Distillation

Distillation is a method of separating the components of a solution which depends upon the distribution of the substances between a gas and a liquid phase, applied to cases where all components are present in both phases. Instead of introducing a new substance into the mixture in order to provide the second phase, as is done in gas absorption or desorption, the new phase is created from the original solution by vaporization or condensation.

In order to make clear the distinction between distillation and the other operations, let us cite a few specific examples. In separation of a solution of common salt and water, the water can be completely vaporized from the solution without removal of salt since the latter is for all practical purposes quite nonvolatile at the prevailing conditions. This is operation of evaporation. Distillation on the other hand, is concerned with the separation of solutions where all the components are appreciably volatile. In this category, consider the separation of the components of a liquid solution of ammonia and water. By contacting ammonia-water solution with air, which is essentially insoluble in the liquid, the ammonia can be stripped or desorbed by processes by desorption operation. Ammonia in this case mixed with water vapor and air and is not obtained in pure form. on the other hand, by application of heat, we can partially vaporize the solution and thereby create a gas phase consisting of nothing but water and ammonia. And since the gas will be richer in ammonia than the residual liquid, a certain amount of separation will have ~~richer~~ resulted. By appropriate manipulation of the phases or by repeated vaporizations and condensations it is then ordinarily possible to make as complete a separation as may be desired, as recovering both components of the mixture in as pure a state as we wish.

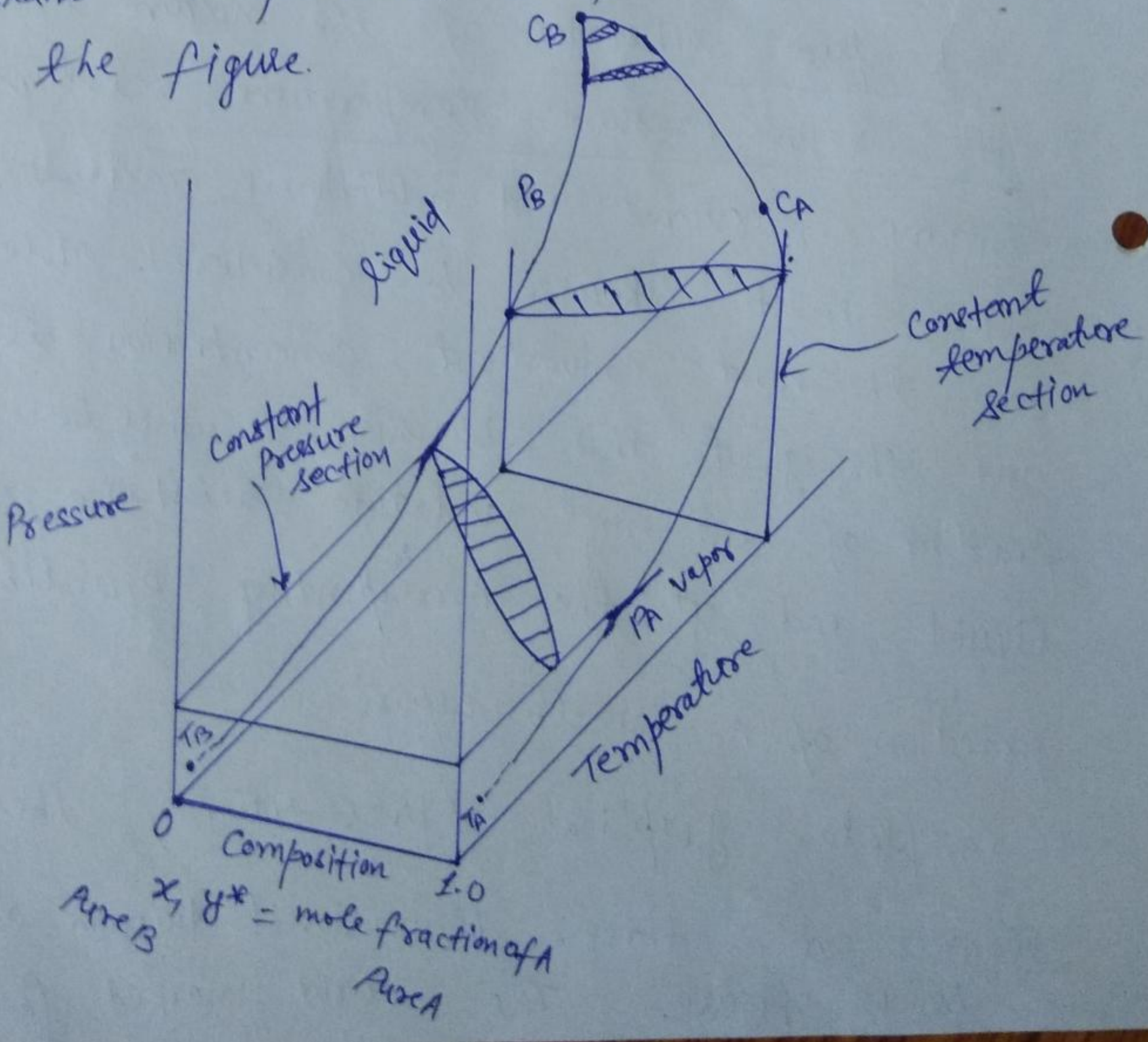
Nevertheless the direct separation, which is ordinarily possible by distillation, into pure products requiring no further processing has made this perhaps the most important of all the mass-transfer operations.

Vapor-liquid Equilibria:- The successful application of distillation methods depends greatly upon an understanding of the equilibria existing between the vapor and liquid phases of the mixtures encountered. A brief review of these is therefore essential.

Pressure- Temperature- concentration Phase Diagram:-

let us first consider binary mixtures which we shall term ordinary, by this is meant that the liquid components dissolve in all proportions to form homogeneous solutions which are not necessarily ideal and that no complications of maximum or minimum boiling point occur. We shall consider component A of the binary mixture A-B as the more volatile, i.e the vapor- pressure of pure A at any temperature is higher than the vapor pressure of pure B. The vapor- liquid equilibrium for each pure substance of the mixture is of course its vapor- pressure- temperature relationship. For Binary mixtures and additional variable, concentration, must likewise be considered. Mole fractions are the most convenient concentration terms to use, and throughout this discussion x will be the mole fraction of the more volatile substance A in the liquid and y^* the corresponding equilibrium mole fraction of A in the vapor.

Complete graphical representation of the equilibria requires a three- dimensional diagram as shown in below figure. The curve marked P_A is the vapor- pressure curve of A, lying entirely in the nearest composition plane at $x = 1.0$. The curve extends from its critical point C_A to its triple point T_A, but the complications of the solid phase which do not enter into distillation operations will not be considered. Similarly curve P_B is the vapor pressure of pure B, in the far plane at $x=0$. The liquid and vapor regions at compositions between $x=0$ and 1.0 are separated by a double surface which extends smoothly from P_A to P_B. The shape of this double surface is most readily studied by considering sections at constant pressure and constant temperature, examples of which are shown in the figure.



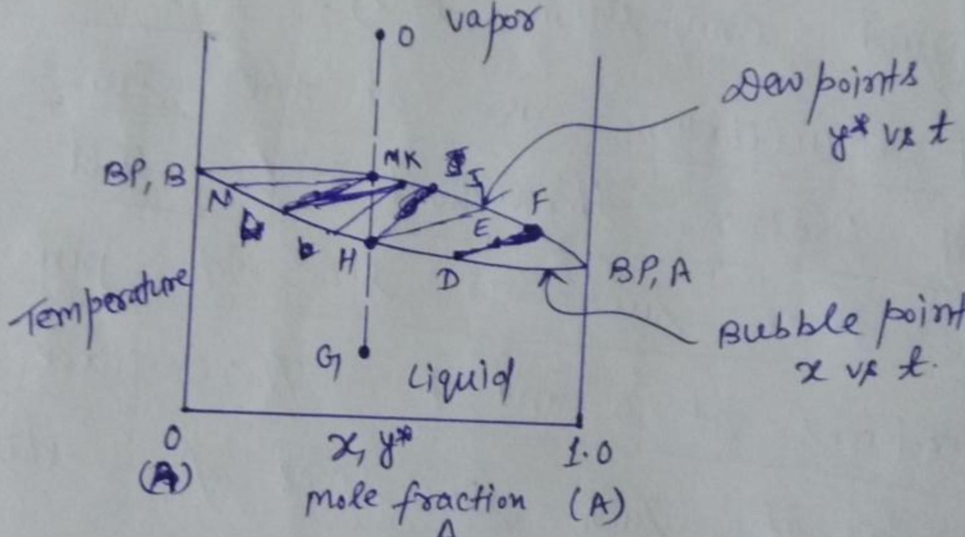
Constant - pressure Equilibria :-

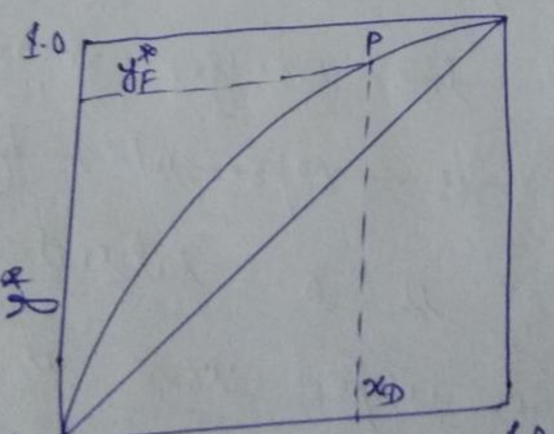
consider first a typical section at constant pressure. The intersection of the double surface of figure with constant - pressure plane produces a looped curve without maxima or minima extending from the boiling point of pure B to that of pure A at the pressure in question. The upper curve provides the temperature - vapor composition ($t-y^*$) relationship, the lower that of the temperature - liquid composition ($t-x$). Liquid and vapor mixtures at equilibrium are at the same temperature and pressure throughout, so that horizontal tie lines such as line DF join equilibrium mixtures at D and F. There are an infinite number of such tie lines for this diagram.

A mixture on the lower curve, as ~~at Pinion such~~ ~~proportions that the average composition of the entire mixture is represented by E~~ as at point D, is a saturated liquid, a mixture on the upper curve as at F, is a saturated vapor. A mixture at E is a two-phase mixture consisting of a liquid phase of composition at D and a vapor phase of composition at F in such proportions that the average composition of the entire mixture is represented by E. The relative amounts of the equilibrium phases are related to the segments of the tie line.

$$\frac{\text{Moles of D}}{\text{Moles of F}} = \frac{\text{Line EF}}{\text{Line DE}}$$

or $$(\text{Moles of D})(\text{Line DE}) = (\text{Moles of F})(\text{line EF})$$





Constant - pressure vapor-liquid equilibria

Consider a solution at G in a closed container which can be kept at constant pressure by moving a piston. The solution is entirely liquid. If it is heated, the first bubble of vapor forms at H and has the composition at J, richer in the more volatile substance, and hence the lower curve is called the bubble-point temperature curve. As more of the mixture is vaporized, more of the vapor forms at the expense of the liquid, giving rise, for example, to liquid L and its equilibrium vapor K, although the composition of the entire mass is still the original as at G. The last drop of liquid vaporizes at M and has the composition at N. Superheating the mixture follows the path MO. The mixture has vaporized over a temperature range from H to M, unlike the single vaporization temperature of a pure substance. Thus, the term boiling point for a solution ordinarily has no meaning since vaporization occurs over a temperature range, i.e. from the bubble point to the dew point.

If the mixture at O is cooled, all the phenomena reappear in reverse order. Condensation, for example, starts at M, whence the upper curve is termed the dew-point curve, and continue to H.

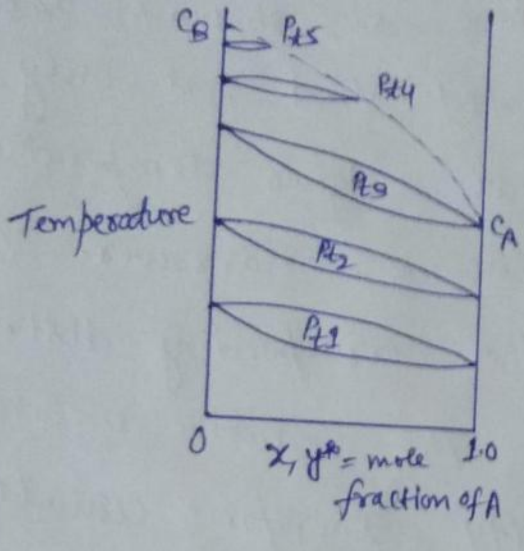
If a solution like that at H is boiled in an open vessel, on the other hand, with the vapors escaping into the atmosphere, since the vapor is richer in the more volatile substance, the liquid residue must therefore become leaner. The temperature and composition of the saturated residual liquid therefore move along the lower curve toward N as the distillation proceeds.

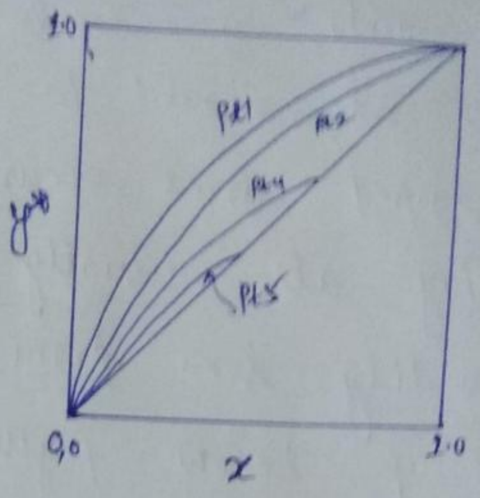
The vapor-liquid equilibrium compositions can also be shown on a distribution diagram (x vs. y^*) as shown in above figure. Point P on the diagram represents the tie line DF, for example. Since the vapor is richer in the more volatile substance, the curve lies above the 45° diagonal line, which has been drawn in for comparison.

Increased pressures :-

At high pressures the sections at constant pressure will of course intersect the double surface at increased temperatures. The intersections can be projected onto a single plane as shown in below figure. It should be noted that not only do the looped curves occur at higher temperatures, but they also usually become narrower. This is readily seen from the corresponding distribution curves of below figure. The relative volatility and hence the separability therefore usually become less at higher pressures. As the critical pressure of one component is exceeded, there is no longer a distinction between vapor and liquid for that component, and for mixtures the looped curves are therefore shorter, as at pressure above P_{t3}, the critical pressure of A in the figure. Distillation separations can be made only in the region where a looped curve exists.

For particular systems, the critical pressure of less volatile substance may be reached before that of the more volatile, and it is also possible that the double surface of figure will extend at intermediate compositions to a small extent beyond the critical pressures of either substance.





Relative volatility :-

The greater the distance between the equilibrium curve and the diagonal line, the greater the difference in liquid and vapor compositions and the easier the separation by distillation. one numerical measure of this is called the separation factor or, particularly in the case of distillation, the relative volatility α. This is the ratio of the vapor to liquid composition ratio of more volatile component (A) to vapor to liquid composition ratio of ~~more~~ less volatile component (B) in a binary mixture.

$$\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B} = \frac{(y_A/y_B)}{(x_A/x_B)}$$

$$\alpha_{AB} = \frac{y_A x_B}{y_B x_A} = \frac{y_A(1-x_A)}{(1-y_A)x_A}$$

$$y_A = \frac{\alpha_{AB} x_A}{1+(\alpha_{AB}-1)x_A}$$

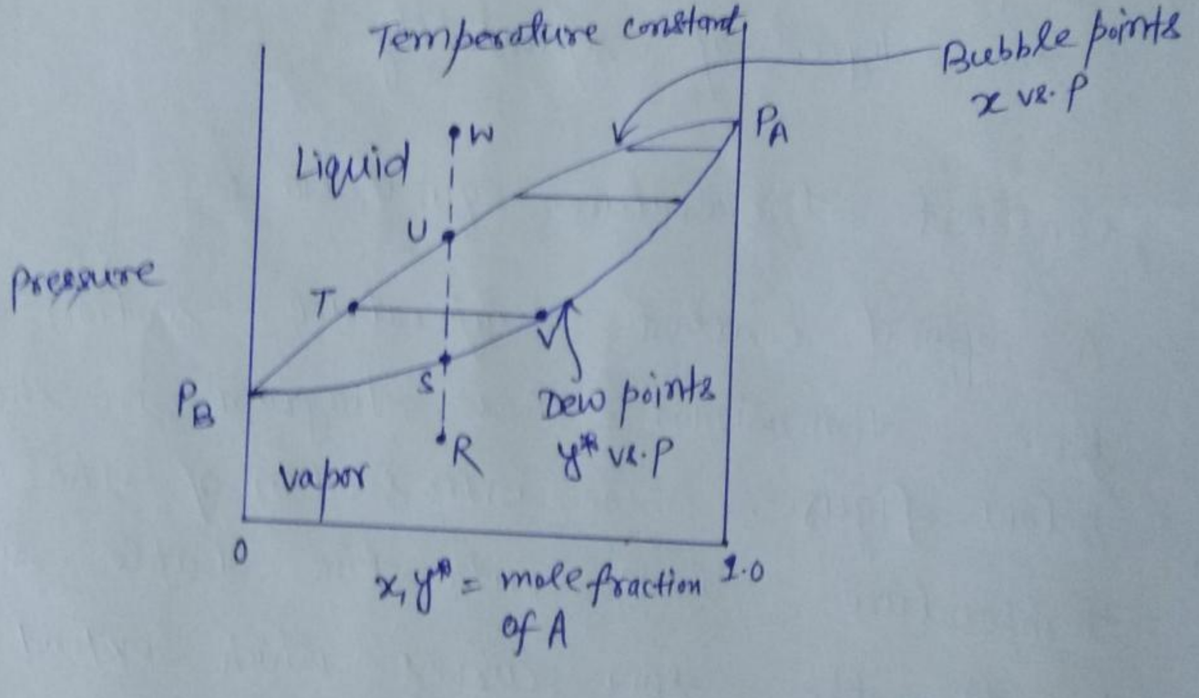
The value of α will ordinarily change as x varies from 0 to 1.0. If $y^* = x$ (except at $x=0$ or 1), $\alpha = 1.0$ and no separation is possible. The larger the value of α above unity, the greater the degree of separability.

Constant temperature equilibria :-

A typical constant- temperature section of the three - dimensional phase diagram in shown in below figure. The intersection of the constant-temperature plane with the double surface provides the two curves which extend without maxima or minima from the vapor pressure of pure B to that of pure A. There are an infinite number of horizontal tie lines, such as TV, which join an equilibrium vapor at V to its corresponding liquid at T.

A solution in a closed container at W is entirely a liquid, and if the pressure is reduced at constant temperature, the first bubble of vapor forms at U, complete vaporization occurs at S, and further reduction in pressure results in a superheated vapor as at R.

vapor-liquid equilibrium data, except in the special situations of ideal and regular solutions, must be determined experimentally.



Constant temperature vapor-liquid equilibria

Ideal solutions - Raoult's law :-

For an ideal solution, the equilibrium partial pressure $\bar{p}^*$ of a constituent at a fixed temperature * and its mole fraction in the liquid.

*(equals the product of its vapor pressure p when pure at

this temperature)

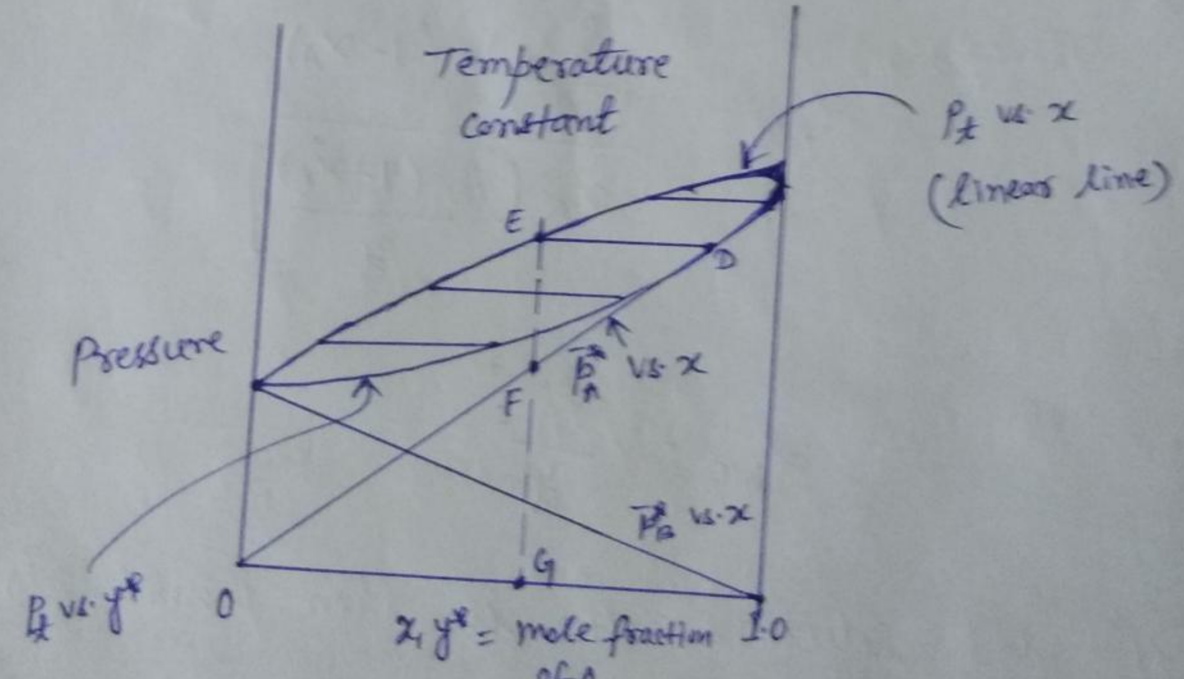
$$\bar{p}_A^* = P_A x_A \quad , \quad \bar{p}_B^* = P_B x_B = P_B(1-x_A)$$

If the vapor phase is also ideal,

$$P_t = \bar{p}_A^* + \bar{p}_B^* = P_A x_A + P_B(1-x_A)$$

$$x_A = \frac{P_t - P_B}{P_A - P_B}$$

The total as well as the partial pressures are linear in x at a fixed temperature. These relationships are shown graphically in below figure



Ideal Solutions

The equilibrium vapor composition can then be computed at this temperature. For example, the value of y^* at point D on the figure equals the ratio of the distances FG to EG,

$$y_A^* = \frac{\bar{p}_A^*}{P_t} = \frac{P_A x_A}{P_t}$$

$$1 - y_A^* = \frac{\bar{p}_B^*}{P_t} = \frac{P_B (1-x_A)}{P_t}$$

The relative volatility α_{AB} is,

$$\alpha_{AB} = \frac{y_A (1-x_A)}{x_A (1-y_A)}$$

Therefore,

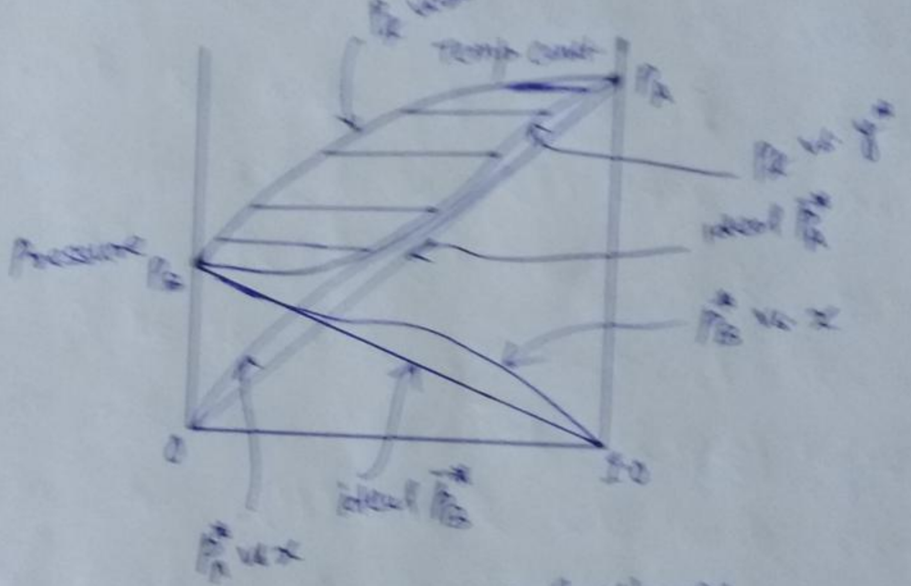
$$\alpha_{AB} = \frac{\left(\frac{P_A x_A}{P_t}\right)(1-x_A)}{x_A \left[\frac{P_B (1-x_A)}{P_t}\right]}$$

$$\alpha_{AB} = \frac{P_A}{P_B}$$

For ideal solutions, it is then possible to compute the entire vapor-liquid equilibria from the vapor pressures of the pure substances. For pressures too high to apply the ideal-gas law, fugacities are used instead of pressures.

Positive deviations from Ideality :-

A mixture whose total pressure is greater than that computed for ideality is said to show positive deviations from Raoult's law. Most mixtures fall into this category. In these cases the partial pressures of each component are larger than the ideal as shown in below figure.

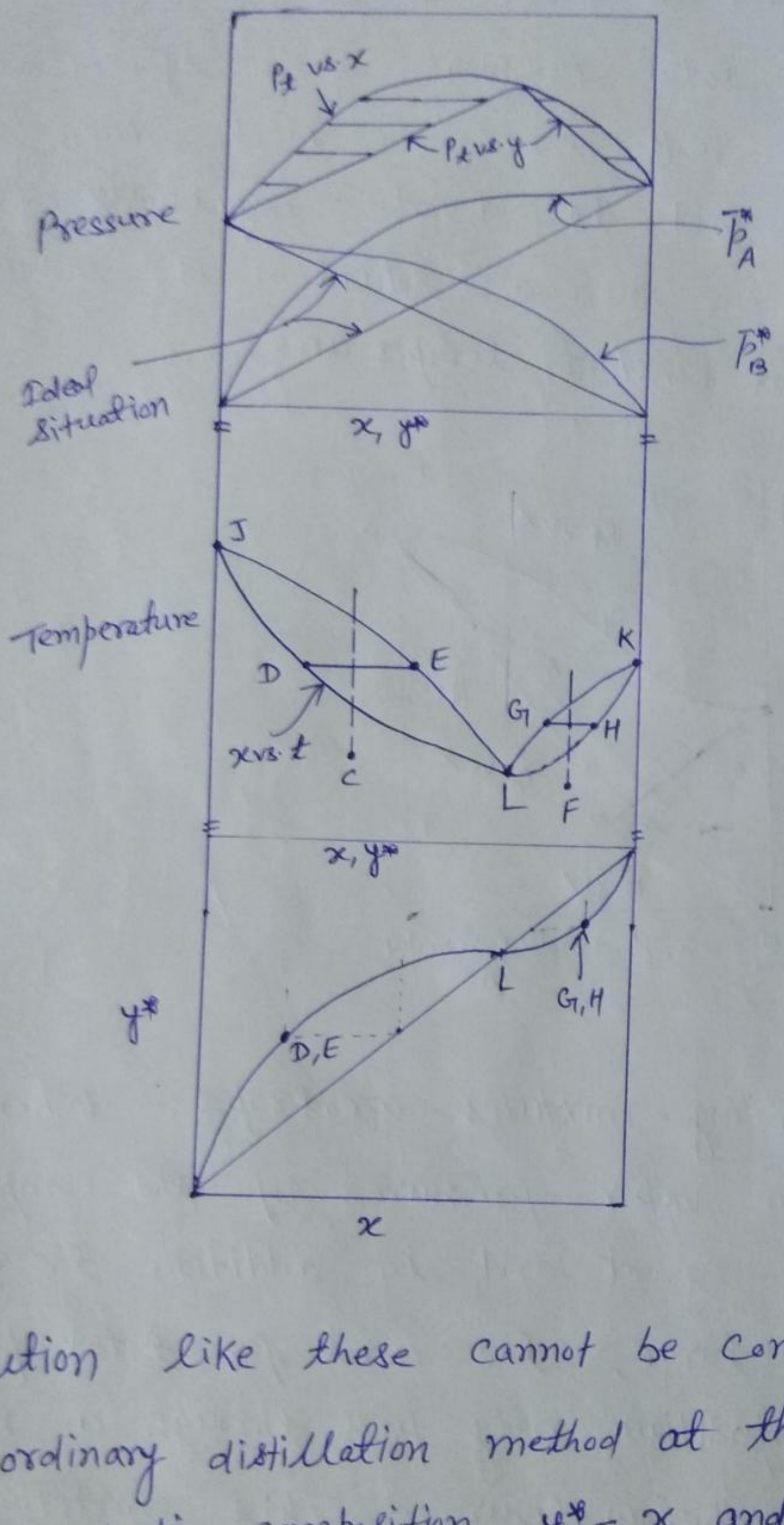


x, y^* = mole fraction of A

Positive deviation from ideality

Minimum-boiling mixtures- azeotropes :-

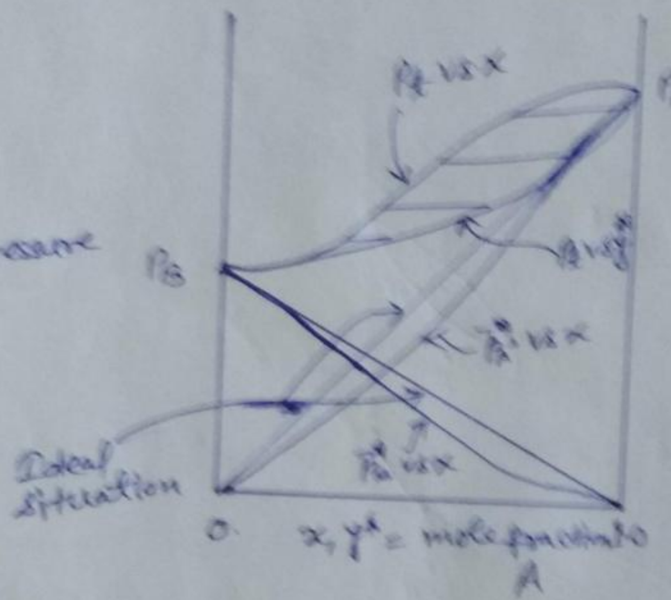
When the positive deviations from ideality are sufficiently large and the vapor pressures of the two components are not too far apart, the total-pressure curves at constant temperature may rise through a maximum at some concentration, as shown in below figure such a mixture is said to form an azeotrop, or constant-boiling mixture. The significance of this is more readily seen by study of the constant-pressure section of below figure. The liquid and vapor composition curves are tangent at point L, the point of azeotropism at this pressure, which represents the minimum boiling temperature for this system. For all mixtures of composition less than L, such as those at C, the equilibrium vapor (E) is richer in the more volatile component than the liquid (D). For all mixtures richer than L, however, such as at F, the equilibrium vapor (G) is less rich in the more volatile substance than the liquid (H). A mixture of composition L gives rise to a vapor of composition identical with the liquid, and it consequently boils at constant temperature and without change in composition. If solutions either D or H are boiled in an open vessel with continuous escape of the vapors, the temperature and composition of the residual liquids in each case move along the lower curve away from point L (toward K for a liquid at H, and toward J for one at D).



Solution like these cannot be completely separated by ordinary distillation method at this pressure, since at azeotropic composition $y^* = x$ and $\alpha = 1.0$. The azeotropic composition y^* as well as its boiling point changes with pressure. In some cases, changing the pressure may eliminate azeotropism from the system.

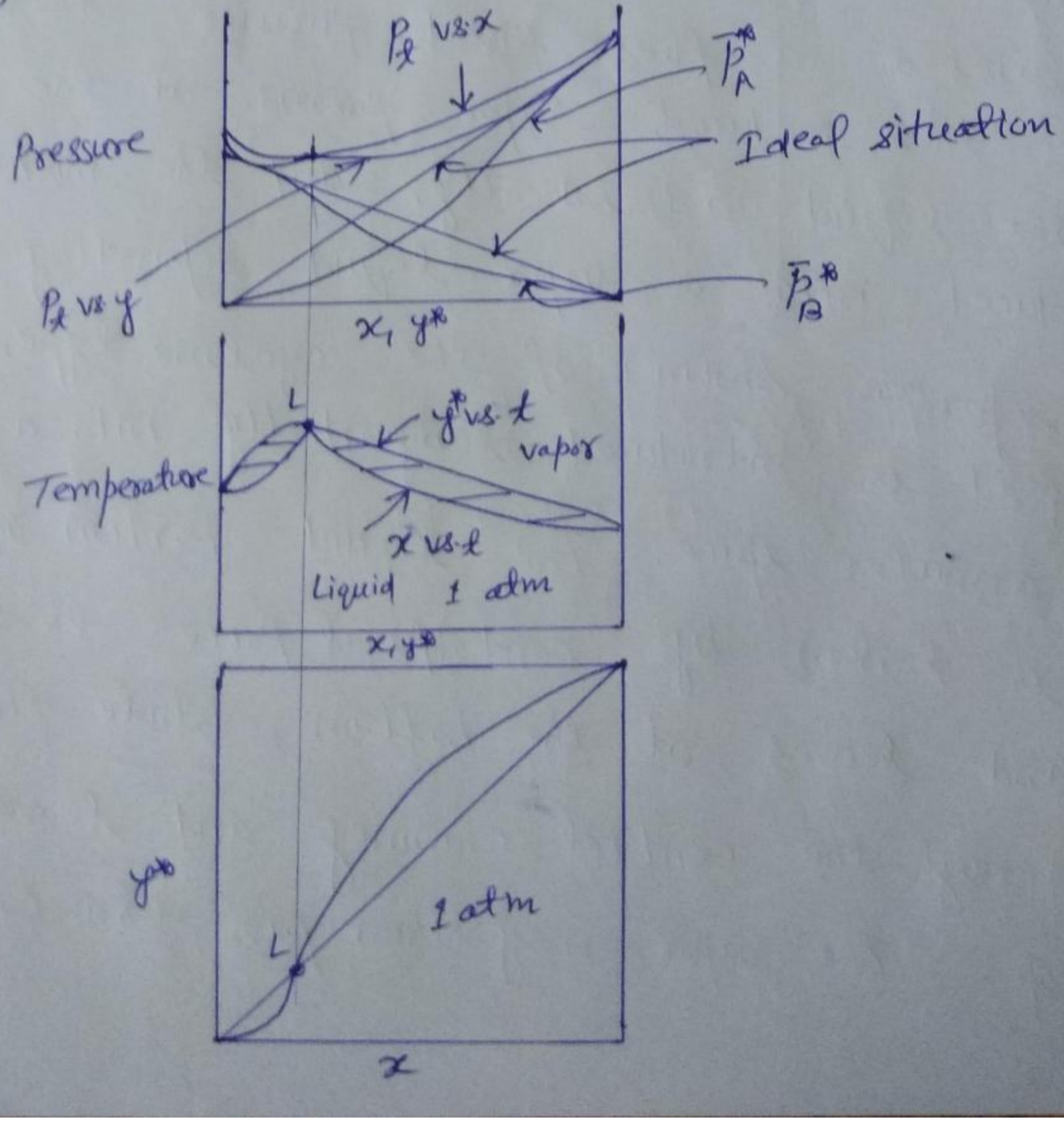
Negative deviations from ideality :-

when the total pressure of a system at equilibrium is less than the ideal value, the system is said to deviate negatively from raoult's law. Such a situation is shown in below figure at constant temperature.



Maximum-boiling mixtures-azeotropes :- When the differences in vapor pressures of the components is not too great and in addition the negative deviations are large, the curve for total pressure against composition may pass through a minimum as shown in below figure. This condition gives rise to a maximum in the boiling temperature, as at point L, and a condition of azeotropism. The equilibrium vapor is leaner in the more volatile substance for liquids whose x is less than the azeotropic composition and greater if x is larger. solutions on either side of the azeotrope, if boiled in an open vessel with escape of vapor, will ultimately leave a residual liquid of the azeotropic composition in the vessel.

Maximum- boiling azeotrops are less common than the minimum type. one which is very well Known is that of $HCl-H_2O$ (11·1 mole% HCl, 110°c, at 1 atm), which can be prepared simply by boiling a solution of any strength of the acid in an open vessel. This is one method of standardizing HCl.

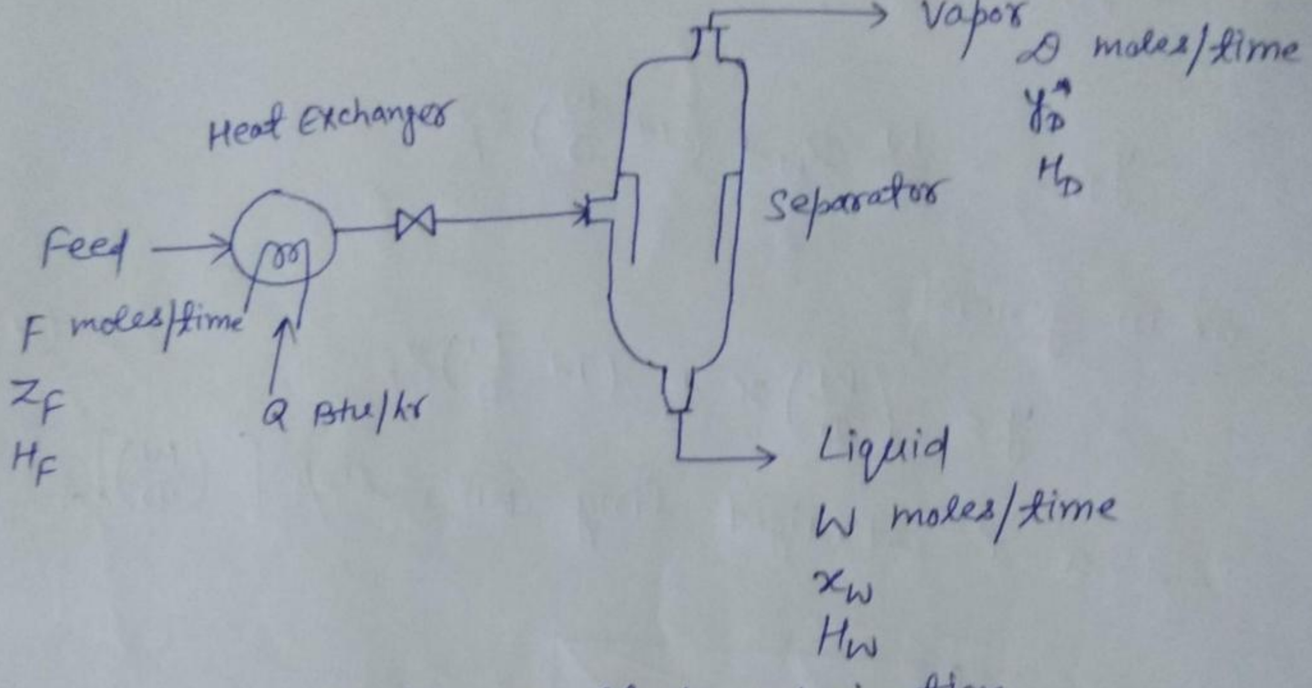


Single - stage operation - Flash vaporization

Flash vaporization, or equilibrium distillation as it is sometimes called, is a single - stage operation wherein a liquid mixture is partially vaporized, the vapor allowed to come to equilibrium with the residual liquid, and the resulting vapor and liquid phases are separated and removed from the apparatus. It may be batchwise or continuous.

A typical flowsheet is shown schematically in below figure for continuous operation. Here the liquid feed is heated in a conventional tubular heat exchanger or by passing through the heated tubes of a fuel - fired furnace. The pressure is then reduced, vapor forms at the expense of the liquid adiabatically, and the mixture is introduced into a vapor - liquid separating vessel. The separator shown is of the cyclone type, where the feed is introduced tangentially into a covered annular space. The liquid portion of the mixture is thrown by centrifugal force to the outer wall and leaves at the bottom, while the vapor rises through the central chimney and leaves at the top. The vapor may then pass to a condenser.

Particularly for flash vaporization of a volatile substance from a relatively nonvolatile one, operation in the separator can be carried out under reduced pressure, but not so low that ordinary cooling water will not condense the vapor product.



Continuous flash vaporization

Overall Material Balance

$$F = D + W \qquad \text{——— (1)}$$

Component balance

$$F z_F = D y_D + W x_W \qquad \text{——— (2)}$$

Heat balance

$$F H_F + Q = D H_D + W H_W \qquad \text{——— (3)}$$

Substituting F from equation (1) into (2), we get:—

$$(D+W)z_F = D y_D + W x_W$$

$$-D y_D = W x_W - (D+W) z_F$$

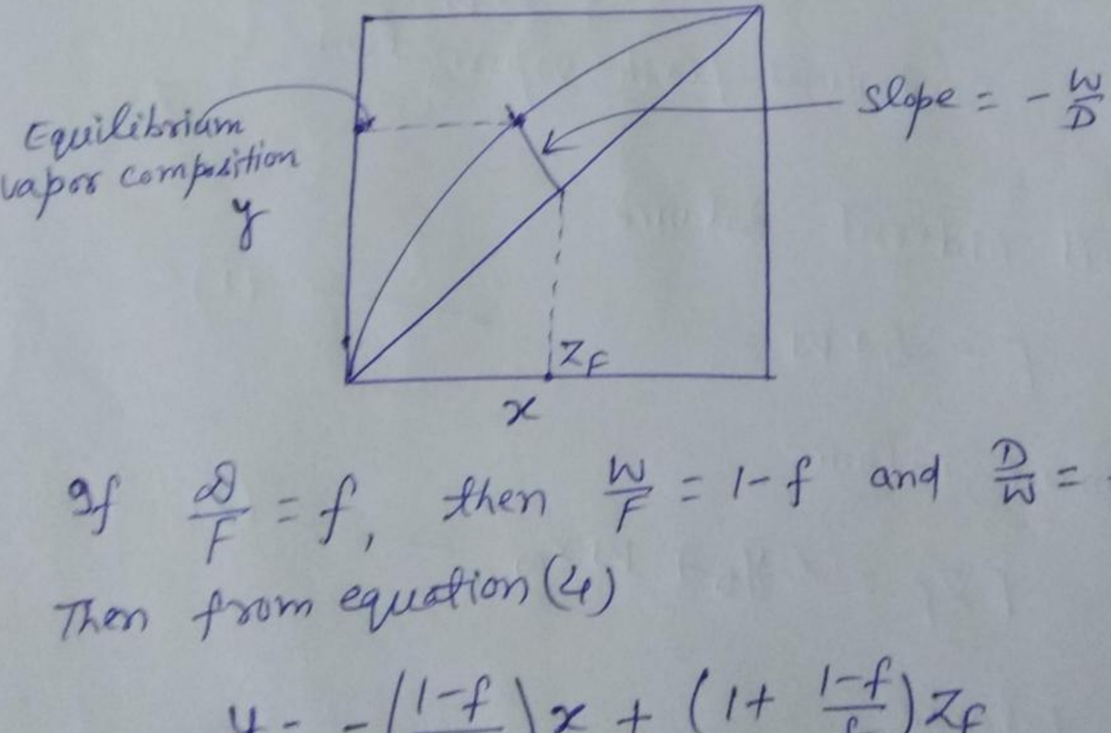
$$-y_D = \frac{W}{D} x_W - \left(1+\frac{W}{D}\right) z_F$$

$$y_D = -\frac{W}{D} x_W + \left(1+\frac{W}{D}\right) z_F$$

or in general

$$y = -\left(\frac{W}{D}\right) x + \left(1+\frac{W}{D}\right) z_F \qquad \text{— (4)}$$

This is a straight ling with slope$\left[-\left(\frac{W}{D}\right)\right]$.



If $\frac{D}{F} = f$, then $\frac{W}{F} = 1-f$ and $\frac{D}{W} = \frac{f}{1-f}$

Then from equation (4)

$$y = -\left(\frac{1-f}{f}\right) x + \left(1+\frac{1-f}{f}\right) z_F$$

$$y = -\left(\frac{1-f}{f}\right) x + \left(\frac{f+1-f}{f}\right) z_F$$

Therefore, $y = -\left(\frac{1-f}{f}\right) x + \frac{z_F}{f}$, from which $y = z_F = x$, The material-balance line crosses the diagonal at $x = z_F$ for all values of f.

Differential or simple distillation :-

If during an infinite number of successive flash vaporizations of a liquid only an infinitesimal portion of the liquid were flashed each time, the net result would be equivalent to a differential, or simple distillation.

In differential distillation, a batch of liquid is charged to a Kettle or still fitted with some sort of heating device such as a steam jacket. The charge is boiled slowely, and the vapors are withdrawn as rapidly as they form to a condenser, where they are liquefied, and the condensate (distillate) is collected in the receiver. The apparatus is essentially a large-scale replica of the ordinary laboratory distillation flask and condenser. The first portion of the distillate will be the richest in the more volatile substance, and as distillation proceeds, the vaporized product becomes leaner. The distillate can therefore be collected in several separate batches, called cuts, to give a series of distilled products of various purities.

consider a binary mixture in which the vapor issuing from a true differential distillation is at any time in equilibrium with the liquid from which it rises but changes continuously in composition.

Assume that at any time during the course of the distillation there are L mole of liquid in the still of composition x mole fraction A and that an amount dD moles of distillate is vaporized, of mole fraction y^* in equilibrium with the liquid. Then we have the following material balances :-

Overall Material balance :-

in - out = accumulation

$$0 - dD = dL$$

Therefore, $-dD = dL$

Material balance of A

$$-y^* dD = d(Lx) = Ldx + xdL$$

or, $y^* dL = Ldx + xdL$

$$(y^*-x)\,dL = L\,dx$$

$$\frac{dL}{L} = \frac{dx}{y^*-x}$$

Integration gives,

$$\int_F^W \frac{dL}{L} = \int_{x_F}^{x_W} \frac{dx}{y^*-x}$$

$$\int_W^F \frac{dL}{L} = \int_{x_W}^{x_F} \frac{dx}{y^*-x}$$

$$\boxed{\ln\left(\frac{F}{W}\right) = \int_{x_W}^{x_F} \frac{dx}{y^*-x}} \quad \text{——} \quad (1)$$

This is known as the Rayleigh equation.

If an average value of relative volatility is given over the concentration range involved, graphical integration can be avoided.

$$\because \quad y = \frac{\alpha x}{1+(\alpha-1)x}$$

By substituting the value of y in equation (4), we get

$$\ln\left(\frac{F}{W}\right) = \int_{x_W}^{x_F} \frac{dx}{\frac{\alpha x}{1+(\alpha-1)x} - x} = \int_{x_W}^{x_F} \frac{dx}{\frac{\alpha x - x - (\alpha-1)x^2}{1+(\alpha-1)x}}$$

$$\ln\left(\frac{F}{W}\right) = \int_{x_W}^{x_F} \frac{(1+(\alpha-1)x)\,dx}{(\alpha-1)(x-x^2)}$$

$$\ln\left(\frac{F}{W}\right) = \int_{x_W}^{x_F} \frac{dx}{(\alpha-1)(x-x^2)} + \int_{x_W}^{x_F} \frac{dx}{1-x}$$

$$\ln\left(\frac{F}{W}\right) = \frac{1}{(\alpha-1)} \ln\left[\left(\frac{x_F}{x_W}\right)\left(\frac{1-x_W}{1-x_F}\right)\right] + \ln\left(\frac{1-x_W}{1-x_F}\right)$$

Therefore,

$$\ln\left(\frac{F}{W}\right) = \frac{1}{\alpha-1} \ln \frac{x_F(1-x_W)}{x_W(1-x_F)} + \ln \frac{1-x_W}{1-x_F}$$

or, $$\ln\left[\left(\frac{F}{W}\right)\left(\frac{1-x_F}{1-x_W}\right)\right] = \frac{1}{\alpha-1} \ln \frac{x_F(1-x_W)}{x_W(1-x_F)}$$

$$(\alpha-1)\left[\ln \frac{F(1-x_F)}{W(1-x_W)}\right] = \ln \frac{x_F(1-x_W)}{x_W(1-x_F)}$$

$$\alpha \ln \frac{F(1-x_F)}{W(1-x_W)} = \ln \frac{x_F(1-x_W)}{x_W(1-x_F)} \cdot \frac{F(1-x_F)}{W(1-x_W)}$$

Therefore,

$$\ln \frac{Fx_F}{Wx_W} = \alpha \ln \frac{F(1-x_F)}{W(1-x_W)}$$

which relates the number of moles of A remaining in the residue, Wx_W, to that of B remaining, $W(1-x_W)$. These expressions are most likely to be valid for ideal mixtures, for which α is most nearly constant.

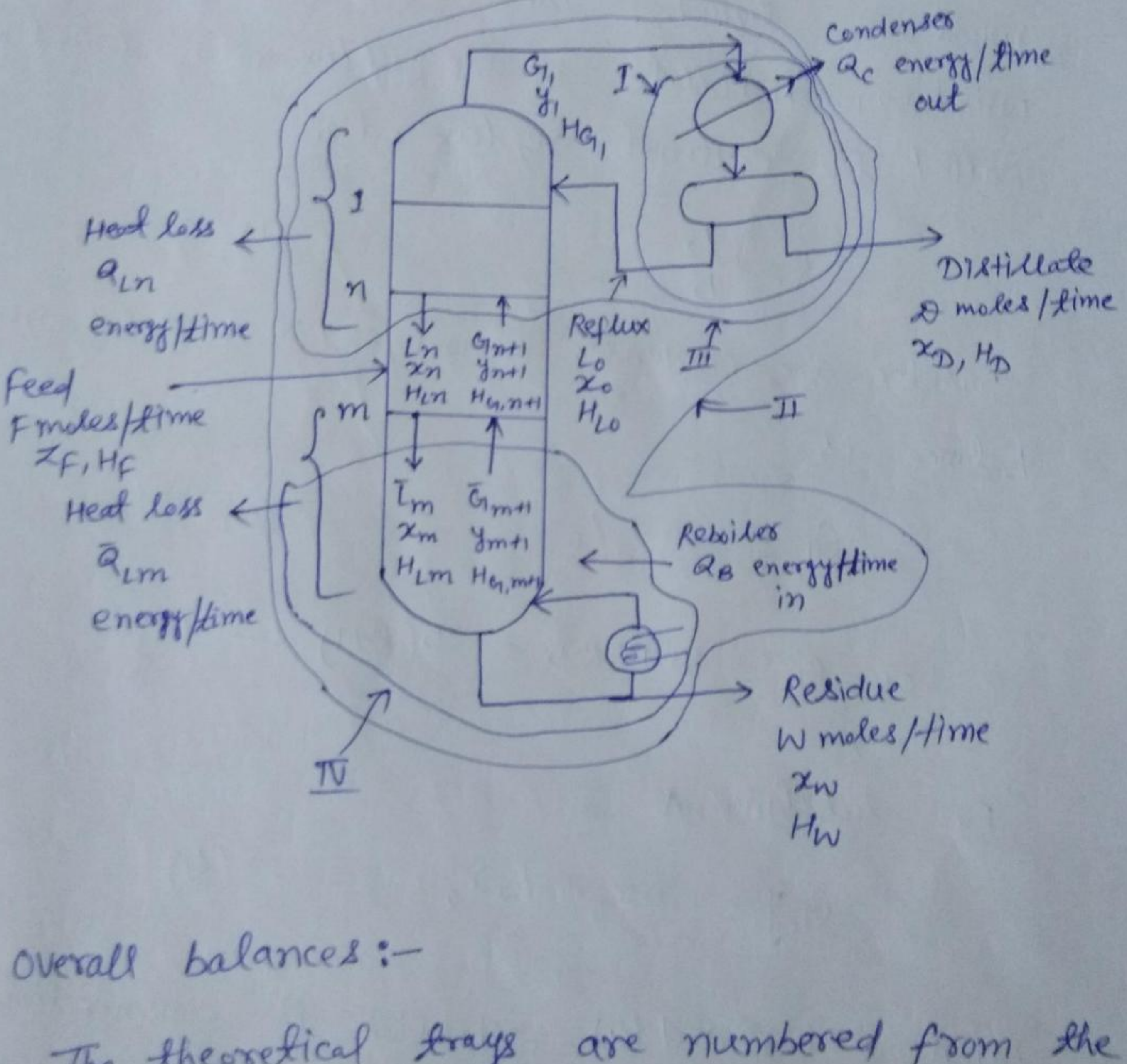
Continuous Rectification - Binary Systems:-

Continuous rectification, or fractionation, is a multi-stage countercurrent distillation operation. For a binary solution, with certain exceptions it is ordinarily possible by this method to separate the solution into its components, recovering each in any state of purity desired.

In distillation as shown in below figure, the feed is introduced more or less centrally into a vertical cascade of stages. Vapor rising in the section above the feed (called the absorption, enriching, or rectifying section) is washed with liquid to remove or absorb the less volatile component. The washing liquid in this case is provided by condensing the vapor issuing from the top, which is rich in more volatile component. The liquid returned to the top of the tower is called reflux, and the material permanently removed is the distillate, which may be a vapor or a liquid, rich in more volatile component. In the section below the feed (stripping or exhausting section), the liquid is stripped of volatile component by vapor produced at the bottom by partial vaporization of the bottom liquid in the reboiler. The liquid removed, rich in less volatile component, is the residue or bottoms. Inside the tower, the liquids and vapors are always at their bubble points and dew points, respectively, so that the highest temperatures are at the bottom, the lowest at the top.

The entire device is called a fractionator.

The purities obtained for the two withdrawn products will depend upon the liquid/gas ratios used and the number of ideal stages provided in the two sections of the tower.



Overall balances :-

The theoretical trays are numbered from the top down as shown in above figure. The subscripts generally indicate the tray from which a stream originates: for example, L_n is mole/time falling from the nth tray. A bar over the quantity indicates that it applies to the section of the column below the point of introduction of the feed. The distillate product may be liquid, vapor or a mixture. The reflux, however, must be liquid. The molar ratio of reflux to withdrawn distillate is the reflux ratio, sometimes called the external reflux ratio,

$$R = \frac{L_0}{D} \quad \text{--- (1)}$$

consider the condenser, envelope I. A total material balance is

$$G_1 = D + L_0 \quad \text{--- (2)}$$

$$\text{or } G_1 = D + RD = D(R+1) \quad \text{--- ③}$$

For substance A

$$G_1 y_1 = D x_D + L_0 x_0 \quad \text{--- (4)}$$

Equations ② and (4) establish the concentrations and quantities at the top of the tower.

An enthalpy balance, envelope I,

$$G_1 H_{G_1} = Q_c + L_0 H_{L0} + D H_D$$

$$Q_c = D\left[(R+1) H_{G_1} - R H_{L0} - H_D\right]$$

Provides the heat load of the condenser. The reboiler heat is then obtained by a complete enthalpy balance about the entire apparatus, envelope II,

$$Q_B = D H_D + W H_W + Q_c + Q_L - F H_F$$

where, Q_L is the sum of all the heat losses.

Two methods namely Ponchon and Savarit; and Mccabe and Thiele methods will be used to develop the relationship between numbers of trays, liquid/vapor ratios, and product compositions.

Multistage tray towers - Method of Mccabe and Thiele :-

This method, although less rigorous than that of Ponchon and Savarit, is nevertheless most useful since it does not require detailed enthalpy data. Except where heat losses or heats of solutions are usually large, the Mccabe-Thiele method will be found adequate for most purposes.

Assumptions of Mccabe-Thiele Method :-

(a) The two components have equal and constant molar latent heats of vaporization.

(b) sensible enthalpy changes and heat of mixing are negligible compared to latent heats of vaporization.

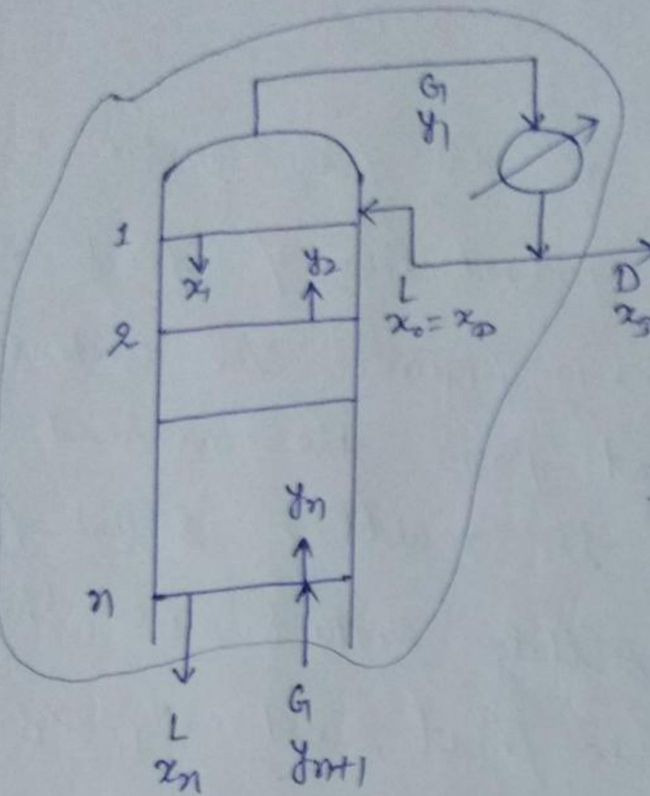
(c) Heat losses are negligible.

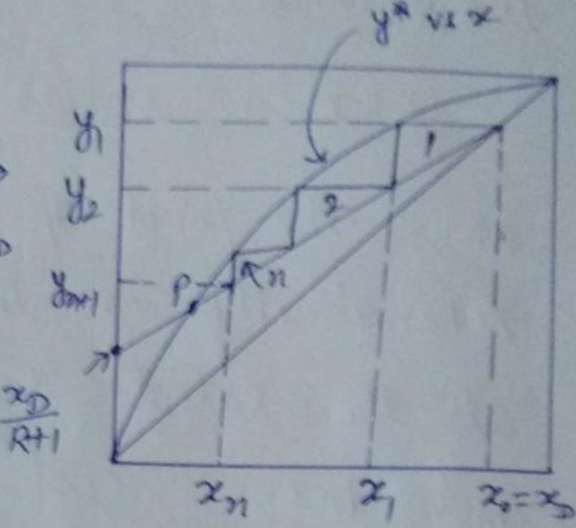
(d) The pressure is uniform throughout the column (negligible pressure drop).

These assumptions, reffered to as the Mccabe-Thiele assumptions, leadsto the condition of constant molar overflow. For constant molar overflow, the analysis of a distillation column is greatly simplified because it is not necessary to consider energy balances in either the rectifying or stripping sections, only Material balances and a VLE curve are required.

Enriching section; total condenser - Reflux at the bubble point :-

consider a section of the fractionator entirely above the point of introduction of feed as shown schematically in below figure. The condenser removes all the latent heat from the overhead vapor but does not cool the resulting liquid further. The reflux and distillate product are therefore liquids at the bubble point, and $y_1 = x_D = x_0$. since the liquid, L mol/h, falling from each tray and the vapor G mol/h, rising from each tray are each constant if the usual simplifying assumptions pertain, subscripts are not needed to identify the source of these streams. The compositions, however, change. The trays shown are theoretical trays, so that the composition y_n of the vapor from the n th tray is in equilibrium with the liquid of composition x_n leaving the same tray. The point (x_n, y_n), on x, y coordinates, therefore falls on the equilibrium curve.





x = mole fraction A in liq

A total material balance for the envelope in the figure is

$$G = L + D = D(R+1)$$

For component A,

$$G y_{n+1} = L x_n + D x_D$$

$$y_{n+1} = \frac{L}{G} x_n + \frac{D}{G} x_D$$

$$y_{n+1} = \frac{L}{L+D} x_n + \frac{D}{L+D} x_D$$

$$y_{n+1} = \frac{L/D}{\frac{L}{D}+1} x_n + \frac{D/D}{L/D + D/D} x_D$$

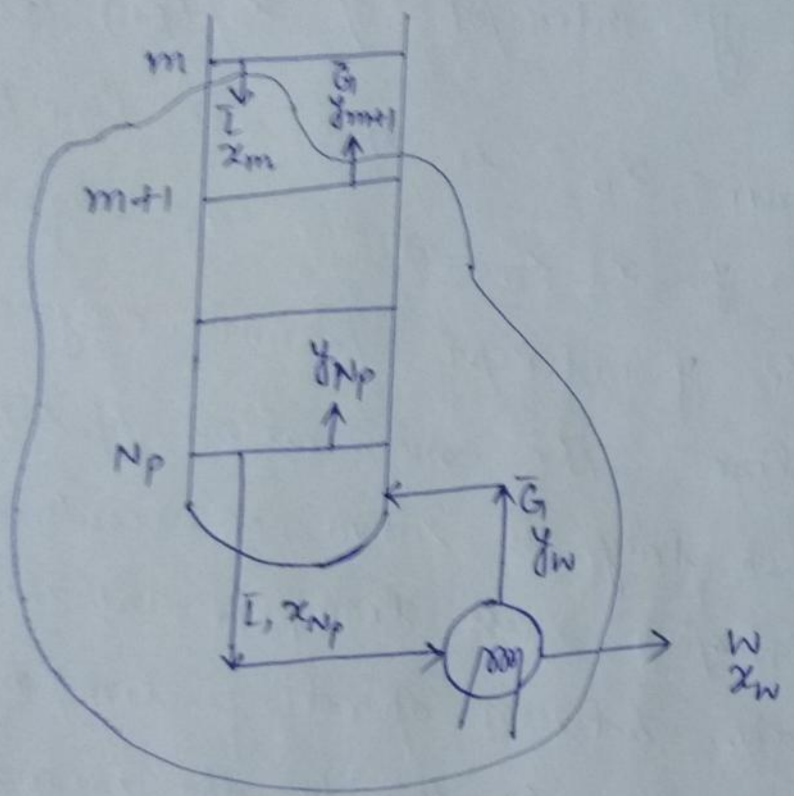
Therefore,

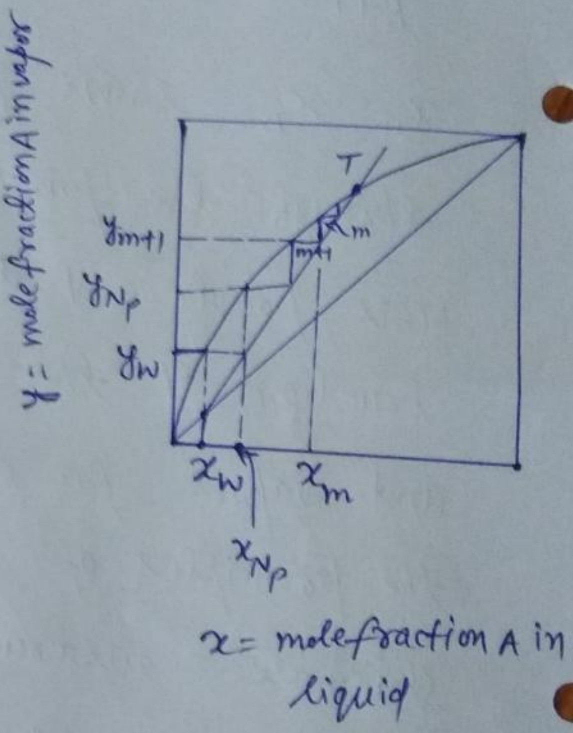
$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$$

The above equation is the operating line of the enriching section. This is the equation of a straight line on x, y coordinates of slope $L/G = \frac{R}{R+1}$ and with a y intercept of $x_D/(R+1)$. Setting $x_n = x_D$ shows $y_{n+1} = x_D$, so that the line passes through the point $y = x = x_D$ on the 45° diagonal. This point and the y intercept permit easy construction of the line. The concentrations of liquids and vapors for each tray is shown in accordance with the principles of interface mass transfer, and the usual staircase construction between operating line and equilibrium curve is seen to provide the theoretical tray- concentration variation. The construction obviously cannot be carried farther than point P.

Exhausting section; Reboiled vapor in equilibrium with residue :-

Consider next a section of the fractionator below the point of introducing the feed as schematically shown in below figure. The trays are again theoretical trays. The rates of flow $\bar{L}$ and $\bar{G}$ are each constant from tray to tray, but not necessarily equal to the values for the enriching section.





A total material balance is

$$\bar{L} = \bar{G} + W$$

and, for component A

$$\bar{L} x_m = \bar{G} y_{m+1} + W x_W$$

These provide the equation of the exhausing-section operating line,

$$y_{m+1} = \frac{\bar{L}}{\bar{G}} x_m - \frac{W}{\bar{G}} x_W$$

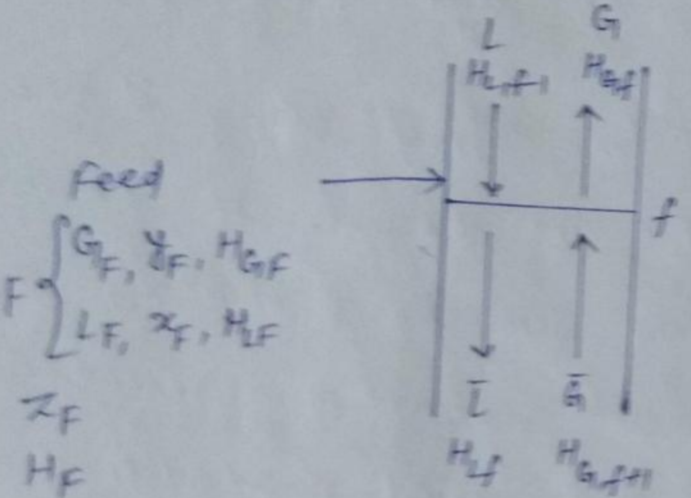
$$y_{m+1} = \frac{\bar{L}}{\bar{L}-W} x_m - \frac{W}{\bar{L}-W} x_W$$

This is a straight line of slope $\bar{L}/\bar{G} = \bar{L}/(\bar{L}-W)$, and since when $x_m = x_W$, $y_{m+1} = x_W$, it passes through $x = y = x_W$ on the 45° diagonal. If the reboiler vapor y_W is in equilibrium with the residue x_W, the first step of the staircase construction represents the reboiler. The steps can be carried no farther than point T.

Introduction of feed :-

The introduction of the feed type influences the Change in slope of the operating lines as we pass from the enriching to the exhausting section of the fractionator.

Consider the section of the column at the tray where the feed is introduced as shown in below figure. The quantities of the liquid and vapor streams change abruptly at this tray, since the feed may consist of liquid, vapor, or a mixture of both. If for example, the feed is a saturated liquid, $\bar{L}$ will exceed L by the amount of the added feed liquid. To establish the general relationship, an overall material balance about this section is



$$F + L + \bar{G} = G + \bar{L} \qquad \text{— (1)}$$

and an enthalpy balance,

$$FH_F + LH_{Lf-1} + \bar{G}H_{Gf+1} = GH_{Gf} + \bar{L}H_{Lf} \qquad \text{— (2)}$$

The vapors and liquids inside the tower are all saturated, and the molal enthalpies of all saturated vapors at this section are essentially identical since the temperature and composition changes over one tray are small. The same is true of the molal enthalpies of the saturated liquids, so that $H_{Gf} = H_{Gf+1}$ and $H_{Lf-1} = H_{Lf}$. Equation (2) then becomes

$$(\bar{L}-L)H_L = (\bar{G}-G)H_G + FH_F$$

combining this with equation (1) gives,

$$\frac{\bar{L}-L}{F} = \frac{H_G - H_F}{H_G - H_L} = q \quad \text{— (3)}$$

The quantity q is thus seen to be the heat required to convert 1 mole of feed from its condition H_F to a saturated vapor, divided by the molal latent heat $H_G - H_L$. The feed may be introduced under any of a variety of thermal conditions ranging from a liquid well below its bubble point to a superheated vapor, for each of which the value of q will be different. Combining equations (1) and (3), we get

$$\bar{G} - G = \bar{L} - L - F = qF - F = F(q-1)$$

which provides a convenient method for determining $\bar{G}$.

Rewriting enriching and stripping section equations without the tray subscripts, we have

$$yG = Lx + Dx_D \quad \text{— (4)}$$

$$y\bar{G} = \bar{L}x - Wx_W \quad \text{— (5)}$$

(5) - (4) gives,

$$(\bar{G}-G)y = (\bar{L}-L)x - (Wx_W + Dx_D)$$

since $$Fz_F = Wx_W + Dx_D$$

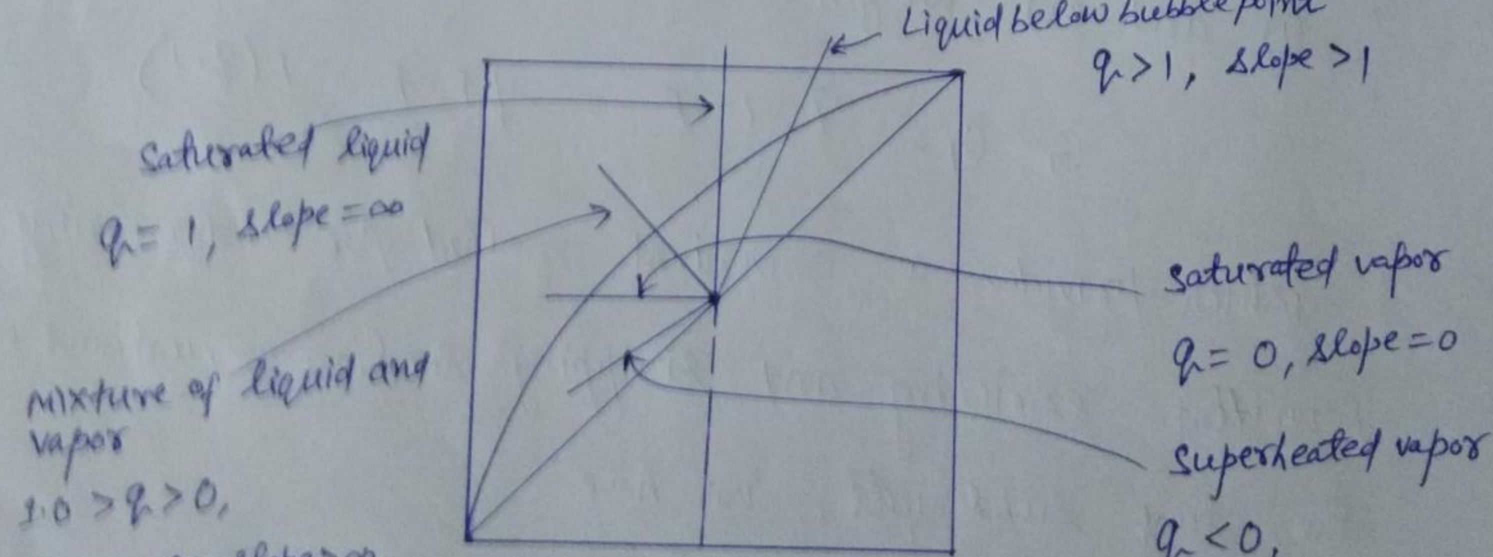
Therefore,

$$(\bar{G}-G)y = (\bar{L}-L)x - Fz_F$$

$$F(q-1)y = qFx - Fz_F$$

$$y = \frac{q}{q-1}x - \frac{z_F}{q-1}$$

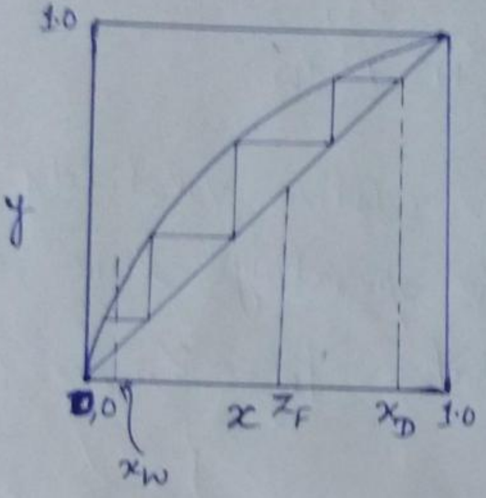
This, the locus of intersection of operating lines (the q line), is a straight line of slope $q/(q-1)$, and since, $y = z_F$, when $x = z_F$, it passes through the point $x = y = z_F$ on the 45° diagonal.



Location of q-line for typical feed conditions

Total Reflux, or Infinite Reflux Ratio :-

As the reflux ratio $R = L/D$ is increased, the ratio L/G increases, until ultimately, when $R = \infty$, $\frac{L}{G} = 1$ and the operating lines of both sections of the column coincide with the 45° diagonal as shown in below figure.



In practice this can be realized by returning all the overhead product back to the column as reflux (total reflux) and reboiling all the residue product, whereupon the forward flow of fresh feed must be reduced to zero. Alternatively such a condition can be interpreted as requiring infinite reboiler heat and condenser cooling capacity for a given rate of feed.

As the operating lines moves farther away from the equilibrium curve with increased reflux ratio, the number of theoretical trays required to produce a given separation becomes less, until at total reflux the number of trays is the minimum N_m.

If the relative volatility is constant or nearly so, the analytical method can be used to calculate minimum trays required at total reflux condition.

Applying relative volatility definition to the residue product gives

$$\frac{y_w}{1-y_w} = \alpha_w \frac{x_w}{1-x_w}$$

where, α_w is the relative volatility at the reboiler. At total reflux the operating line coincide with the 45° diagonal so that $y_w = x_{N_m}$. Therefore,

$$\frac{x_{N_m}}{1-x_{N_m}} = \alpha_w \frac{x_w}{1-x_w}$$

similarly for the last tray of the column, where α_{N_m} pertains,

$$\frac{y_{N_m}}{1-y_{N_m}} = \alpha_{N_m} \frac{x_{N_m}}{1-x_{N_m}} = \alpha_{N_m} \alpha_w \frac{x_w}{1-x_w}$$

This procedure can be continued up the column until ultimately

$$\frac{y_1}{1-y_1} = \alpha_1 \alpha_2 \cdots \alpha_{N_m} \alpha_w \frac{x_w}{1-x_w}$$

If some average relative volatility α_{av}, can be used,

$$\frac{x_D}{1-x_D} = \alpha_{av}^{N_m+1} \frac{x_W}{1-x_W}$$

or

$$N_m + 1 = \frac{\log \frac{x_D}{1-x_D} \frac{1-x_W}{x_W}}{\log \alpha_{av}}$$

which is known as Fenske's equation. The total minimum number of theoretical stages to produce products x_D and x_W is N_m+1, which then includes the reboiler. For small variations in α, α_{av} can be taken as the geometric average of the values for the overhead and bottom products, $\sqrt{\alpha_1 \alpha_W}$. The expression can be used only with nearly ideal mixtures, for which α is nearly constant.

Minimum Reflux Ratio :-

The minimum reflux ratio R_m is the maximum ratio which will require an infinite number of trays for the separation desired, and it corresponds to the minimum reboiler heat and condenser cooling capacity for the separation. As the slope of the enriching section depends on reflux ratio. As the reflux ratio is decreased, the slope of the enriching operating line becomes less, and the number of trays required increases. When operating line passes through the point of intersection of the q-line and the equilibrium curve, corresponds to the minimum reflux ratio and an infinite number of trays would be required to reach at pinch point from either end of the tower. In some cases, the minimum reflux operating line will be tangent to the equilibrium curve in the enriching section. A tangent operating line in the exhausting section may also set the minimum reflux ratio because of the interdependence of the liquid/vapor ratios in the two sections of the column

When the equilibrium curve is always concave downward, the minimum reflux ratio can conveniently be calculated analytically. The required relationship can be developed by solving equations of enriching section operating line and q-line simultaneously to obtain the coordinates (x_a, y_a) of the point of intersection of the enriching operating line and the q-line. When the tray-number designated is dropped, we have

$$y_a = \frac{R}{R+1} x_a + \frac{x_D}{R+1} \quad \text{— (1)}$$

$$y_a = \frac{q}{q-1} x_a + \frac{-z_F}{q-1} \quad \text{— (2)}$$

Solving equations (1) & (2) we get,

$$\frac{R}{R+1} x_a + \frac{x_D}{R+1} = \frac{q}{q-1} x_a - \frac{z_f}{q-1}$$

$$\left(\frac{R}{R+1} - \frac{q}{q-1}\right) x_a = -\left(\frac{x_D}{R+1} + \frac{z_f}{q-1}\right)$$

$$x_a = \frac{\left(\frac{x_D}{R+1} + \frac{z_f}{q-1}\right)}{\frac{q}{q-1} - \frac{R}{R+1}}$$

$$x_a = \frac{x_D(q-1) + z_F(R+1)}{q(R+1) - R(q-1)}$$

$$\therefore \quad x_a = \frac{x_D(q-1) + z_f(R+1)}{R+q}$$

Now,

$$y_a = \frac{R}{R+1}\left[\frac{x_D(q-1) + z_F(R+1)}{R+q}\right] + \frac{x_D}{R+1}$$

$$y_a = \frac{R x_D q - R x_D + R z_F(R+1) + x_D R + x_D q}{(R+1)(R+q)}$$

$$y_a = \frac{(R+1)(Rz_F + x_D q)}{(R+1)(R+q)}$$

$$\therefore \; y_a = \frac{Rz_F + q x_D}{R+q}$$

At the minimum reflux ratio R_m, these coordinates are equilibrium values since they occur on the equilibrium curve. Therefore, from the definition of α.

$$\frac{y_a}{1-y_a} = \alpha \frac{x_a}{1-x_a}$$

$$\frac{\dfrac{R_m z_F + q x_D}{R_m + q}}{1 - \dfrac{R_m z_F + q x_D}{R_m + q}} = \alpha \left[\frac{\dfrac{x_D(q-1) + z_F(R_m+1)}{R_m+q}}{1 - \dfrac{x_D(q-1) + z_F(R_m+1)}{R_m+q}} \right]$$

$$\frac{R_m z_F + q x_D}{R_m(1-z_F) + q(1-x_D)} = \frac{\alpha\left[x_D(q-1) + z_F(R_m+1)\right]}{R_m + q - x_D(q-1) - z_F(R_m+1)}$$

$$\frac{R_m z_F + q x_D}{R_m(1-z_F) + q(1-x_D)} = \frac{\alpha\left[x_D(q-1) + z_F(R_m+1)\right]}{R_m + q - x_D(q-1) - z_F(R_m+1) + 1 - 1}$$

$$\frac{R_m z_F + q x_D}{R_m(1-z_F) + q(1-x_D)} = \frac{\alpha\left[x_D(q-1) + z_F(R_m+1)\right]}{(R_m+1)(1-z_F) + (q-1)(1-x_D)} \quad -(3)$$

This conveniently can be solved for R_m for any value of q. Thus, for example :

for $q = 1$ (feed liquid at the bubble point)

Equation (3) gives,

$$\frac{R_m z_F + x_D}{R_m(1-z_F) + 1 - x_D} = \frac{\alpha z_F (R_m+1)}{(R_m+1)(1-z_F)} = \frac{\alpha z_F}{1-z_F}$$

$$R_m z_F + x_D - R_m z_F^2 - x_D z_F = \alpha R_m z_F - \alpha R_m z_F^2 + \alpha z_F - \alpha x_D z_F$$

$$R_m\left[z_F - z_F^2 - \alpha z_F + \alpha z_F^2\right] = x_D z_F - x_D + \alpha z_F - \alpha x_D z_F$$

$$R_m\left[z_F(1-z_F) - \alpha z_F(1-z_F)\right] = -x_D(1-z_F) + \alpha z_F(1-x_D)$$

$$R_m\left[(z_F - \alpha z_F)(1-z_F)\right] = -x_D(1-z_F) + \alpha z_F(1-x_D)$$

$$R_m\left[-(\alpha-1)z_F(1-z_F)\right] = -x_D(1-z_F)+\alpha z_F(1-x_D)$$

$$R_m(\alpha-1) = \frac{x_D(1-z_F)}{z_F(1-z_F)} - \frac{\alpha z_F(1-x_D)}{z_F(1-z_F)}$$

$$\therefore\ R_m = \frac{1}{\alpha-1}\left[\frac{x_D}{z_F} - \frac{\alpha(1-x_D)}{(1-z_F)}\right]$$

For $q=0$ (feed vapor at the dew point)

from equation (3),

$$\frac{R_m z_F}{R_m(1-z_F)} = \frac{-\alpha x_D+\alpha z_F(R_m+1)}{(R_m+1)(1-z_F)-1+x_D}$$

$$\frac{z_F}{1-z_F} = \frac{\alpha z_F(R_m+1)-\alpha x_D}{(R_m+1)(1-z_F)-1+x_D}$$

$$(R_m+1)z_F(1-z_F)-z_F+x_D z_F = \alpha z_F(R_m+1)-\alpha x_D$$
$$-\alpha z_F^2(R_m+1)+\alpha x_D z_F$$

$$(R_m+1)\left[z_F(1-z_F)-\alpha z_F+\alpha z_F^2\right] = z_F-x_D z_F-\alpha x_D+\alpha x_D z_F$$

$$(R_m+1)\left[z_F(1-z_F)-\alpha z_F(1-z_F)\right] = z_F(1-x_D)-\alpha x_D(1-z_F)$$

$$(R_m+1)\left[(1-\alpha)\, z_F(1-z_F)\right] = z_F(1-x_D) - \alpha x_D(1-z_F)$$

$$(R_m+1)(\alpha-1) = \frac{\alpha x_D(1-z_F)}{z_F(1-z_F)} - \frac{z_F(1-x_D)}{z_F(1-z_F)}$$

$$(R_m+1)(\alpha-1) = \frac{\alpha x_D}{z_F} - \frac{1-x_D}{1-z_F}$$

$$\therefore\ R_m = \frac{1}{\alpha-1}\left(\frac{\alpha x_D}{z_F} - \frac{1-x_D}{1-z_F}\right) - 1$$

In each case, the α is that prevailing at the intersection of the q-line and the equilibrium curve.

Enthalpy- concentration Diagrams :-

Binary vapor- liquid equilibria can also be plotted on coordinates of enthalpy vs. concentration at constant pressure. Liquid- solution enthalpies include both sensible- heat and heat of mixing the components

$$H_L = C_L(t_L - t_0)\, M_{av} + \Delta H_s$$

Where C_L is the heat capacity of the solution, and

ΔH_s is the heat of solution at t_o and the prevailing concentration referred to the pure liquid components. For saturated liquid, t_L is the bubble point corresponding to the liquid concentration at the prevailing pressure. If heat is evolved on mixing, ΔH_s will be negative, and for ideal solutions it is zero. For ideal solutions, the heat capacity is the weighted average of those for the pure components.

For present purposes, saturated vapor enthalpies can be calculated adequately by assuming that the unmixed liquids are heated separately as liquids to the gas temperature t_G (the dew point), each vaporized at this temperature, and the vapors mixed.

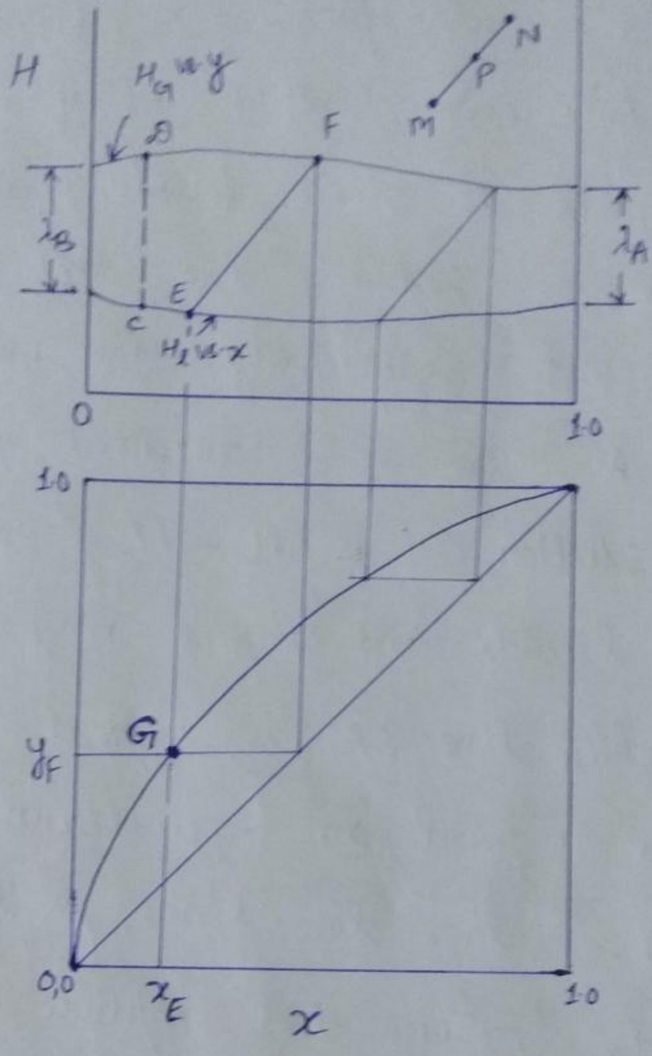
$$H_G = y\left[C_{L,A} M_A (t_G - t_o) + \lambda_A M_A\right] + (1-y)\left[C_{L,B} M_B (t_G - t_o) + \lambda_B M_B\right]$$

where, λ_A and λ_B are latent heats of vaporization of pure substances at t_G in energy per mole and $C_{L,A}$ and $C_{L,B}$ are heat capacities of pure liquids.

In below figure, which represents a typical binary mixture, the enthalpies of saturated vapors at their dew points have been plotted vs. y and those of the saturated liquids at their bubble points vs. x. The vertical distances between the two curves at x = 0 and 1 represent, respectively, the molar latent heats of B and A. The heat required for complete vaporization of solution C is $H_D - H_C$ energy/mole solution. Equilibrium liquids and vapors may be joined by tie lines, of which line EF is typical. The tie line EF will be a point on equilibrium curve (as shown a point G). other tie lines, when projected to the xy plot, produce the complete equilibrium-distribution curve.

Characteristics of the Hxy and xy diagrams:-

Let point M on below figure represent M mol of a mixture of enthalpy H_M and concentration z_M, and similarly N is N mol of a mixture of properties H_N, z_N. Adiabatic mixing of M and N will produce P mole of a mixture of enthalpy H_P and concentration z_P. A total material balance is



$$M + N = P \qquad \text{——} \quad (I)$$

and a balance for component A is

$$MZ_M + NZ_N = PZ_P \qquad \text{——} \quad (II)$$

An enthalpy balance is

$$MH_M + NH_N = PH_P \qquad \text{——} \quad (III)$$

Eliminating P between equations (I) & (II) and between (I) & (III) yields,

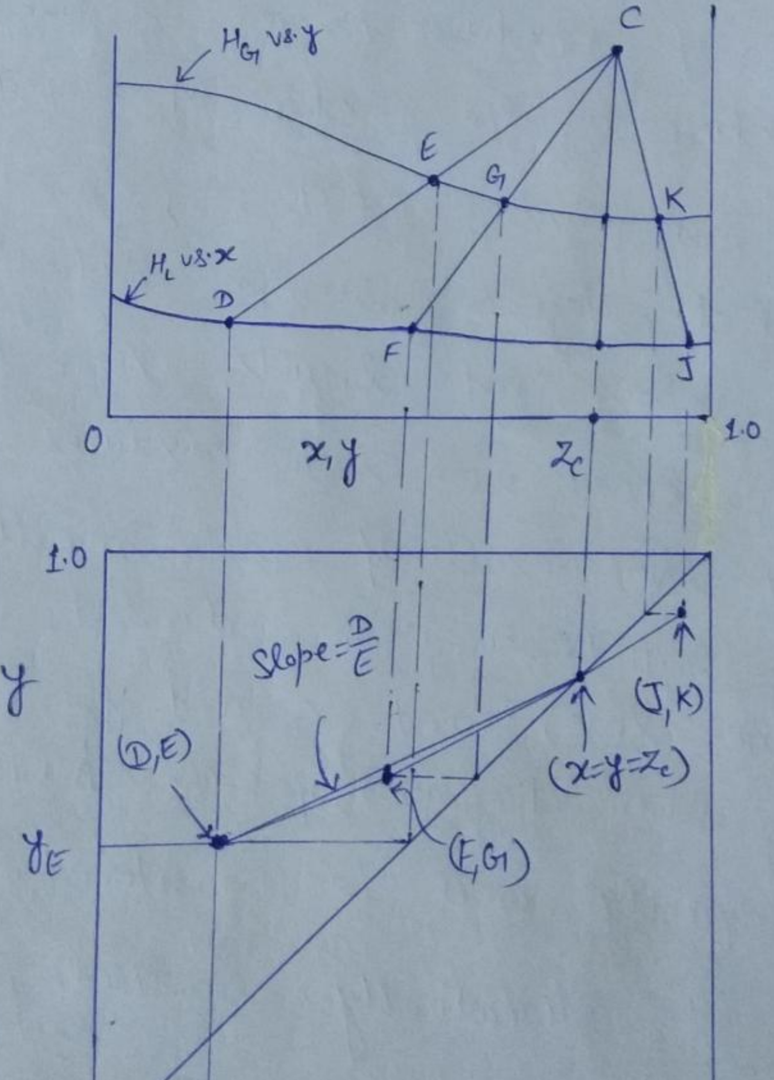
$$\frac{M}{N} = \frac{Z_N - Z_P}{Z_P - Z_M} = \frac{H_N - H_P}{H_P - H_M}$$

This is the equation of a straight line on the enthalpy-concentration plot, passing through points (H_M, Z_M), (H_N, Z_N), and (H_P, Z_P). Point P is therefore on the straight line MN, located so that $\frac{M}{N} = \frac{\text{line } NP}{\text{line } PM}$. Similarly if mixture N were removed adiabatically from mixture P, the mixture M would result.

Consider now mixture $C(H_C, Z_C)$ in below figure. It is useful to describe such a mixture in terms of saturated vapors and liquids, since distillation is mostly concerned with such mixtures. C can be considered the result of adiabatically removing saturated liquid D from saturated vapor E (DE is not a tie line), and x_D and y_E can be located on the lower diagram of the below figure. But C can equally well be considered as having been produced by adiabatically subtracting F from G or J from K, or indeed by such a combination of saturated liquids and vapors given by any line from C which intersects the saturated-enthalpy curves.

These when projected to the lower diagram, form the curve shown there. Thus any point c on the Hxy diagram can be represented by the difference between saturated vapors and liquids and in turn also by a curve on the xy plot. For the combination E-D=C, a material balance shows

$$\frac{D}{E} = \frac{z_C - y_E}{z_C - x_D} = \frac{\text{line } CE}{\text{line } CD}$$



This is the equation on the xy diagram of the chord of slope D/E drawn between point (y_E, x_D) and $y = x = z_C$ on the 45° line. Similarly, the ratios F/G and J/K would be shown by the slopes of chords drawn from these points to $y = x = z_C$.

Consideration of the geometry of the diagram will readily show the following :-

(a) If the $H_G y$ and $H_L x$ curves are straight parallel lines (which will occur if the molar latent heats of A and B are equal, if the heat capacities are constant over the prevailing temperature range, and if there is no heat of solution), then $D/E = F/G = J/K$ for adiabatic subtraction, since the line-segment ratios are then equal, and the curve on xy representing C becomes a straight line.

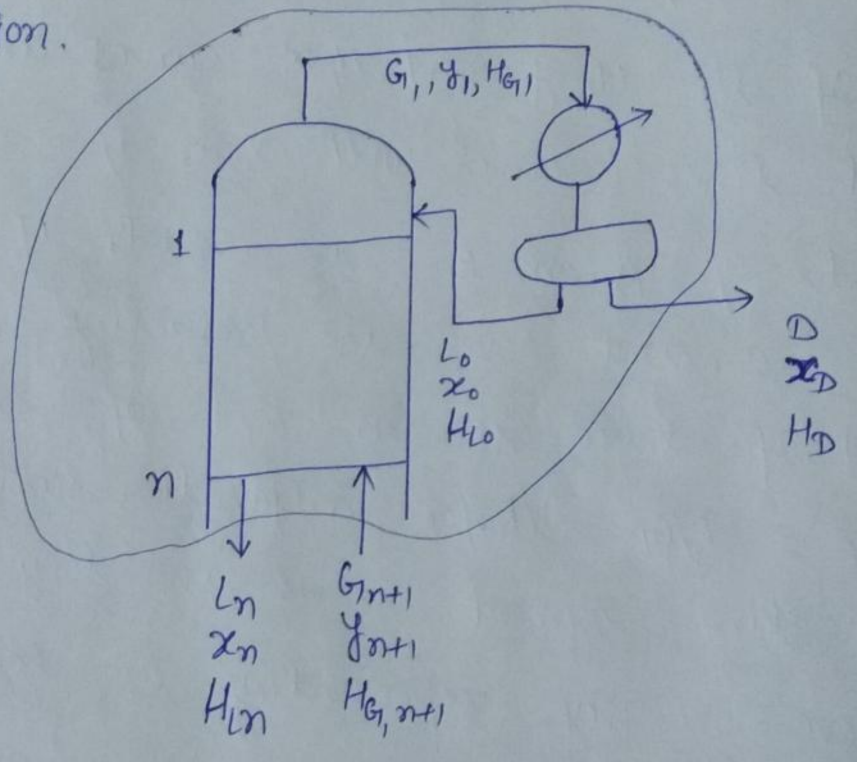
(b) If point C is moved upward, the curve on xy becomes steeper, ultimately coinciding with the 45° line when C is at infinite enthalpy.

(c) If point C is on the $H_G y$ curve, the curve on xy becomes a vertical straight line.

Multistage (Tray) Towers - The Method of Ponchon and Savarit :-

The method will first be developed for the case of negligible heat losses.

The enriching section :- consider the enriching section through tray n. Tray n is any tray in this section.



Material balances for the section are, for total material

$$G_{n+1} = L_n + D \quad \text{—— (1)}$$

and for component A

$$G_{n+1} y_{n+1} = L_n x_n + D x_D \quad \text{—— (2)}$$

$$G_{n+1} y_{n+1} - L_n x_n = D x_D \quad \text{—— (3)}$$

The left-hand side of equation (3) represents the difference in rate of flow of component A, up-down, or the net flow upward. Since for a given distillation the right-hand side is constant, it follows that the difference, or net rate of flow of A upward is constant, independent of tray number in this section of the tower, and equal to that permanently withdrawn at the top.

An enthalpy balance, with heat loss negligible, is

$$G_{n+1} H_{G_{n+1}} = L_n H_{Ln} + Q_c + DH_D \qquad -(4)$$

Let Q' be the heat removed in the condenser and the permanently removed distillate, per mole of distillate. Then

$$Q' = \frac{Q_c + DH_D}{D} = \frac{Q_c}{D} + H_D \qquad -(5)$$

and

$$G_{n+1} H_{G,n+1} - L_n H_{Ln} = DQ' \qquad -(6)$$

The left-hand side of equation (6) represents the difference in rate of flow of heat, up-down, or the net flow upward. Since for a given set of circumstances the right-hand side is constant, the difference, or net rate of flow upward, is constant, independent of tray number in this section of the tower, and equal to that permanently taken out at the top with the distillate and at the condenser.

Elimination of D between equations (1) and (2) and between equations (1) and (6) yields

$$\frac{L_n}{G_{n+1}} = \frac{x_D - y_{n+1}}{x_D - x_n} = \frac{Q' - H_{G_{n+1}}}{Q' - H_{L_n}} \quad —(7)$$

L_n / G_{n+1} is called the internal reflux ratio.

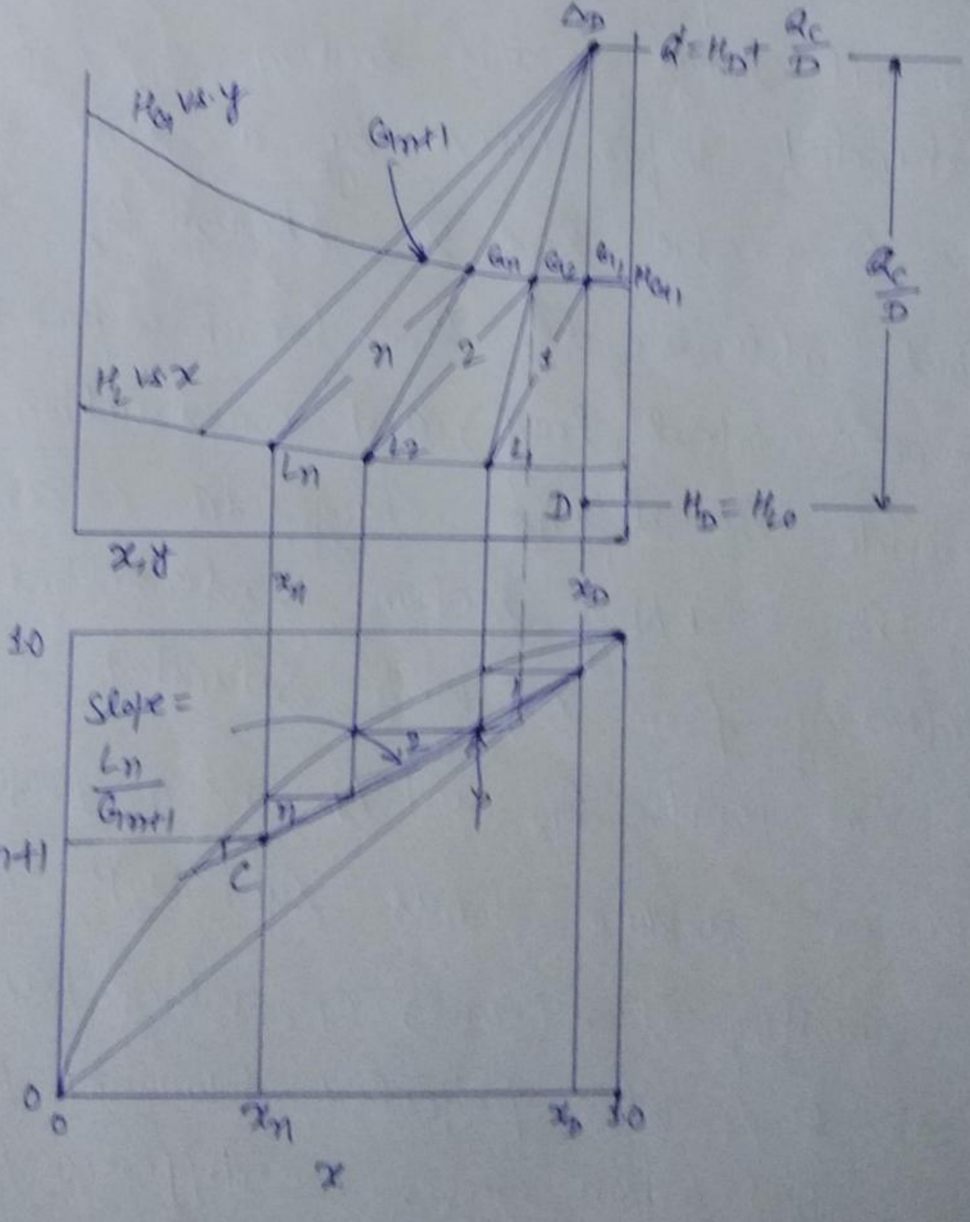
on Hxy diagram equation (7) is the equation of a straight line through $(H_{G_{n+1}}, y_{n+1})$ at G_{n+1}, (H_{L_n}, x_n) at L_n and (Q', x_D) at Δ_D. The last is called a difference point, since its coordinates represent differences in rates of flow:

$$\Delta_D \begin{cases} Q' = \dfrac{\text{difference in heat flow, up-down}}{\text{net moles total substance out}} = \dfrac{\text{net heat out}}{\text{net moles out}} \\[2em] x_D = \dfrac{\text{difference in flow of component A, up-down}}{\text{net moles total substance out}} = \dfrac{\text{net moles A out}}{\text{net moles out}} \end{cases}$$

Δ_D then represents a fictitious stream, in amount equal to the net flow outward (in this case D) and of properties (Q', x_D) such that

$$G_{n+1} - L_n = \Delta_D$$

On the xy diagram equation (7) is the equation of straight line of slope L_n/G_{n+1}, through (y_{n+1}, x_n) and $y = x = x_D$. These are plotted on below figure, where both diagrams are shown.



Above figure is drawn for a total condenser. The distillate D and reflux L_0 then have identical coordinates and are plotted at point D. The location shown indicates that they are below the bubble point. If they were at the bubble point, D would be on the saturated-liquid curve. The saturated vapor G_1 from the top tray, when totally condensed, has the same composition as D and L_0. Liquid L_1 leaving ideal tray 1 is in equilibrium with G_1 and is located at the end of tie line 1. Since equation (7) applies to all trays in this section, G_2 can be located on saturated vapor curve by a line drawn from L_1 to Δ_D; tie line 2 through G_2 locates L_2, etc. Thus, alternate tie lines (each representing the effluents from an ideal tray) and construction lines through Δ_D provide the stepwise changes in concentration occurring in the enriching section. Intersections of the lines radiating from Δ_D with saturated-enthalpy curves, such as points G_2 and L_2, when projected to the lower diagram, produce points such as P. These in turn produce the operating line (curve) CP, which passes through $y=x=x_D$. The tie lines, when projected downward, produce the equilibrium distribution curve. The difference point Δ_D is used in this manner for all trays in the enriching section, working downward until the feed tray is reached.

At any tray n the L_n/G_{n+1} ratio is given by the ratio of lengths $\Delta_D G_{n+1} / \Delta_D L_n$ on the upper diagram of above figure, or by the slope of the chord as shown on the lower diagram. Elimination of G_{n+1} between equations (1) and (7) provides

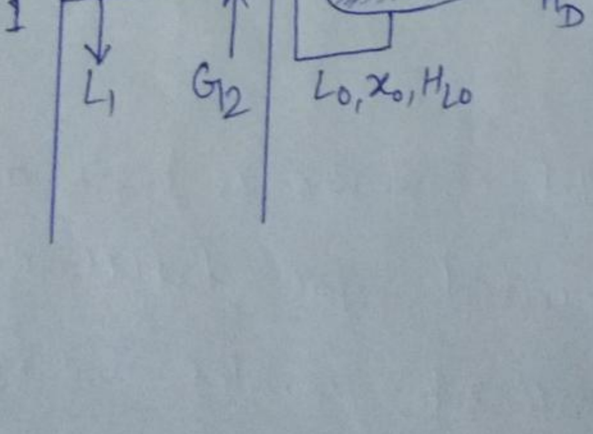
$$\frac{L_n}{D} = \frac{Q' - H_{G_{n+1}}}{H_{G_{n+1}} - H_{L_n}} = \frac{x_D - y_{n+1}}{y_{n+1} - x_n} \quad \text{— (8)}$$

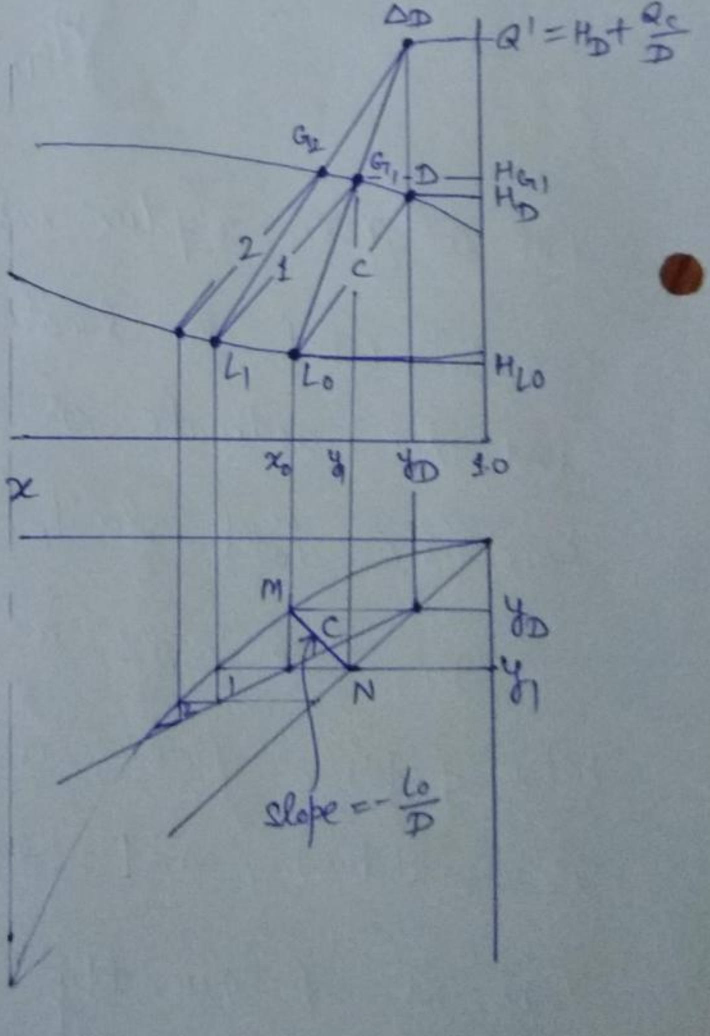
Applying this to the top tray provides the external reflux ratio, which is usually the one specified :-

$$R = \frac{L_0}{D} = \frac{Q' - H_{G_1}}{H_{G_1} - H_{L_0}} = \frac{\text{line } \Delta_D G_1}{\text{line } G_1 L_0} = \frac{\text{line } \Delta_D G_1}{\text{line } G_1 D} \quad \text{— (9)}$$

For a given reflux ratio, the line length of equation (9) can be used to locate Δ_D vertically on above figure, and the ordinate Q' can then be used to compute the condenser heat load.

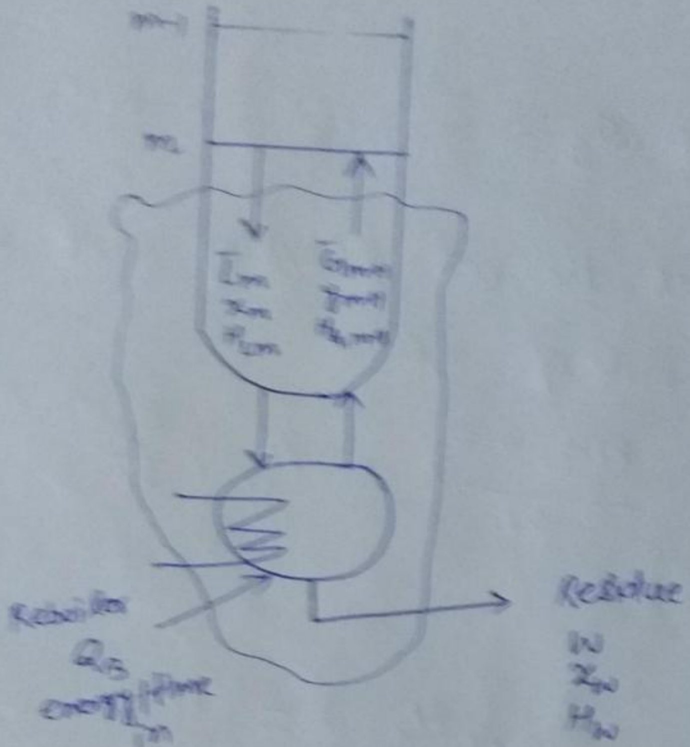
In some cases a partial condenser is used, as in below figure. Here a saturated vapor distillate D is withdrawn, and the condensate provides the reflux. This is frequently done when the pressure required for complete condensation of vapor G_1 at reasonable condenser temperature, would be too large. The Δ_D plotted at an abscissa y_D corresponding to the composition of the withdrawn distillate. Assuming that an equilibrium-condensation is realized, reflux L_0 is at the end of the tie line C. G_1 is located by the construction line $L_0\Delta_D$, etc. In the lower diagram, the line MN solves the equilibrium-condensation problem. The reflux ratio $R = L_0/D$ = Line $\Delta_D G_1$ / line $G_1 L_0$. It is seen that the equilibrium partial condenser provides one equilibrium tray's worth of rectification. However, it is safer not to rely on such complete enrichment by the condenser but instead to provide trays in the tower equivalent to all the stages required.





The stripping section :-

Consider the envelop shown on below figure, where tray m is any tray in the stripping section.



A balance for total material is

$$\bar{L}_m = \bar{G}_{m+1} + W \quad — (1)$$

and, for component A,

$$L_m x_m = \bar{G}_{m+1} y_{m+1} + W x_W \quad — (2)$$

$$L_m x_m - \bar{G}_{m+1} y_{m+1} = W x_W \quad — (3)$$

The left-hand side of equation (3) represents the difference in rate of flow of component A, down-up, or net flow downward.

Since right-hand side is a constant for a given distillation, the difference is independent of tray number in this section of the tower and equal to the rate of permanent removal of A out the bottom.

An enthalpy balance is

$$\bar{L}_m H_{Lm} + Q_B = \bar{G}_{m+1} H_{G_{m+1}} + W H_W \quad \text{— (4)}$$

define Q'' as the net flow of heat outward at the bottom, per mole of residue

$$Q'' = \frac{W H_W - Q_B}{W} = H_W - \frac{Q_B}{W} \quad \text{— (5)}$$

whence,

$$\bar{L} H_{Lm} - \bar{G}_{m+1} H_{G_{m+1}} = W Q'' \quad \text{— (6)}$$

The left-hand side of equation (6) is the difference in rate of flow of heat, down up which then equals the constant net rate of heat flow out the bottom for all trays in this section.

Elimination of W between equations (1) and (2) and between equations (1) and (6) provides

$$\frac{\bar{L}_m}{\bar{G}_{m+1}} = \frac{y_{m+1} - x_W}{x_m - x_W} = \frac{H_{G_{m+1}} - Q''}{H_{Lm} - Q''} \quad \text{—(7)}$$