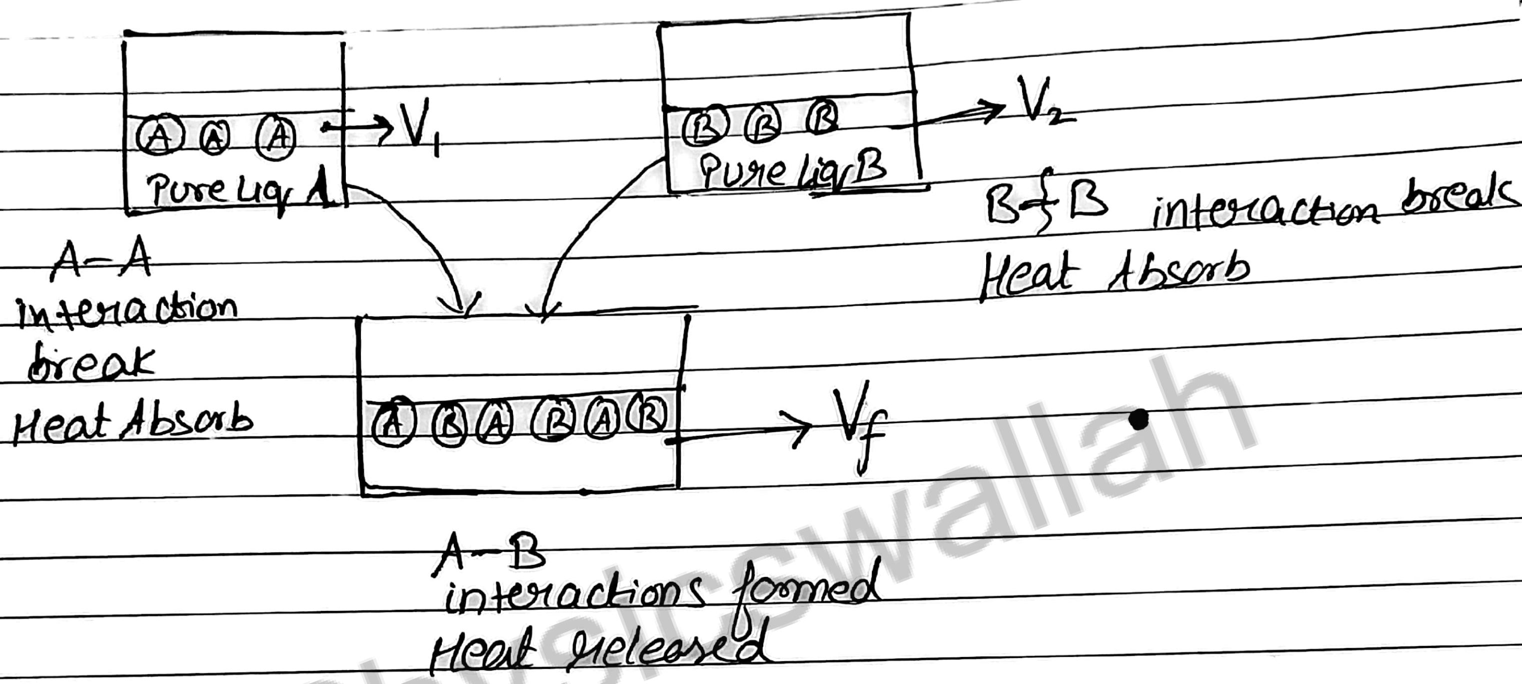
Ideal & Non-Ideal Solutions

Formation of Solution



$\Delta V_{mix} = V_f - (V_1 + V_2)$ change in volume on mixing

$\Delta H_{mix} =$ Heat (Enthalpy) change in mixing

$\Delta S_{mix} =$ Entropy change in mixing $\boxed{\Delta S_{mix} > 0}$ Always

$\Delta G_{mix} =$ Gibb's free energ change in mixing $\boxed{\Delta G_{mix} < 0}$ Always

($\Delta S_{mix} > 0$ as no. of particles increase
entropy depends on no. of particles)

($\Delta G_{mix} < 0$ → for any spontaneous process)

On the basis of ΔV_{mix} & ΔH_{mix}, solutions are classified as — Ideal & Non Ideal Solutions.

① Ideal Solution :

i) which follows Rault's Law at all concentration and Temperature

$$\underset{\substack{\text{(from manometer)} \\ \text{experimentally}}}{P_{observed}} = P^o_A X_A + P^o_B X_B$$

$$P_{A\,observed} = P^o_A X_A \qquad P_{B\,observed} = P^o_B X_B$$

All. $\underset{\text{from experiments}}{P_{observed}} = \underset{\text{from Rault's Law}}{P_{calculated}}$

ii) $\Delta V_{mix} = 0$

Reason:

$(A-A)_{interactions} = (B-B)_{interactions} = (A-B)_{interactions}$

Force of Attraction of both Liquids is same as Force of Attraction of Solution molecules (A-B)

So, molecules neither come closer, nor moves aways

$\Rightarrow V_f = V_1 + V_2$ & $\Delta V_{mix} = 0$

iii) $\Delta H_{mix} = 0$

Reason: Heat Absorbed to break (A-A) & (B-B) = Heat Released to form (A-B) interaction

iv) $\Delta S_{mix} > 0$ v) $\Delta G_{mix} < 0$

vi) $(A-A)_{interactions} = (B-B)_{interactions} = (A-B)_{interactions}$

example ① $CH_3OH + C_2H_5OH$

same polarity (polar Nature) & nearly same Molecular Size

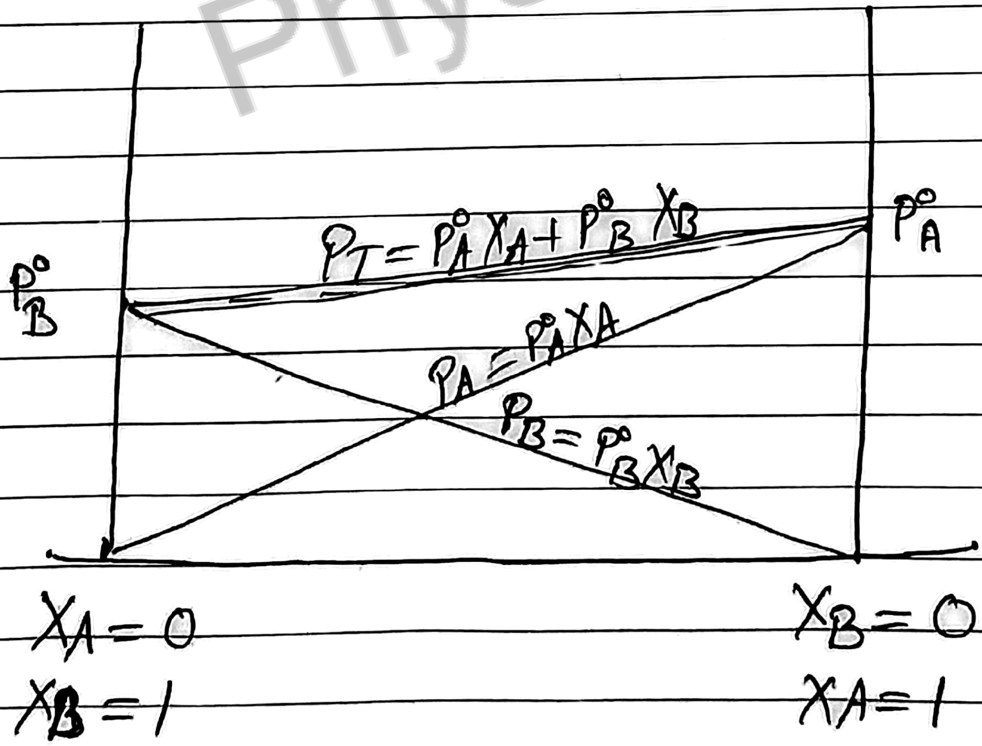
② $C_6H_6 + C_6H_5CH_3$
Benzene Toluene

③ $C_2H_5Cl + C_2H_5Br$ → nearly same size & polar Nature

④ $C_2H_4Br_2 + C_2H_4Cl_2$

⑤ $C_2H_5Cl + C_2H_5I$ → ✗ Cl & I diff in size

⑥ n-hexane + n-heptane



Non-Ideal Solutions :

i) which do not follow Rault's Law

$$P_{observed} \neq P_A^o \chi_A + P_B^o \chi_B$$

$P_{A\,obs} \neq P_A^o \chi_A$ $\qquad$ $P_{B\,obs} \neq P_B^o \chi_B$

ii) $\Delta V_{mix} \neq 0$

Reason: $\left.\begin{matrix}(A-A)\\(B-B)\end{matrix}\right\}$ interactions $\neq$ $(A-B)$ interactions

either FOA increases or decreases, so molecules may come closer or move further

$V_f \neq V_1 + V_2$

iii) $\Delta H_{mix} \neq 0$

Reason: Heat absorbed to break $A-A$ & $B-B$ $\neq$ Heat Released in formation of $A-B$

iv) $\left.\begin{matrix}(A-A)\\(B-B)\end{matrix}\right\}$ interactions $\neq$ $(A-B)$ interactions

v) $\Delta S_{mix} > 0$ $\qquad$ $\Delta G_{mix} < 0$ $\qquad$ Always.

चाहे Ideal हो या Non-Ideal.

Types of Non-Ideal Solution

→ +ve deviation from Rault's Law

→ -ve deviation from Rault's Law

① Non-Ideal Solution Showing -ve deviation from Rault's Law

i) $P_{observed \text{ experimentally}} < P_A^0 X_A + P_B^0 X_B$

$P_{A\,obs} < P_A^0 X_A$ $\qquad$ $P_{B\,obs} < P_B^0 X_B$

ii) (A–B) interactions > (A–A), (B–B) interactions

Force of Attraction Increases on mixing ⇒ Thus Vapour Pressure Decrease
(FOA)

iii) $\Delta V_{mix} < 0$

Reason: FOA Increases thus molecules come closer & volume decreases $V_f < V_1 + V_2$

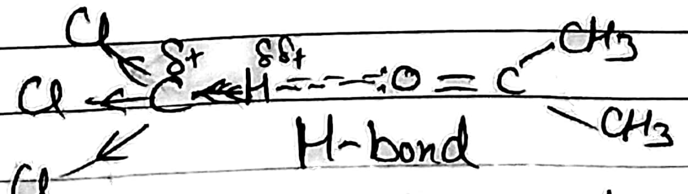
(iv) $\Delta H_{mix} < 0$

(A–A) (B–B) weaker — Less Heat absorbed

(A–B) stronger — More Heat released

examples

① $CHCl_3 + CH_3\overset{\overset{O}{\|}}{C}-CH_3$



new Interaction in Solution

H-bond banne se FOA Increases↑ -

(2) $CHBr_3$ + CH_3COCH_3

OR

CHX_3 + (O,N) containing compounds

(3) Strong Acid + water

$HClO_4$ + H_2O

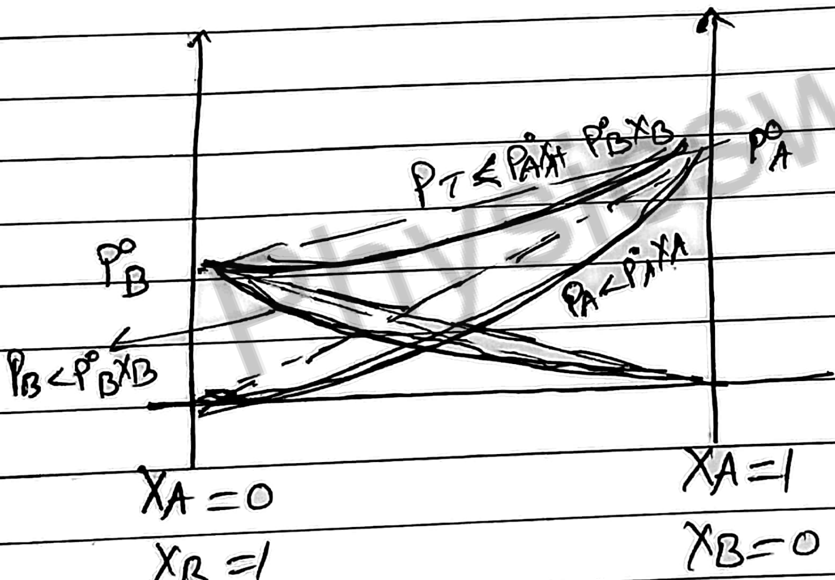
H_2SO_4 + H_2O

HNO_3 + H_2O

HI + H_2O

HCl + H_2O

HBr + H_2O



$P_A < P^o_A X_A$

$P_B < P^o_B X_B$

$P_T < P^o_A X_A + P^o_B X_B$

(2) Non-Ideal Solution Showing +ve deviation from Rault's Law

i) $P_{observed}$ (Total) $> P^o_A X_A + P^o_B X_B$

P_A observed $> P^o_A X_A$ (Rault's law) P_B obs $> P^o_B X_B$ (Rault's law)

ii) FOA decreases on mixing ⇒ Vapour Pressure Increases

$$\begin{matrix}(A-A) \\ (B-B)\end{matrix} > (A-B)$$

interactions interactions

iii) $\Delta V_{mix} > 0$

Reason:

FOA decreases ⇒ Molecules moves away → volume Increases

iv) $\Delta H_{mix} > 0$

Heat absorbed to break A-A & B-B (stronger) > Heat released in formation of A-B (weaker)

example. ① $H_2O + C_6H_6$

H-bonding

Solution $H_2O - C_6H_6$ NO H bonding

Interactions Decreases

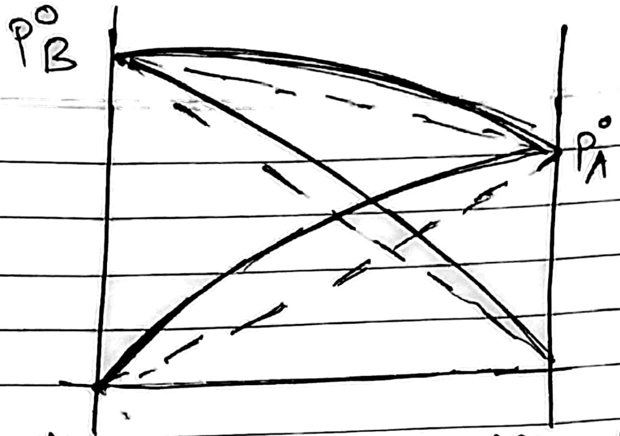
② $H_2O + C_6H_5CH_3$
Toluene

③ $CH_3OH + C_6H_6$

④ $C_2H_5OH + C_6H_5CH_3$

⑤ $H_2O + CH_3OH$

⑥ $H_2O + C_2H_5OH$



$P_T > P^o_A X_A + P^o_B X_B$

$P_A > P^o_A X_A$

$P_B > P^o_B X_B$

obs calculated

$X_A = 0$ $X_B = 1$ Pure B

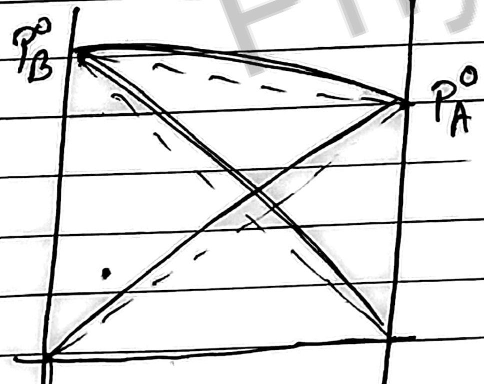
$X_A = 1$ $X_B = 0$ Pure A

dotted lines → Rault's Law

dark lines → experiment observed

Two types of Non-Ideal Solutions Showing +ve Deviation

Type I



$X_A = 0$ $X_B = 1$ Pure B

$X_A = 1$ $X_B = 0$ Pure A

Here, P_T is never greater than P^o_B

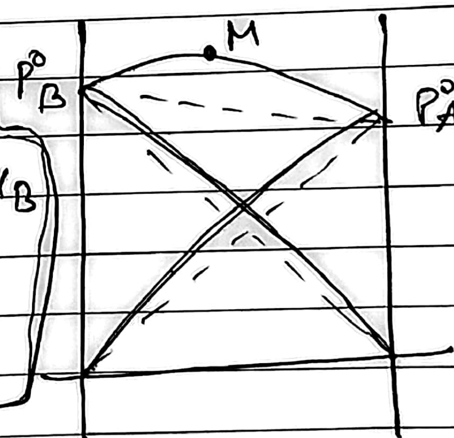
For Both

$P_T > P^o_A X_A + P^o_B X_B$

$P_A > P^o_A X_A$

$P_B > P^o_B X_B$

Type II



$X_A = 0$ $X_B = 1$ Pure B

$X_A = 1$ $X_B = 0$ Pure A

Here, P_T is at some point (M) greater than even P^o_B