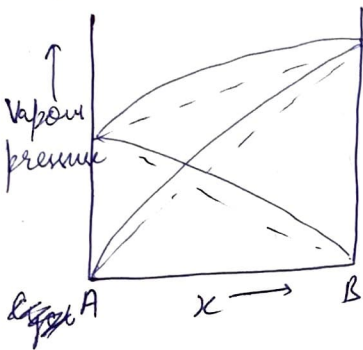


## Real or Non-Ideal Solution

Very few solutions obey Raoult's law over entire range of composition. Non-ideality arise due to either vapour phase or solution.

Type I : Small positive deviation

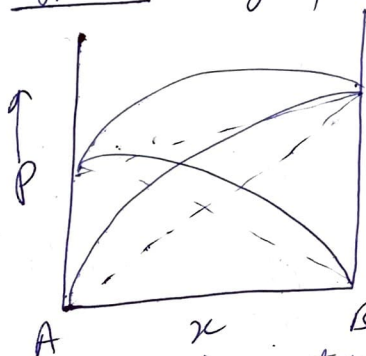


Total vapour pressure remains always within vapour pressure of pure components.

only slightly greater value of vapour pressure than predicted by Raoult's law

B - CCl4, A - cyclohexane

Type II : large positive deviation



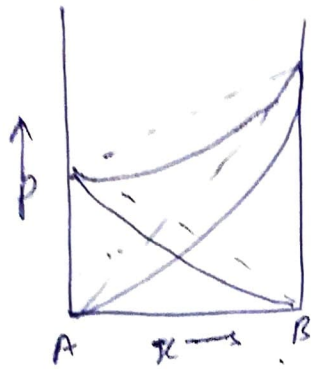
H2O - propyl alcohol, acetaldehyde - CS2  
ethyl alcohol - CH4, acetone - CS2

$\Delta H_{mixing} = \text{positive}$   $\Delta V_{mixing} = \text{positive}$

- Difference in polarity of molecules or difference in length of hydrocarbon chain or analogous grouping of molecule.

Difference in intermolecular forces of attraction. There is association of either of constituent in liquid state. i.e. components have quite ~~strong~~ <sup>weak</sup> interactions than their pure forms & hence solution is more volatile & can be easily converted to vapour form & hence quite high vapour pressure of solution than the individual pure components.

Type III large negative deviation



$H_2O - H_2SO_4$ ,  $H_2O - HNO_3$ , acetone- $CS_2$ ,  
 For a certain composition, total vapour pressure of mixture is below vapour pressure of each of components. This is because of stronger interaction between pure A & B leading to less volatile solution & hence its total vapour pressure is less than individual components.

$\Delta H_{mixing} = \text{negative}$ ,  $\Delta V_{mixing} = \text{negative}$ .

Vapour Pressure - Composition & Boiling point - Composition curves of completely miscible binary solution

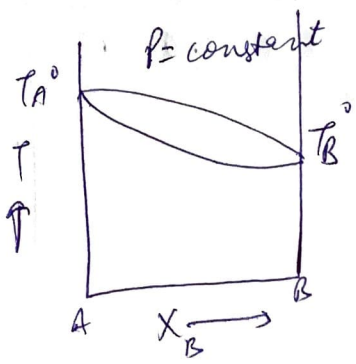
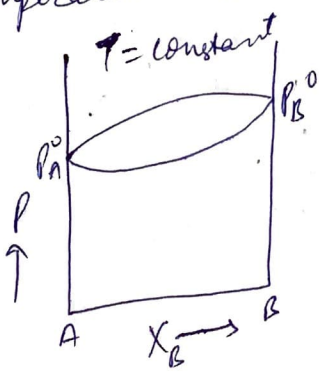
On heating under constant pressure (atmospheric pressure), solution will start boiling at a temperature at which its total vapour pressure becomes equal to atmospheric pressure.

$P = P_A + P_B$

Since solutions of different compositions have different vapour pressure, it follows that they will boil at different temperature.

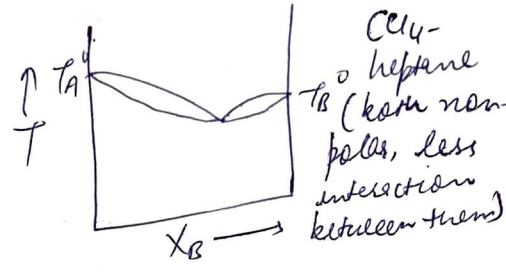
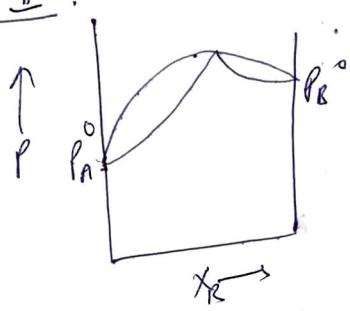
A solution of high vapour pressure will boil at lower temperature & vice-versa.

Type I:



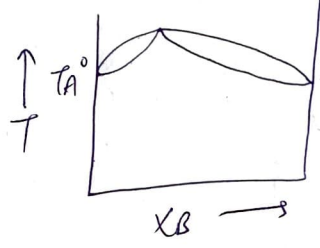
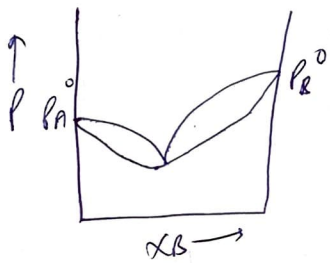
Vapour phase will be richer in more volatile component B. Composition of vapour phase will always be richer in B than that of liquid phase. That's why vapour composition will lie above liquid composition curve.

Type I :



CCl<sub>4</sub>-heptane (kiss non-polar, less interaction between them)

Type II :



HCl/HNO<sub>3</sub> → acid reacts with water so give non-volatile ions...

Some eg. of Type III :

ethyl ether & acetone having boiling points 293K & 303K, respectively. Heptane & C<sub>2</sub>H<sub>5</sub>OH at 323K.

Some eg. of Type IV :

- Pyridine & formic or acetic or propanoic acid. (base + acid → reactive & more interactions between molecules & hence less tendency to escape & hence less total vapour pressure)  
 - Halomethane (eg. CCl<sub>4</sub>) with O or N containing compound (eg: ketone, ether, ester or amine) Partial association between them is through hydrogen bonding.