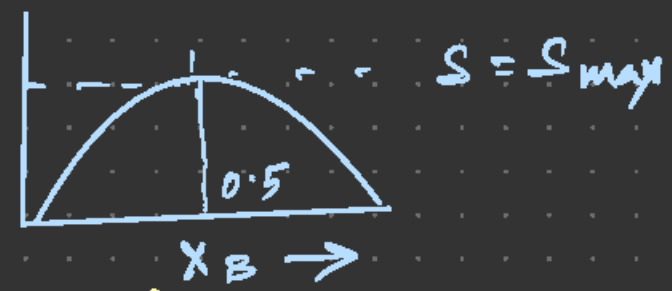
$$\therefore \Gamma \left(\ln \Gamma - x_A \ln \Gamma_A - x_B \ln \Gamma_B \right)$$

$$= \Gamma \left(x_A \ln \Gamma - x_A \ln \Gamma_A + x_B \ln \Gamma - x_B \ln \Gamma_B \right)$$

$$= -\Gamma \left(x_A \ln \frac{\Gamma_A}{\Gamma} + x_B \ln \frac{\Gamma_B}{\Gamma} \right)$$

$$= -\Gamma \left(x_A \ln x_A + x_B \ln x_B \right)$$

$$S = k_B \ln \Omega$$



$$= -k_B N \left(x_A \ln x_A + x_B \ln x_B \right)$$

ff N = Avogadro number

$$N k_B = R$$

$$x_B = x$$

$$x_A = 1 - x$$

$$\therefore \quad S = -R \left(x_A \ln x_A + x_B \ln x_B \right)$$

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

Also $S = S_{max}$ when $x_A = x_B = \frac{1}{2}$

Ideal solution - Ideal gas mixture

$$\Delta S_{m,mix} = -R \sum_{i=1}^{c} x_i \ln x_i$$

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

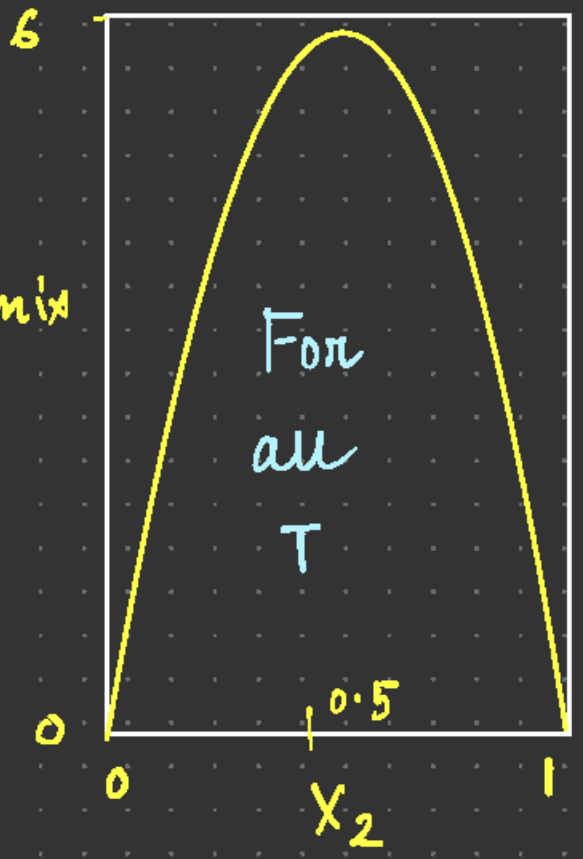
$$\Delta G_m = \Delta H_m - T\Delta S_m$$

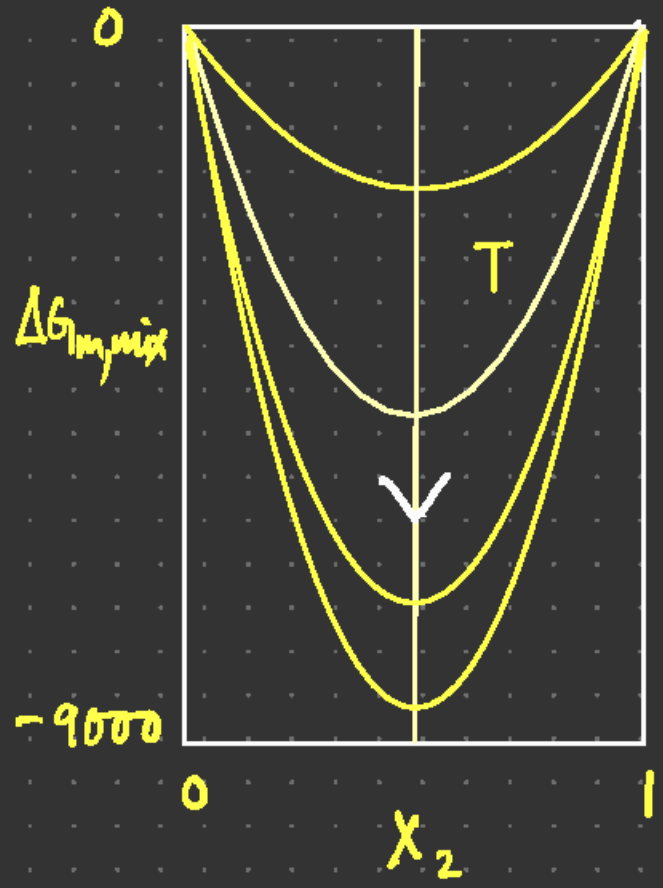
$$\Delta H_{m,mix} = 0$$

$$\Delta V_{m,mix} = 0$$

$$\Delta U_{m,mix} = 0$$

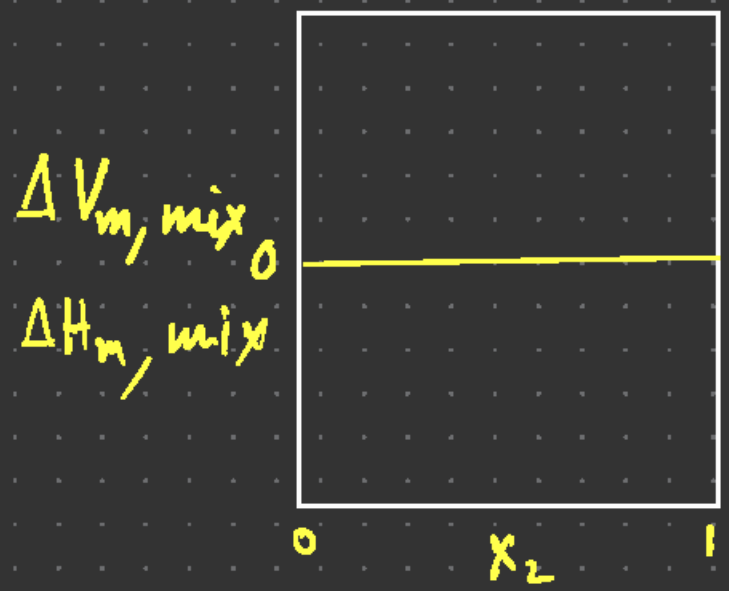
$$\Delta F_{m,mix} = RT \sum_{i=1}^{c} x_i \ln x_i$$





$X_1 = X_2 = 0.5$

$\Delta S_{m,mix}$ is maximum when $X_1 = X_2 = 0.5$



Ideal Solution.

For Ideal Gas

$$\bar{V}_k = \frac{RT}{P}$$

Real Gas: $\alpha_k = \bar{V}_k - \frac{RT}{P}$

$$\Delta\mu_k = \int_{p}^{P_k} \bar{V}_k \, dP$$

$$= \int_{p}^{P_k} \left(\alpha_k + \frac{RT}{P} \right) dP$$

$$= \int_{p}^{p_k} \alpha_k \, dP + RT \ln \frac{p_k}{p}$$

$$\Delta\mu_k = \mu_k - \mu_k^{o} = RT \ln \frac{f_k}{p}$$

Fugacity of component k

$$= \int_{p}^{p_k} \alpha_k \, dP + RT \ln \frac{p_k}{p}$$

$$RT \ln \frac{f_k}{p} \cdot \frac{p}{p_k} = \int_{p}^{p_k} \alpha_k \, dP$$

$$RT \ln \left(\frac{f_k}{p_k} \right) = \int_{p}^{p_k} \alpha_k \, dP$$

$$\ln \frac{f_k}{p_k} = \frac{1}{RT} \int_p^{p_k} \alpha_k \, dp$$

$$f_k = p_k \exp \left[\frac{1}{RT} \int_p^{p_k} \alpha_k \, dp \right]$$

$$\alpha_k \to 0 \; ; \; f_k \to p_k$$

f_k – fugacity of component k

$$\mu_k - \mu_k^{\circ} = \Delta\mu_k = RT \ln a_k = RT \ln \frac{f_k}{P}$$

$$a_k = \frac{f_k}{P}$$

P is the pressure in the reference state for component k

Fugacity – Gas mixture

$$\overline{\Delta G}_k = \Delta\mu_k = RT \ln a_k$$

$$\begin{cases} a_k = X_k & \text{Ideal} \\ \gamma_k = 1 & \text{Solution} \end{cases}$$

$$\left(\frac{\partial \Delta\mu_k}{\partial T}\right)_{P, n_k} = R \ln a_k + RT\left(\frac{\partial \ln a_k}{\partial T}\right)_{P, n_k}$$

$$\left(\frac{\partial \Delta\mu_k}{\partial P}\right)_{T, n_k} = RT\left(\frac{\partial \ln a_k}{\partial P}\right)_{T, n_k}$$

$$X_1 d\Delta\mu_1 + X_2 d\Delta\mu_2 = 0$$

$$\Delta\mu_1 = -\int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d\Delta\mu_2}{dX_2} dX_2$$

$X_1 d\Delta\mu_1 + X_2 d\Delta\mu_2 = 0$

$$\ln a_1 = -\int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d\ln a_2}{dX_2} dX_2$$

$$d\Delta\mu_1 = RT\, d\ln a_1$$

$$d\Delta\mu_2 = RT\, d\ln a_2$$

As $a_2 \to 0$

$$\ln a_2 \longrightarrow -\infty$$

$$a_k = \gamma_k x_k$$

$$\Delta \bar{G}_k = \Delta \mu_k = RT \ln \gamma_k x_k$$

$$= \underbrace{RT \ln \gamma_k}_{\text{Departure from ideality}} + \underbrace{RT \ln x_k}_{\text{Ideality}}$$

Deviation from ideality

$$\Delta \bar{G}_k = \Delta \bar{G}_k^{xs} + \Delta \bar{G}_k^{id}$$

or, $$\Delta \mu_k = \Delta \mu_k^{xs} + \Delta \mu_k^{id}$$

$$= RT \ln \gamma_k + RT \ln X_k$$

Say $\gamma_k > 1$

Apparent concentration of 'k'

> Actual concentration of 'k'

X_k

Positive deviation

When $\gamma_k < 1$ $\quad a_k = \gamma_k X_k$

$$\Delta \bar{G}_k^{xs} = \Delta \mu_k^{xs} = RT \ln \gamma_k < 0$$

Apparent concentration of 'k'

< Actual concentration of 'k'

Negative deviation from ideality

$$\left(\frac{\partial \Delta\mu_k}{\partial T}\right)_{P,n_k} = R\ln\gamma_k + RT\left(\frac{\partial \ln\gamma_k}{\partial T}\right)_{P,n_k} + R\ln X_k$$

$$\left(\frac{\partial \Delta\mu_k}{\partial P}\right)_{T,n_k} = RT\left(\frac{\partial \ln\gamma_k}{\partial P}\right)_{T,n_k}$$

Gibbs Duhem

$$X_1 d\Delta\mu_1 + X_2 d\Delta\mu_2 = 0$$

$\Delta\mu_1 = RT\ln(\gamma_1 X_1)$ $\quad$ $\Delta\mu_2 = RT\ln(\gamma_2 X_2)$

$$d\Delta\mu_k = RT\, d\ln\gamma_k + RT\, d\ln X_k$$

$$X_1 RT\left(d\ln\gamma_1 + d\ln X_1\right) + X_2 RT\left(d\ln\gamma_2 + d\ln X_2\right)$$

$$= 0$$

$$X_1 d\ln X_1 + X_2 d\ln X_2$$

$$= dX_1 + dX_2 \qquad \because X_1 + X_2 = 1,\ dX_1 = -dX_2$$

$$= 0$$

$$\therefore X_1 d\ln\gamma_1 + X_2 d\ln\gamma_2 = 0$$

$$\ln \gamma_1 = -\int_{x_2=0}^{x_2} \frac{x_2}{x_1} \frac{d \ln \gamma_2}{dx_2} dx_2$$

Dilute Solutions

Raoult's law for Solvent

'1' – Solvent

'2', '3', ... 'c' — Solutes

Ideal Solution

$a_k = X_k$

$\gamma_k = 1$

$$\lim_{X_1 \to 1} a_1 = X_1$$ (Raoult's law)

Any component $a_i = X_i$

'2' – solute

$X_2 \to 0$

⇒ Dilute solution

Henry's law for solute

$$\lim_{X_2 \to 0} a_2 = \gamma_2^0 X_2 = K_H X_2$$

γ_2^0 is independent of concentration and is called Henry's Law Constant (applicable in dilute range)

γ_2^0 : depends on both solute and solvent

Raoult's law



Ratio of partial vapour pressure of each component to its vapour pressure as a pure liquid/solid solvent is approximately

$$p_i = x_i p_i^0$$

'i' - pure solvent

Mixture of two liquids or two solids A and B

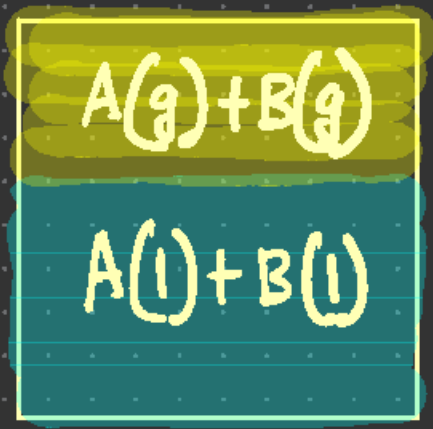
Use * for pure substance

μ_A^o – Standard chemical potential of A in vapour phase

$$\mu_A^* = \mu_A^o + RT \ln p_A^* \quad -(1)$$

Solution of A+B

$$\mu_A = \mu_A^o + RT \ln p_A \quad -(2)$$



$$\mu_A(g) = \mu_A(l)$$

$$\mu_A^o = \mu_A^* - RT \ln p_A^* \quad (\text{pure A})$$

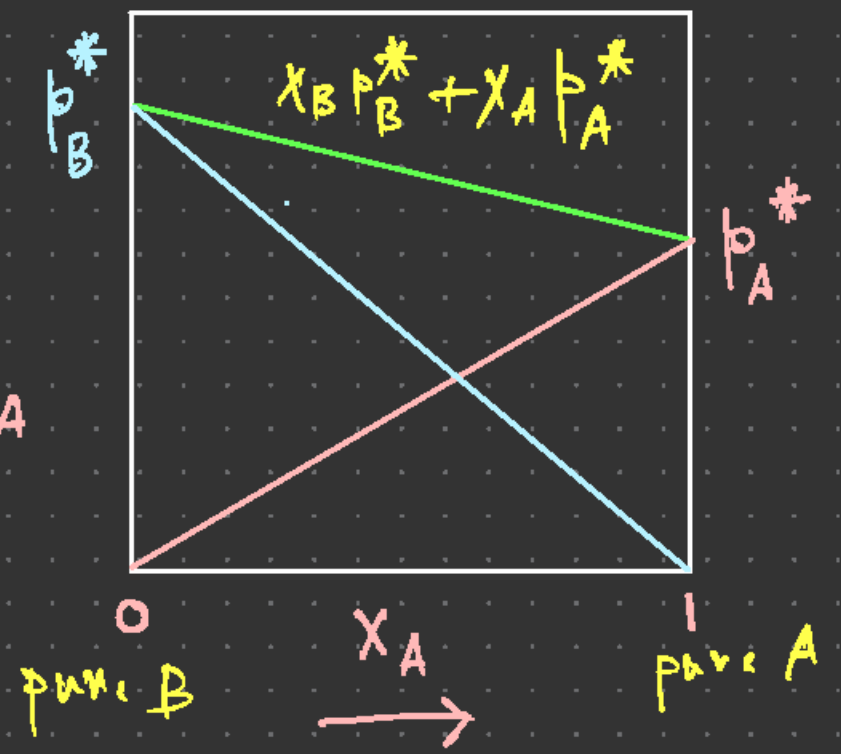
$$= \mu_A - RT \ln p_A \quad (\text{A+B soln.})$$

$$\therefore \quad \mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

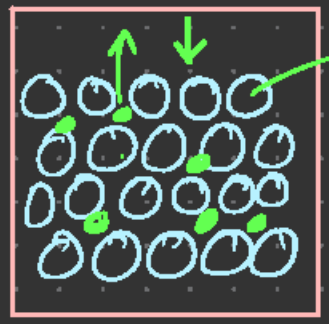
$p_A^* \rightarrow$ vapour pressure of pure liquid A

$p_A \rightarrow$ partial vapour pressure of component A

$$p_A = X_A p_A^*$$



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



Rate of vaporization $= k X_A$

Rate of condensation $= k' p_A$

$k' p_A = k X_A$ at equilibrium

$$p_A = \frac{k}{k'} X_A$$

Pure liquid/solid $X_A = 1$

$$\therefore \quad p^* = \frac{k}{k'} \qquad p_A = X_A p_A^*$$

Thus,

$$p_A = X_A p_A^*$$

Solute and solvent both obey Raoult's law when solution is ideal

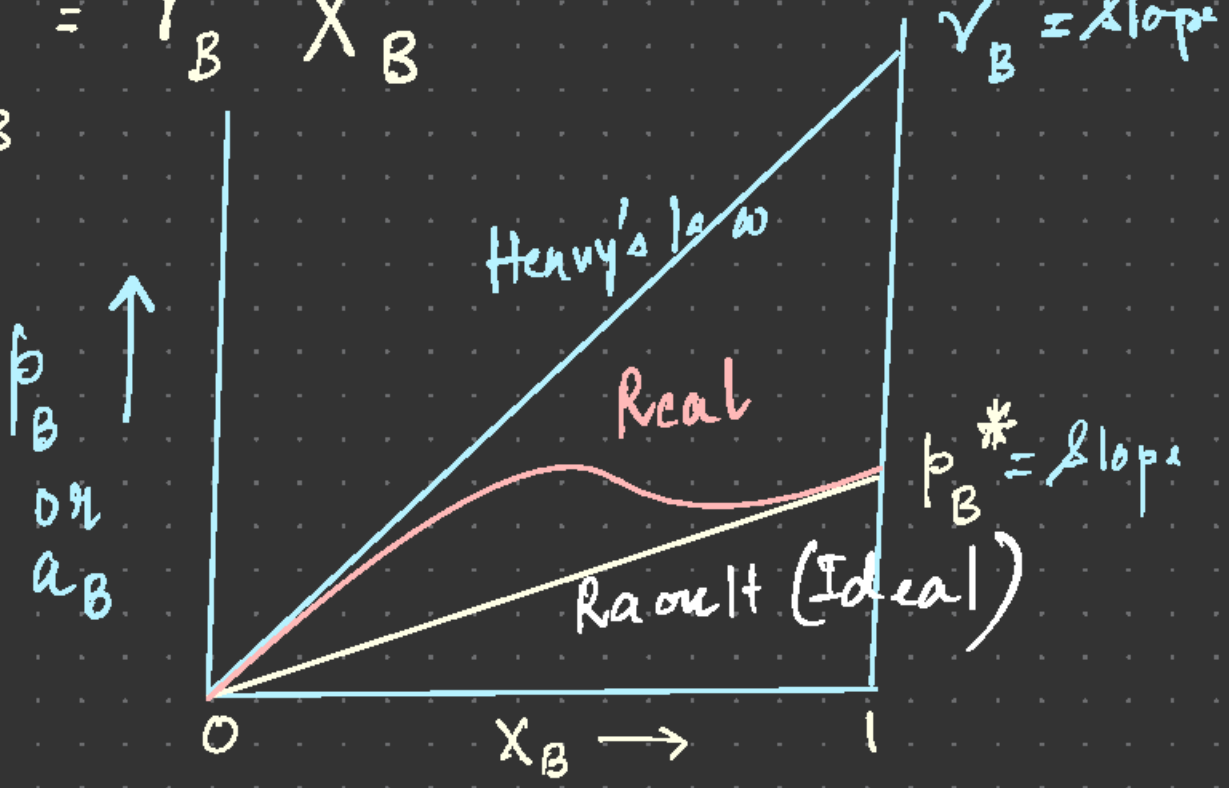
Henry's law - Real solution at low concentration of solute

Vapour pressure of solute proportional to the mole fraction of solute

$$p_B = \gamma_B^{\circ} X_B$$

$$a_B = \gamma_B^{\circ} X_B$$

$$p_B = p_B^{*} X_B$$



Ideal dilute Solutions

- Solvent obeys Raoult's law
- Solute obeys Henry's law

See the table

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

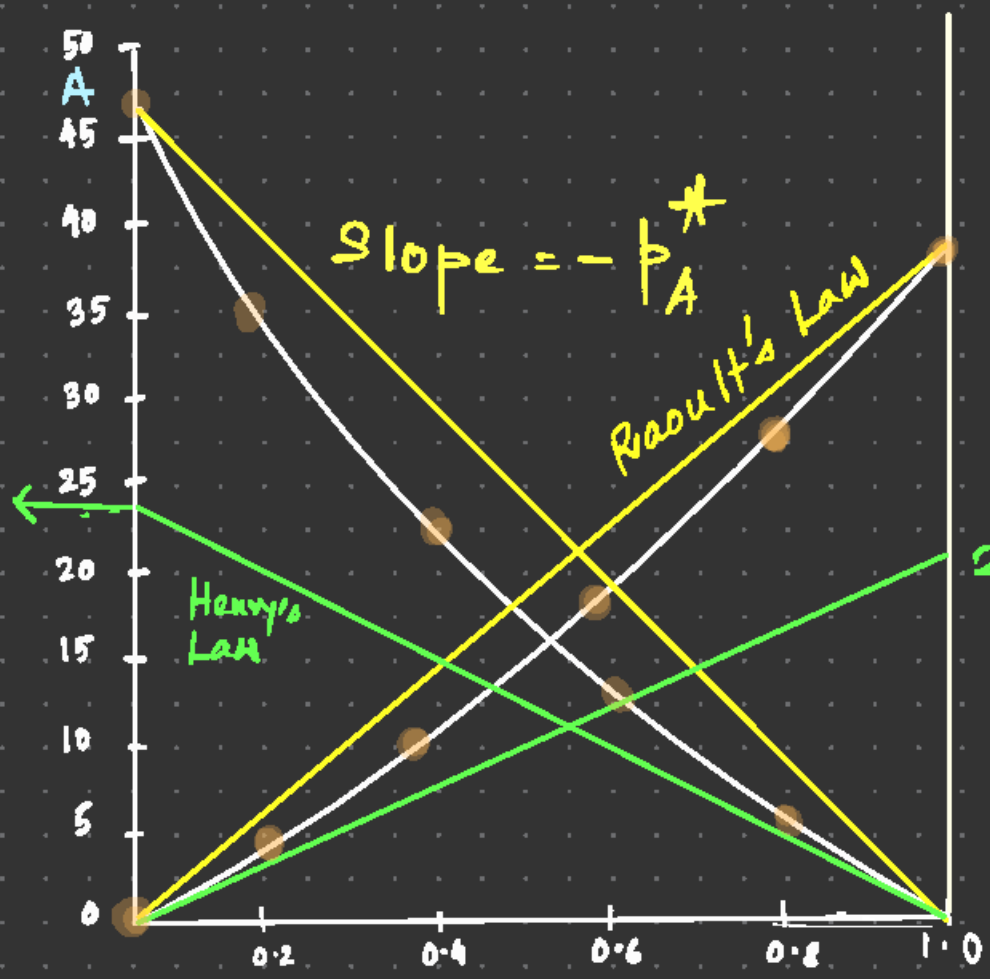
x_C	0	0.2	0.4	0.6	0.8	1
p_C (kPa)	0	4.7	11	18.9	26.7	36.4
p_A (kPa)	46.3	33.3	23.3	12.3	4.9	0

Raoult's law

$$p_A = p_A^* x_A$$

$$= p_A^* (1 - x_C)$$

$$p_C = p_C^* x_C$$



p ↑

$\gamma_A^0 = 23.3$

$22.0 = \gamma_C^0$

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)

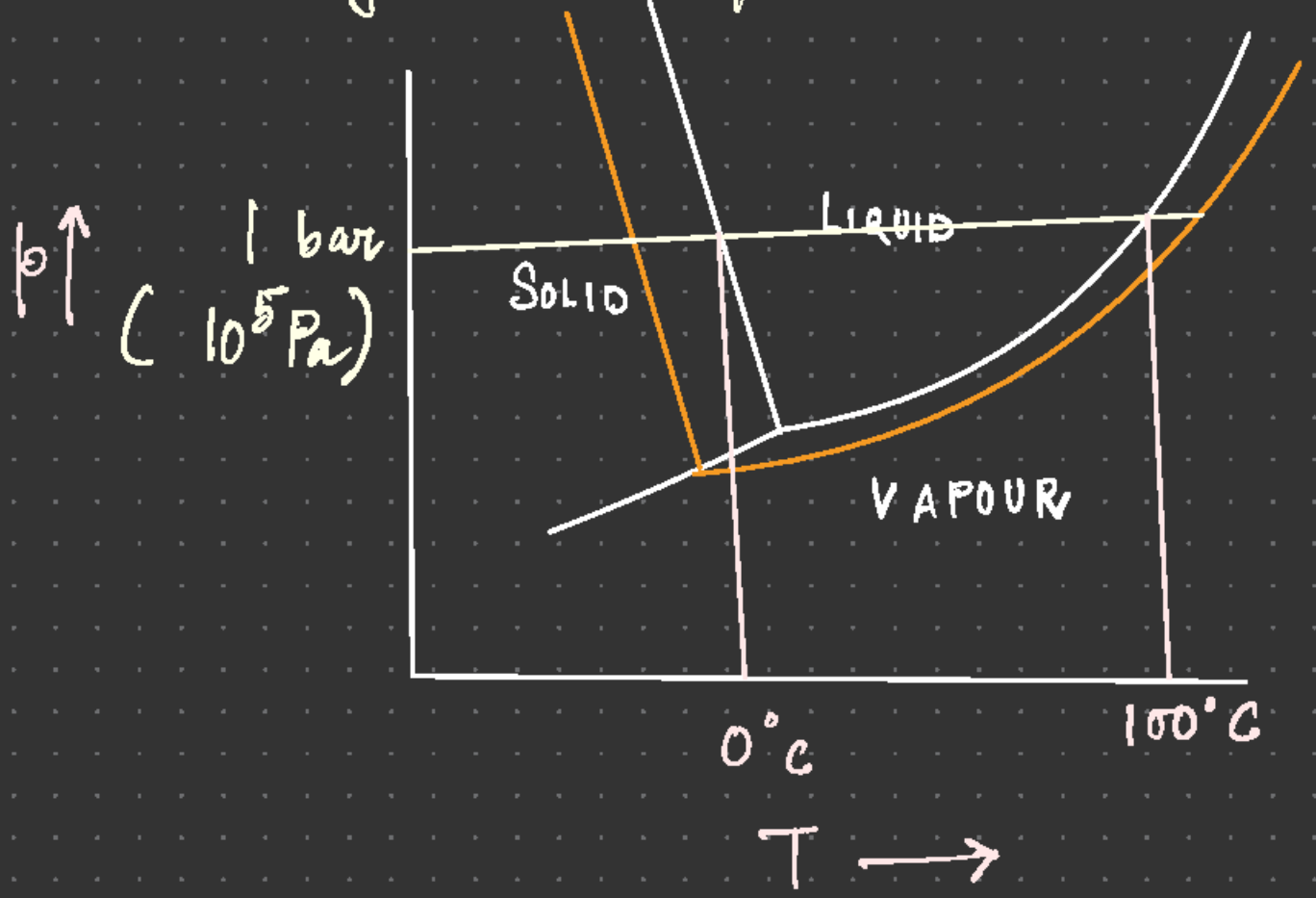
$p_B = k_B b_B \qquad k_{O_2} = 7.9 \times 10^4\ kPa\ kg\ mol^{-1}$

b_B (molality)

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

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

Colligative properties



$$p = x p^*$$

Elevation of boiling point

Solvent A

Solute B

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

$$T_b \rightarrow T_b^* + \Delta T$$

$$\Delta T = K_H X_B$$

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

Gibbs-Helmholtz equation

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

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

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

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

$$\frac{d(\Delta G^{vap}/T)}{dT} = R \frac{d \ln X_A}{dT}$$

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

At $X_A = 1$ (pure A)

$\ln X_A = 0$

$$\int_{0\ (\text{pure A})}^{\ln X_A} d \ln X_A = -\frac{1}{R} \int_{T_b^*}^{T_b} \frac{\Delta H^{vap}}{T^2} dT$$

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

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

$X_B \ll 1$ (Dilute solution)

or, $X_B \to 0$

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

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

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

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

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

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

$$\mu_A(s) = \mu_A(l)$$

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

$$\Delta T = K_H' X_B$$

$$K_H' = \frac{RT_f^{*2}}{\Delta H^{fusion}}$$

Solubility

$X_B = 1$ at $T = T_f$

$$\mu_B^*(s) = \mu_B(l)$$

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

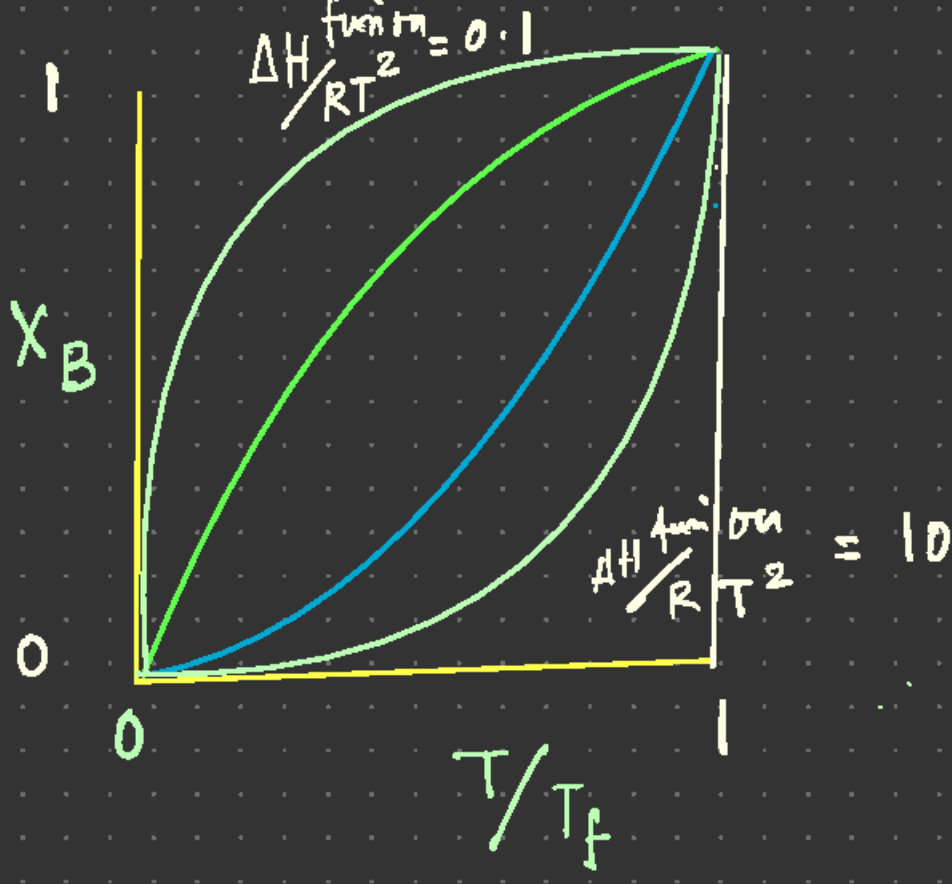
$$\ln X_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT}$$

$B(s) \rightarrow B(l)$

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

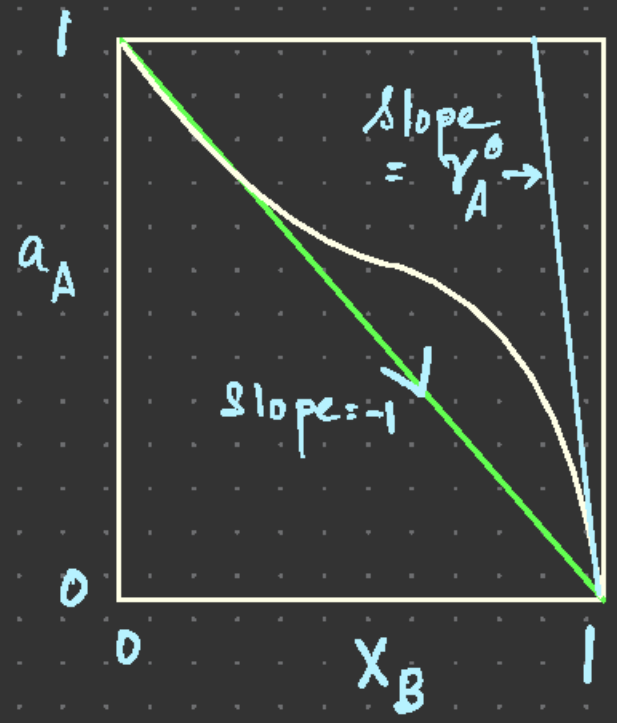
$$\int_0^{\ln X_B} d \ln X_B = -\frac{1}{R} \int_{T_f}^{T} \frac{\Delta H^{fusion}}{T^2} dT$$

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



No solvent property

Deviation from ideality



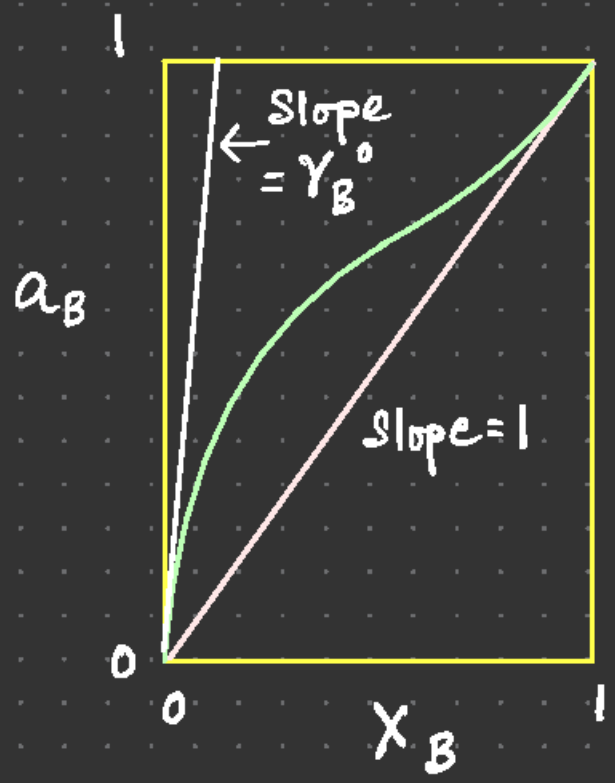
$$a_A = \gamma_A x_A$$

Raoult's law

$$a_A = x_A$$

Henry's law

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



Raoult' law

$a_B = X_B$

Henry's law

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

Regular Solution models

$$\Delta S_{m,mix} = \Delta S^{ideal}_{m,mix} = -R \sum_{i=1}^{c} x_i \ln x_i$$

$$\Delta H_{m,mix} = \Delta H^{xs}_{m,mix}\left(x_1, x_2, \cdots, x_c\right)$$

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

$$= \Delta H_{m,mix}\left(x_1, x_2, \cdots, x_c\right)$$

$$\Delta \mu_k^{xs} = \Delta \bar{G}_k^{xs} = \Delta \bar{H}_k = RT \ln \gamma_k$$

$$\gamma_k = e^{\Delta \bar{H}_k / RT}$$

$$\Delta H_{m,mix} = a_0 X_1 X_2 = \Delta G_{m,mix}^{xs}$$

$$\therefore \Delta G_{m,mix} = \Delta G_{m,mix}^{xs} + \Delta G_{m,mix}^{id}$$

$$= a_0 X_1 X_2 + RT\left(X_1 \ln X_1 + X_2 \ln X_2\right)$$

$$\Delta \bar{H}_1 = \Delta \bar{G}_1^{xs} = a_0 X_2^2$$

$$\Delta \bar{H}_2 = \Delta \bar{G}_2^{xs} = a_0 X_1^2$$

$$\therefore \quad \gamma_1 = e^{a_0 x_2^2 / RT}$$

$$\gamma_2 = e^{a_0 x_1^2 / RT}$$

if $x_2 \rightarrow 0$ or $x_1 \rightarrow 1$

$$\gamma_2^0 = e^{a_0 / RT}$$

$$\gamma_1^0 = 1$$