M.Sc. Semester II

Forensic Science

FS-201: Forensic Analyticl Chemistry

DISTILLATION

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1. It is used for the separation of components of liquid mixture.
2. Depends on the distribution of components between liquid mixture and the vapour in equilibrium with the mixture.
3. The two phases exist by the formation of vapour phase through partial evaporation of the liquid mixture.
4. Each phase can be recovered separately with the more volatile component concentrated in the vapour, while the less volatile ones are in greater concentration in the liquid.
5. **Distillation is defined** as the partial vaporization of liquid in a still or retort and the subsequent collection of vapour as condensate in a separate vessel.
6. Gibb's Phase rule $F= C-P+2$
7. Thus, according to Gibb's phase rule for a two component system we need two independent variables which must be specified to describe the system completely. Since for distillation pressure of the system is maintained constant, there must be an unequivocal relationship between the composition of the liquid and vapour phase and the temperature.
8. It can be expressed as **temperature -composition diagram**. In the diagram, the curve ADB represents the boiling points of mixtures of benzene and toluene whose composition is expressed in mole fractions. The curve ACB represents the composition of the vapour which is in equilibrium with the liquid at a given temperature.

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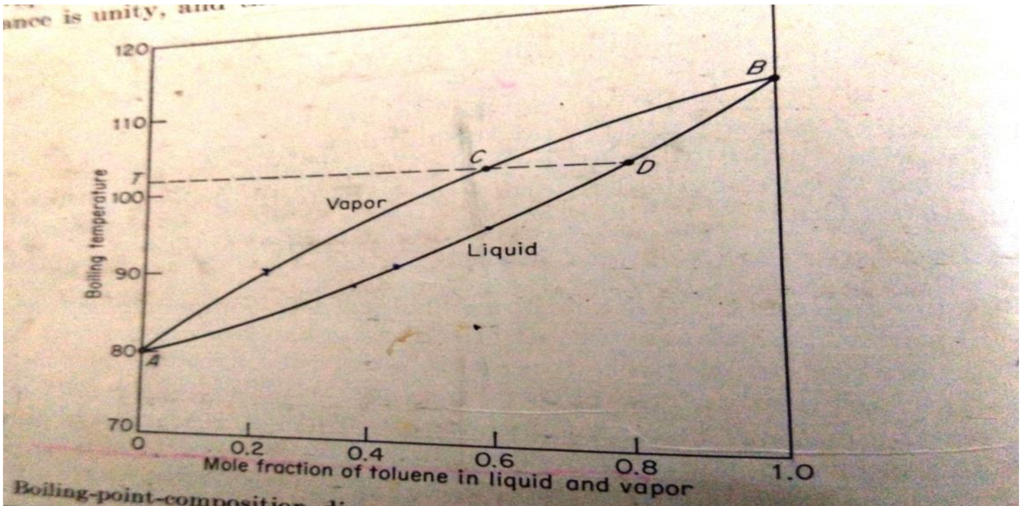


Boiling-point-composition diagram for mixture of benzene and toluene
mercury pressure.

Thus, the composition of the vapour in equilibrium with a solution of composition D is given by C. Thus, vapour phase is richer in the more volatile component than the liquid phase in equilibrium with it.

9. Hence, **distillation is a separation process based on the difference in composition between liquid and vapour in equilibrium with it.** The separation efficiency of a distillation process is directly proportional to this difference. Hence, it is highly desirable to introduce a concept of volatility which expresses the relationship between the compositions of the liquid and the vapour phases when the two phases are equilibrated.

10. Roult's Law

$P_A=X_A P^0_A$ 1

$P_B= X_B P^0_B$ 2

P_A- V.P. exerted by molecules of A
P_B - V.P. exerted by molecules of B
P^0_A & P^0_B are the V.P. of the pure components at the temperature of the system.
X_A & X_B represent mole fraction of components in the liquid phase for A & B respectively.

$$P = P_A + P_B = X_A P^0_A + X_B P^0_B$$

P- Total Pressure

This law only valid for ideal solutions. Ideal behaviour most likely observed if the two components are chemically similar or for highly dilute solutions.

11. It is important to consider the composition of vapour which is escaping from the solution.
    Let Y_A and Y_B represent the mole fraction of components A& B in the vapour phase.
    By Dalton's Law

$$P_A / P_T = Y_A \text{ ....}3$$

$$P_B / P_T = Y_B \text{ ....}4$$

Combining 1, 2, 3 and 4

$$P_A / P_B = Y_A / Y_B = X_A P^0_A / X_B P^0_B = \alpha X_A / X_B$$

α is relative volatility of A w.r.t B

$$\alpha = P^0_A / P^0_B$$

If the component A more volatile than component B then $P^0_A > P^0_B$ therefore Y_A / Y_B greater than X_A / X_B

This is the fundamental principle of fractional distillation, that is in the process of boiling, the vapour becomes enriched in the more volatile component.

12. **Volatility** (V) of a given component is given as

$$V = Y/X$$

Where X and Y represent the mole fraction of the component in the liquid and vapour phase respectively.

$$V_A = Y_A/X_A$$

$$V_B = Y_B/X_B$$

$$\alpha = V_A/V_B = Y_A X_B / Y_B X_A$$

On rearranging,

$$Y_A/Y_B = \alpha X_A/X_B$$

OR

$$Y_A/1-Y_A = \alpha X_A/1-X_A$$

where α is relative volatilty

$$\log \alpha = 8.9 T_B - T_A / T_A + T_B$$

T_A & T_B are normal B.P.s of two constituents in absolute degrees.

Concept of relative volatility widely used, since it provides a measure of the separability of binary mixture by distillation.

13. Theory of Fractional Distillation:

The simplest example is of a miscible binary mixture. Suppose a mixture of composition x_1 were partially volatilized at temperature t_1 and a portion of the vapour in equilibrium with the liquid were condensed at t_2 to give a liquid of composition x_2. The change in liquid composition from x_1 to x_2 corresponds to change in one equilibrium stage. If the liquid of composition x_2 in its turn was partially vaporized at temperature t_2 , the composition of new condensate would be x_3, etc. Hypothetically these successive distillations can be repeated until an infinitely small sample of very pure A was obtained.

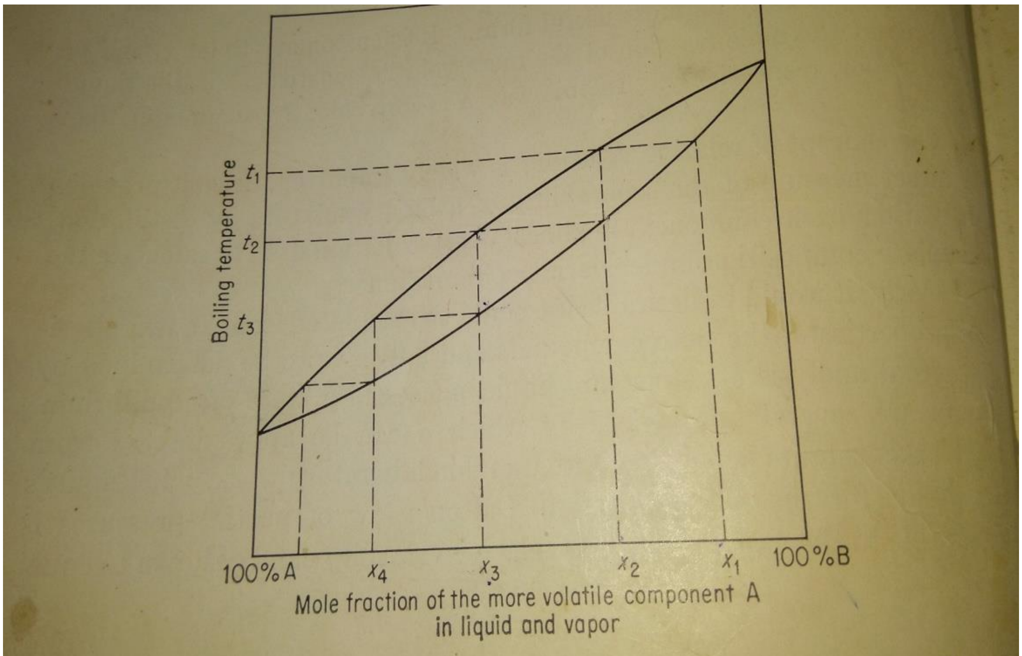


FIG. 2.2. Fractional distillation illustrated with the temperature-composition diagram

14. The enrichment of finite samples can be obtained by using a distillation column so designed that excellent contact is made between vapour rising through the column and condensate (reflux) falling through the column.
15. A distillation column is assumed to be made up of number of theoretical plates. **Efficiency** expressed in terms of theoretical plates in the column, a theoretical plate being the length of column required to give the same change in composition of liquid as that brought about one equilibrium stage in the temperature- composition diagram.
16. The **height equivalent of a theoretical plate (HETP)** would be given by HETP= length of column/ total number of plates
17. Theoretically, any two liquids can be separated by fractional distillation if their V.P.s are different at a given temperature or if their B.P.s are different at a given pressure.
18. **Reflux Ratio:** ratio of moles of reflux per unit time to the moles of product withdrawn from the top of the column per unit time.

19. **Hold up:** That portion of original liquid introduced into the stillpot which is actually in the column as vapour or reflux at any given time.
20. **Throughput:** Rate at which vapour is passing up the column or desirable yield per unit time.

21. Analysis of steady- state condition (continuous distillation):

a) Mathematical analysis of steady state condition is done to determine the conditions existing at any point in the column at any given time and by knowing these conditions we can predict optimum operating conditions for the distillation.

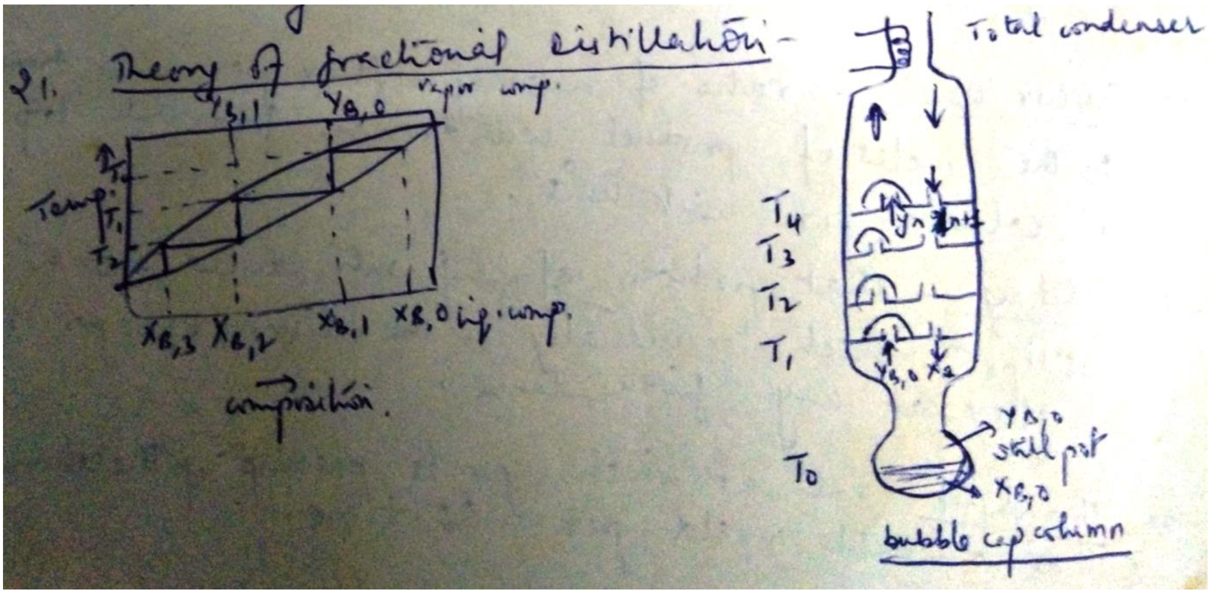
b) Fenske and Underwood independently derived an expression which relates the distillate composition to the relative volatility of the components, number of theoretical plates in the column, and the still composition when the column is operated under total reflux, that is, in a steady state.

(One must keep in mind that in total reflux no product withdrawn and so it is of no practical importance)

c) In **continuous distillation** the preheated material to be fractionated is fed into the middle of the column while the lower boiling fractions are withdrawn from the top and the higher boiling fractions from the bottom. The rate of sample introduction is adjusted so that the volume of feed is equal to the total volume of takeoff from the top and bottom of the column. Under such conditions the composition of phases will be constant at any given time in the column during course of distillation and is amenable to mathematical treatment.

d) **Derivation:**

The number of theoretical plates, n, required to enrich a binary mixture of A and B originally containing concentrations $X_{A,0}$ and $X_{B,0}$ to a given degree of purity, $X_{A,f}$ can be computed from relative volatility, α**.** It is assumed α is constant over the range of concentration considered.



21. Theory of fractional distillation-

The vapour from the first vaporization in the still pot gives

$$Y_{A,0}/Y_{B,0} = \alpha X_{A,0}/X_{B,0}$$

Or

$$Y_{A,0}/1- Y_{A,0} = \alpha X_{A,0}/1- X_{A,0}$$

When the vapour from the still pot condenses in the first plate, its concentration does not change, that is $Y_{A,0} = X_{A,1}$

It evaporates from the first plate

$$Y_{A,1}/1- Y_{A,1} = \alpha X_{A,1}/1- X_{A,1}= \alpha Y_{A,0}/1- Y_{A,0}= \alpha^2 X_{A,0}/1- X_{A,0}$$

After n such plates, giving n+1 repetitive evaporation- condensations

$$Y_{A,n}/1- Y_{A,n}= \alpha^{n+1} X_{A,0}/1- X_{A,0}$$

This is Fenske equation.

α^n is known as enrichment factor.

e) Taking log, of Fenske equation and rearranging

$$\log (Y_{A,n}/1- Y_{A,n})= (n+1) \log \alpha + \log (X_{A,0}/1- X_{A,0})$$

When the vapour in the nth plate condenses, the composition of the final distillate will be $Y_{A,n} = X_{A,f}$

Therefore, $\log (X_{A,f}/1- Y_{A,f}) = (n+1) \log \alpha + \log (X_{A,0}/1- X_{A,0})$

Or

$$(n+1)= \log (X_{A,f}/1- X_{A,f}) - \log (X_{A,0}/1- X_{A,0}) \bigg/ \log \alpha$$

Or

$$n+ 1= \log [X_{A,f} (1- X_{A,0})/ X_{A,0} (1- X_{A,f})] \bigg/ \log \alpha$$

From these mathematical expressions we can calculate minimum number of plates required to achieve desired separation or can calculate from known distillate and distilland compositions, number of theoretical plates in the column.

References and Suggested Reading:

1. Physical and Chemical Methods of Separation, E.W. Berg, Mc Graw-Hill Book Company.
2. Modern Methods of Chemical Analysis, R.L. Pecsok, John Wiley and Sons.
3. Wikepedia
4. Google