Non-ideal mixtures & Azeotropes:

For ideal binary mixtures, the solute-solvent interaction is a same as the solute-solute & solvent-solvent interactions. For such mixtures, Raoult's law can provide the partial pressure & total pressure in the vapor phase.

i.e.
$$x_i P_i^{vap}(T) = P_i = y_i P$$

$$\Rightarrow P = \sum_{i=1}^{n} x_i P_i^{vap}(T) \quad \text{for an } n\text{-component ideal mixture.}$$

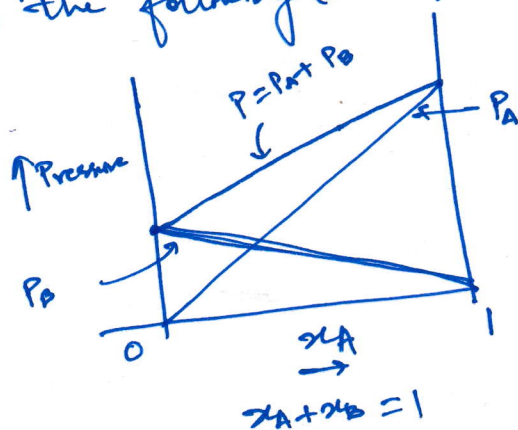For an ideal binary mixture, the partial pressure & total pressure is given by:

$$P_A = x_A P_A^{vap} \quad \& \quad P_B = x_B P_B^{vap} = (1-x_A) P_B^{vap}$$

$$\& \quad \boxed{P = P_A + P_B = x_A P_A^{vap} + (1-x_A) P_B^{vap}}$$

A plot of partial pressures & total pressure as a function of x_A is the following (@ a fixed temperature T)

• Note that straight lines are obtained for partial & total pressures.

$$x_A + x_B = 1$$

Non ideal mixtures:

Non-ideal mixtures show difference in the solute-solvent interactions (compared to solute-solute & solute-solvent interactions) & thus may show a positive or negative deviation from ideal mixtures.

(a) Negative Deviation: Example: Acetone + chloroform
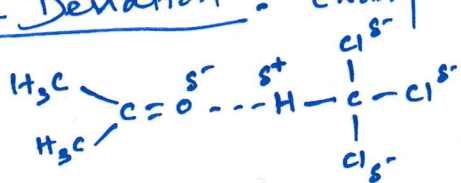
[Due to the hydrogen bonding, the interaction between acetone & chloroform is stronger; thus showing negative deviation

Positive Deviation :

Ex: CS_2 + Acetone   ← On this case, the net intermolecular
(non-polar)   (polar)   forces between CS_2 & acetone, than
                             their respective pure solutions, resulting
                             in positive deviation.

Positive deviation from ideality : On this case, the partial pressure of
each component & the total pressure are larger than the ideal
mixture. Positive deviation takes place if atleast one component
gives a higher partial pressure than the calculated values from
Raoult's law.

That is: $P(actual) > \sum_{i=1}^{n} x_i P_i^{vap}$
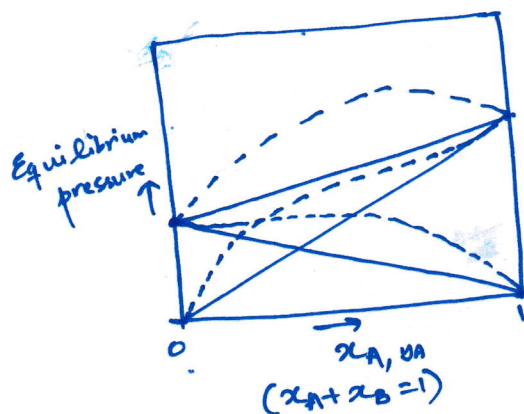
Solid lines: For ideal mixture

Dotted lines: Non-ideal mixture
(curve)   that show positive
              deviation.

Equilibrium
pressure ↑

x_A, y_A
$(x_A + x_B = 1)$
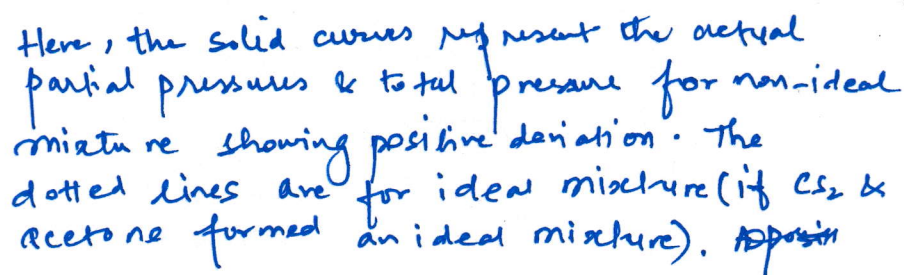
Note, for $x_A \to 1$ & $x_B \to 1$, the partial pressure of the respective
component approach ideality tangentially.

Minimum boiling mixtures - azeotropes : when the positive
deviation from ideality is sufficiently large & the vapor
pressure of the components are not very different, then the
total pressure curves at a constant Temperature passes
through a maxima at some concentration. Such a mixture
is called the minimum boiling azeotropic mixture (constant
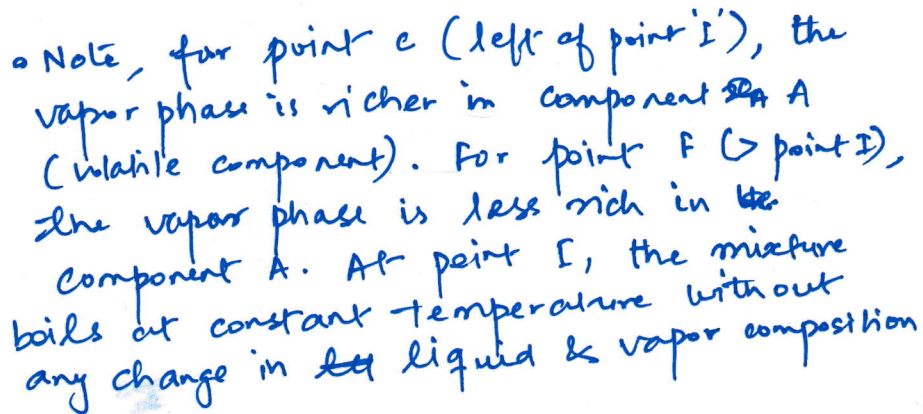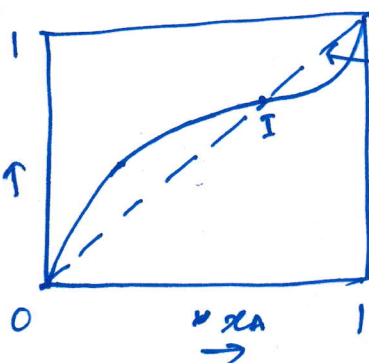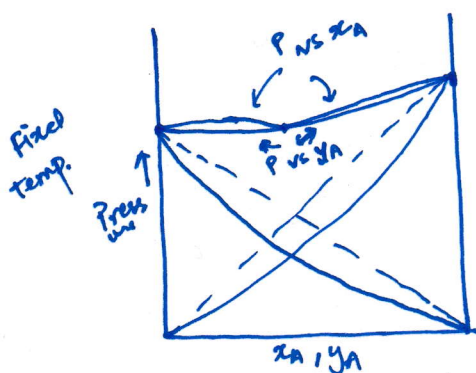boiling mixture).

Let us look at the ~~Better~~, ~~P-x-y~~ ~~x-x-y plots~~   ③
plots for the minimum & boiling azeotropic mixture.

At constant temperature.

Here, the solid curves represent the actual partial pressures & total pressure for non-ideal mixture showing positive deviation. The dotted lines are for ideal mixture (if CS_2 & acetone formed an ideal mixture). ~~Apositi~~

At constant pressure

o Note, for point e (left of point 'I'), the vapor phase is richer in component ~~x~~ A (volatile component). For point F (> point I), the vapor phase is less rich in ~~the~~ component A. At point I, the mixture boils at constant temperature without any change in ~~the~~ liquid & vapor composition

At constant pressure


Note, & $y = x$ line & the y^* vs x (equilibrium curve) intersect at point I. Therefore, at point 'I' the liquid & vapor have same composition. For $x_A < I$, $y_A^* > x_A$. For $x_A > I$, $y_A^* < x_A$.

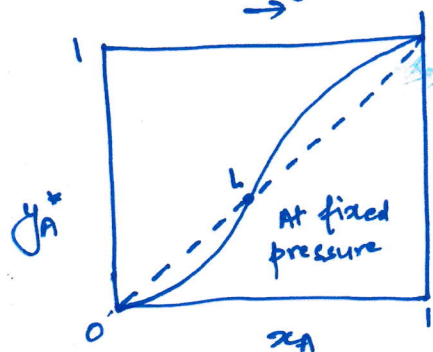Mixtures like these cannot be separated by ordinary distillation.

<u>Negative Deviation from Ideality</u>: As mentioned previously, when the total pressure of a system ~~is~~ at equilibrium is lower than that of the ideal mixture, the mixture is said to exhibit negative deviation.

P vs x_A

P vs y_A

Fixed Temp.

Press. line

x_A, y_A

- In this case, the partial pressures of components & the total pressure is less than that of the ideal mixture. The total pressure goes through a minima at a given concentration


Vapor y_A vs T

L

liquid x_A vs T

Temp. T

At fixed pressure

0 $x_A, y_A \rightarrow$ 1
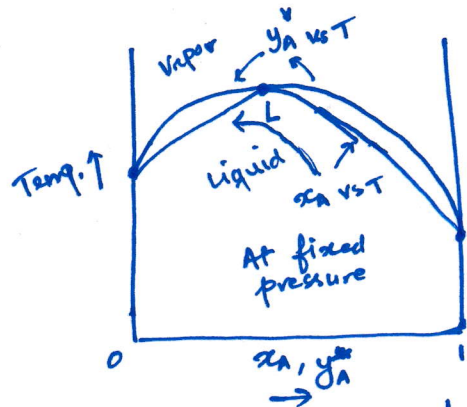
- The boiling point goes through a maxima. In this case, the vapor phase is rich in volatile component on the right side of point 'L' & vice versa.

1

y_A^*

L At fixed pressure

0 x_A 1

- At point 'L', The composition of the liquid & vapor phases are same. The mixture boils at this point L without any separation between vapor & liquid composition. Therefore, mixtures like these cannot be separated by ordinary distillation.

Partial liquid miscibility :

Some liquids are not miscible in all proportions & ~~tead~~ form two immiscible liquids in a certain concentration range. These are referred to as the 'partially miscible liquids'.

Fixed pressure

Temp. T

vapor

Liquid K A

L

P 2-phase liquid Q

0 $x_A, y_A \rightarrow$ 1
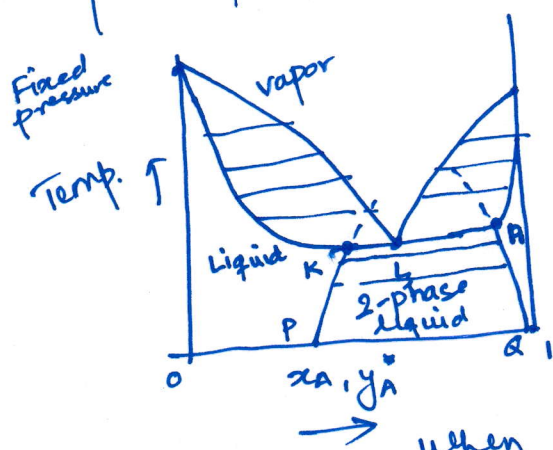
- for example, in this figure, these two components form immiscible liquids (2 phase liquids) when x_A lies between point P & Q. [Two separate liquid phases similar ~~to~~ to what you observe when you mix oil & water]. Similarly, ~~tos~~ two immiscible liquid phases exist between point K & A. When such a two-~~mi~~immiscible phase is heated, the vapor composition remains same (for x_A varying between K & A). In this case, this vapor composition is given by point 'L'.

The y_A^* vs x_A plot for this case is given as shown. ⑤
below:
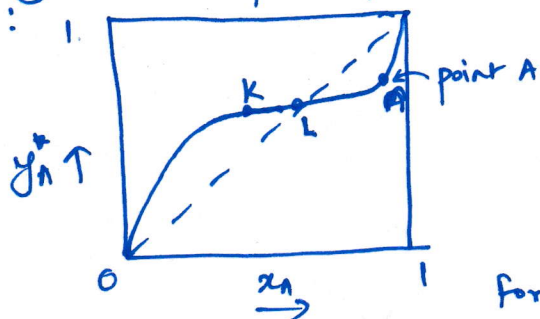
Between K & A, the mixture boils at same temperature & the vapor composition remains same.

for $x_A < K$ & $x_A > A$, plots similar to what discussed previously is observed.

for such immiscible liquids, the vapor pressure of either component can not be influenced by the presence of other component & each component exerts its true vapor pressure at the prevailing temperature.

$$P = P_A^{vap} + P_B^{vap}$$

(& As long as both the components are present).

○ Note, that if one component disappears, then the boiling point changes to the boiling point of the component that remains.

○ In steam distillation, a high boiling organic liquid can be vaporized at low temperature (using the property mentioned above).

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