

Real or non ideal Solutions

- A solution obtained on mixing two liquids is said to be non ideal if the solute-solvent interactions are weaker or stronger than solute-solute or solvent-solvent interaction.
- When two volatile liquids A & B form solution in such a way that A---B interaction is more or less than the A---A or B---B interaction then solution of A & B liquids is said to be <sup>non</sup>ideal solution.
- For a non ideal solution,
  - (i) it does not obey Raoult's law
  - (ii)  $\Delta V_{mix} \neq 0$
  - (iii)  $\Delta H_{mix} \neq 0$

There are two types of non ideal solutions.

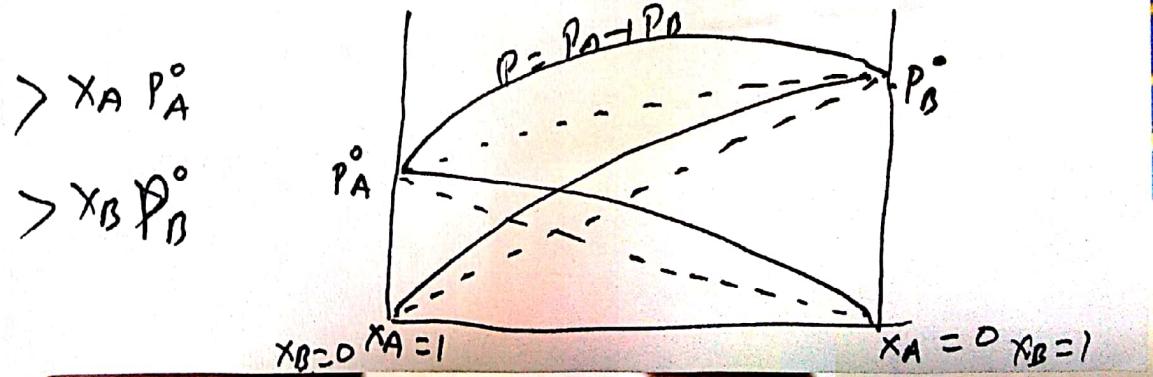
(i) Non ideal solutions showing positive deviation from Raoult's law

When a binary solution of A & B is formed by mixing of two liquids A & B such that A-B interaction is weaker than A---A & B---B interactions then solution is said to show positive deviation from ideal behaviours.

- For such solution,  $\Delta H_{\text{mixing}}$  is positive as energy required to overcome the bond between molecules hence results Cooling effect  $\therefore \Delta H_{\text{mix}} > 0$
- As molecules held together less tightly hence  $\Delta V_{\text{mixing}} > 0$
- vapour pressure - composition curve can be shown as

$$P_A > x_A P_A^{\circ}$$

$$P_B > x_B P_B^{\circ}$$

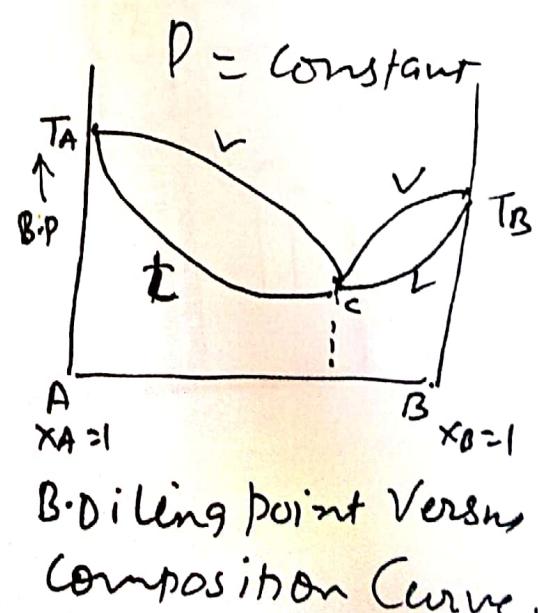
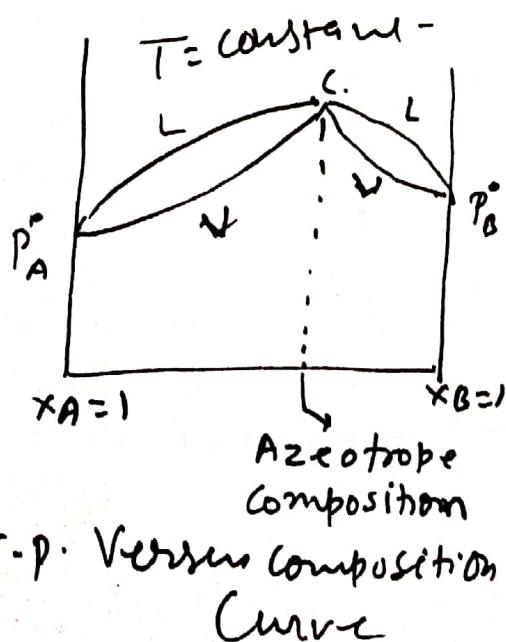


- Examples of non-ideal solutions showing positive deviation

- Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) + Acetone ( $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{H}}}-\text{CH}_3$ )
  - $\text{C}_2\text{H}_5\text{OH}$  +  $\text{H}_2\text{O}$
  - Acetone +  $\text{CS}_2$
  - Chloroform +  $\text{C}_2\text{H}_5\text{OH}$
  - Water + Chloroform
- 

- Such solution is said to form minimum boiling Azeotrope mixture in certain composition.

- At definite composition, solution boils at certain temperature at which total vapour pressure becomes equal to atmospheric pressure.



## ⑪ Non ideal solution showing negative deviation from ideal behaviour

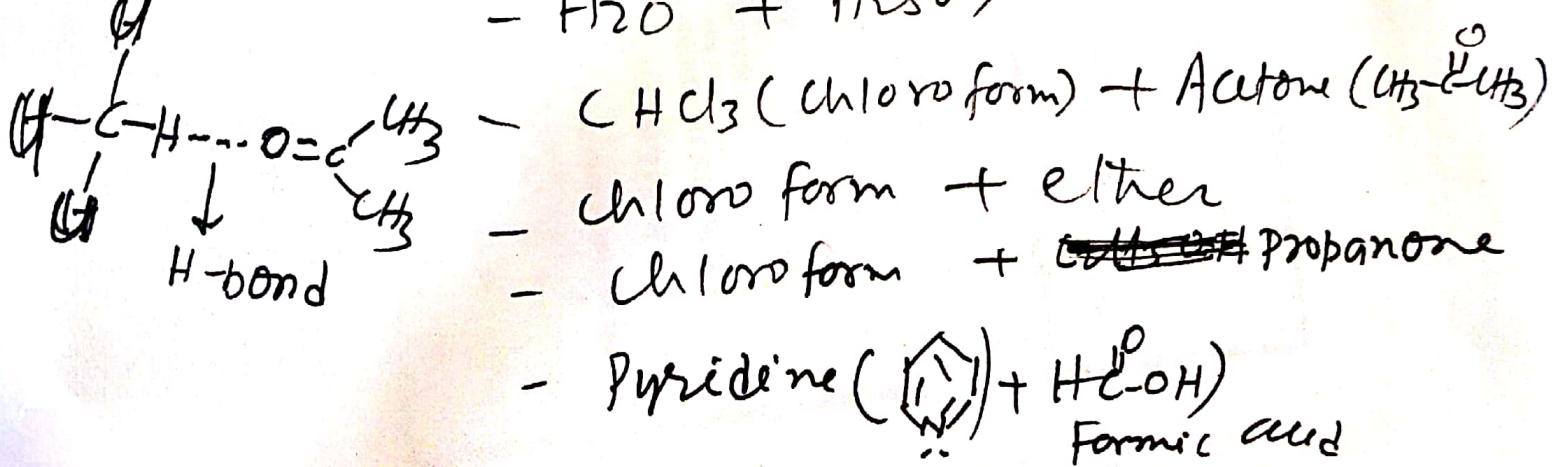
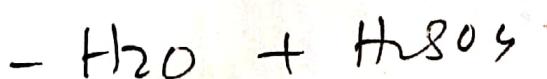
A binary solution of liquid A & B is said to show negative deviation from ideal behaviour if A---B interactions are stronger than A--A & B--B interactions.

- The total vapour pressure of this solution becomes less than the corresponding V.P. of ideal solution. & show deviation from Raoult's law

$$P_A < P_A^\circ X_A$$

$$P_B < P_B^\circ X_B$$

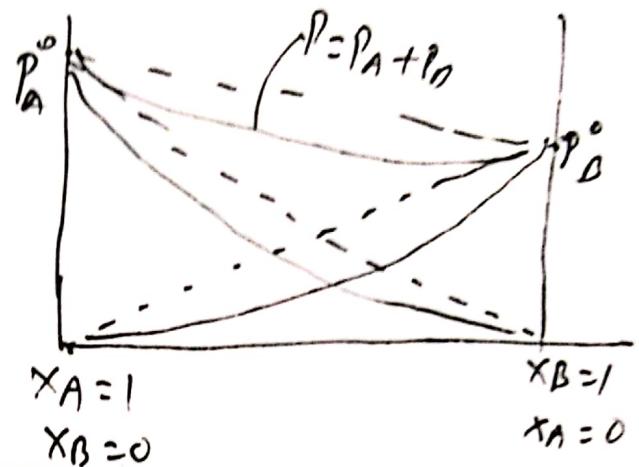
- $\Delta H_{mix} < 0$  (heating effect occurs)
- $\Delta V_{mix} < 0$  (volume contraction)
- Ex -  $H_2O + HCl$



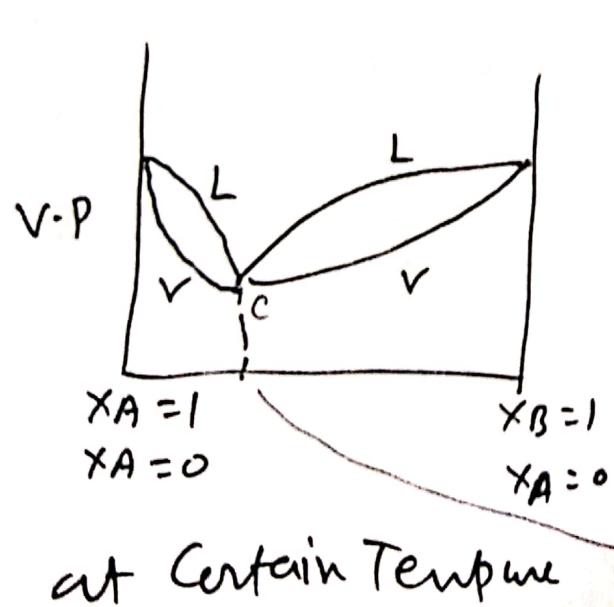
— Vapour pressure - Composition Curve for solution showing negative deviation

$$P_A < X_A P_A^{\circ}$$

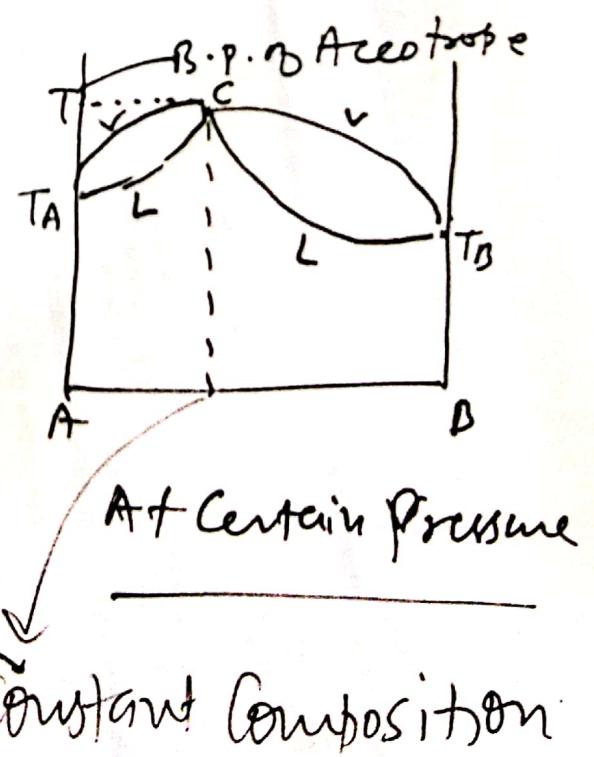
$$P_B < X_B P_B^{\circ}$$



— Binary Solution Showing -ve deviation from maximum boiling Acetone mixture in certain composition.



at Certain Temperature



Constant Composition

## Azeotrope mixture

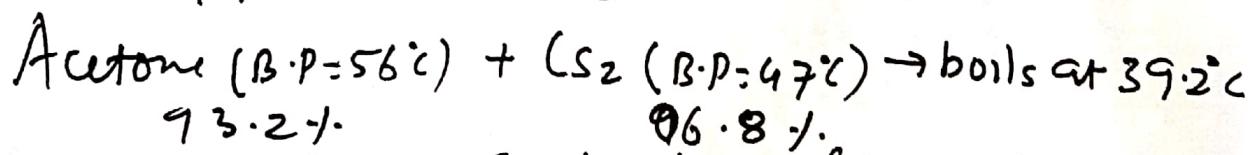
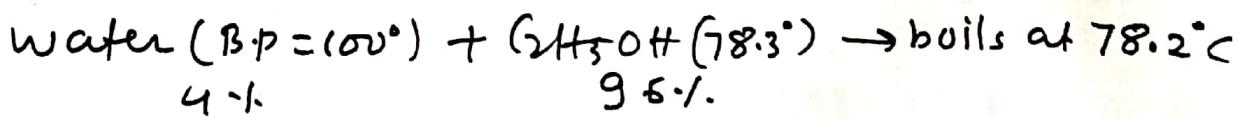
# A mixture of volatile liquids

~~at~~ in certain composition which like a pure component boils at constant temperature & distills over completely at the same temperature without any change in composition is known as constant boiling.

Mixture or Azeotrope mixture.

- As Azeotrope mixture boils at certain constant Temp.
  - Azeotrope mixture hence can't be separated by fractional distillation.

Azeotrope mixture has lower distillation boiling point than any components when solution is non ideal showing positive deviation



- non ideal solution showing  
-ve deviation has higher B.P.  
than any components

