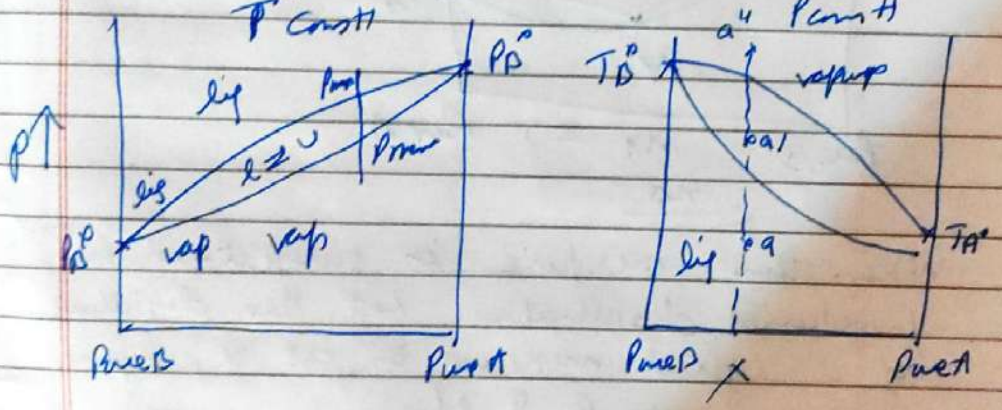
Temp-VS Composition Diagram of Non Ideal Solutions

A Non ideal sol. are of two types

(1) Little Deviation from ideality

(2) very large Deviation from Ideality

(1) For little deviation, the V.P. Vs Composition curve and B.Pt VS Composition are similar to those of an ideal solution. The total V.P. of liquid mixture lies bet^n those of pure components. B.pt ↑ or ↓ according to the composition of mix. Hence b.pt lies between pure components & ↑ or ↓ according to change in composition.

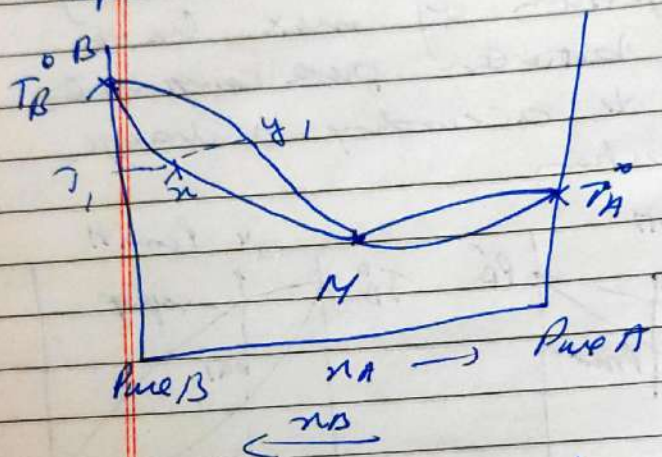


(2) very large deviation from Ideality

In this solution exhibits either max. or min. in P Vs Composition curve Since B.Pt is inversely related to V.P. so solution will exhibit min. or max. in b.p.T. curve at a conc^n where there is max.

or maximum in total V.P
Hence vapour & liquids curve in Temp vs Composition diagram meet each other at max. or min. pt so that both the phases have same composition at that pt.
∴ V. Phase is stable at higher temps

(a) If solution exhibits a max. in V.P curve then it will exhibit in bpt & Temp vs. composition will be



When this mixture is subjected to fractional distillation Let the distillation of a liquid mixture is at x, lying between pt. B & M.
Liquid mixture will start boiling at temp T & vapour which appeared on boiling will have composition y_1
Since vapour phase carries more of A. & remaining liquid will contain more of the constituent B & will boil at higher temp.

As the distillation proceeds composition of liquid phase will move along y, M i.e toward pt M. At pt M liquid & vapour phase have same composition.

Hence condensing the vapour & distillation of resultant solution will not yield any seperation of the constituents. The liquid will boil at constt. temp. as if it is consists of a single constituent.

The fractional distillation of liquid mixt of composition x_1 will yield vapour of composition corresponding to pt M & pure liquid B. vapour of A is collected from top of the fractionating column & the latter from bottom of the column.

When composition of liquid mixture lies between A & M i.e x_2 As distillation proceeds, the vapour phase will contain more & more of B & acquire composition corresponding to pt M & liquid phase contains more & more of A & yield pure A.

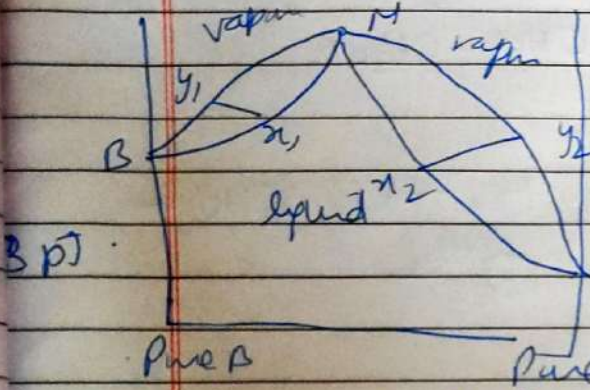
Fractional distillation of liquid mixt will yield vapour corresponding to pt M which can be collected from top of the fractionating column & liquid of liquid of pure constituent A which can be collected from bottom of the column.

Fractionating distillation of a solution exhibiting min in the bpt yield

Distillate: A Const. boiling liquid mixture of composition corresponding to a pt M

Residue → Pure A if the composition of liquid mixture lies betn A & M or pure B if the composition lies between B & M

Solutions exhibiting a max. in the bpt



Consider a liquid mixture of x_1, when it starts boiling, the vapour has a composition of y_1. Since vapour is relatively richer in constituent B, the remaining liquid becomes richer in A. During distillation the composition of liquid phases moves along x_1, M & vapour phase moves along y_1, B.

Distillate: Pure A if the composition of liquid mix. lies between A & M or pure B lie betn B & M

Residue → A Const. boiling liquid mixture of composition corresponding to pt M

Azeotropic Mixture → The liquid mixture of composition M corresponds to min- or max- bpt, boils at const. T

and can be distilled without any change of composition. Such a liquid mixture known as azeotropic mixture. On boil unchanges

For a given pair of liquids at a given P, the composition of azeotropic mixture & corresponding bpt is definite. Their values changes as external P is changed.

eg $H_2O - C_2H_5OH$, $H_2O - C_2H_5OC_2H_5$

$CCl_4 - CH_3OH$, $CHCl_3 - CH_3OH$

Minimum

Max $H_2O - HNO_3$, $H_2O - HCl$, $CHCl_3 - CH_3COCH_3$,  -