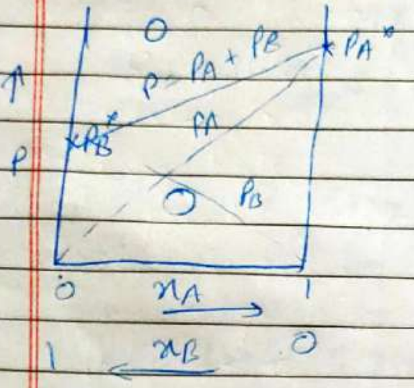
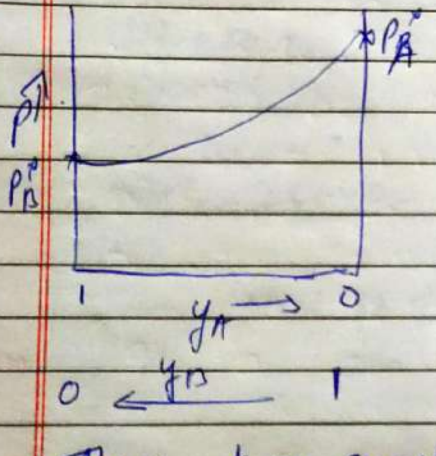
Vapour Pressure Composition Diagram of a Binary Liquid Solution

We have already studied graph of Total V.P. vs composition at a particular temperature

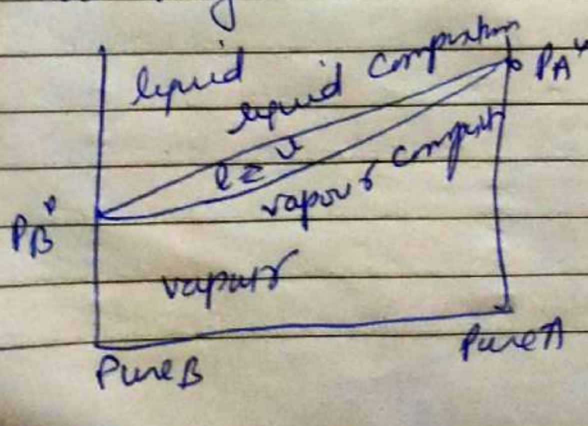


If in a binary solution P > Peq v.p. then there is only liquid phase. Any pt. above P = PA+PB give liquid phase. Any pt. below this line is a vapour phase.



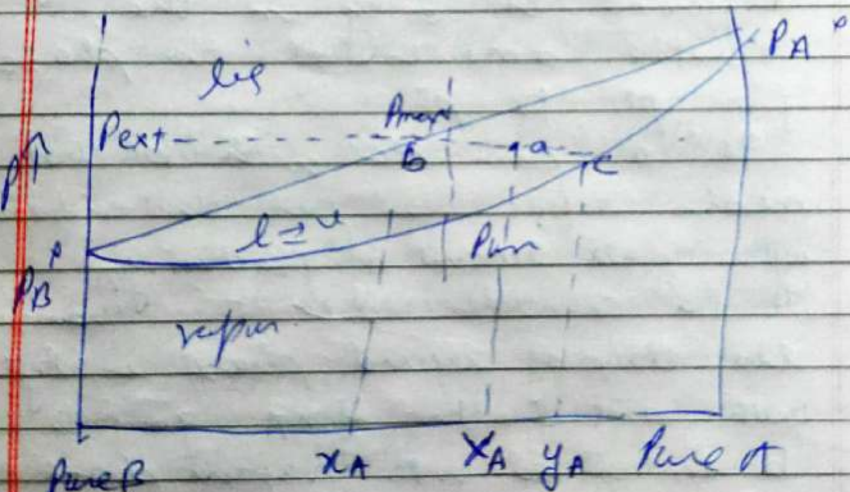
This is plot of P vs y_A the composition in vapour phase.

These two graphs shows that two phases liquid & vapour are in equilibrium with each other so they can be combined



Temp is fixed

The upper curve is called liquidus curve & above this curve only liquid exist & below curve is called vapourous curve & only vapour exist.
A pt in between these curves represents the system in which liquid & vapour coexist in equilibrium with each other.
For a particular composition, the points on liquidus & vapours curves represent max. & min pressure, within which 2 phases can exist in equilibrium with each other.
If $P_{system} > P_{max}$ liquid exists
$P_{system} < P_{min}$ vapour exist
$P_{max} > P_{system} > P_{min}$ liquid ⇌ vapour



Tie line
If component A composition is to be determined in liquid & vapour then a horizontal line is drawn known as ~~tiee~~ tie line to the liquidus & vapours curve

Date ______
Page ______

Since A is chosen as the describing variable, then intersection of a vertical line from x_A with liquidus curve i.e. pt. 'b' gives the value of 'P' & horizontal line from P_e cutting the vaporous curve 'c' gives vapour composition y_A i.e.

Lever Rule

A point within the liquid & vapour phases shows $l \rightleftharpoons v$ in equilibrium. From pt 'a', the amount fraction of the constituent A in the liquid is given by pt- 'b' & vapour phase is given by 'c'.

Tie line bc represents the composition of liquid & vapour phases x_A & y_A. Difference is only in the relative amounts of two phases from pt to pt.

(1) If 'a' coincides with 'b' that means vapour has just started forming with small amount of fraction y_A.

(2) If 'a' coincides with 'c' then last drop of liquid phase is left with amt fraction of x_A going to be converted into vapour phase.

(3) If we move from 'b' to c more & more of liquid phase changes to vapour phase.

(4) Distance 'ba' represents amt of vapour formed since as we move from

b to c more & more of vapour is formed formed.

(5) Similarly as we move from c to b more & more of liquid is formed distance ac represents the amt of liquid formed.

distance ab $\propto$ amt of vapour formed
distance ac $\propto$ amt. of liquid formed
Take Ratio

$$\frac{ab}{ac} = \frac{\text{Amt of vapour formed}}{\text{Amt of liquid formed}}$$

If a lies very close to b, then ab is very small $n_v << n_l$ ie system consist of liquid phase.
If a lies very close to c, $n_v >> n_l$
system consists of vapour phase.

Isothermal Fractional Distillation of an Ideal Binary solution
$l \Rightarrow v$, vapour is richer in the more voltaile component out of 2.

$$y_A = \frac{x_A P_A^\circ}{x_A P_A^\circ + x_B P_B^\circ} \Rightarrow \frac{y_A}{x_A} = \frac{1}{x_A + x_B\left(\frac{P_B^\circ}{P_A^\circ}\right)} \quad -①$$

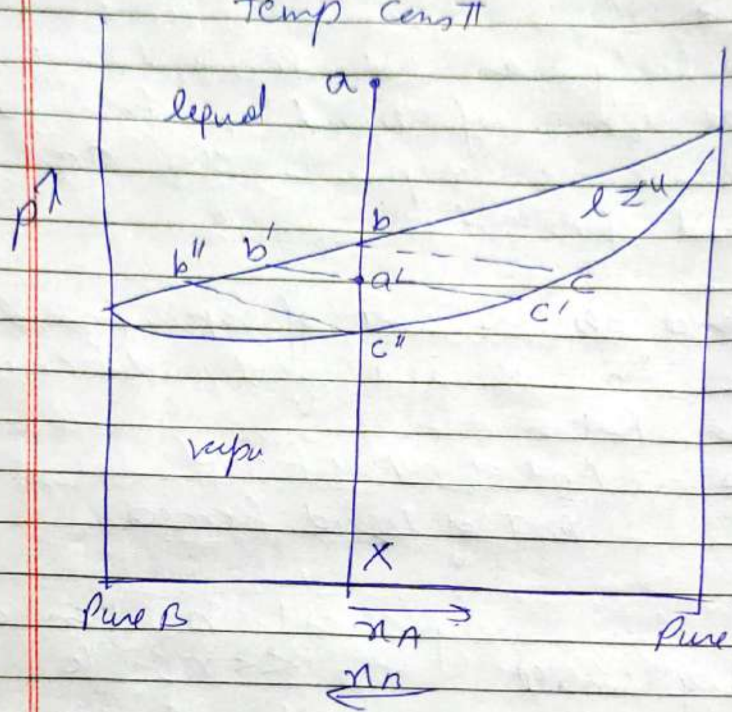
If A > B more voltaile (A) $P_A^\circ > P_B^\circ$

$\frac{P_B^\circ}{P_A^\circ} < 1$, so eq ① deno. is < 1

since $x_A + x_B = 1$

$\therefore y_A > x_A$

When Pressure is reduced isothermally
Temp Const



Let the system is in liquid phase given by point 'a' & pressure of system is reduced isothermally,
system moves along a a' a'' line
(1) System will remain in liquid phase till pt 'b' is reached
(2) At the pt 'b', vapour phase just started forming & its composition corresponds to pt. 'c'. The vapour phase is more rich in the component A (since it is more volatile than B)
(3) Component A is ~~retro~~ vapours are removed & liquid phase becomes rich in component B, composition of liquid phases moves along b b'

(4) If vaporization is to be continued, the pressure of the system must be lowered. The overall state will move along the same vertical line by pt. a'.

(5) At the pt a', the composition of liquid & vapour phases is given by b' & c' respectively. The relative amounts of two phases is given by lever rule

$$\frac{\text{Amount in liquid phase}}{\text{Amount in vapour phase}} = \frac{a'c'}{a'b'}$$

(6) If P is further reduced & then the pt c'' where there is negligible trace of liquid b'' is left & vapour phase has same composition x which is same as that of starting liquid

(7) As P is further reduced, 2 phase system is converted into one phase system consisting of vapour phase

Procedure of Isothermal Fractional Distillation -

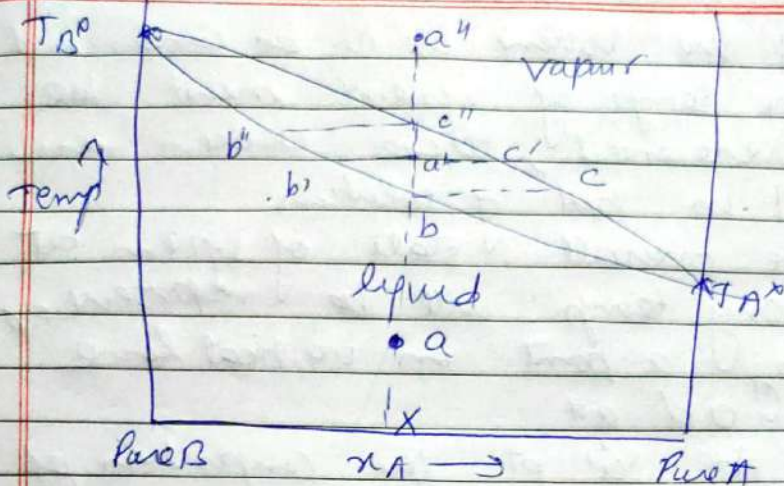
vapour which are formed, are removed & condensed separately. The new liquid composed is richer in more volatile constituents. Vapour which are formed will be richer in volatile component & liquid left

Date
Page

still richer in more voltaile component
If this removing of vapour from solution & condensing is repeated several times, then a stage is reached when vapour consists of only ~~one~~ of the more voltaile constituents & liquid that of less voltaile component
separation of constituents is achieved

Temperature composition Diagram of Binary liquid solution
Def. B.pt. Normal B.pt
A liquid which has a higher V.P will have lower B.pt. since less heating is required to attain V.P = external Pressure.
A liquid with lower V. P. will have high B. pt.
Bpt of a solution have a definite relation with the composition of the solution
So the graph between Temp & composition will be reverse of previous graph & no graph is a straight line

P (constt)



(1) Lower portion of graph represent liquid phase as its stable at lower temp. lower curve is liquidus curve
upper portion represents vapour phase & is stable at higher temp. vapour curve
(2) B.pt of B > A ie V.P of B is lower than A.
(3) central region $l \rightleftharpoons v$

When a liquid mix is heated at constt P. on increasing the temp the state of system moves along vertical line $a a' a''$
(1) The system will remain of one phase till temp T is reached where the liquid starts boiling with the vapour composition corresponding to the point C'
(2) vapour phase is richer of A than liquid phase since A has lower b.pt. Vapour of A are removed & hence solution becomes richer in B so, composition moves along bb'

(3) If the boiling is to be continued, the temp of system must be increased, there occurs an ↑ in bpt of solution

(4) The overall state of system at any temp. will be represented by a point on vertical line a a''
At 'a'' pt. the composition of liquid & vapour phases are represented by pt. 'b' & c'.
Relative amt of 2 phases is given by lever rule

$$\frac{\text{Amt in liquid phase}}{\text{Amt in vapour phase}} = \frac{a'c'}{a'b'}$$

(5) Temp is further increased, system reaches to pt a'' where only a last trace of liquid of composition b'' is left & vapour phase has composition X

(6) If temp. of system is slightly increased, the liquid phase disappears completely & system becomes of one phase comprising of vapour phase

eg Fractionating column.

4.13 ISOBARIC FRACTIONAL DISTILLATION OF AN IDEAL BINARY SOLUTION

Underlying Principle The isobaric process of distillation in which the external pressure is kept constant instead of temperature is more convenient and is often employed for the separation of constituents of a binary liquid system. The principle of separation of constituents using the isobaric fractional distillation may be explained with the help of temperature-composition diagram shown in Fig. 4.13.1.

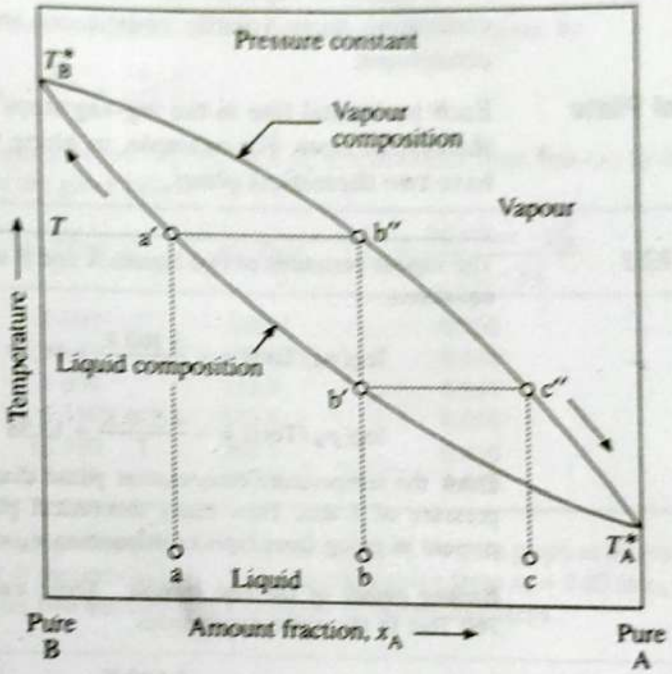


Fig. 4.13.1 Principle of isobaric distillation

- Let the starting composition of the solution to be distilled be represented by the point a. Let the temperature of the solution be raised till it starts boiling. At this stage, the vapour pressure of the solution is equal to the external pressure, which is kept constant throughout the distillation process. Usually the atmospheric pressure of 1 atm is employed for this purpose. The vapour which appeared at the boiling point T is represented by b″. Since the latter is richer in the constituent A (the more volatile constituent), the residual liquid will become richer in the constituent B and will boil at a slightly higher temperature.
- Let the vapour formed at T be removed and condensed separately to yield distillate b. Let this new distillate be heated till it starts boiling. the vapour which now emerges is represented by c″ and is still richer in the constituent A.
- If the above sequence of collecting the vapour, condensing them to give a new distillate and heating the new distillate to its boiling point is repeated several times, the vapour will continue to contain more and more of the constituent A and ultimately a stage would be reached where it would contain only this constituent.

The residual liquid at any stage can be mixed with the previous residual liquid and can be treated in the same way. The residual liquid continues to contain lesser and lesser of the more volatile constituent and thus more and more of the lesser volatile constituent. When the process is repeated several times, a stage would be reached when the residual liquid would contain only the lesser volatile constituent.

Thus, we see that by carrying out the above fractional distillation process, it is possible to separate the two constituents of a binary liquid mixture; vapour containing more volatile constituent and the liquid containing less volatile constituent.

Theoretical Plate

Each horizontal line in the zig-zag steps shown in Fig. 4.13.1 is known as the *theoretical plate*. For example, in going from liquid of composition a to c, we have two theoretical plates.

**e Fractionating
olumn**

The process of fractional distillation is extremely tedious and involves more time and labour as the separation is carried out in batches and in a discontinuous manner. However, these difficulties can be overcome by employing a fractionating column, which essentially carries the distillation in a continuous manner. Figure 4.13.3 displays one such column commonly employed in industry. This is known as the *bubble-cap column*. It consists of a long tube carrying a large number of bubble-cap plates and is attached to a boiler at the bottom and to a condenser at the top. Each plate can hold a thin layer of liquid and has an overflow mechanism through which the excess liquid can pass to the plate just below it. It also has many bubble-caps through which the vapour passes upward after bubbling through the liquid. There is a temperature gradient along the length of the column, the top being cooler than the bottom. The various plates are thus situated at different temperatures and also hold the liquid at that temperature.

Principle Underlying Fractionating Column The principle of bubble-cap column can be illustrated very nicely with the help of temperature-composition diagram (Fig. 4.13.4).

Let the liquid be boiled at the bottom, say at temperature T_0. The vapour issuing has composition v_0. When this vapour is passed through the first plate, it is cooled to temperature T_1 and thus its state is moved to the point a. At this state, some of the vapour condenses to form liquid of composition l_1 and the

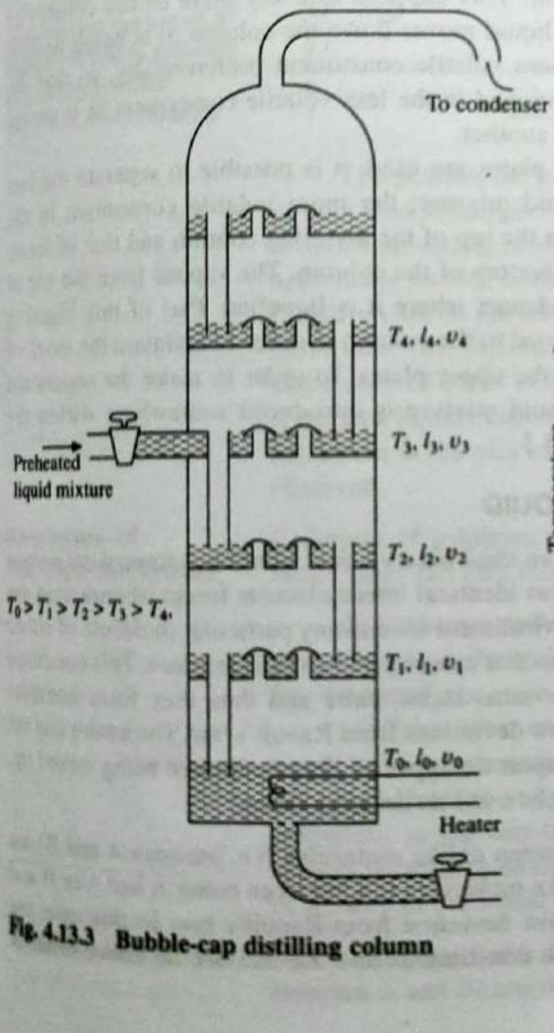


Fig. 4.13.3 Bubble-cap distilling column

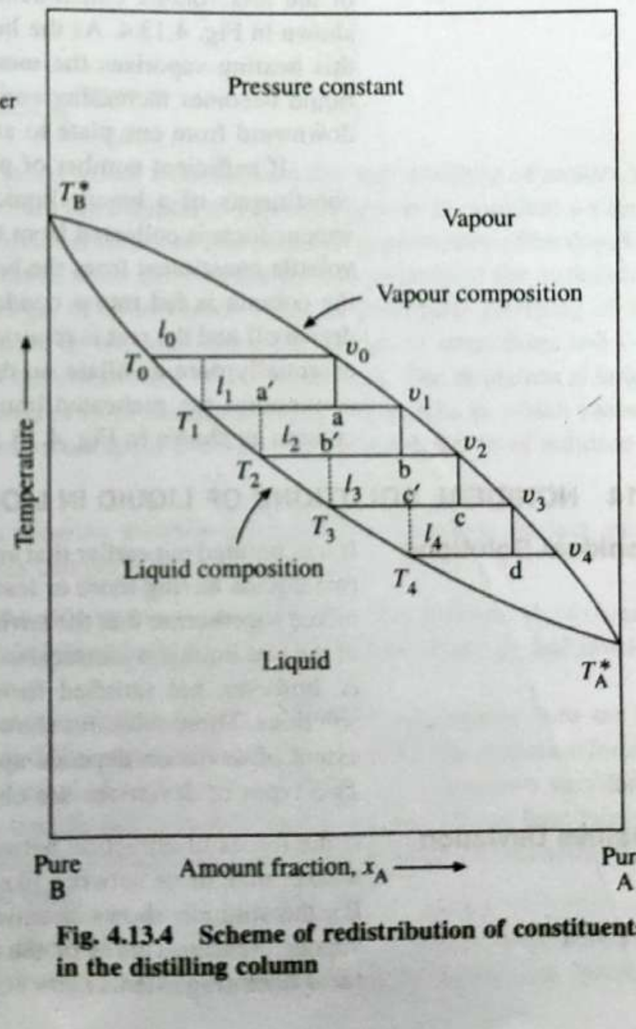


Fig. 4.13.4 Scheme of redistribution of constituents in the distilling column

remaining vapour has composition v_1. The liquid formed contains more of the less volatile constituent. Next, the vapour of composition v_1 is passed through the second plate whose temperature is $T_2 (T_2 < T_1)$. Here the vapour is cooled to T_2 and thus the state of system is moved from v_1 to b. At this state, again part of the vapour is condensed to give liquid of composition l_2 and the remaining vapour has composition v_2. Now the vapour has become more enriched in the more volatile constituent. This happens at every plate of the column as is also shown in Fig. 4.13.4. As the vapour moves up the column, it is being cooled; this cooling condenses the less volatile component preferentially, so that the vapour becomes increasingly enriched in the more volatile component as it passes upward from one plate to another.

Similarly, as the liquid flows down, its temperature is increased and again there is a redistribution of the constituents. For example, the liquid of composition l_3 has flown from the plate 3 to plate 2. The liquid has been heated from T_3 to T_2 and thus the state of the system has moved from l_3 to b′. Thus part of the liquid vaporizes to yield vapour of composition v_2 containing more of the more volatile constituent. The resultant liquid has a composition of l_2 and thus contains more of the less volatile constituent. This happens at every plate of the column as shown in Fig. 4.13.4. As the liquid moves down the column, it is being heated; this heating vaporizes the more volatile constituent preferentially, so that the liquid becomes increasing enriched in the less volatile component as it moves downward from one plate to another.

If sufficient number of plates are used, it is possible to separate the two constituents of a binary liquid mixture; the more volatile constituent in the vapour form is collected from the top of the distilling column and that of lesser volatile constituent from the bottom of the column. The vapour from the top of the column is fed into a condenser where it is liquefied. Part of this liquid is drawn off and the rest is returned to the column in order to maintain the stock of essentially pure distillate on the upper plates. In order to make the separation continuous, the preheated liquid mixture is introduced somewhere within the column as shown in Fig. 4.13.3.