

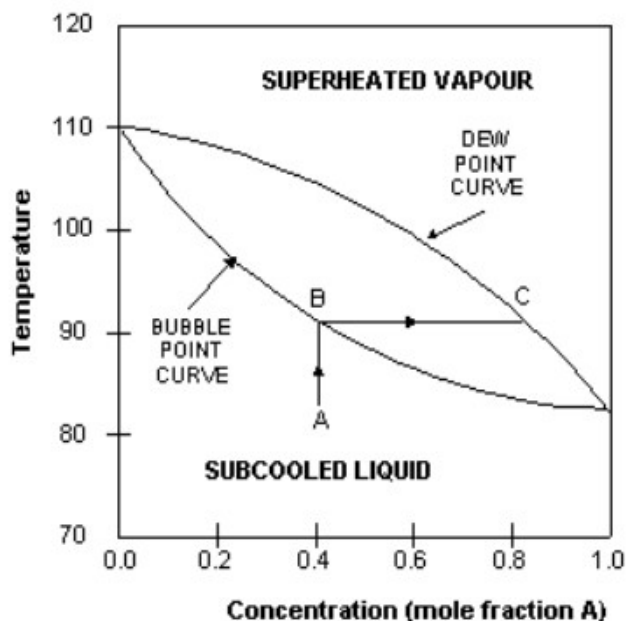
VAPOR PRESSURE AND BOILING

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

Here are some important points regarding vapor pressure:

- Energy input raises vapor pressure
- Vapor pressure is related to boiling
- A liquid is said to 'boil' when its vapor pressure equals the surrounding pressure
- The ease with which a liquid boils depends on its volatility
- 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.

THE BOILING POINT DIAGRAM



- The Boiling Point Diagram The boiling point diagram shows how the equilibrium compositions of the components in a liquid mixture vary with temperature at a fixed pressure.
- Consider an example of a liquid mixture containing 2 components (A and B) - a binary mixture..

The boiling point of A is that at which the mole fraction of A is 1. The boiling point of B is that at which the mole fraction of A is 0. In this example, A is the more volatile component and therefore has a lower boiling point than B.

The upper curve in the diagram is called the dew-point curve while the lower one is called the bubble-point curve.

- Dew-point: is the temperature at which the saturated vapor starts to condense.
- Bubble-point: is the temperature at which the liquid starts to boil.

- The region above the dew-point curve shows the equilibrium composition of the superheated vapor while the region below the bubble-point curve shows the equilibrium composition of the sub-cooled liquid.
- 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. TM
- 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.
- The relative volatility of component 'i' with respect to component 'j' is defined as

$$\alpha_{ij} =$$

y_i = mole fraction of component 'i' in the vapour

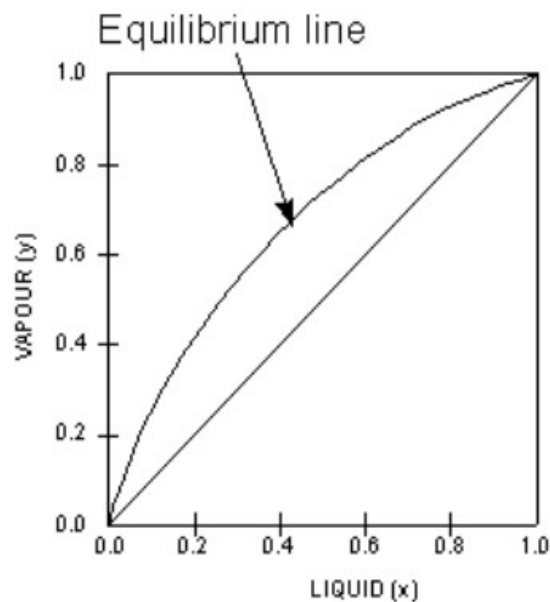
x_i = mole fraction of component 'i' in the liquid

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.

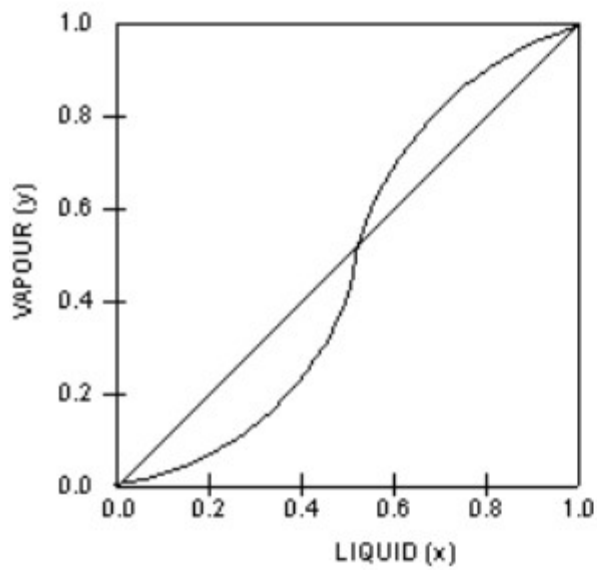
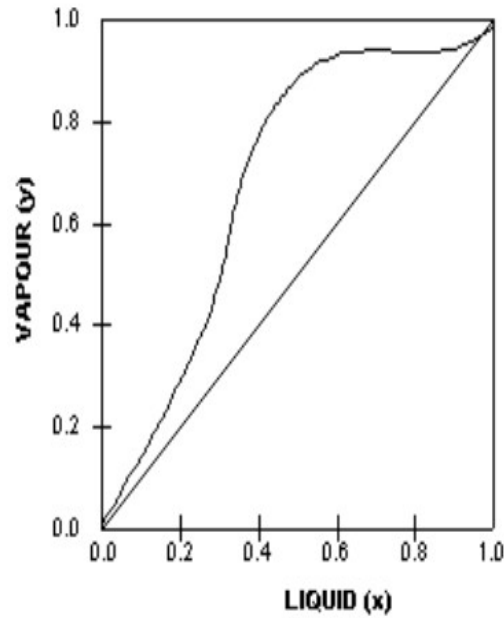
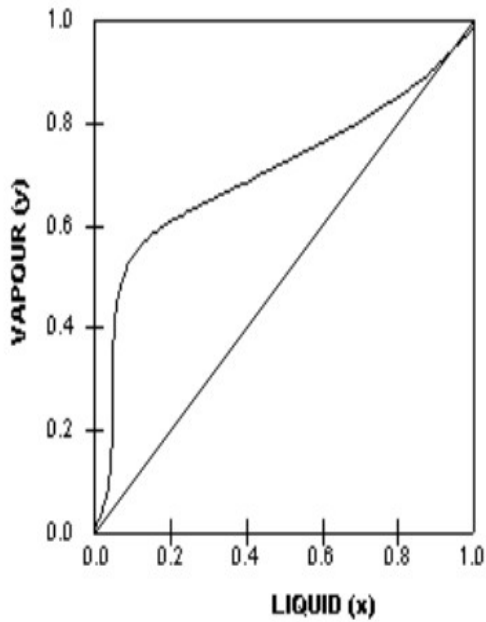
Distillation columns are designed based on the boiling point properties of the components in the mixtures being separated. Thus the sizes, particularly the height, of distillation columns are determined by the vapor liquid equilibrium (VLE) data for the mixtures.

Vapor-Liquid-Equilibrium (VLE) Curves

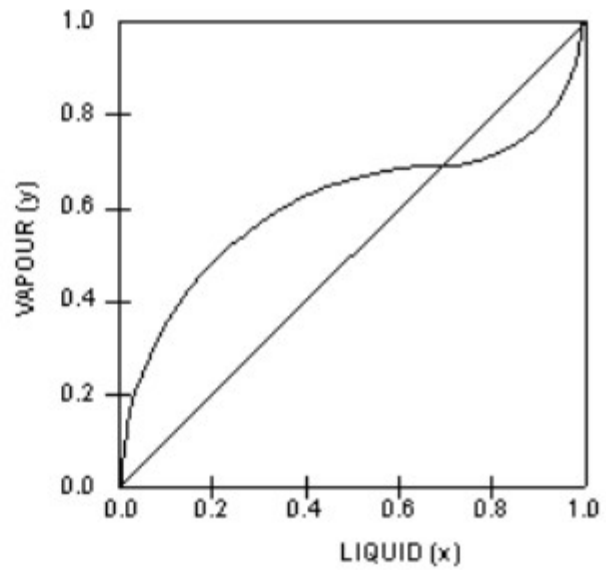
Constant pressure VLE data is obtained from boiling point diagrams. VLE data of binary mixtures is often presented as a plot, as shown in the figure. The VLE plot expresses the bubble-point and the dew-point of a binary mixture at constant pressure. The curved line is called the equilibrium line and describes the compositions of the liquid and vapour in equilibrium at some fixed pressure



The previous particular VLE plot shows a binary mixture that has a uniform vapor-liquid equilibrium that is relatively easy to separate. The next two VLE plots below on the other hand, shows non-ideal systems which will present more difficult separations.



Maximum Boiling Point



Minimum Boiling Point

The most intriguing VLE curves are generated by azeotropic systems. An azeotrope is a liquid mixture which when vaporised, produces the same composition as the liquid. The two VLE plots below, show two different azeotropic systems, one with a minimum boiling point and one with a

maximum boiling point. In both plots, the equilibrium curves cross the diagonal lines, and this are azeotropic points where the azeotropes occur. In other words azeotropic systems give rise to VLE plots where the equilibrium curves crosses the diagonals

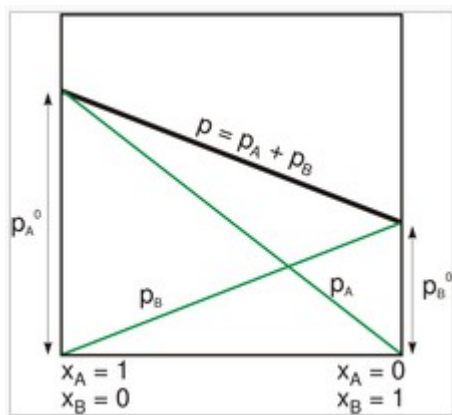
Raoult's law

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.

Mathematically, Raoult's law for a single component in an ideal solution is stated as

$$p_i = p_i^* x_i$$

where p_i is the partial vapor pressure of the component i in the gaseous mixture (above the solution), p_i^* is the vapor pressure of the pure component i , and x_i is the mole fraction of the component i in the mixture (in the solution).



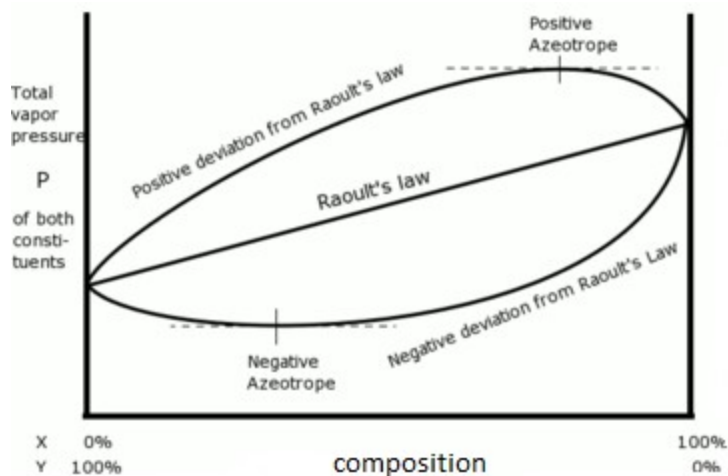
Once the components in the solution have reached equilibrium, the total vapor pressure of the solution can be determined by combining Raoult's law with Dalton's law of partial pressures to give

$$p = p_A^* x_A + p_B^* x_B + \dots$$

If a non-volatile solute (zero vapor pressure, does not [evaporate](#)) is dissolved into a solvent to form an ideal solution, the vapor pressure of the final solution will be lower than that of the pure solvent.

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

Real solutions: Solutions which deviate from Raoult's 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

Positive deviation

When the cohesive forces between like molecules are greater than the adhesive forces between dissimilar molecules, the dissimilarities of polarity leads both components to escape solution more easily. Therefore, the vapor pressure is greater than expected from the Raoult's law, showing positive deviation. If the deviation is large, then the vapor pressure curve shows a maximum at a particular composition and form a positive azeotrope. Some mixtures in which this happens are (1) [benzene](#) and [methanol](#), (2) [carbon disulfide](#) and [acetone](#), and (3) [chloroform](#) and [ethanol](#)

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

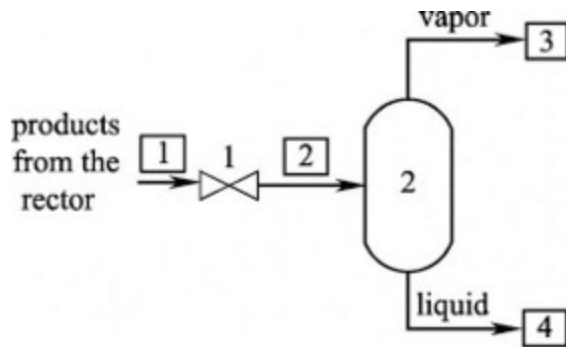
Continuous columns can be further classified according to:

- 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.

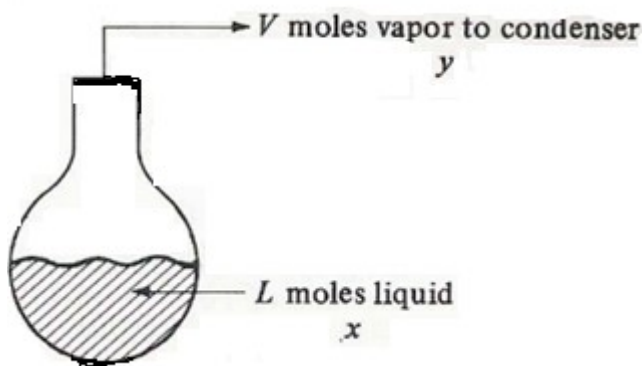
Defining f as the molar fraction of the feed that is vaporized (i.e. $f = V/F$), the material balance for the flash drum gives:



$$y = -[(1-f)/f]x + x_f/f$$

Equilibrium relation: $y = f(x)$ Solved simultaneously for x and y

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):

$\ln =$

Where L_1 is the original moles charged

L_2 : the moles left in the still

x_1 : the original composition of liquid

x_2 : the final composition of liquid

$y = f(x)$ is needed From equilibrium relation

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

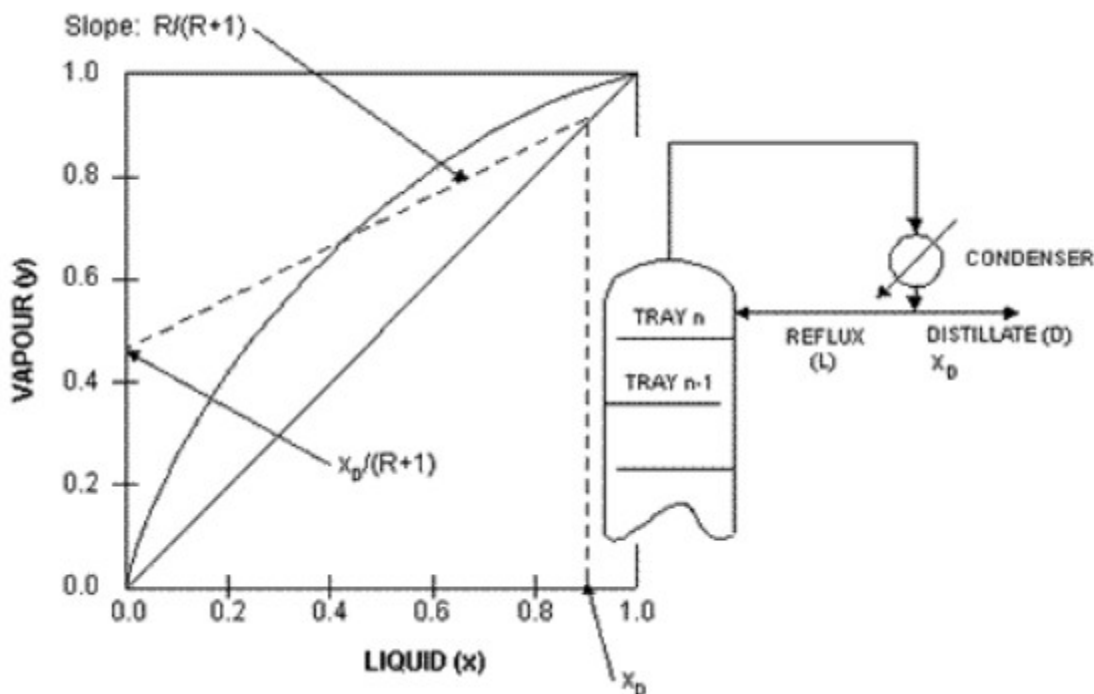
The design procedure is simple. Given the VLE diagram of the binary mixture, operating lines are drawn first.

- 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 one 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.

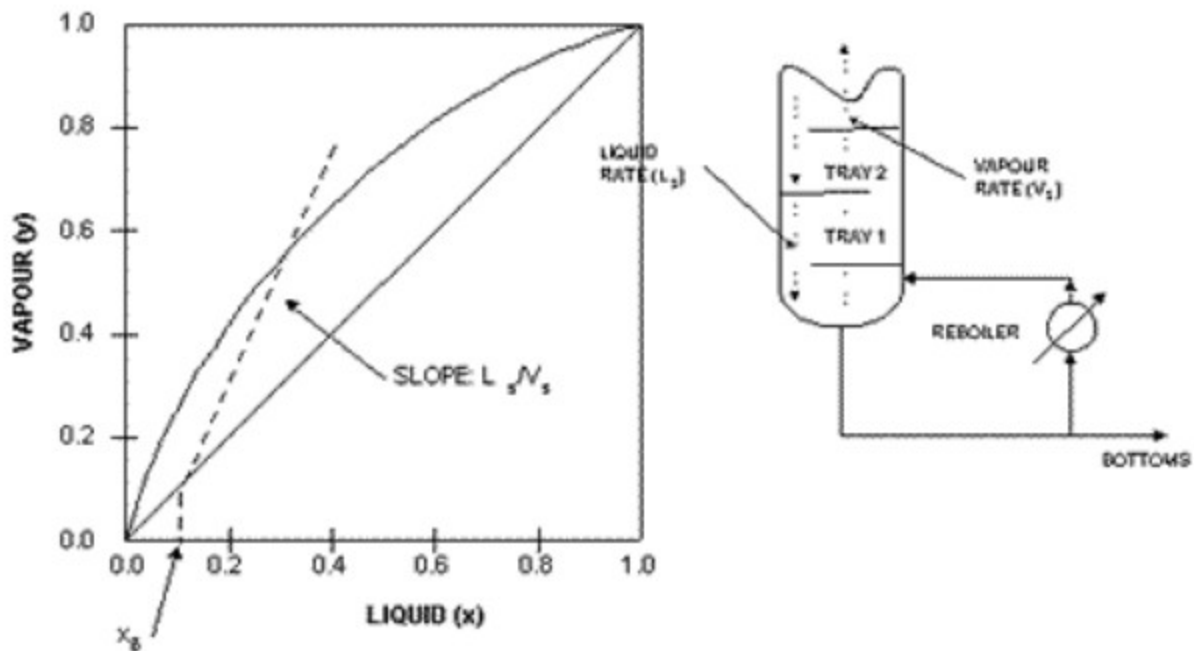
Operating Line for the Rectification Section

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 intersection 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.

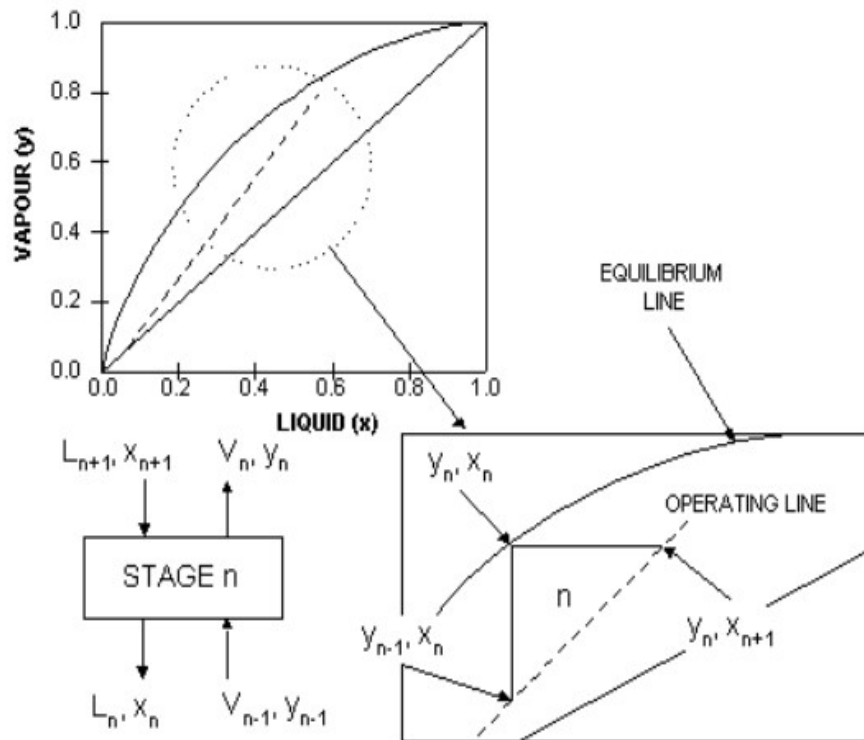


Operating Line for the Stripping Section

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 L_s/V_s is drawn as illustrated in the diagram below. L_s is the liquid rate down the stripping section of the column, while V_s 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.

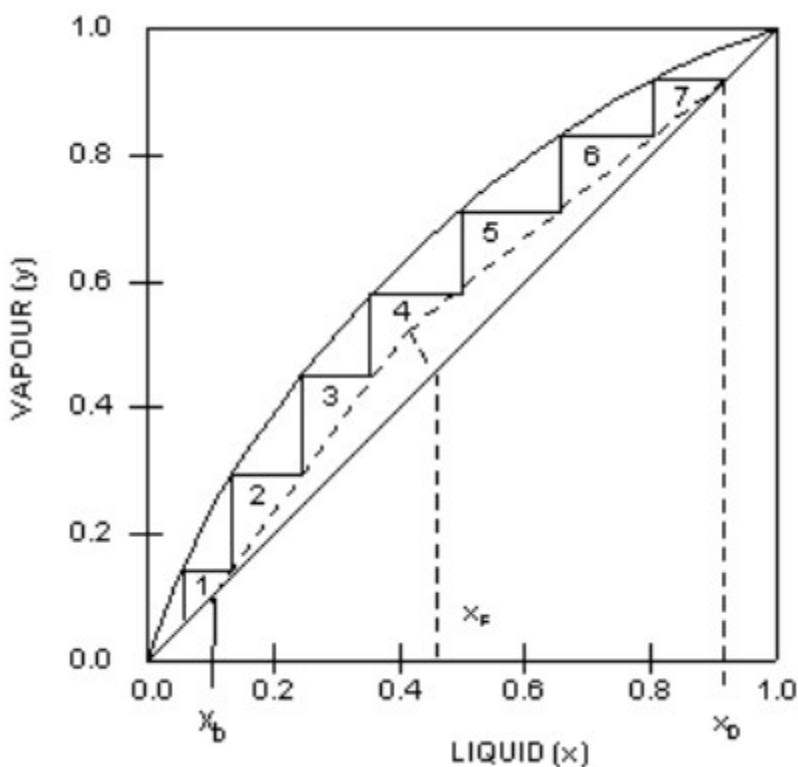


Equilibrium and Operating Lines TMThe McCabe-Thiele method assumes that the liquid on a tray and the vapor above it are in equilibrium. How this is related to the VLE plot and the operating lines is depicted graphically in the diagram on the right.



TM

A magnified section of the operating line for the stripping section is shown in relation to the corresponding n'th stage in the column. L's are the liquid flows while V's are the vapor flows. x and y denote liquid and vapor compositions and the subscripts denote the origin of the flows or compositions. That is 'n-1' will mean from the stage below stage 'n' while 'n+1' will mean from the stage above stage 'n'. The liquid in stage 'n' and the vapor above it are in equilibrium, therefore, x_n and y_n lie on the equilibrium line. Since the vapor is carried to the tray above without changing composition, this is depicted as a horizontal line on the VLE plot. Its intersection with the operating line will give the composition of the liquid on tray 'n+1' as the operating line defines the material balance on the trays. The composition of the vapor above the 'n+1' tray is obtained from the intersection of the vertical line from this point to the equilibrium line



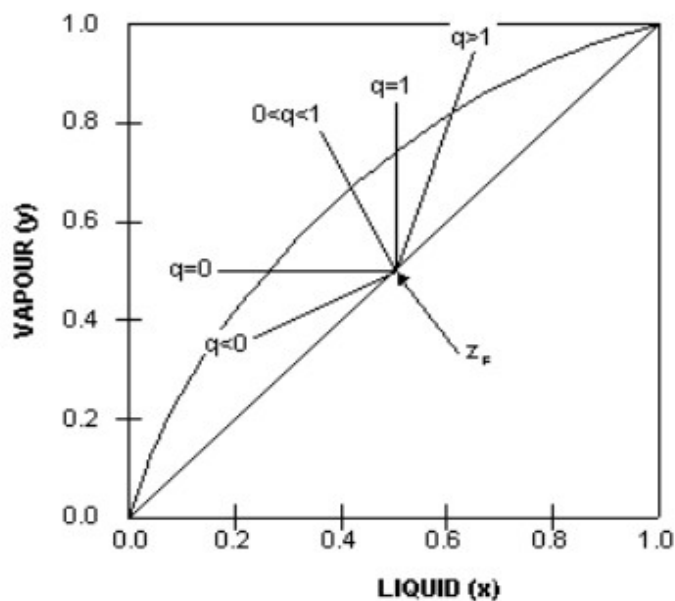
Doing the graphical construction repeatedly will give rise to a number of 'corner' sections, and each section will be equivalent to a stage of the distillation. This is the basis of sizing distillation columns using the McCabeThiele graphical design methodology as shown in the following example. sections, the graphical construction described above was applied. This particular example shows that 7 theoretical stages are required to achieve the desired separation. The 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: $(\text{number of theoretical trays}) / (\text{tray efficiency})$

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 accommodate 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 4th 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)

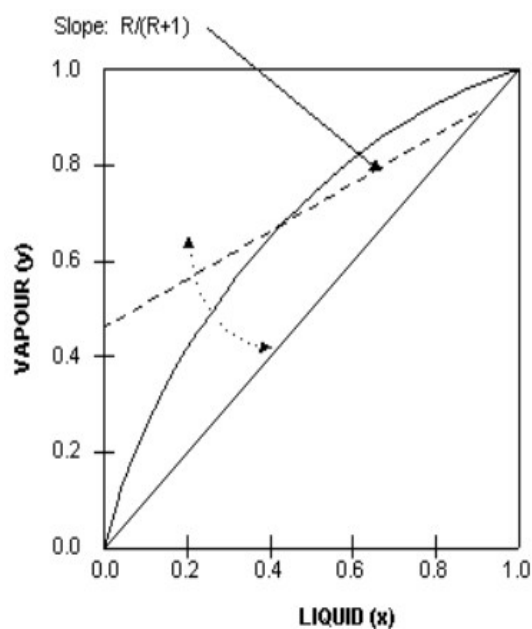
The q-lines for the various feed conditions are shown in the diagram above.

Using Operating Lines and the Feed Line in McCabe-Thiele Design If we have information about the condition of the feed mixture, then we can construct the q-line and use it in the McCabe-Thiele design. However, excluding the equilibrium line, only two other pairs of lines can be used in the McCabe-Thiele procedure. These are:

- feed-line and rectification section operating line
- feed-line and stripping section operating line
- stripping and rectification operating lines

This is because these pairs of lines determine the third.

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. On the other hand, as reflux is decreased, the operating line for the rectification section moves towards the equilibrium line. The 'pinch' between operating and equilibrium lines becomes more pronounced and more and more trays are required. This is easy to verify using the McCabeThiele method.

The limiting condition occurs at minimum reflux ratio, when an infinite number of trays will be required to effect separation. Most columns are designed to operate between 1.2 to 1.5 times the minimum reflux ratio because this is approximately the region of minimum operating costs (more reflux means higher reboiler duty).

Vapor Flow Conditions

Adverse vapor flow conditions can cause:

- Foaming
- Entrainment
- Weeping/dumping
- Flooding

Foaming

Foaming refers to the expansion of liquid due to passage of vapour or gas. Although it provides high interfacial liquid-vapour contact, excessive foaming often leads to liquid buildup on trays. In some cases, foaming may be so bad that the foam mixes with liquid on the tray above. Whether foaming will occur depends primarily on physical properties of the liquid mixtures, but

is sometimes due to tray designs and condition. Whatever the cause, separation efficiency is always reduced.

Entrainment

Entrainment refers to the liquid carried by vapor up to the tray above and is again caused by high vapor flow rates. It is detrimental because tray efficiency is reduced: lower volatile material is carried to a plate holding liquid of higher volatility. It could also contaminate high purity distillate. Excessive entrainment can lead to flooding. 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.

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.

Steam distillation:

At atmospheric pressure, high-boiling liquids cannot be purified by distillation, since components of the liquid may decompose at the high temperatures required. - Often the high-boiling substances are essentially insoluble in water, so a separation at lower temperatures can be obtained by simple steam distillation. Steam distillation is often used to separate a high-boiling component from small amounts of non volatile.

If a layer of liquid water (A) and an immiscible high-boiling component (B) such as hydrocarbon are boiled at 101.3 kPa, then the phase rule, for the three phases (2 L and 1 V) and two components,

$F = C - P + 2 = 2 - 3 + 2 = 1$ degree of freedom Hence, if the total pressure is fixed, the system is fixed • Since there are two liquid phases, each will exert its own vapor pressure at the prevailing temperature, and cannot be influenced by the presence of the other.

When the sum of the separate vapor pressures equals the total pressure, the mixture boils and

$p_A + p_B = P$ where p_A is vapor pressure of pure water

p_B is vapor pressure of pure B

Vapor composition: $y_A = p_A / P$ $y_B = p_B / P$

As long as the two liquid phases are present, the mixture will boil at the same temperature, giving a vapor of constant composition. ^TNote: as long as liquid water is present, the high-boiling

component B vaporizes at a temperature well below its normal boiling point without vacuum. TM
The vapors of water (A) and high-boiling component (B) are usually condensed in a condenser and the resulting two immiscible liquid phases are separated. TM

Disadvantage: large amounts of heat must be used to simultaneously evaporate the water with the high-boiling compound TMUsed in the food industry for the removal of volatile taints and flavors from edible fats and oils.

Azeotropic, Extractive and Molecular distillation

An azeotrope is a liquid mixture which when vaporised, produces the same composition as the liquid. An azeotrope that contains one liquid phase in contact with vapour is called a homogenous azeotrope. A homogenous azeotrope cannot be separated by conventional distillation. However, vacuum distillation may be used as the lower pressures can shift the azeotropic point. Alternatively, an additional substance may be added to shift the azeotropic point to a more 'favourable' position.

Azeotropic distillation: When this additional component appears in appreciable amounts at the top of the column, the operation is called azeotropic distillation.

Extractive distillation: When the additional component appears mostly at the bottom of the column, the operation is called extractive distillation.

Molecular distillation: Distillation that is carried out under a high vacuum in an apparatus so designed as to permit molecules escaping from the warm liquid to reach the cooled surface of the condenser before colliding with other molecules and consequently returning to the liquid and that is used in the purification of substances of low volatility (as in the separation of vitamin A and vitamin E from fish-liver oils)