

$$P_t = \alpha(P_A - P_B) + P_B$$

$$\alpha = \frac{P_t - P_B}{P_A - P_B}$$

$$y_A^* = \frac{P_A \alpha}{P_t} = \frac{\alpha P_A}{P_B + \alpha(P_A - P_B)}$$

Complete the V-L-E Data

Ex 1

mix { m-Heptane } at 1 atm.
 { n-Octane. }

T.B.P. n-Heptane \rightarrow 98.4°C (A) \rightarrow more volatile
 n-Octane \rightarrow 125.6°C (B)

at Compute V.P at different T.

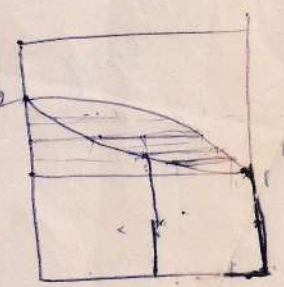
Ex at 110°C V.P of A $P_A = 1050$ mmHg
 $P_B = 484$ mmHg
 $P_t = 760$ mmHg.

$$\alpha_A = \frac{P_t - P_B}{P_A - P_B} = \frac{760 - 484}{1050 - 484} = 0.487 \text{ A is lighter}$$

$$y_A = \frac{P_A \alpha}{P_t} = \frac{1050 \times 0.487}{760} = 0.674 \text{ — vap.}$$

$$\alpha = \frac{P_A}{P_B} = \frac{1050}{484} = 2.17$$

T	P_A	P_B	α	y_A	α_1
98.4	760	333	2.28	1	
105					
110					
115					
120					
125.6	1540	760	2.02	0	

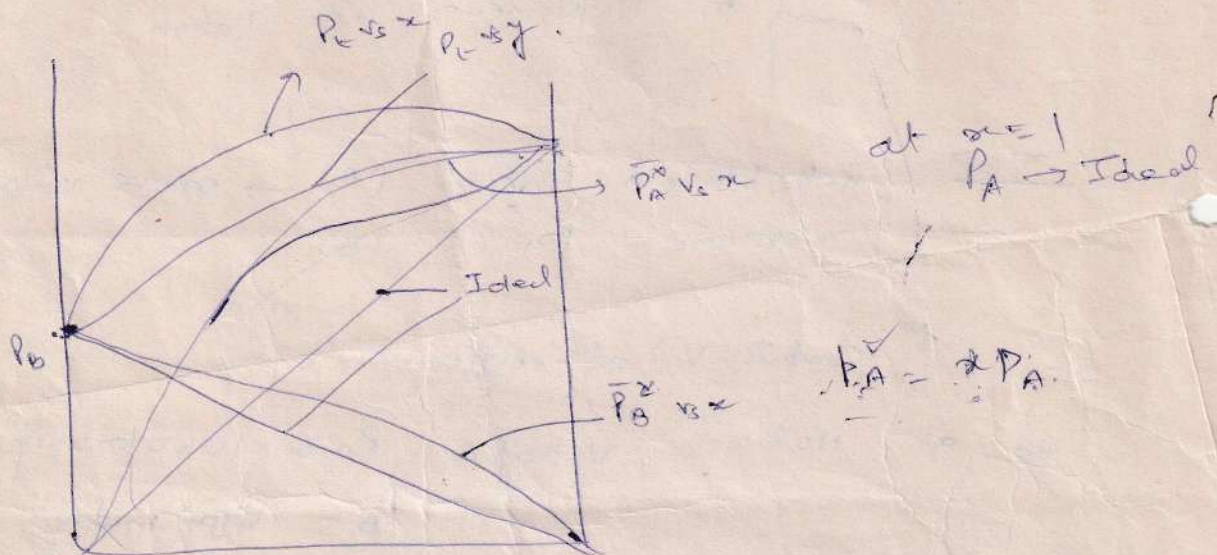


So. Calculate $\bar{\alpha} = \frac{q_1 + \alpha_L - \dots}{n} = 2.16$

eqm relationship

$$y^* = \frac{\alpha x}{1 + (\alpha - 1)x}$$

Positive deviation from ideality.



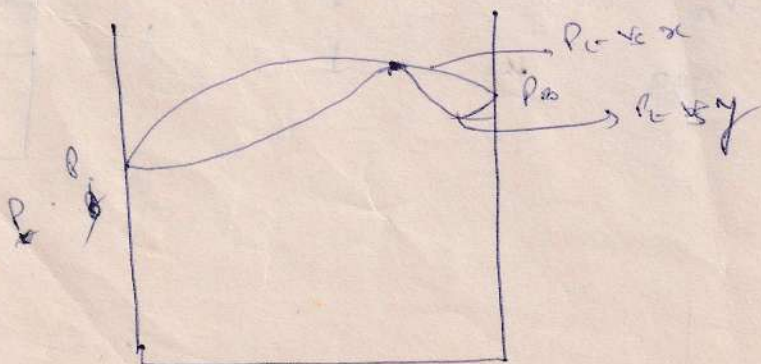
$$\frac{\text{Actual Press}}{\text{Ideal Press}} = \frac{\bar{P}_A^*}{P_A^*} = \gamma = \text{activity coefficient}$$

$\gamma > 1 \Rightarrow \ln \gamma > 0 \Rightarrow$ positive deviation from ideality.

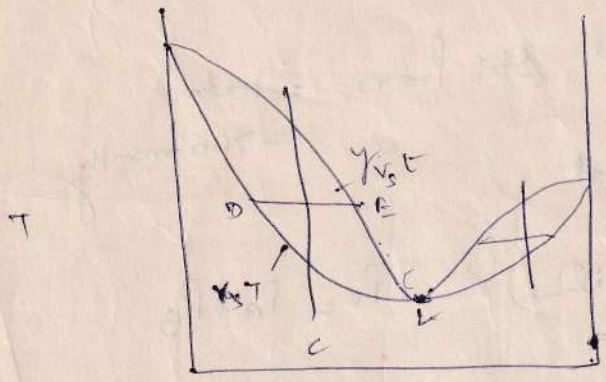
minimum boiling azeo mix \Rightarrow azeotrope (const boiling mix)

① when (v.e.D.R) is sufficient

large. ② v.p are not too far



x, y^*



right to L $\alpha < 1$
 so. generally we use $\frac{1}{\alpha}$

mix of composition L gives rise to a vap of composition identical with the liquid.

it consequently boils at const temp. without change in composition.

$$y^* = x \quad \alpha = 1$$

can eliminate azeotrope by changing the press.

ex ethanol - water azeotrope \leftarrow 1 atm
 89.4% ethanol
 78.2°C

below 70 mm Hg Azeotrope disappears

Insoluble liquids \rightarrow Steam distillation

ex. hydrocarbon + water

the vapour pressure of either component cannot be influenced by the presence of other

(partial press = vap. press)

$$P_c = P_A + P_B$$

$y^* = \frac{P_A}{P_c} \Rightarrow$ mix will boil at same temp and produce a vap of const composition.

ex

Ex 50 g water \Rightarrow 2.78 gmol
 + 50 g ethylaniline \Rightarrow 0.412 gmol
 } boil at std. pres. = 1 atm.
 = 760 mmHg

t	P_A water	P_B (ethylaniline)	$P_T = P_A + P_B$
38.5	51.5	1	
64.4	199.7	5	52.5
80.8	363.9	10	205
96	657.6	20	374
99.15	737.2	22.8	678
113.2	1225	40	760
204		760	1265

mix boils at $T = 99.15^\circ\text{C}$
 with composition

$$y^* = \frac{P_A}{P_T} = \frac{737.2}{760} = 0.97 \text{ mole fraction of water}$$

1 mole contain $\begin{cases} 0.97 \text{ water} \\ 0.03 \text{ ether} \end{cases}$

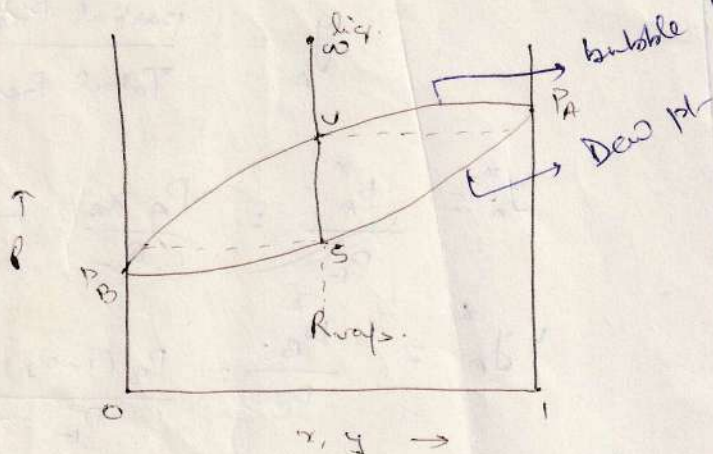
whole water will evaporated with

the temp will then rise to 204°C and the equilibrium vap will be pure ethylaniline -
 $2.78 \times \left(\frac{0.03}{0.97}\right) = 0.086 \text{ gmol ethylaniline}$

0.97 mole of water \rightarrow 0.03 mole of ethylaniline
 $2.78 \rightarrow \left(\frac{0.03}{0.97} \times 2.78\right) \checkmark$

Constant temp equilibria ①

in a closed container entire liq will vaporise as P_{ext} is reduced at const. temp.



U: first bubble of vap form
 S: complete vaporisation occurs
 R = heated vaps.

Relative volatility:

numerical measure: ratio of A and B in one phase to that in other phase. i.e.

$$\alpha = \frac{y^A / (1 - y^A)}{x / (1 - x)} \quad \text{or} \quad \frac{y^A \cdot (1 - x)}{x \cdot (1 - y^A)}$$

graphically: greater the distance b/w equilibrium curve and diagonal line

α will change as x varies 0, to 1, and $y^A = x \Rightarrow \alpha = 1$ but not valid for $x=0$, or 1

greater diff. in liq and vaps composition $(\alpha > 1)$

easier separation by distillation.

relation is not correct for 0 and 1

to calculate $\alpha = P_A / P_B$ if $\alpha = 1 \Rightarrow$ no separation possible

$(y^A = x)$ Raoult's

Ideal solus. - (Raoult's law) at fixed temp.

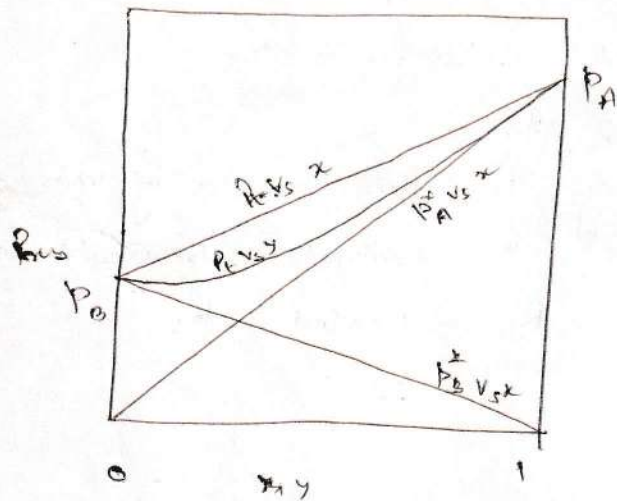
equilibrium partial pres $P_A^* = x_A P_A^0$
 $P_B^* = P_B^0 (1 - x_A)$

if vapour phase is also ideal

$$P_{tot} = P_A^* + P_B^* = P_A^0 x_A + P_B^0 (1 - x_A)$$

if pressure too high then obey fugacities instead of P pres.

So, Total press is linear with x at fixed temp.



because for ideal gas

mole fraction

$$y_A = \frac{\text{partial } P_{\text{tot}}}{\text{Total } P_{\text{tot}}} = \frac{P_A^*}{P_{\text{tot}}}$$

$$y_A^* = \frac{P_A^*}{P_{\text{tot}}} = \frac{P_A x_A}{P_{\text{tot}}} \quad \text{--- (1)}$$

$$x_A^* = \frac{P_B^*}{P_{\text{tot}}} = \frac{P_B (1-x_A)}{P_{\text{tot}}} \quad \text{--- (2)}$$

α value does not vary much for ideal solution and for non-ideal system does not define

from both eqn

$$\frac{P_A}{P_B} = \alpha = \frac{(y_A)}{(x_A)} \times \frac{(1-x)}{x}$$

$$y = \frac{\alpha x}{1 + (\alpha - 1)x}$$

Positive Deviation from Ideality: (most mixture)

$$P_{\text{act}} > P_{\text{ideal}}$$

$$P_{\text{act}} > P_{\text{ideal}}$$

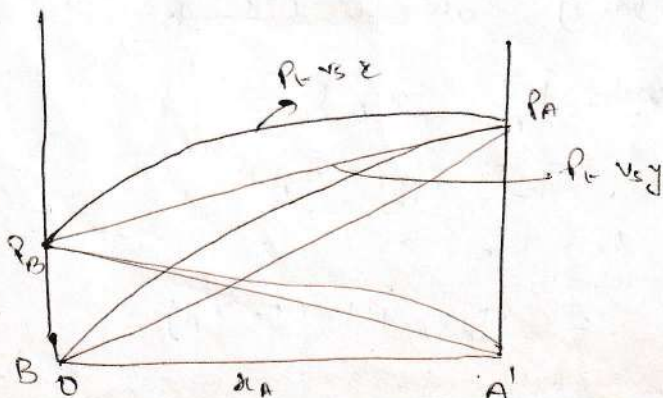
ideal soln = $P^* = P x$

non-ideal soln = $P^* = r P x$

$$r = \frac{P^*}{P x}$$

r = activity coefficient

if $r > 1 \Rightarrow \ln r \Rightarrow (+ve) \Rightarrow$ Positive deviation



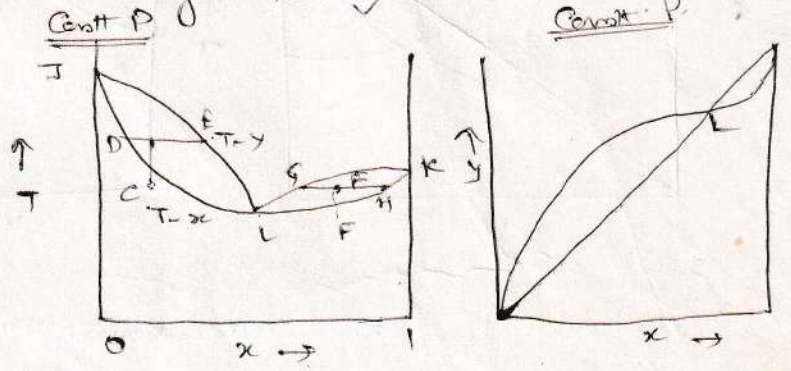
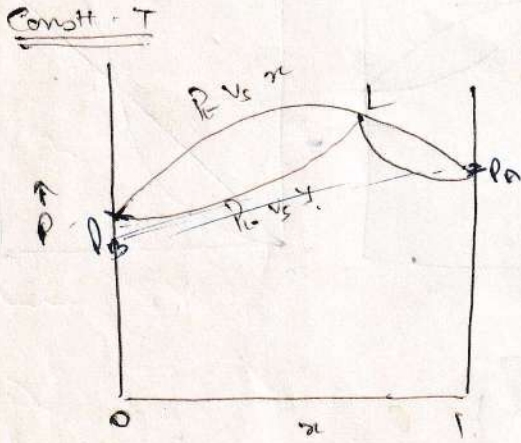
Minimum Boiling mixture

- Positive deviation from ideality are sufficiently large
- vapour pressures are closer

So total Press is max at some Conc.

↓
formation of Azeotrope.

or
Constt boiling mixture



Point less than L such as e
equim vapo. (y_A) > liq. (x_A)
(E) (D)

Point higher than L such as f
equim vapo G is < liq. (H)

at L ⇒ y = x boils at constt Temp
without change in composition.

solns. either D or H boil will move along lower curve
↓ ↓
J K.

So of this type soln can not be completely separated ⇒ Azeotrope formation
↓
So we can do separation by changing press

ex ethanol - water

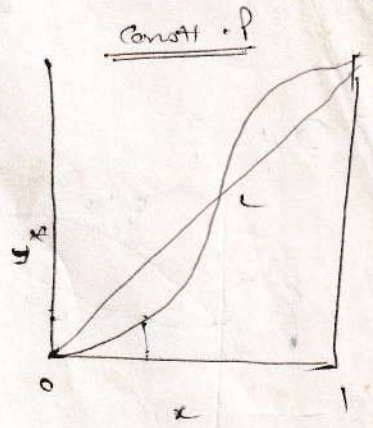
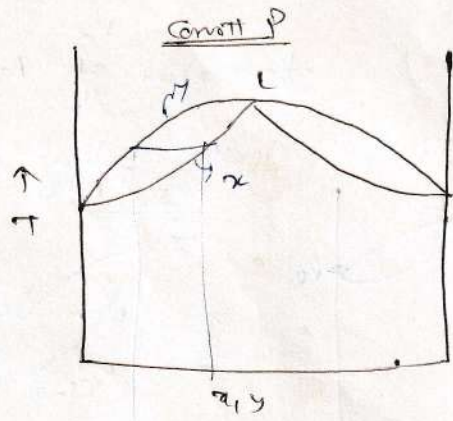
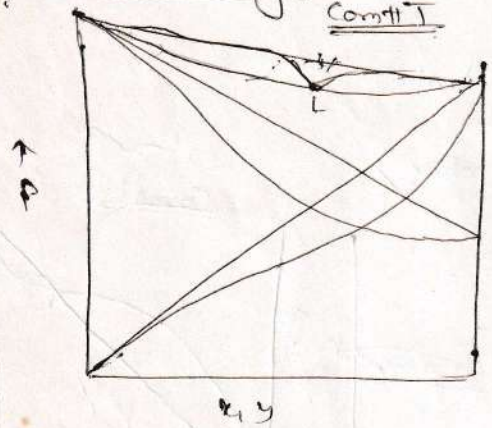
Azeotrope → P = 1 atm, T = 78.2°C
ethanol → 89.4 mole % or 95.6 wt %

∴
So Azeotrope disappears at press below 70 mm Hg.

Negative Deviation from ideality

equilibrium $P_{\text{act}} < P_{\text{ideal}}$

max. boiling mixture \rightarrow
Const. T



min Press L \Rightarrow max boiling Temp L
 \Downarrow
 max boiling Azeotrope (Less common)

Ex. HCl - water
 11%
 at 110°C , $P = 1\text{atm}$

for ideal soln.