VAPOR PRESSURE AND BOILING

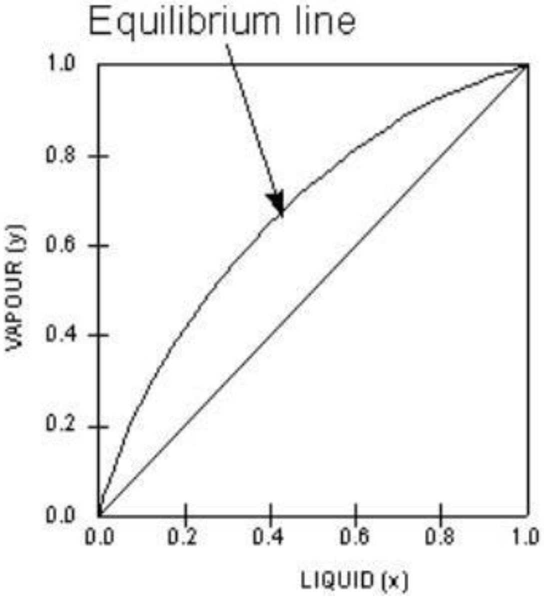
The vapor pressure of a liquid at a particular temperature is the equilibrium pressure exerted by molecules leaving and entering the liquid surface.

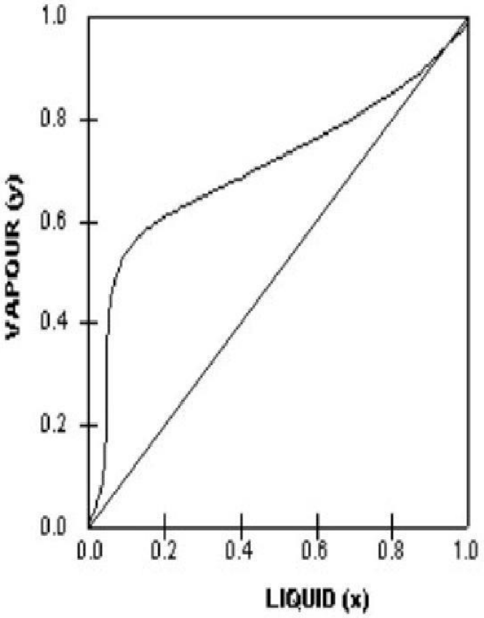
Liquids with high vapor pressures (volatile liquids) will boil at lower temperatures The vapor pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture Distillation occurs because of the differences in the volatility of the components in the liquid mixture.

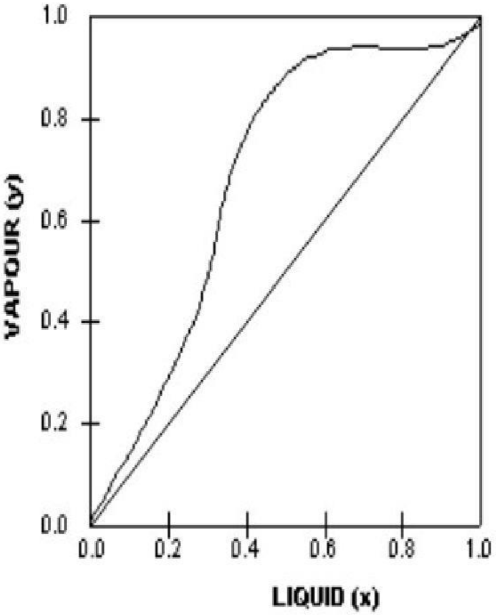
For example, when a subcooled liquid with mole fraction of A=0.4 (point A) is heated, its concentration remains constant until it reaches the bubble-point (point B), when it starts to boil. The vapors evolved during the boiling has the equilibrium composition given by point C, approximately 0.8 mole fraction A. This is approximately 50% richer in A than the original liquid. ™ This difference between liquid and vapor compositions is the basis for distillation operations.

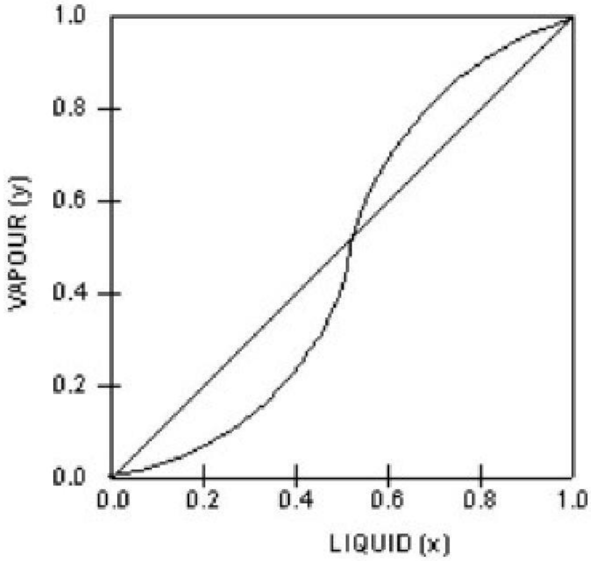
Relative Volatility

Relative volatility: is a measure of the differences in volatility between 2 components, and hence their boiling points. It indicates how easy or difficult a particular separation will be. Thus if the relative volatility between 2 components is very close to one, it is an indication that they have very similar vapor pressure characteristics. This means that they have very similar boiling points and therefore, it will be difficult to separate the two components via distillation.

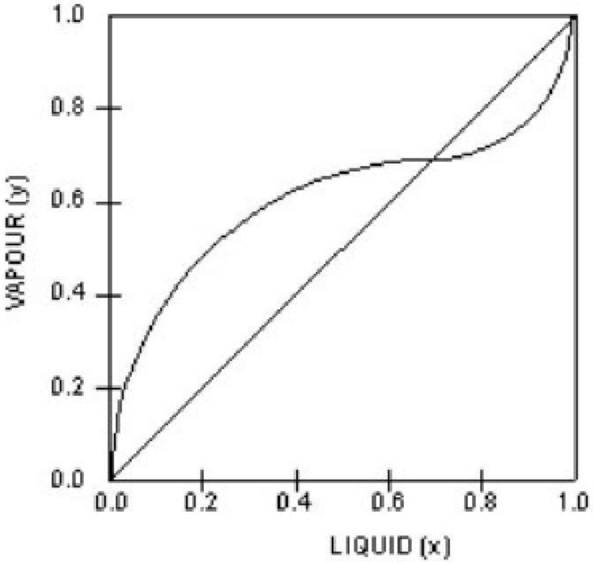








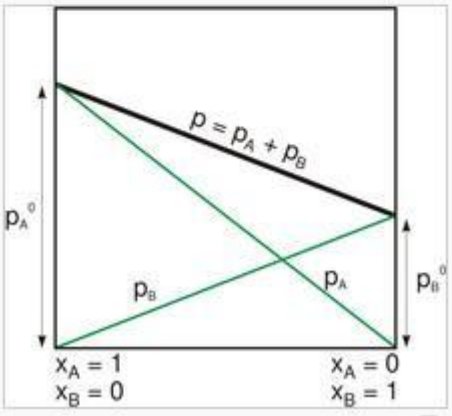
Maximum Boiling Point



Minimum Boiling Point

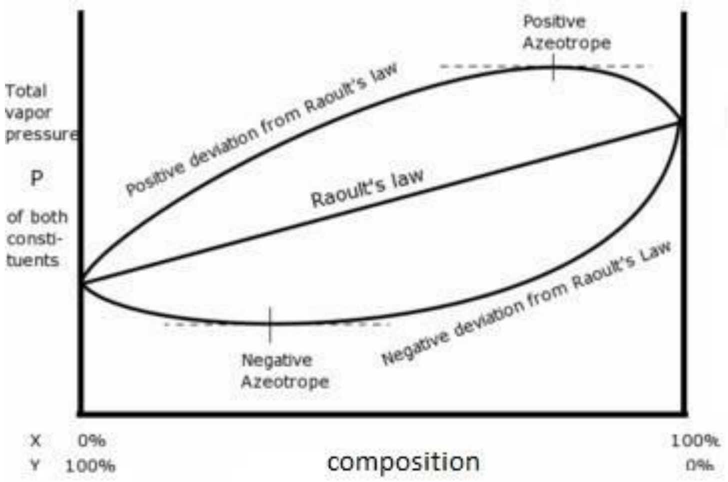
Raoult's law

It states that the partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.



Ideal solution: An ideal solution will obey Raoult's Law,

Real solutions: Solutions which deviate from Raoults law are called as real solutions. Many pairs of liquids are present in which there is no uniformity of attractive forces, i.e., the adhesive and cohesive forces of attraction are not uniform between the two liquids, so that they deviate from the Raoult's law.



Negative deviation:

If the vapor pressure of a mixture is lower than expected from Raoult's law, there is said to be a negative deviation. This is evidence that the adhesive forces between different components are stronger than the average cohesive forces between like components. In consequence each component is retained in the liquid phase by attractive forces that are stronger than in the pure liquid so that its partial vapor pressure is lower.

For example, the system of chloroform ($CHCl_3$) and acetone(CH_3COCH_3) has a negative deviation from Raoult's law

TYPES OF DISTILLATION COLUMNS

There are many types of distillation columns, each designed to perform specific types of separations, and each design differs in terms of complexity.

Batch and Continuous Columns

One way of classifying distillation column type is to look at how they are operated. Thus we have: batch and continuous columns.

Batch Columns In batch operation, the feed to the column is introduced batch-wise. That is, the column is charged with a 'batch' and then the distillation process is carried out. When the desired task is achieved, a next batch of feed is introduced.

Continuous columns

They process a continuous feed stream. No interruptions occur unless there is a problem with the column or surrounding process units. They are capable of handling high throughputs and they are most common of the two types.

Types of Continuous Columns

Continuous columns can be further classified according to:

The nature of the feed that they are processing,

- binary column - feed contains only two components
- multi-component column - feed contains more than two components The number of product streams they have
- Multi-product column - column has more than two product streams

- Extractive distillation - where the extra feed appears in the bottom product stream

Where the extra feed exits when it is used to help with the separation,

- azeotropic distillation - where the extra feed appears at the top product stream

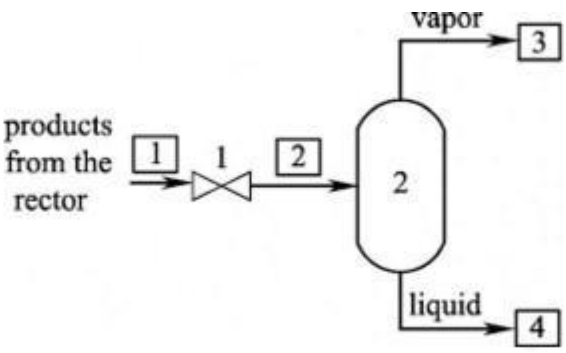
The type of column internals

- tray column - where trays of various designs are used to hold up the liquid to provide better contact between vapor and liquid, hence better separation
- packed column - where instead of trays, 'packings' are used to enhance contact between vapor and liquid

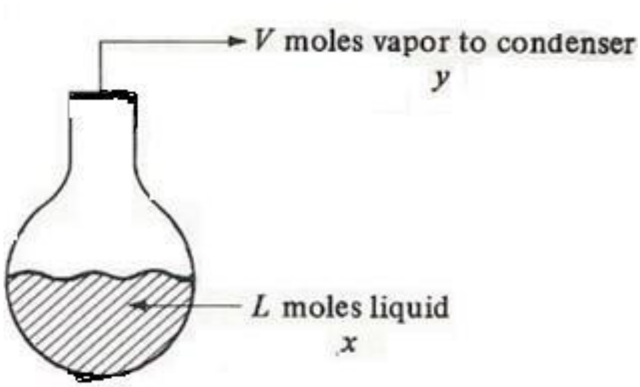
Equilibrium or Flash Distillation

This is type of distillation that occurs in a single-stage in which a liquid mixture is partially vaporized. The vapor is allowed to come to equilibrium with the residual liquid and the resulting vapor and liquid phases are separated and removed from the apparatus. Consider a binary mixture of A and B flowing at a rate of F mol/h into a heater partial vaporization.

Defining f as the molar fraction of the feed that is vaporized (i.e. f = V/F), the material balance for the flash drum gives:



Simple batch or Differential Distillation



liquid is first charged to a heated kettle - The liquid charge is boiled slowly and the vapors are withdrawn as rapidly as possible to a condenser, where the condensed vapor (distillate) is collected - The first portion of vapor condensed is richest in the more volatile component A. - As vaporization proceeds, the vaporized product becomes leaner in A. Following is the design equation for the batch distillation (material balance):

DISTILLATION COLUMN DESIGN

Distillation columns are designed using VLE data for the mixtures to be separated. The vapor-liquid equilibrium characteristics (indicated by the shape of the equilibrium curve) of the mixture will determine the number of stages, and hence the number of trays, required for the separation. This is illustrated clearly by applying the McCabe-Thiele method to design a binary column.

McCABE-THIELE DESIGN METHOD

The McCabe-Thiele approach is a graphical one, and uses the VLE plot to determine the theoretical number of stages required to effect the separation of a binary mixture. It assumes constant molar overflow and this implies that:

Molal heats of vaporization of the components are roughly the same

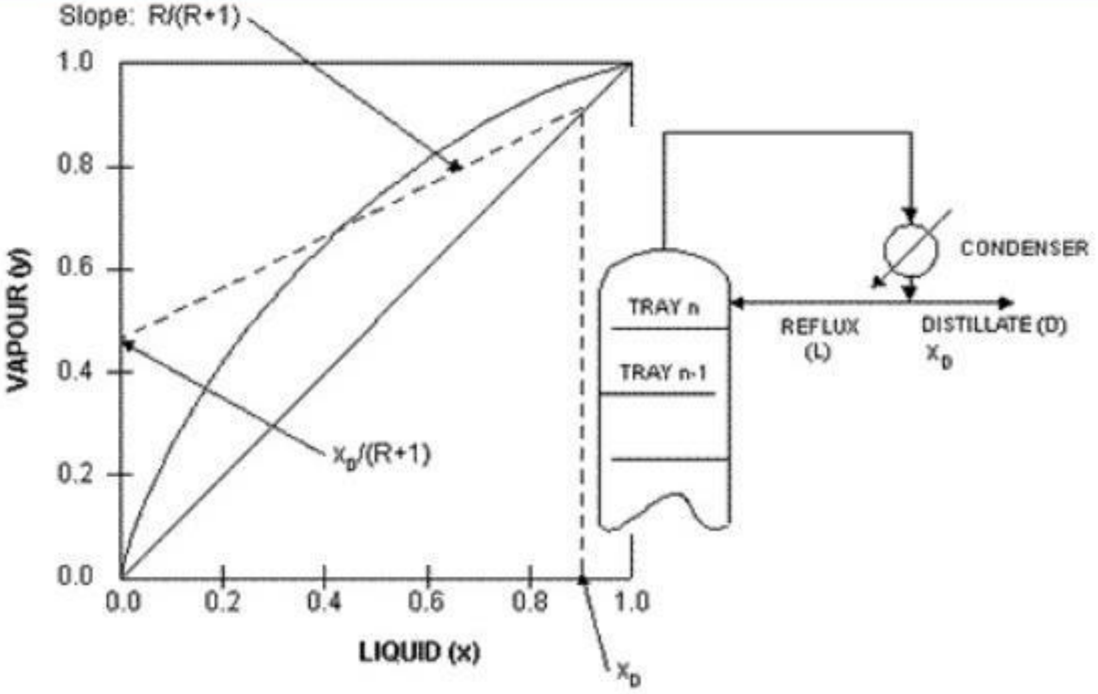
Heat effects (heats of solution, heat losses to and from column, etc.) are negligible for every mole of vapour condensed, 1 mole of liquid is vaporised

The design procedure is simple. Given the VLE diagram of the binary mixture, operating lines are drawn first.

- Operating lines define the mass balance relationships between the liquid and vapor phases in the column.
- There is one operating line for the bottom (stripping) section of the column, and on for the top (rectification or enriching) section of the column.
- Use of the constant molar overflow assumption also ensures the operating lines are straight lines.

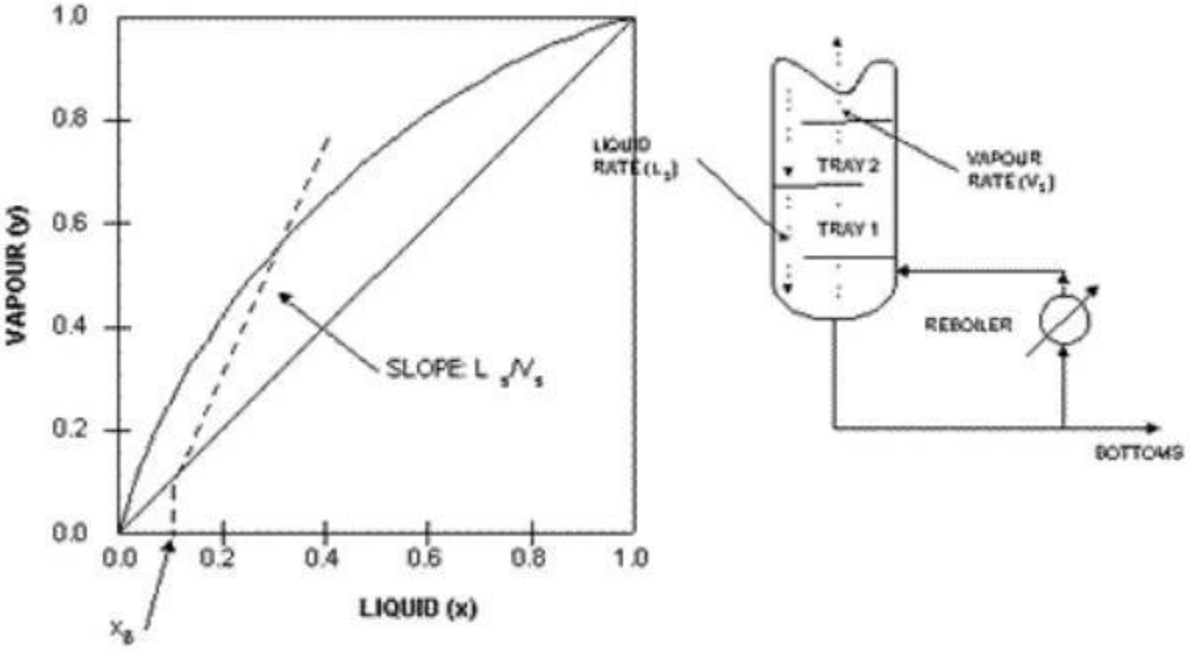
Operating Line for the Rectification Section

The operating line for the rectification section is constructed as follows: ™First the desired top product composition is located on the VLE diagram, and a vertical line produced until it intersects the diagonal line that splits the VLE plot in half. A line with slope R/(R+1) is then drawn from this instersection point as shown in the diagram below. R is the ratio of reflux flow (L) to distillate flow (D) and is called the reflux ratio and is a measure of how much of the material going up the top of the column is returned back to the column as reflux.



Operating Line for the Stripping Section ™

The operating line for the stripping section is constructed in a similar manner. However, the starting point is the desired bottom product composition. A vertical line is drawn from this point to the diagonal line, and a line of slope Ls/Vs is drawn as illustrated in the diagram below. Ls is the liquid rate down the stripping section of the column, while Vs is the vapor rate up the stripping section of the column. Thus the slope of the operating line for the stripping section is a ratio between the liquid and vapor flows in that part of the column.



Equilibrium and Operating Lines ™The McCabe-Thiele method assumes that the liquid on a tray and the vapor above it are in equilibrium. How this is related to the VLE plot and the operating lines is depicted graphically in the diagram on the right.

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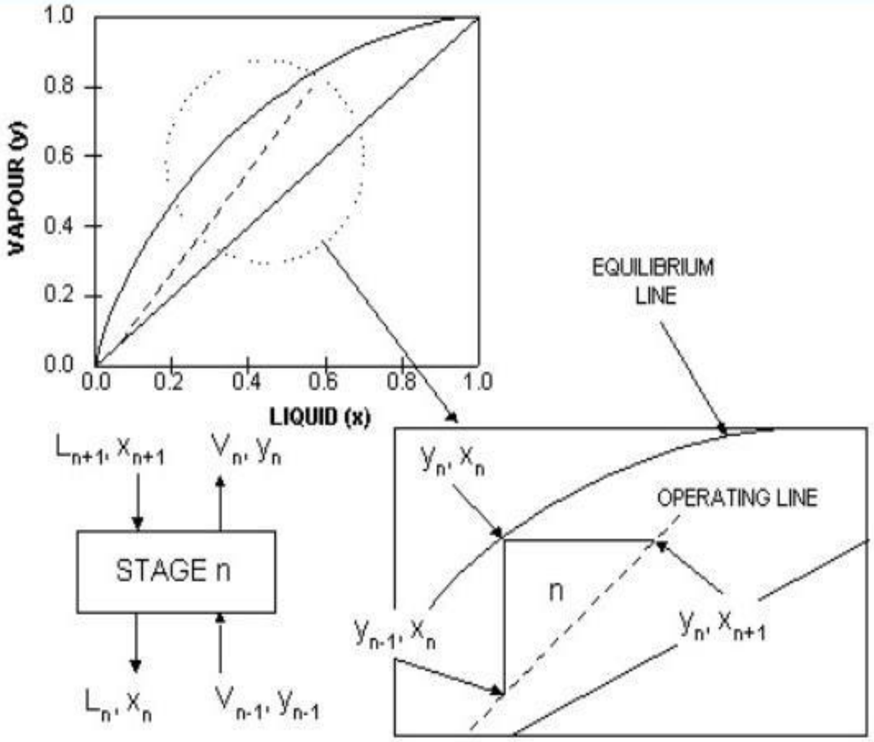

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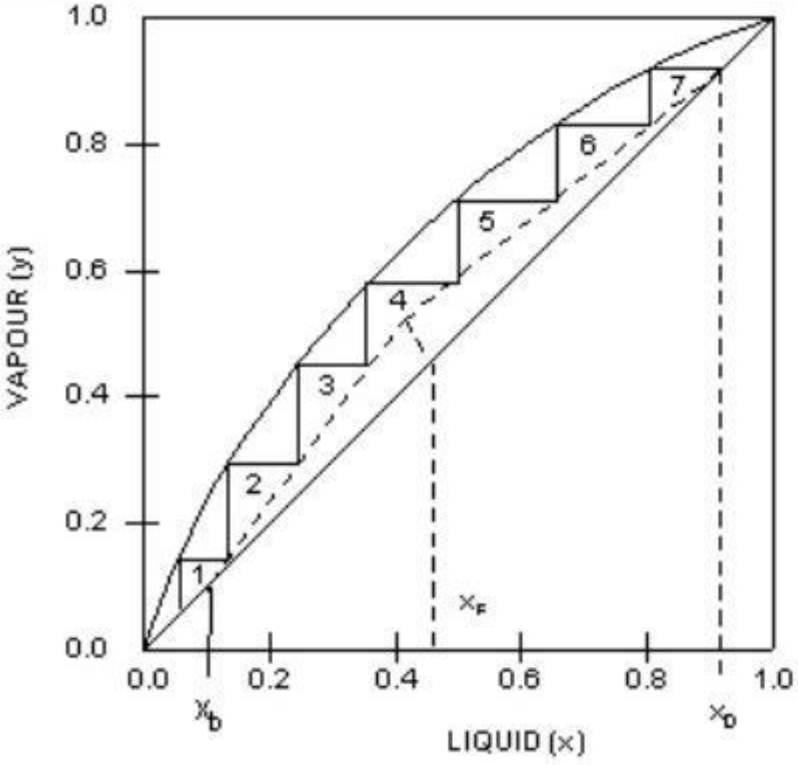
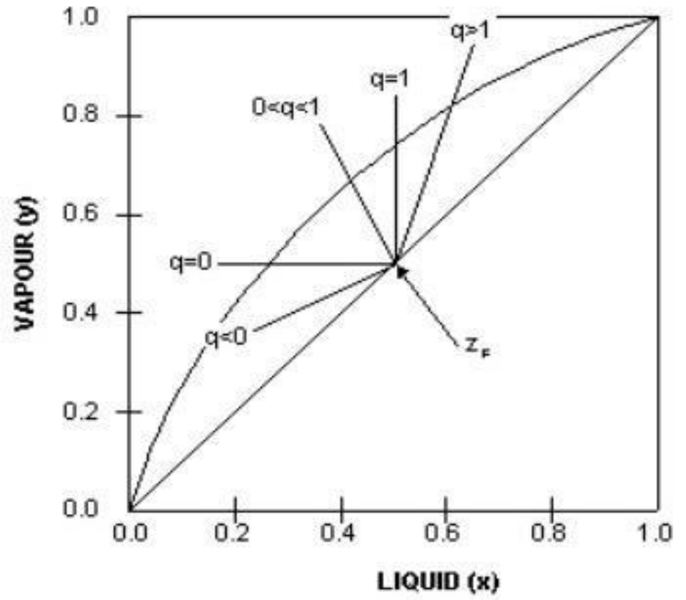


Doing the graphical construction repeatedly will give rise to a number of 'corner' sections, and each section will be equivalent to a stage of the distillation. This is the basis of sizing distillation columns using the McCabeThiele graphical design methodology as shown in the following example. sections, the graphical construction described above was applied. This particular example shows that 7 theoretical stages are required to achieve the desired separationThe required number of trays (as opposed to stages) is one less than the number of stages since the graphical construction includes the contribution of the reboiler in carrying out the separation.

The actual number of trays required is given by the formula: (number of theoretical trays)/(tray efficiency)

Typical values for tray efficiency ranges from 0.5 to 0.7 and depends on a number of factors, such as the type of trays being used, and internal liquid and vapor flow conditions. Sometimes, additional trays are added (up to 10%) to accomodate the possibility that the column may be under-designed.

The Feed Line (q-line)



The diagram above also shows that the binary feed should be introduced at the 4'th stage. However, if the feed composition is such that it does not coincide with the intersection of the operating lines, this means that the feed is not a saturated liquid. The condition of the feed can be deduced by the slope of the feed line or q-line. The q-line is that drawn between the intersection of the operating lines, and where the feed composition lies on the diagonal line. ™Depending on the state of the feed, the feed lines will have different slopes.

For example:

q = 0 (saturated vapor)

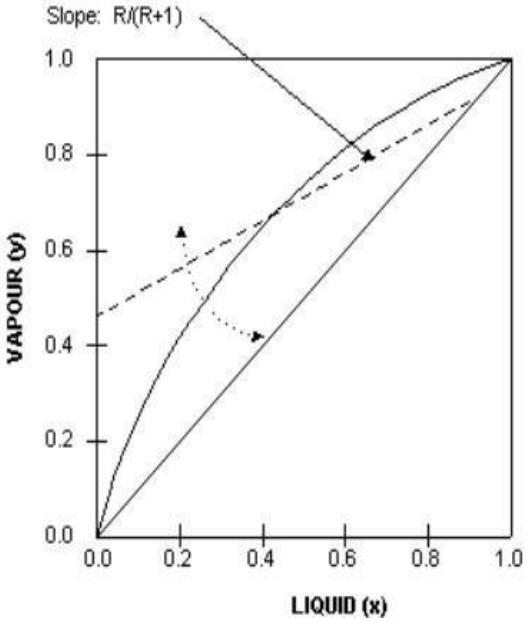
q = 1 (saturated liquid)

0 < q < 1 (mix of liquid and
vapor) q > 1 (subcooled liquid)

q < 0 (superheated vapour)

The q-lines for the various feed conditions are shown in the diagram above.

Reflux Conditions



As the reflux ratio is increased, the gradient of operating line for the rectification section moves towards a maximum value of 1. Physically, what this means is that more and more liquid that is rich in the more volatile components are being recycled back into the column. Separation then becomes better and thus less trays are needed to achieve the same degree of separation. Minimum trays are required under total reflux conditions, i.e. there is no withdrawal of distillate. 9 On the other hand, as reflux is decreased, the operating line for the rectification section moves

Weeping/Dumping

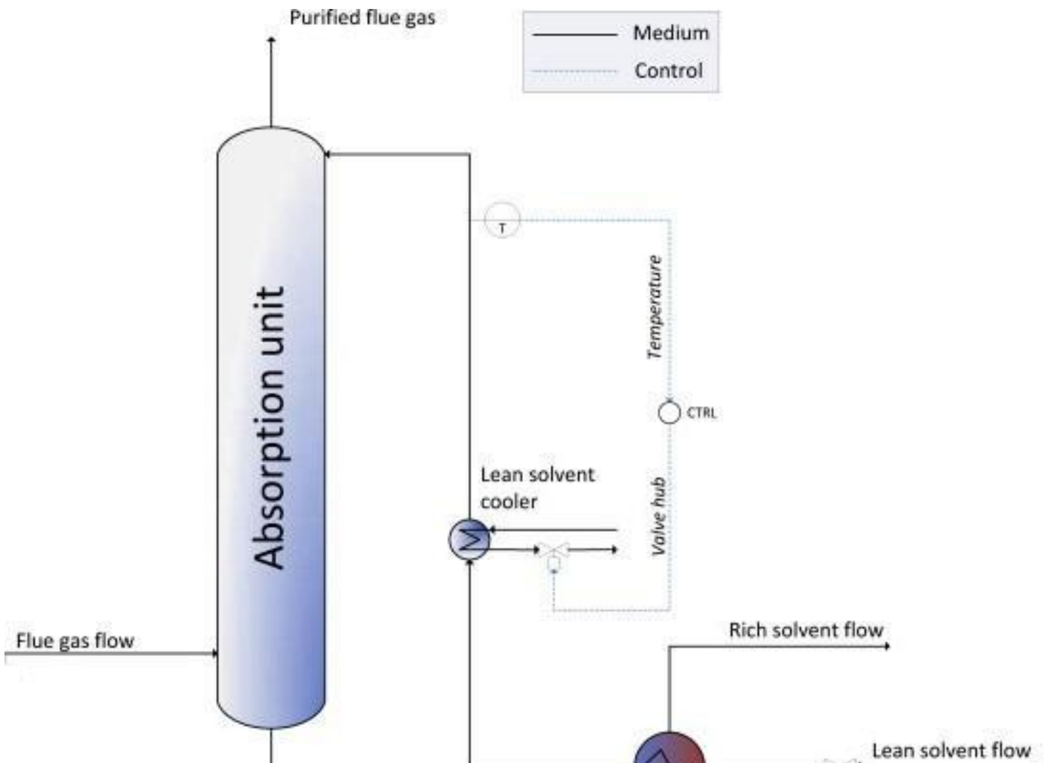
This phenomenon is caused by low vapor flow. The pressure exerted by the vapour is insufficient to hold up the liquid on the tray. Therefore, liquid starts to leak through perforations. Excessive weeping will lead to dumping. That is the liquid on all trays will crash (dump) through to the base of the column (via a domino effect) and the column will have to be re-started. Weeping is indicated by a sharp pressure drop in the column and reduced separation efficiency.

Flooding:

Flooding is brought about by excessive vapor flow, causing liquid to be entrained in the vapor up the column. The increased pressure from excessive vapor also backs up the liquid in the downcomer, causing an increase in liquid holdup on the plate above. Depending on the degree of flooding, the maximum capacity of the column may be severely reduced. Flooding is detected by sharp increases in column differential pressure and significant decrease in separation efficiency.

ABSORPTION

Absorption refers to an operation in which the transfer of material is from a gas phase to a liquid phase. A gas is absorbed by means of liquid in which the solute gas is more or less soluble from its mixture with an inert gas as well as more or less insoluble gas. The liquid is essentially immiscible in the gas phase.



Selection of solvent for absorption and stripping

(A) Gas Solubility: High solubility of a gas in the solvent is preferred, utilizing low quantity of solvent. Absorbent should not dissolve carrier gas. Similar chemical nature of solute and absorbent (solvent) gives a good solubility. If chemical reaction takes place between solute and solvent, rate of absorption is extremely high. But the reaction should be reversible to recover solvent during desorption.

Volatility: Low volatility or low vapor pressure of the solvent enhances the adsorption operation as solvent loss with carrier gas is very small. Sometimes, a second less volatile solvent is used to recover the first solvent.

Viscosity: For better absorption, a solvent of low viscosity is required. In mechanically agitated absorber, greater amount of power is required for high viscous solvent and flooding is also caused at lower liquid and gas flow rates.

Corrosiveness: Non-corrosive or less corrosive solvent reduces equipment construction cost as well as maintenance cost.

Cost: The solvent should be cheap so that losses will be insignificant and should be easily available.

Toxicity and Hazard: The solvent should be non-toxic, non-flammable, non-hazardous and should be chemically stable.

Types of Absorbers

Tray column

Packed column

Packing Materials

Packing materials are utilized to provide large interfacial area of contact between two phases. These are made from either of ceramics, metals or plastics. A number of packing materials with various size, shape and performance are available. These are classified into three types, namely, **dumped or random**, **structured** and **grid**.

The packing materials have following characteristics:

Cost: The cost of the packing materials should be very low.

Surface area: A large interfacial area of contact is always recommended. In that case, pressure drop will be more.

Void volume: A high void volume is needed to maintain low pressure drop.

Fouling resistance: Packing materials should not trap suspended solids present in liquid. Bigger packing materials generally give low fouling resistance.

Mechanical strength: Good mechanical strength is desired for choosing packing materials as this will not break or deform during filling or operation.

Uniform flow of streams: Stack of packing materials should have uniform void spaces through which both the streams (gas and liquid) can flow uniformly. Nonuniform flow of streams leads to stagnant liquid pool which in turn gives low mass transfer.

(a) Raschig rings;

(b) Lessing rings and modified Raschig rings (Cross-partition rings)

(c) Berl saddle

(a) Intalox saddle and modification

(b) Pall ring and modification

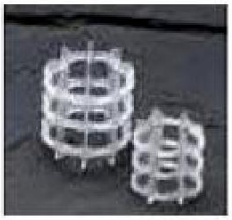
(a) Intalox Metal Tower Packing (IMTP)

(b) Nutter ring

(c) Cascade Mini-Ring (CMR)

(d) Jaeger Tripac

(e) Koch Flexisaddle



(f) Nor-Pac

(g) Hiflow ring

Structured Packings

These materials are used widely as packing materials in packed tower due to low gas pressure drop and improved efficiency. Corrugated metal sheet structured packing and Wire mesh structured packing materials are widely used in the industries.

Mellapak

Flexipak

Montez Corrugated metal sheet

Wire mesh packing

Design of packed tower based on overall mass transfer Coefficient

From overall mass transfer equation, $N_A = K_y(y_{AG} - y_A^*)$ one can write for packed tower as

$N_A = K_y(y - y^*)$

Then,

$$dh = -\frac{G' dy}{K_y \bar{a}(1-y)(y-y^*)}$$

where, y^* is solute concentration in gas phase that is capable of remaining in equilibrium with a liquid having a bulk concentration of x.

Therefore,

where, y^* is solute concentration in gas phase that is capable of remaining in equilibrium with a liquid having a bulk concentration of x.

Therefore,

$$h_T = \int_0^{h_T} dh = \int_{y2}^{y1} \frac{G^{/} dy}{K_y \, \overline{a} (1-y)(y-y^*)}$$

$$= \int_{y2}^{y1} \frac{G^{/} dy}{k_G \, \overline{a} P (1-y)(y-y_i)}$$

$$= \int_{x2}^{x1} \frac{L^{/} dx}{k_L \, \overline{a} (C_{av})(1-x)(x_i-x)}$$

Graphical integration of right hand side of Equation (4.11):

Operating line AB is drawn in xy plane. Any point (x,y) is taken in operating line. A vertical line is drawn upto equilibrium line to get y^*.

$$h_T = \int_{x2}^{x1} \frac{L^{/} dx}{K_x \, \overline{a} (1-x)(x^*-x)} = \int_{y2}^{y1} \frac{G^{/} dy}{K_G \, \overline{a} P (1-y)(y-y^*)} = \int_{x2}^{x1} \frac{L^{/} dx}{k_L \, \overline{a} (C_{av})(1-x)(x^*-x)}$$

Equation 4.7 can be written as

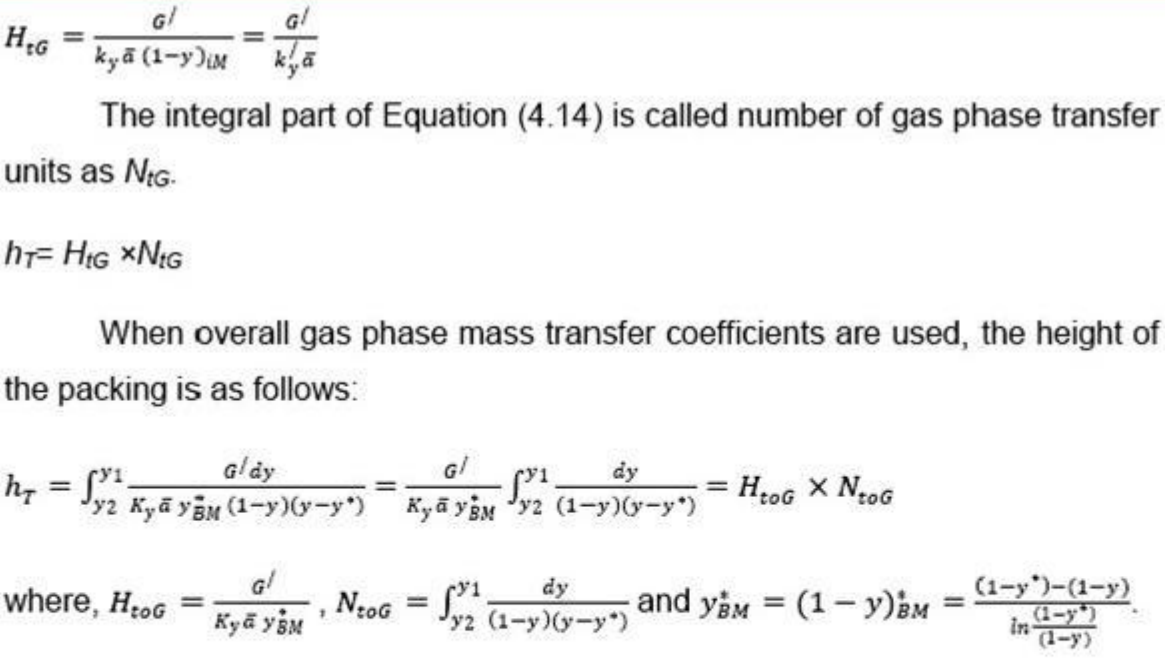
$$h_T = \int_0^{h_T} dh = \int_{y2}^{y1} \frac{G^{/} y_{iBM} \, dy}{k_y \bar{a} \, y_{iBM} \, (1-y)(y-y_i)} = \int_{y2}^{y1} \frac{G^{/} (1-y)_{iM} \, dy}{k_y \bar{a} \, (1-y)_{iM} \, (1-y)(y-y_i)}$$

where, $y_{iBM} = (1-y)_{iM} = \frac{(1-y_i)-(1-y)}{ln \frac{(1-y_i)}{(1-y)}}$

$$h_T = \frac{G^{/}}{k_y \bar{a} \, (1-y)_{iM}} \int_{y2}^{y1} \frac{(1-y)_{iM} \, dy}{(1-y)(y-y_i)}$$

As, $\frac{G^{/}}{k_y \bar{a} \, (1-y)_{iM}}$ remains constant at the packing section though G/ varies. This quantity is called 'height if transfer units' (HTU) and designated as H_{tG}. It is important to measure the separation effectiveness of the particular packings for a particular separation process. It also describes the mass transfer coefficient. Larger mass transfer coefficient leads to the smaller value of HTU.

Hence,



$$H_{tG} = \frac{G'}{k_y \bar{a}\,(1-y)_{iM}} = \frac{G'}{k'_y \bar{a}}$$

The integral part of Equation (4.14) is called number of gas phase transfer units as N_{tG}.

$h_T = H_{tG} \times N_{tG}$

When overall gas phase mass transfer coefficients are used, the height of the packing is as follows:

$$h_T = \int_{y2}^{y1} \frac{G'\,dy}{K_y \bar{a}\, y^*_{BM} (1-y)(y-y^*)} = \frac{G'}{K_y \bar{a}\, y^*_{BM}} \int_{y2}^{y1} \frac{dy}{(1-y)(y-y^*)} = H_{toG} \times N_{toG}$$

where, $H_{toG} = \frac{G'}{K_y \bar{a}\, y^*_{BM}}$, $N_{toG} = \int_{y2}^{y1} \frac{dy}{(1-y)(y-y^*)}$ and $y^*_{BM} = (1-y)^*_{BM} = \frac{(1-y^*)-(1-y)}{ln\frac{(1-y^*)}{(1-y)}}$.

Define NTU

Height of Packing (z) = NTU x HTU

Where,

NTU = number of transfer units - dimensionless
HTU = height of transfer units - dimension of length

The number of transfer units (NTU) required is a measure of the difficulty of the separation. A single transfer unit gives the change of composition of one of the phases equal to the average driving force producing the change. The NTU is similar to the number of theoretical trays required for tray column. Hence, a larger number of transfer units will be required for a very high purity product.

Height of Transfer Units (HTU)

Height Equivalent to Theoretical Plate (HETP)

For a specified separation job, in packed tower, the height of packing is to be determined and in tray tower, numbers of ideal trays are determined. The ratio between packing height to number of trays required for the same separation is called height equivalent to theoretical plate (HETP).

$$HETP = \frac{h_T}{N_T} = \frac{Height\ of\ packing}{Number\ of\ ideal\ trays}$$

Height of packing (Z) = HETP x Number of trays

HETP varies with size and type of packing, flow rate of gas and liquid, concentration of solute, physical and transport properties as well as equilibrium relationship and uniformity of liquid and gas distribution. HETP is used to characterize the packing. A good packing has small HETP.

Absorption Factor

Where A is absorption factor and is defined as $A = L/(mG)$.

Henry's Law

A law stating that the mass of a dissolved gas in a given volume of solvent at equilibrium is proportional to the partial pressure of the gas

Where, H is the Henry's constant, is the partial pressure of A in gas phase, is the concentration of component A in the liquid phase.

Stripping or Desorption

Mass transfer occurs from liquid to gas phase.

The solute is removed from the liquid solution by contacting with gas.

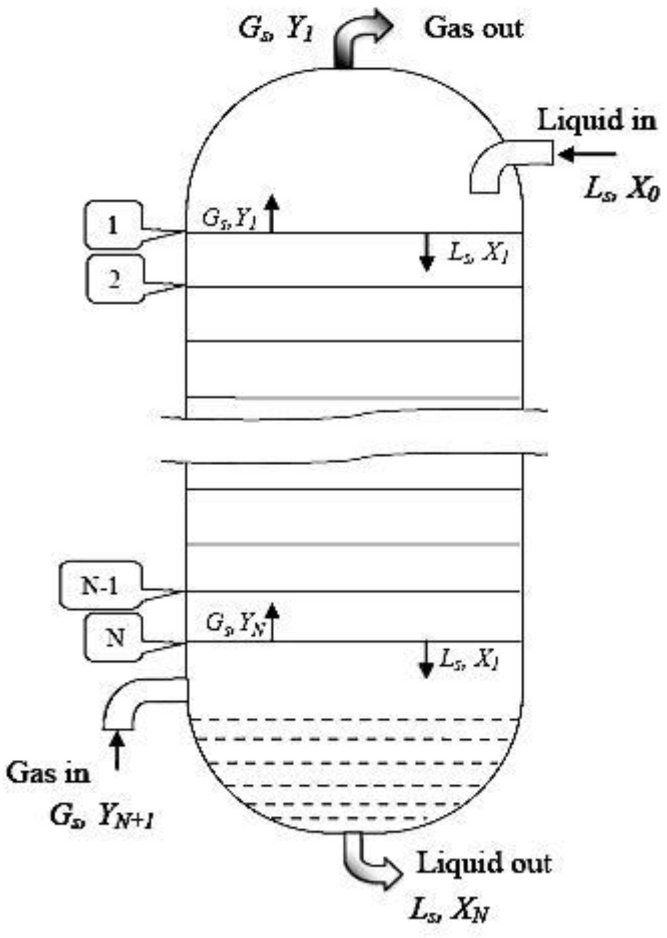
Single stage counter current Unit

G_1, G_2 : molar flow rates of entering and leaving gas

G_S: molar flow rate of inert gas

L_1, L_2 are the molar flow rates of leaving and entering liquid

L_S is the molar flow rate of pure solvent



X,Y are the mole ratios of solute to **inert component** in liquid and gas phase respectively

x,y are the mole ratio of solute in liquid and gas phases

Making Material Balance

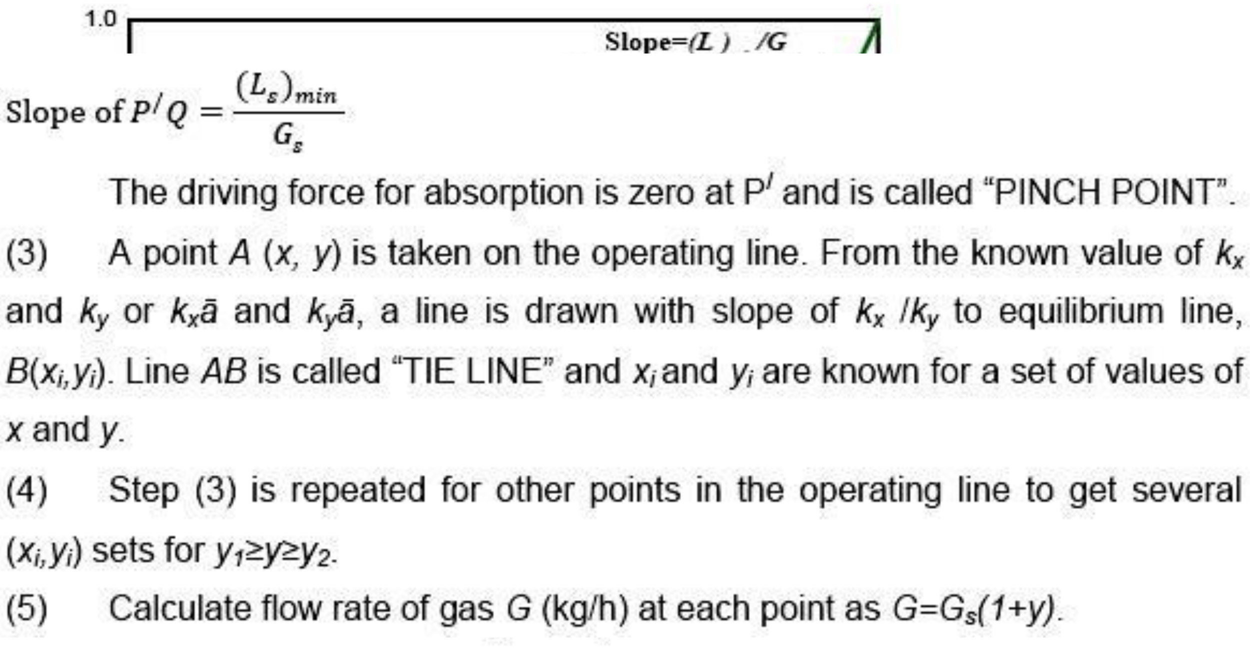
STEP-BY-STEP PROCEDURE

(1) For a particular gas-liquid system, draw equilibrium curve on *X-Y* plane.

(2) Draw operating line in *X-Y* plane (*PQ*) using material balance Equation. Lower terminal *Q* (*X2, Y2*) and upper terminal *P* (*X1, Y1*) are placed in *x-y* plane.

Making Material Balance

If liquid mass flow rate, *Ls* is not known, minimum liquid mass flow rate *(Ls)min* is to be determined. *Ls* is generally 1.2 to 2 times the *(Ls)min*.



Slope of $P^{/}Q = \frac{(L_s)_{min}}{G_s}$

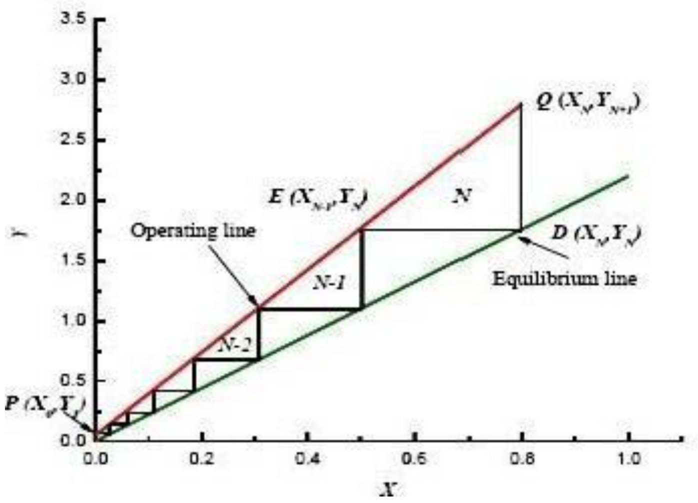
The driving force for absorption is zero at P$^{/}$ and is called "PINCH POINT".

(3) A point *A* (*x, y*) is taken on the operating line. From the known value of k_x and k_y or $k_x\bar{a}$ and $k_y\bar{a}$, a line is drawn with slope of k_x / k_y to equilibrium line, $B(x_i, y_i)$. Line *AB* is called "TIE LINE" and x_i and y_i are known for a set of values of *x* and *y*.

(4) Step (3) is repeated for other points in the operating line to get several (x_i, y_i) sets for $y_1 \geq y \geq y_2$.

(5) Calculate flow rate of gas *G* (kg/h) at each point as $G=G_s(1+y)$.

The following parameters should be known for the determination of “number of stages” (1) Gas feed rate, (2) Concentration of gas at inlet and outlet of the tower, (3) Minimum liquid rate; actual liquid rate is 1.2 to 2 times the minimum liquid rate, (4) Equilibrium data for construction of equilibrium curve now,



Z = No of trays x HETP

Example

A gas stream containing 90 mol% N_2 and 10% CO_2 is passed through an absorber, in which pure and cool water at 5^oC is used as a solvent The operation is assumed to be isothermal at 5 o C and isobaric at 10 atm The liquid flow rate is 1.5 times the minimum liquid flow rate Determine the number of equilibrium stages required to absorb 92 mol% of CO_2 Given Henry’s constant of CO_2 in water at 5^oC of 876 atm/mole fraction.

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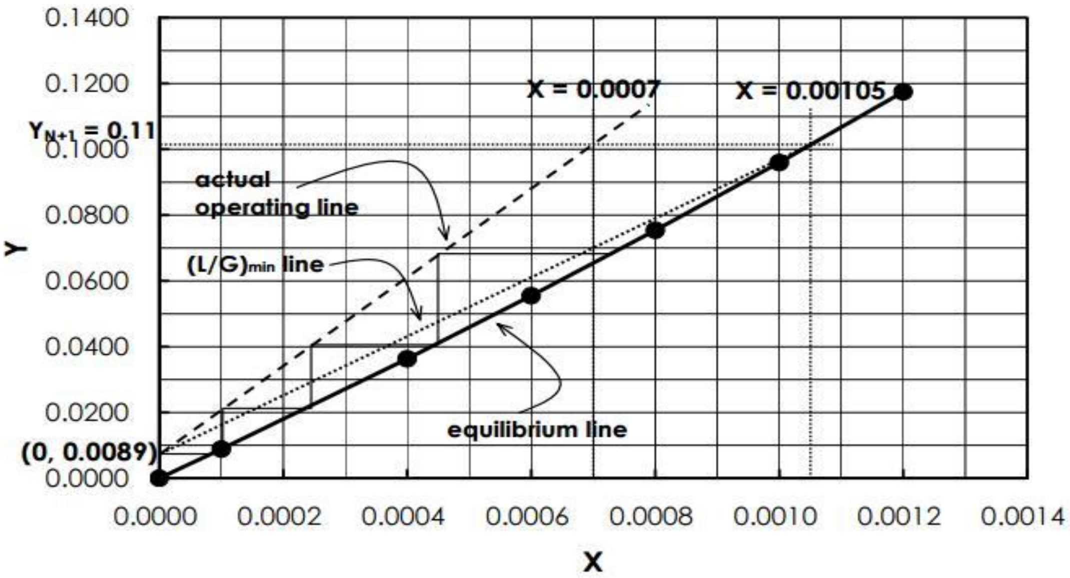
the equilibrium or the y-x data can be computed

x	**0**	**0.0001**	**0.0004**	**0.0006**	**0.0008**	**0.0010**	**0.0012**
y	**0**	**0.00876**	**0.0350**	**0.0526**	**0.0701**	**0.0876**	**0.1051**
X	**0**	**0.0001**	**0.0004**	**0.0006**	**0.0008**	**0.0010**	**0.0012**
Y	**0**	**0.00884**	**0.0363**	**0.0555**	**0.0754**	**0.0960**	**0.1175**



The slope of the min L/G minimum is found to be 97.2

Hence, the slope of the actual operating line is 1.5 times of minimum = 1.5 x 97.2 = 145. 8

X_1 = 0.0007

Yields the number of equilibrium stages of ~3.8 = 4