

# Distillation

***Distillation*** is a method of separating the components of a solution which depends upon the distribution of the substances between a gas (vapour) and a liquid phase, applied to cases where all components are present in both phases.

**Distillation vs. Evaporation**

**Distillation as a Mass Transfer Operation**

**Distillation vs. Absorption/Desorption**

# Vapour-Liquid Equilibria (V-LE)

Successful application of distillation methods depends greatly upon an understanding of the equilibrium existing between the vapour and liquid phases of the mixtures encountered.

Phase rule applies to Vapour-Liquid systems:

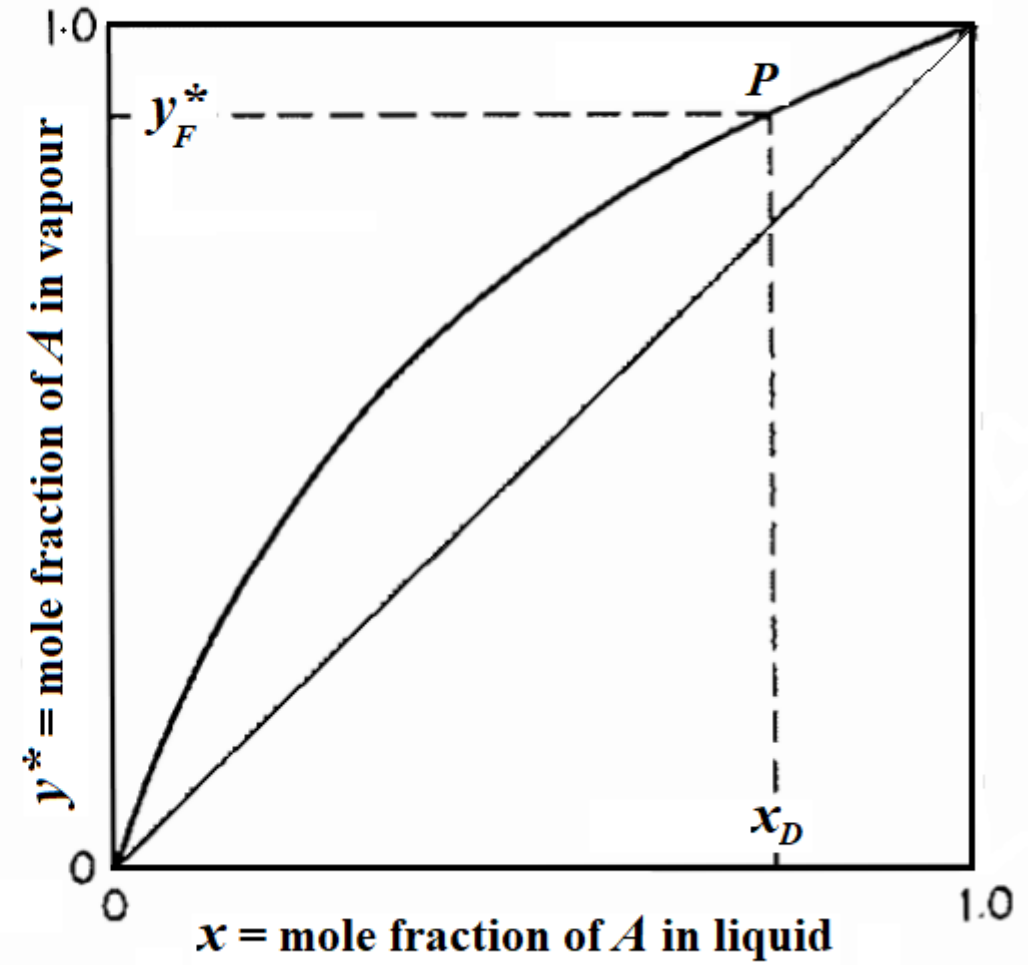
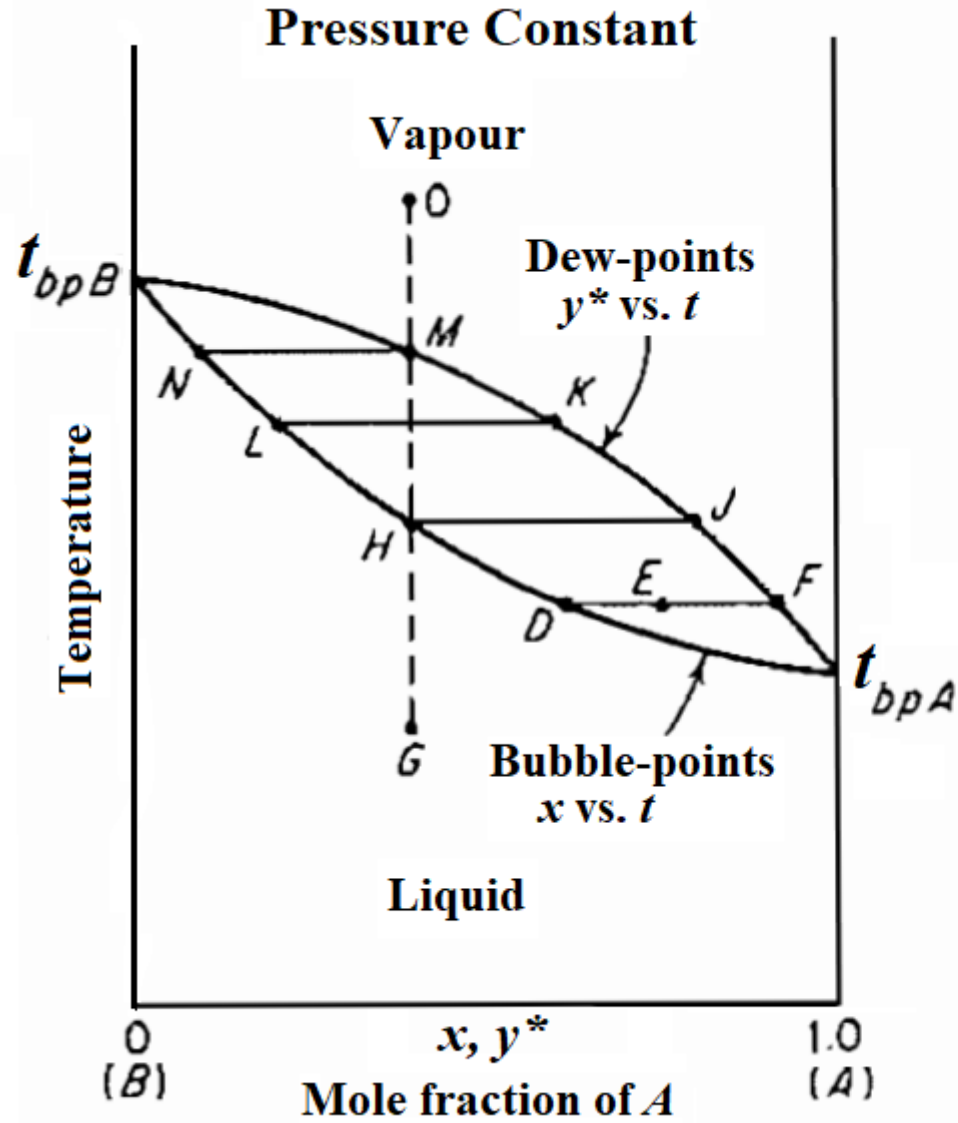
$$F = C - P + 2$$

For binary systems:

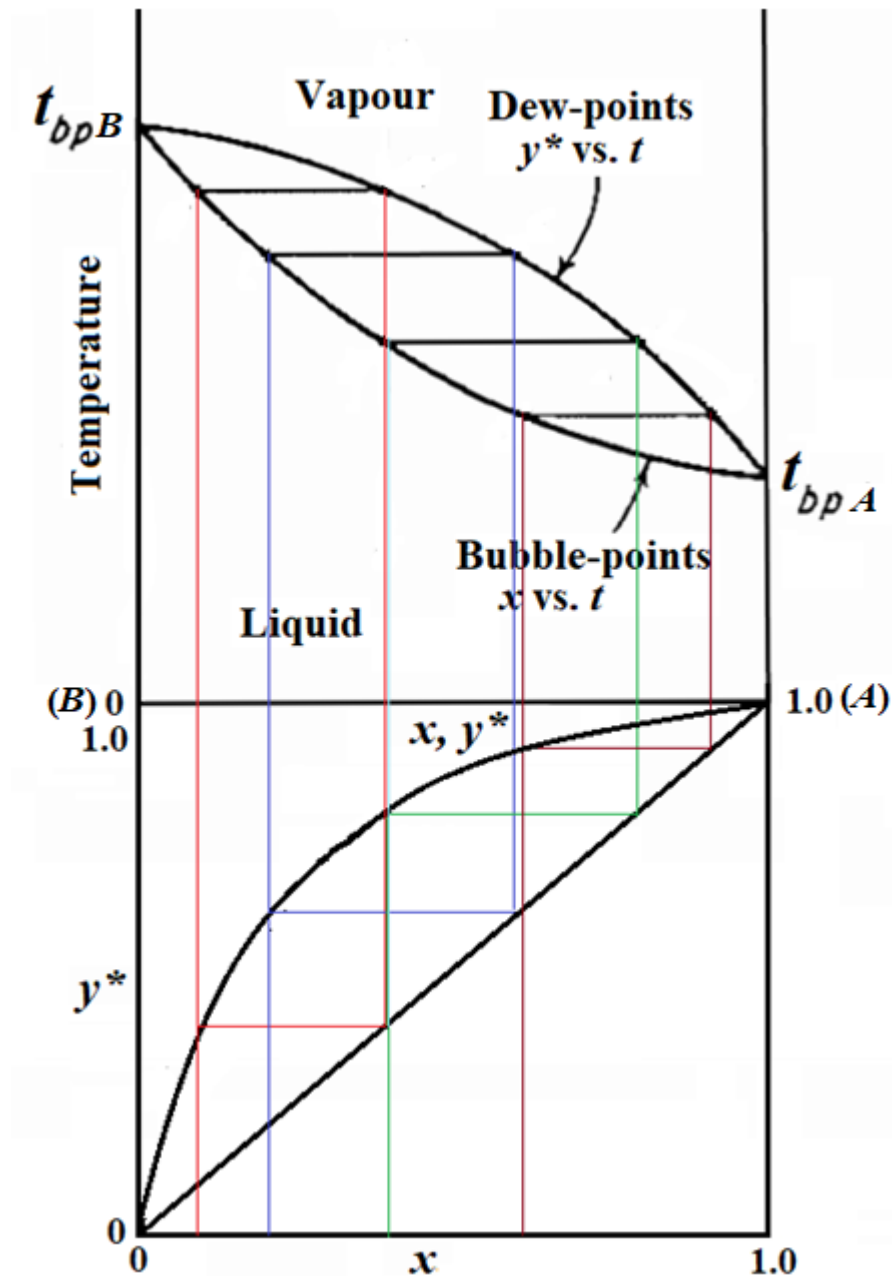
Variables are: Pressure, Temperature and Concentrations of one component in the liquid and vapour phases

But, Degrees of Freedom,  $F = 2$ .

If the pressure is fixed, only one variable, e.g., liquid phase concentration, can be changed independently and temperature and vapour phase concentration follow.



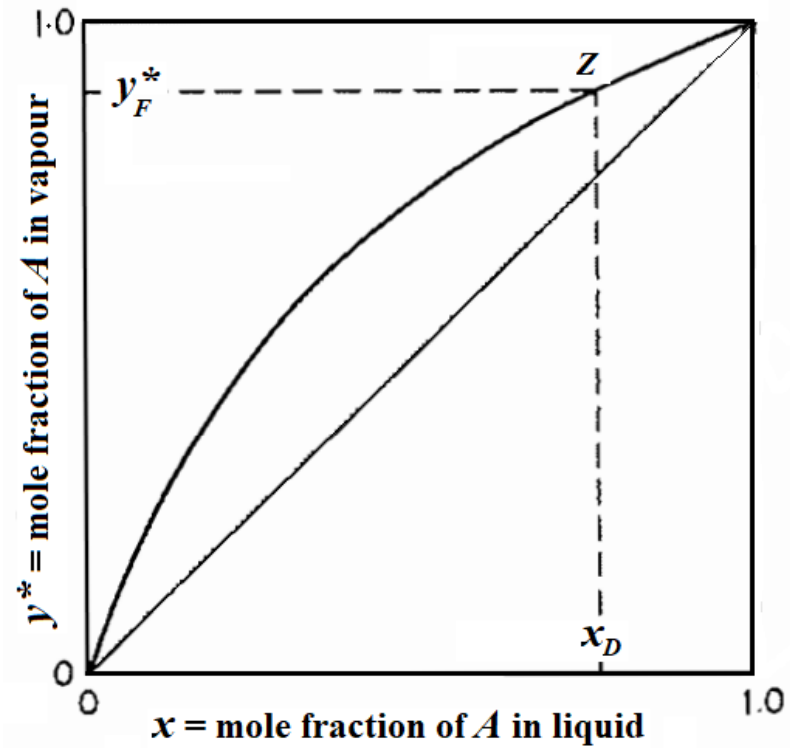
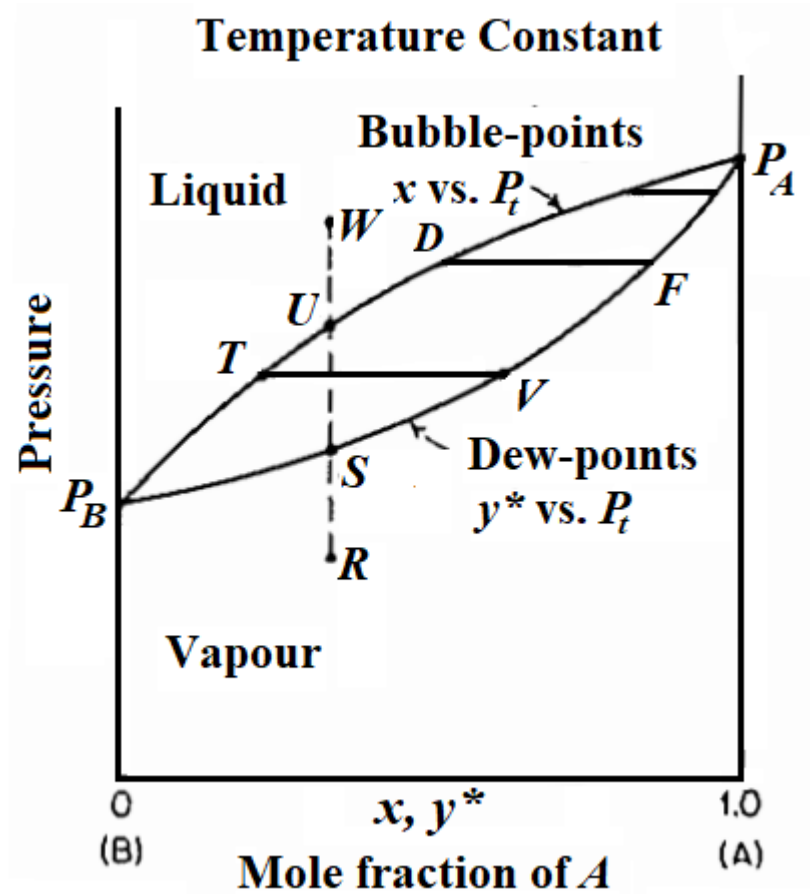
**Constant pressure vapour-liquid equilibria**



**Relative volatility:**

$$\alpha_{AB} = \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{y^*(1-x)}{x(1-y^*)}$$

The larger the value of  $\alpha_{AB}$  above unity, the greater the degree of separability.



**Constant temperature vapour-liquid equilibria**

## Ideal Solutions – Raoult's Law

$$p_A^* = P_A x \quad p_B^* = P_B (1 - x)$$

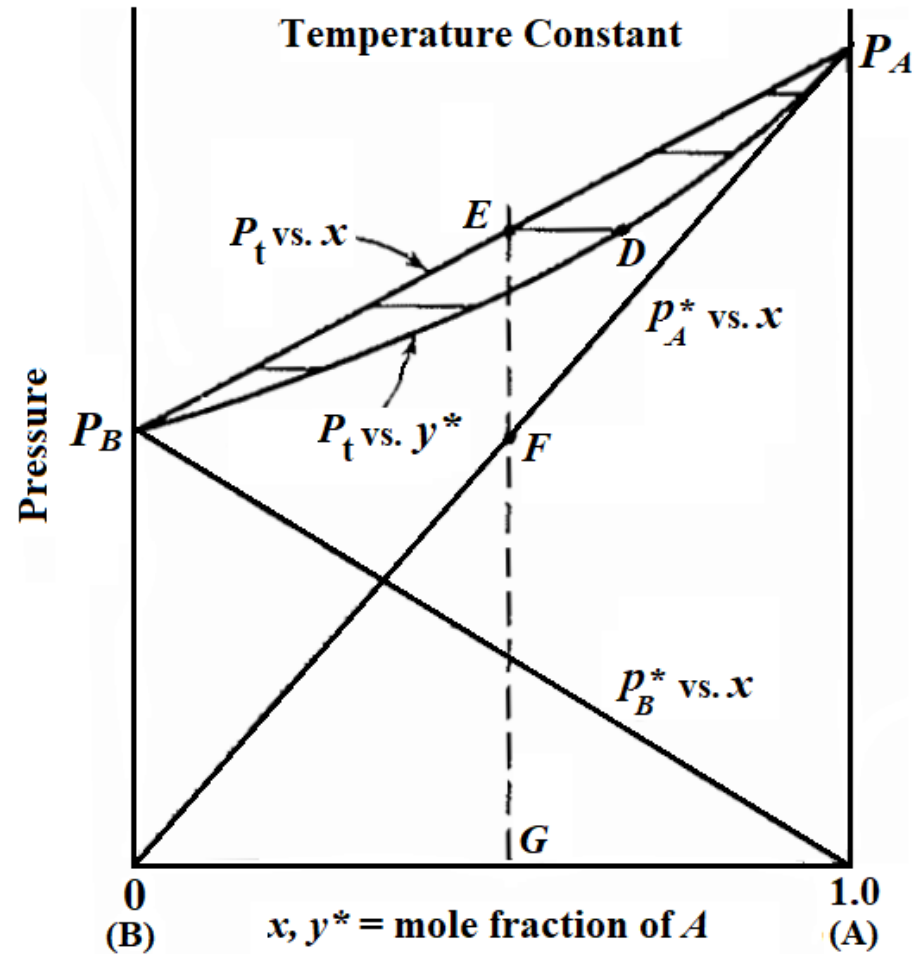
For Ideal vapour phase:

$$\begin{aligned} P_t &= p_A^* + p_B^* = P_A x + P_B (1 - x) \\ &= P_B + (P_A - P_B) x \end{aligned}$$

$$y^* = \frac{p_A^*}{P_t} = \frac{P_A x}{P_t}$$

$$1 - y^* = \frac{p_B^*}{P_t} = \frac{P_B (1 - x)}{P_t}$$

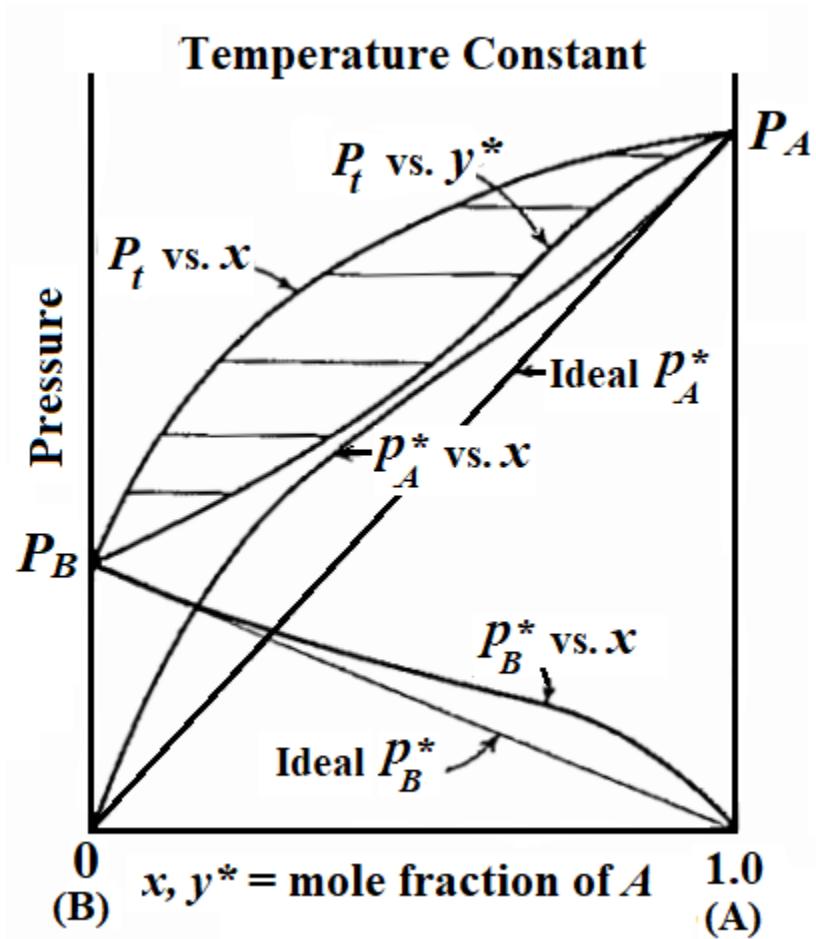
$$\alpha_{AB} = \frac{P_A}{P_B}$$



$$y^* = \frac{\alpha_{AB} x}{1 + (\alpha_{AB} - 1) x}$$

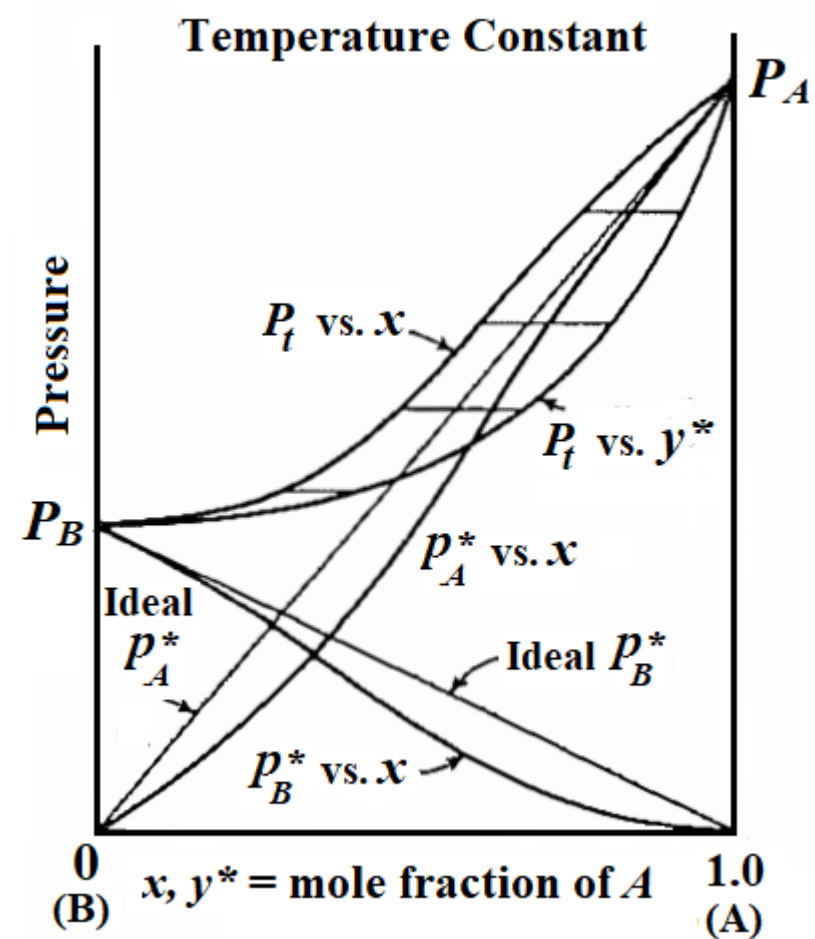
## Positive Deviations from Ideality

$$P_t > p_A^* + p_B^*$$



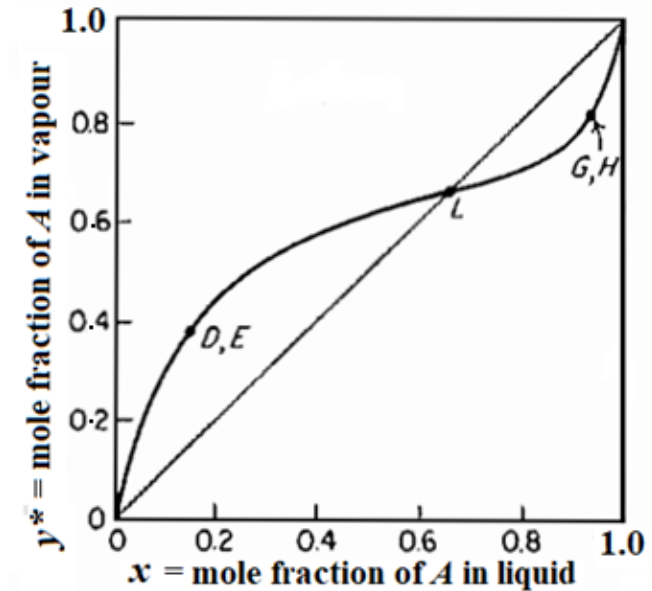
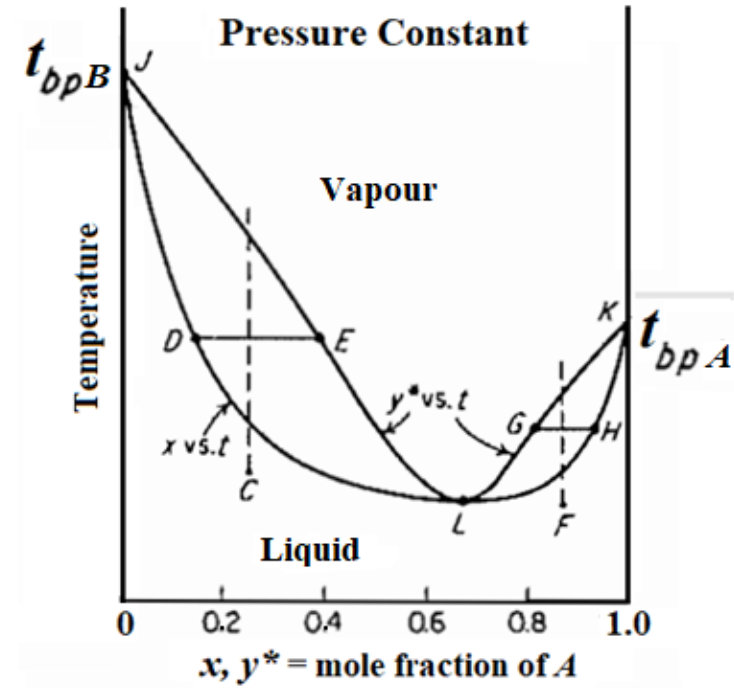
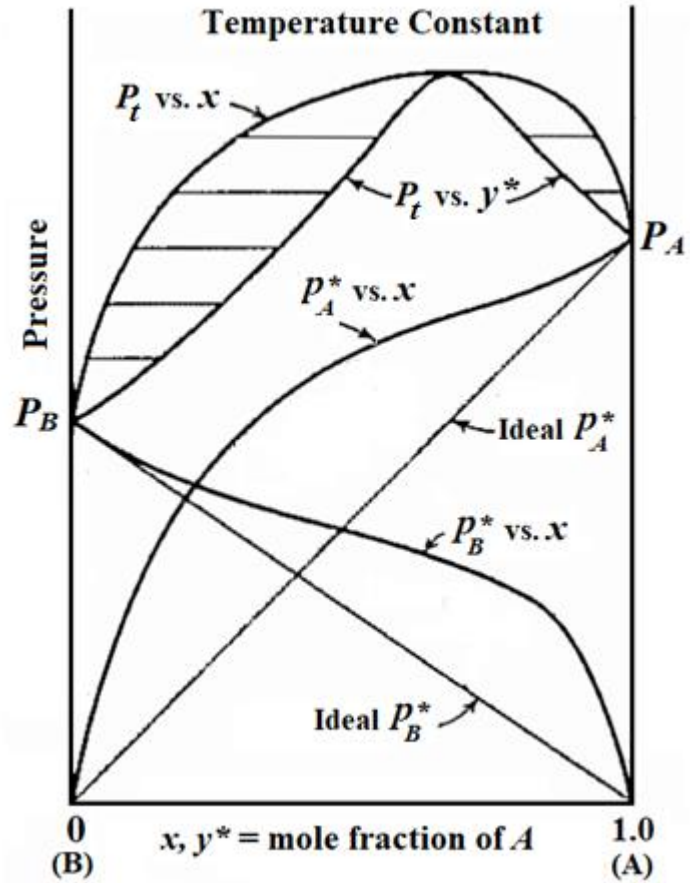
## Negative Deviations from Ideality

$$P_t < p_A^* + p_B^*$$





# Minimum Boiling Azeotropes



## Examples:

$\text{CS}_2$  (46.2 °C) – Water (100 °C) ---- Azeotrope (39.25 °C, 61 mol%  $\text{CS}_2$ )

Ethanol (78.4 °C) - Water (100 °C) ---- Azeotrope (78.15 °C, 89.4 mol% EtOH)

Acetic acid (118.1 °C) – Toluene (110.8 °C)

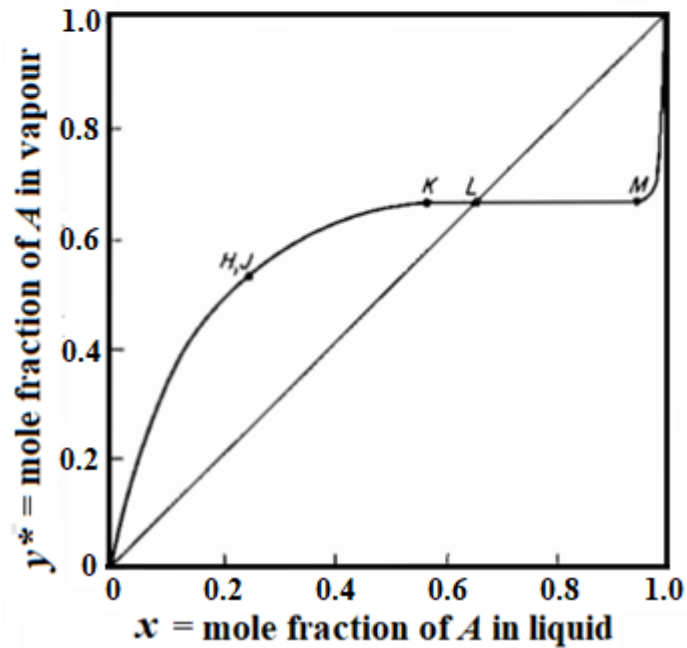
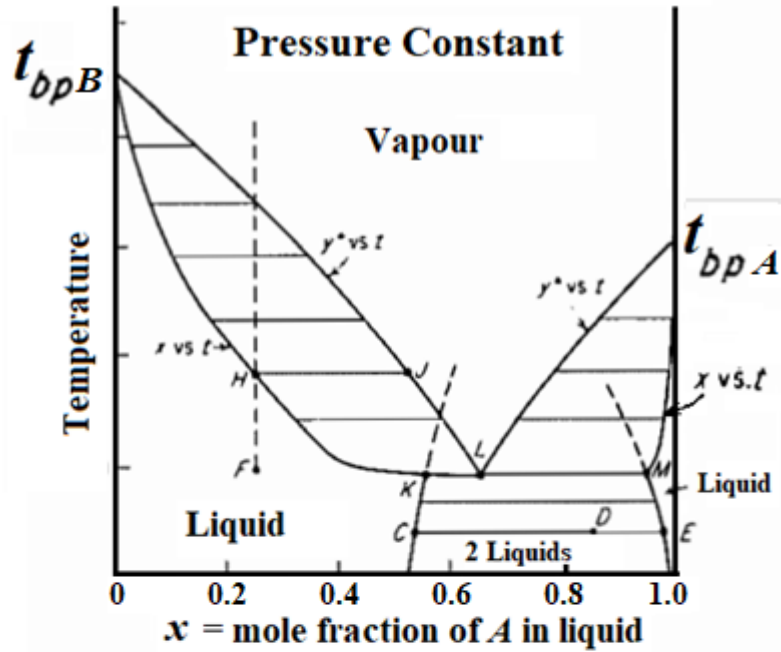
---- Azeotrope (105.4 °C, 62.7 mol% Acetic acid)

# Heteroazeotrope

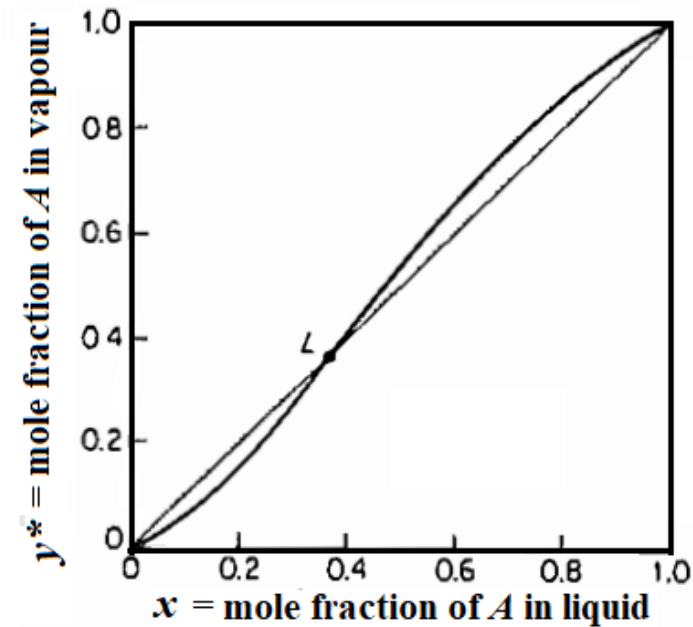
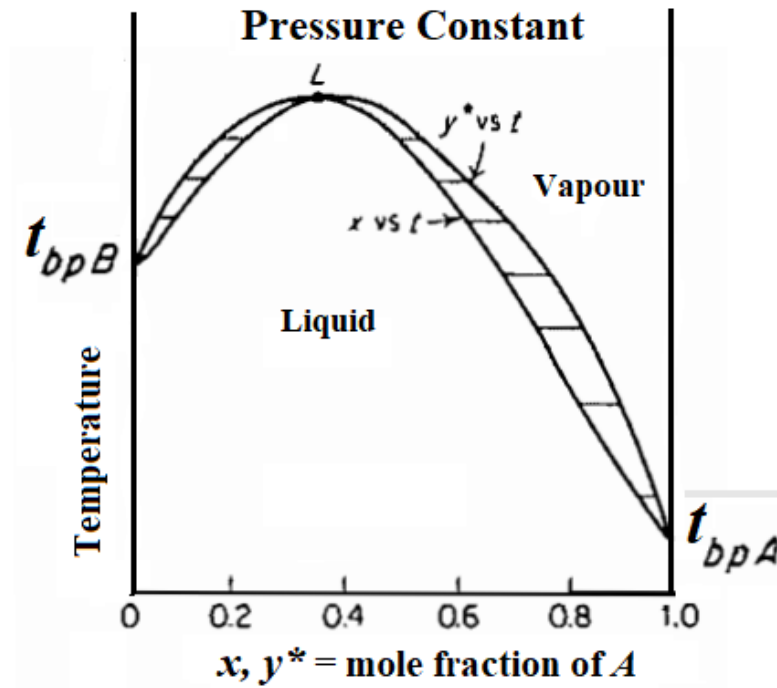
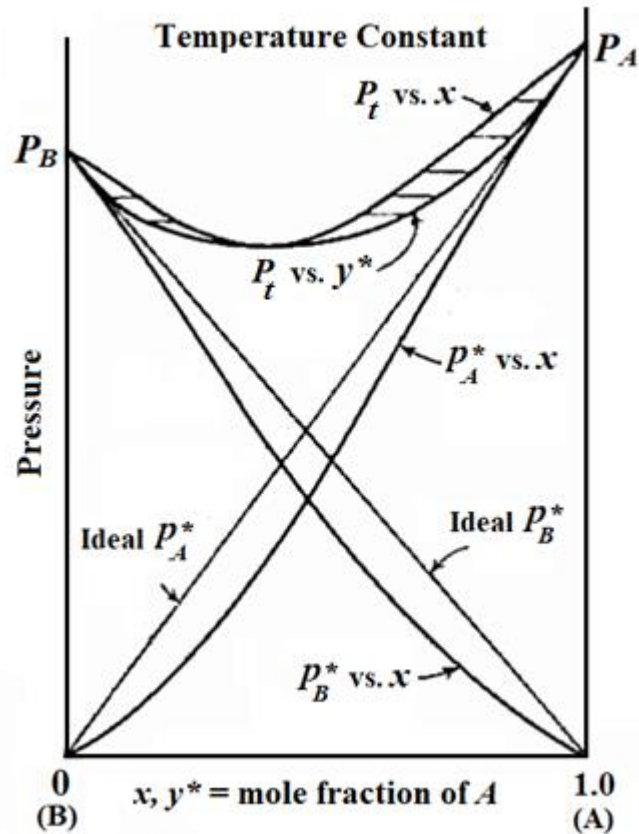
Examples:

Isobutanol - Water

Toluene - Water



# Maximum Boiling Azeotropes



## Examples:

HCl (85 °C) – Water (100 °C) ---- Azeotrope (110 °C, 11.1 mol% HCl)

Acetone (56.5 °C) - Chloroform (61.2 °C)

---- Azeotrope (64.5 °C, 65.5 mol% Chloroform)

Water(100 °C) – Formic acid (100.8 °C)

---- Azeotrope (107.1 °C, 56.7 mol% Formic acid)

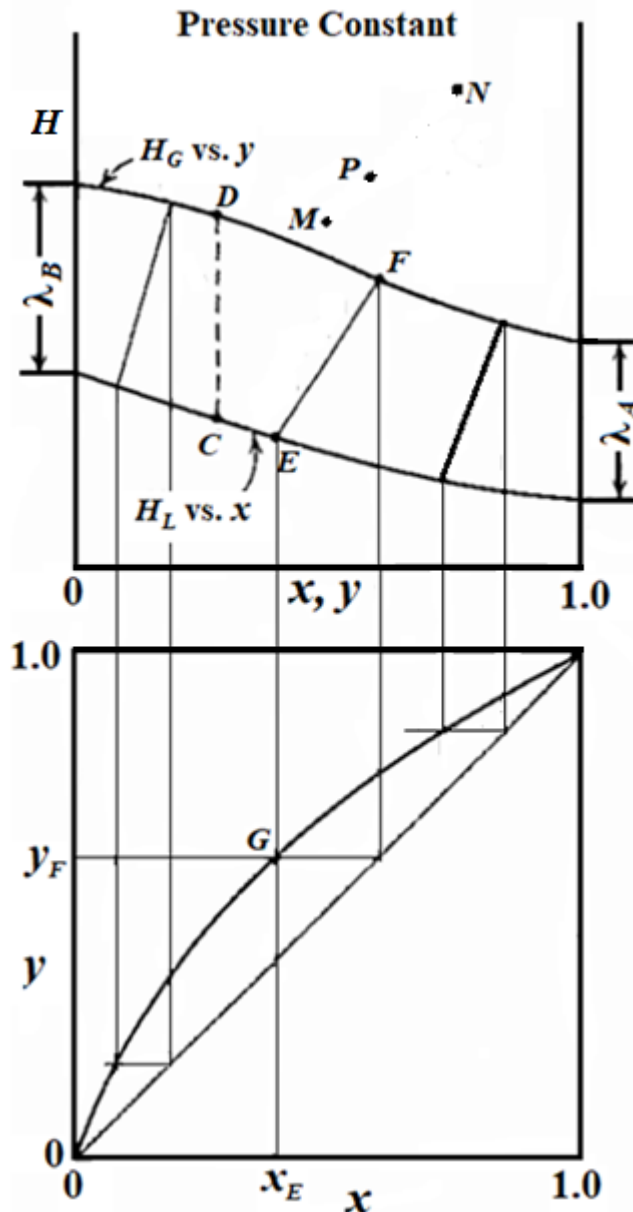
# Enthalpy–Concentration ( $H$ - $x$ , $y$ ) Diagrams

**Liquid Enthalpy:**

$$H_L = C_L (t_L - t_o) M_{av} + \Delta H_S$$

**Saturated Vapour Enthalpy:**

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



**Overall material balance:**

$$M + N = P \quad \dots (1)$$

**A balance for component A gives:**

$$M z_M + N z_N = P z_P \quad \dots (2)$$

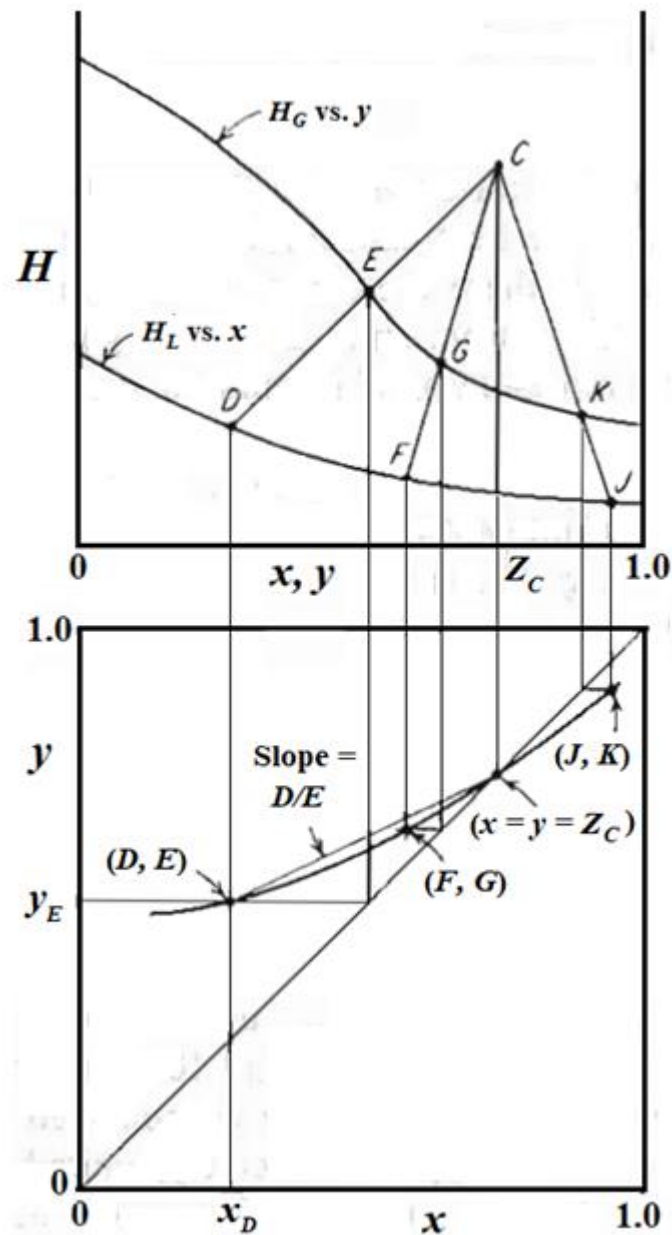
**An enthalpy balance gives:**

$$M H_M + N H_N = P H_P \quad \dots (3)$$

**Elimination of  $P$  between eqs. (1) & (2) and between eqs. (1) & (3) yields:**

$$\frac{M}{N} = \frac{z_N - z_P}{z_P - z_M} = \frac{H_N - H_P}{H_P - H_M} \quad \dots (4)$$

This is the equation of a straight line on the enthalpy-concentration plot, passing through points  $M (H_M, z_M)$ ,  $N (H_N, z_N)$  and  $P (H_P, z_P)$ . Point  $P$  is, therefore, on the straight line  $MN$ , located so that  $M/N = \text{line } NP / \text{line } MP$ .



For the combination  $E - D = C$ , a material balance gives

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

# Multicomponent Systems

For multicomponent system particularly, it is customary to describe the equilibrium data by means of the distribution coefficient,  $m$ . For component  $J$ ,

$$m_J = \frac{y_J^*}{x_J}$$

The relative volatility  $\alpha_{I,J}$  of component  $I$  with respect to  $J$  is

$$\alpha_{I,J} = \frac{y_I^* / x_I}{y_J^* / x_J} = \frac{m_I}{m_J}$$

For ideal solutions,  $m_J = \frac{P_J}{P_t}$  and  $\alpha_{I,J} = \frac{P_I}{P_J}$

## Bubble Point:

For the bubble point vapour,  $\sum y_i^* = 1.0$  Or,  $m_A x_A + m_B x_B + m_C x_C + \dots = 1.0$

With component  $J$  as a reference component,  $\frac{m_A x_A}{m_J} + \frac{m_B x_B}{m_J} + \frac{m_C x_C}{m_J} + \dots = \frac{1.0}{m_J}$

$$\Rightarrow \alpha_{A,J} x_A + \alpha_{B,J} x_B + \alpha_{C,J} x_C + \dots = \sum \alpha_{i,J} x_i = \frac{1}{m_J}$$

The equilibrium bubble-point vapour composition is given by

$$y_i = \frac{\alpha_{i,j} x_i}{\sum \alpha_{i,j} x_i}$$

**Dew Point:**

For the dew point liquid,  $\sum x_i^* = 1.0$

$$\text{Or, } \frac{y_A}{m_A} + \frac{y_B}{m_B} + \frac{y_C}{m_C} + \dots = 1.0$$

With component  $J$  as a reference component,

$$\frac{m_J y_A}{m_A} + \frac{m_J y_B}{m_B} + \frac{m_J y_C}{m_C} + \dots = m_J$$

$$\Rightarrow \frac{y_A}{\alpha_{A,J}} + \frac{y_B}{\alpha_{B,J}} + \frac{y_C}{\alpha_{C,J}} + \dots = \sum \frac{y_i}{\alpha_{i,j}} = m_J$$

The dew-point liquid composition is given by

$$x_i = \frac{y_i / \alpha_{i,j}}{\sum (y_i / \alpha_{i,j})}$$

# Distillation Methods

Simple Distillation

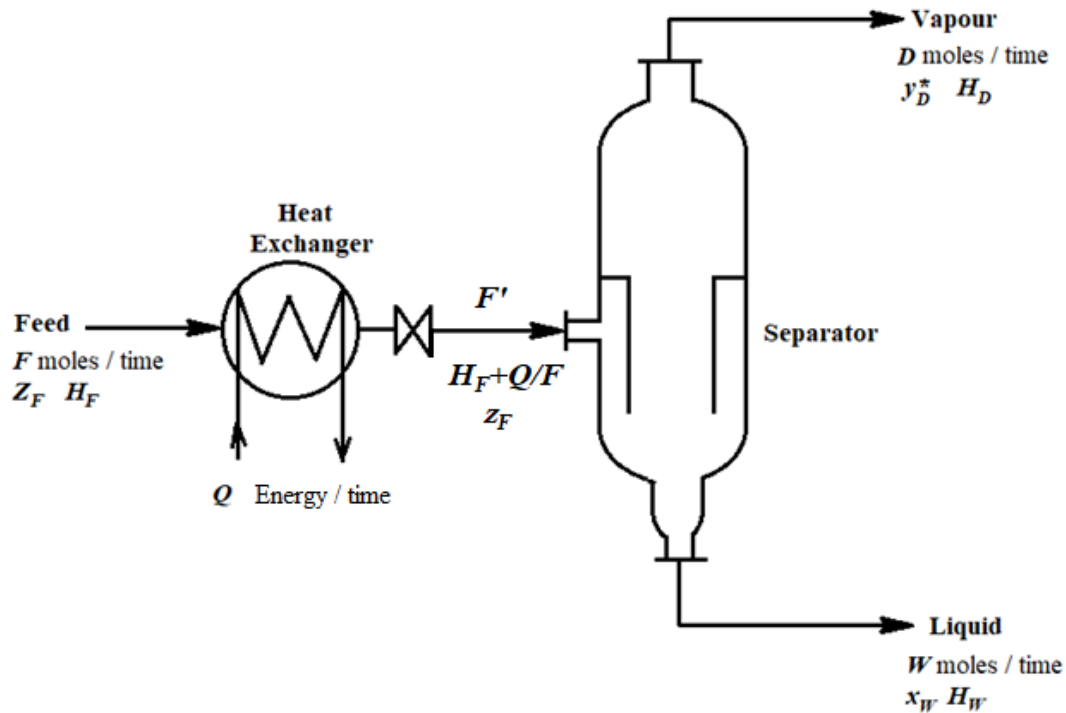
Fractional Distillation **or** Continuous Rectification



## **SIMPLE DISTILLATION METHODS**

- 1. Equilibrium or Flash Distillation**
- 2. Simple Batch or Differential Distillation**
- 3. Steam Distillation**

# Equilibrium or Flash Distillation



**Overall material balance:**

$$F = D + W \quad \dots (5)$$

**A balance for component A gives:**

$$F z_F = D y_D + W x_W \quad \dots (6)$$

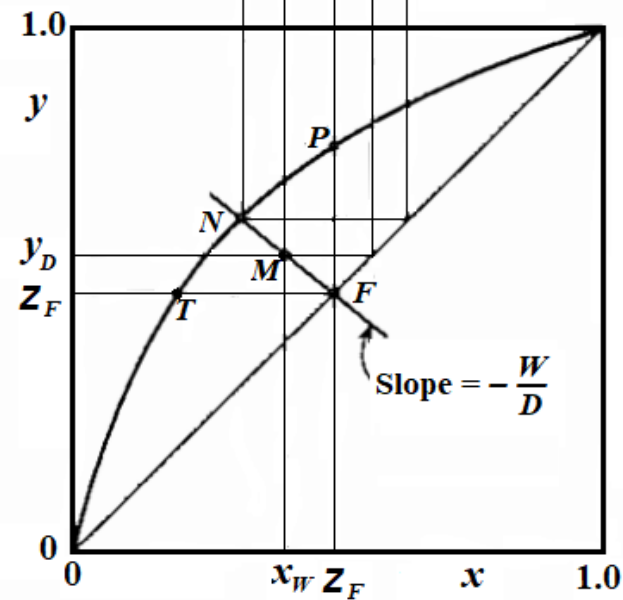
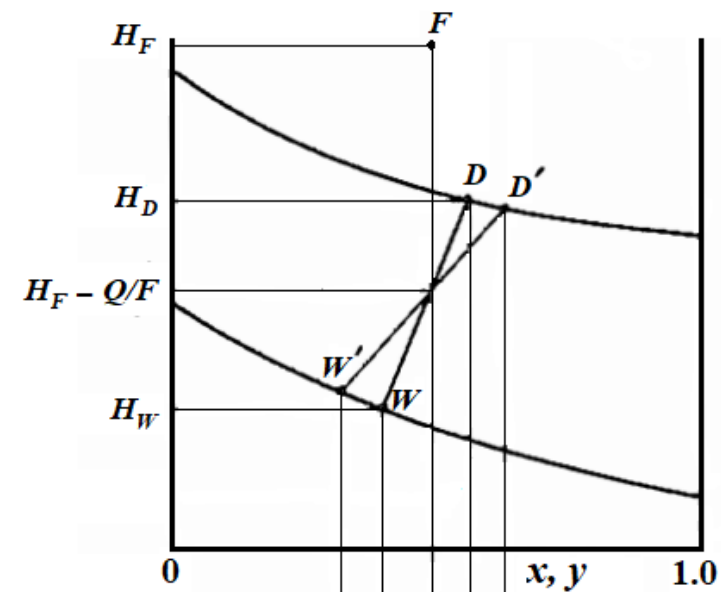
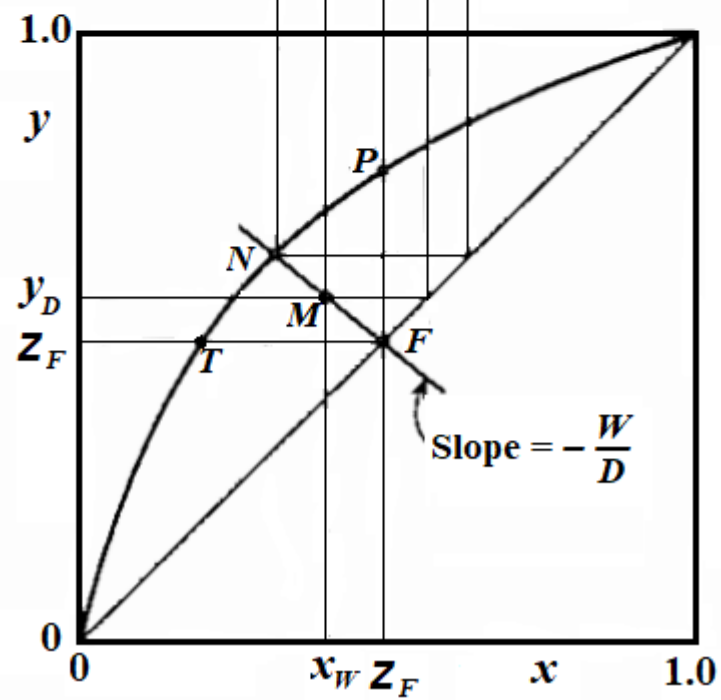
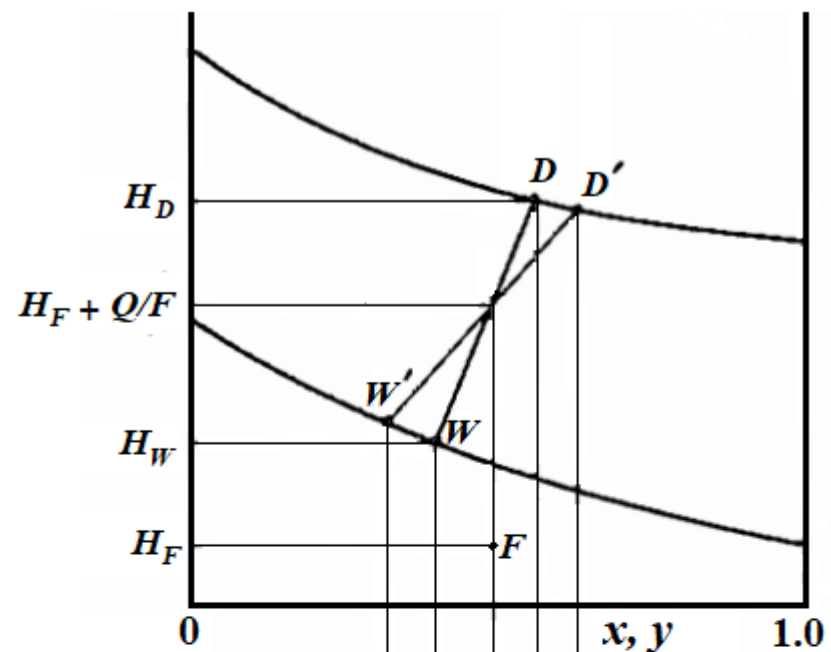
**An enthalpy balance gives:**

$$\begin{aligned} F H_F + Q &= D H_D + W H_W \\ \Rightarrow F (H_F + Q/F) &= D H_D + W H_W \quad \dots (7) \end{aligned}$$

**Solving simultaneously, these yields:**

$$-\frac{W}{D} = \frac{y_D - z_F}{x_W - z_F} = \frac{H_D - (H_F + Q/F)}{H_W - (H_F + Q/F)} \quad \dots (8)$$

On the H-x,y diagram, this represents a straight line through points  $D (H_D, y_D)$ ,  $W (H_W, x_W)$  and  $F' (H_F + Q/F, z_F)$  representing the feed mixture after it leaves the heat exchanger.



**Partial Condensation**

## Multicomponent Systems - Ideal Solutions

For mixtures leaving an equilibrium stage containing components  $A, B, C$ , etc., the equilibrium relation for any component  $J$  can be written as

$$y_{J,D}^* = m_J x_{J,W} \quad \dots (9)$$

Equation (8) also applies for each of the components, and when combined with equation (9) for any component  $J$ , for an equilibrium stage gives

$$\frac{W}{D} = \frac{m_J x_{J,W} - z_{J,F}}{z_{J,F} - x_{J,W}} = \frac{y_{J,D}^* - z_{J,F}}{z_{J,F} - y_{J,D}^* / m_J} \quad \dots (10)$$

This provides the following expression, useful for equilibrium vaporization,

$$y_{J,D}^* = \frac{z_{J,F}(W/D + 1)}{1 + W/D m_J} \quad \dots (11a)$$

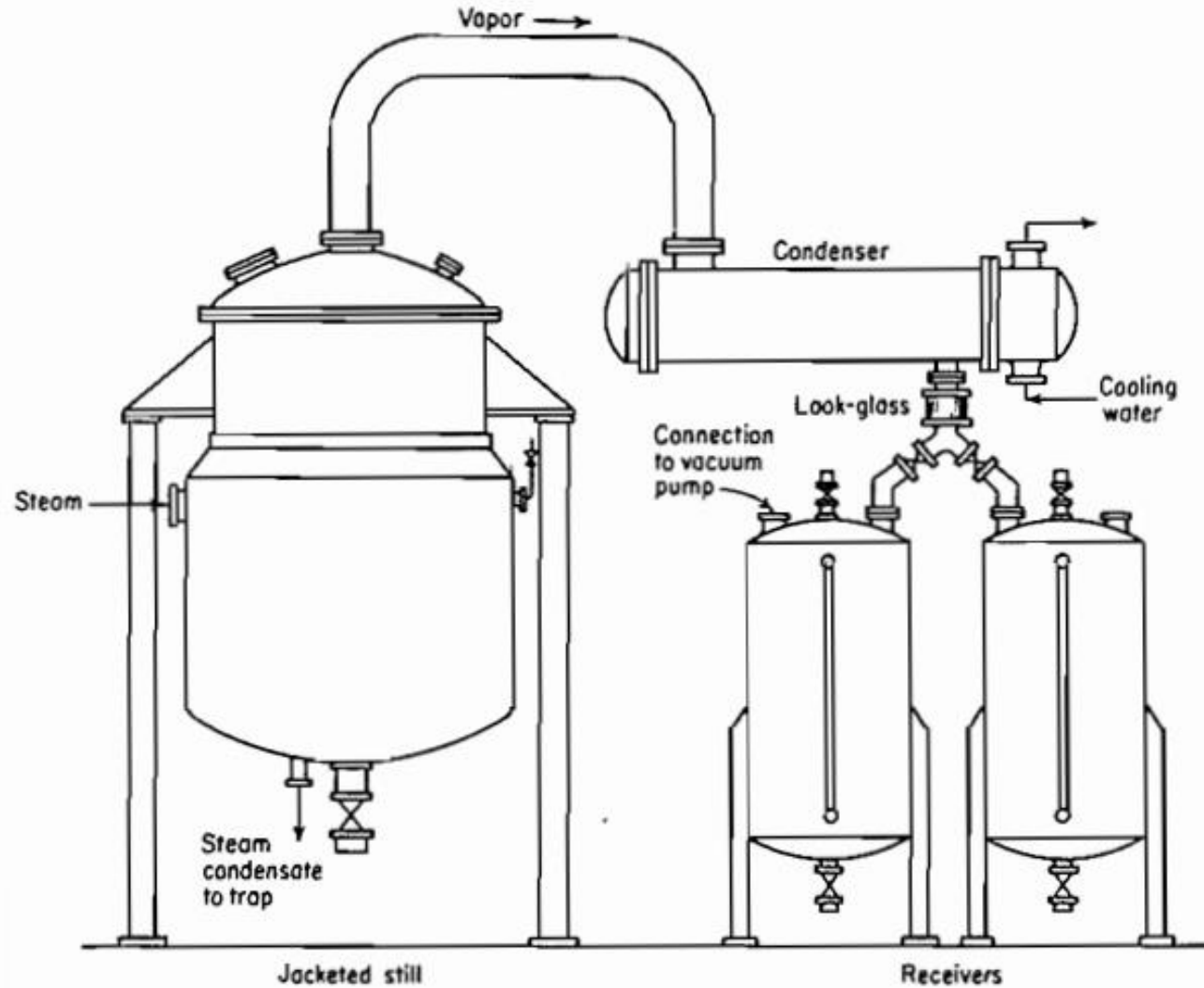
$$\sum y_D^* = 1.0 \quad \dots (11b)$$

and for partial condensation

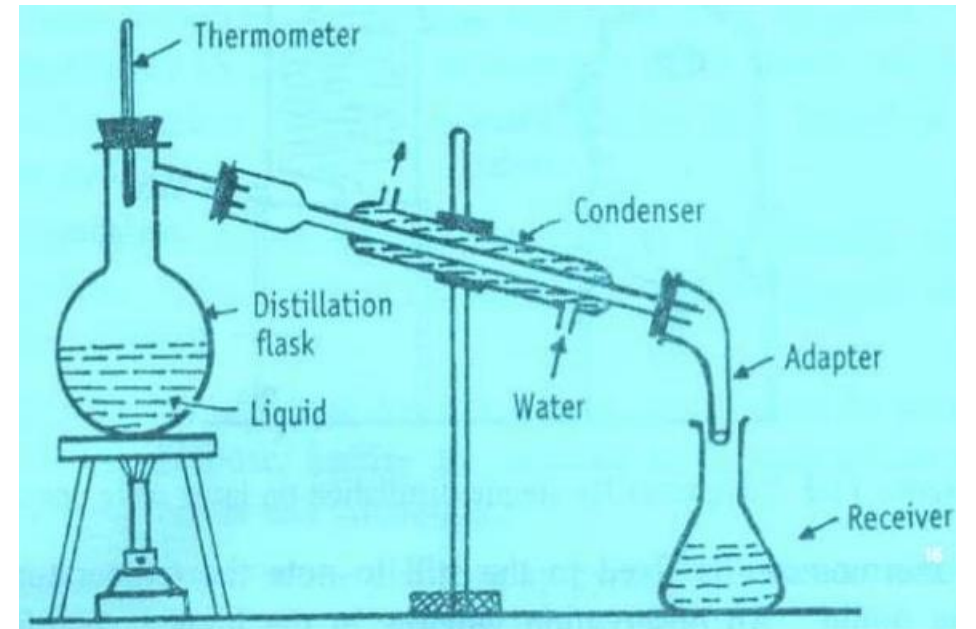
$$x_{J,W} = \frac{z_{J,F}(W/D + 1)}{m_J + W/D} \quad \dots (12a)$$

$$\sum x_W = 1.0 \quad \dots (12b)$$

# Simple Batch or Differential Distillation

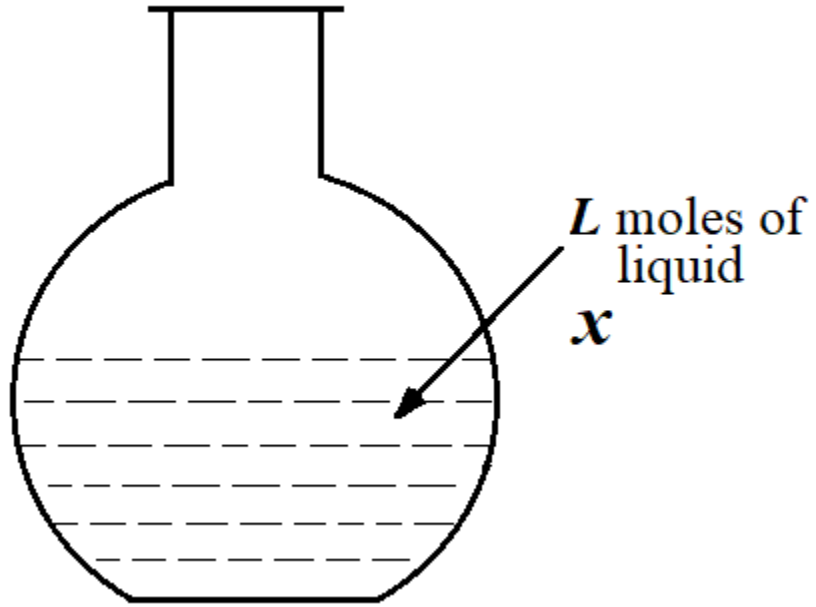


**Batch Still**



**Laboratory Batch Distillation Set-up**

## Differential Distillation



	Total material	Component A
Moles in	0	0
Moles out	$dD$	$y^* dD$
Moles accumulated	$dL$	$d(Lx)$
In – Out = Accumulation	$0 - dD = dL$	$0 - y^* dD = L dx + x dL$

$$y^* dL = L dx + x dL \quad \dots (13)$$

$$\int_W^F \frac{dL}{L} = \ln \frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{y^* - x} \quad \dots (14)$$

## Differential Condensation

$$\ln \frac{F}{D} = \int_{y_F}^{y_D} \frac{dy}{y - x^*} \quad \dots (16)$$

## Rayleigh Equation

$$F x_F = D y_{D,av} + W x_W \quad \dots (15)$$

## Constant Relative Volatility

If we can describe the equilibrium relation at constant pressure by use of some average relative volatility,  $\alpha_{av}$  over the concentration range involved as

$$y^* = \frac{\alpha_{av} x}{1 + (\alpha_{av} - 1) x} \quad \dots (16)$$

then graphical integration can be avoided. Substituting this in Rayleigh equation yields

$$\begin{aligned} \ln \frac{F}{W} &= \int_{x_W}^{x_F} \frac{dx}{y^* - x} = \int_{x_W}^{x_F} \frac{1 + (\alpha_{av} - 1) x}{\alpha_{av} x - x - (\alpha_{av} - 1) x^2} dx \\ &= \int_{x_W}^{x_F} \frac{1 + (\alpha_{av} - 1) x}{x(1 - x)(\alpha_{av} - 1)} dx = \frac{1}{\alpha_{av} - 1} \int_{x_W}^{x_F} \frac{dx}{x(1 - x)} + \int_{x_W}^{x_F} \frac{dx}{1 - x} \\ &= \frac{1}{\alpha_{av} - 1} \left[ \int_{x_W}^{x_F} \left( \frac{dx}{x} + \frac{dx}{1 - x} \right) \right] + \ln \frac{1 - x_W}{1 - x_F} \\ \Rightarrow \ln \frac{F}{W} &= \frac{1}{\alpha_{av} - 1} \left[ \ln \frac{x_F (1 - x_W)}{x_W (1 - x_F)} \right] + \ln \frac{1 - x_W}{1 - x_F} \quad \dots (17) \end{aligned}$$

This can be rearranged to another useful form:

$$\log \frac{F x_F}{W x_W} = \alpha_{av} \log \frac{F(1 - x_F)}{W(1 - x_W)} \quad \dots (18)$$

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

## Multicomponent Systems - Ideal Solutions

For multicomponent systems forming ideal liquid solutions, Eqn. (18) can be written for any two components. Ordinarily one component is chosen on which to base the relative volatilities, whereupon Eqn.(18) is written once for each of the others. For example, for substance  $J$ , with relative volatility based on substance  $B$ ,

$$\log \frac{F x_{J,F}}{W x_{J,W}} = \alpha_{JB} \log \frac{F x_{B,F}}{W x_{B,W}} \quad \dots (19)$$

and

$$\sum x_W = 1.0 \quad \dots (20)$$

Where  $x_{J,F}$  is the mole fraction of  $J$  in the feed and  $x_{J,W}$  is that in the residue.



## Steam Distillation

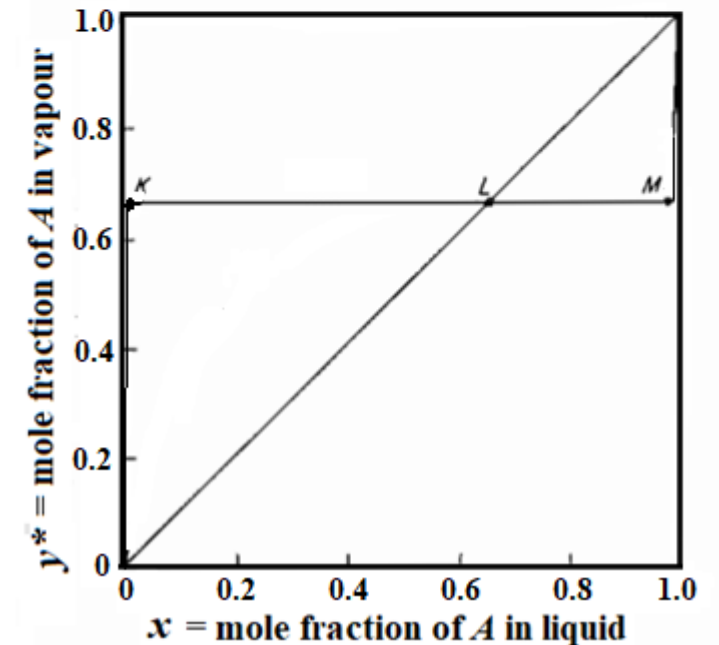
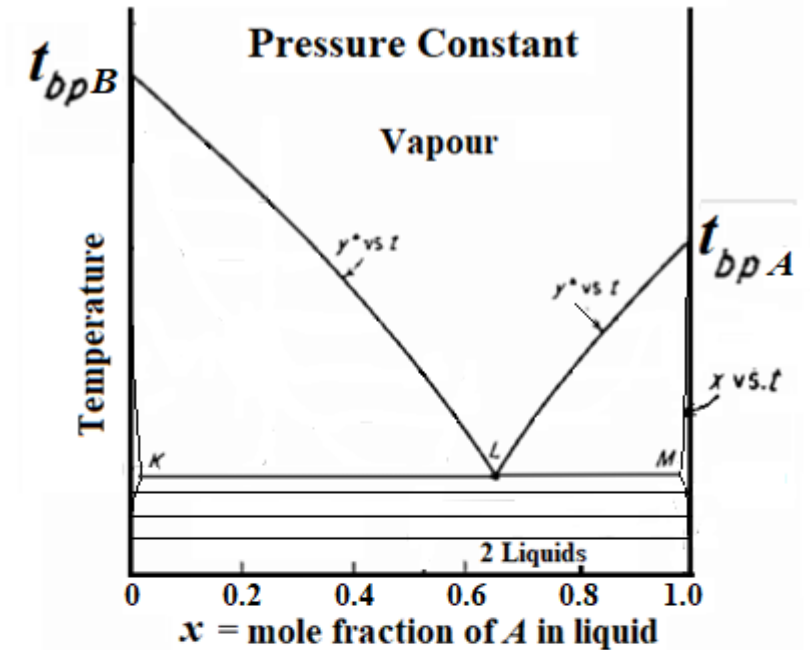
Steam Distillation is often used to separate a high boiling component from relatively non-volatile impurities.

It is used for the recovery of volatile compounds with high boiling point, from inert and complex matrices, solid or liquid, using saturated or superheated steam as separation and energy agent.

Steam distillation has been the traditional method to isolate volatiles from fragrant plant materials. It is used to isolate the [essential oils](#) from [lavender](#) or from [rose petals](#).

Steam distillation is also used for the isolation of **antioxidant** and **antimicrobial** compounds from **herbs and species** such as clove, rosemary, sage and thyme.

At atmospheric pressure high boiling liquids cannot be purified by distillation since the 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 steam distillation.



If a layer of liquid water (*A*) and an immiscible high boiling component (*B*) such as a hydrocarbon are boiled at 1 atm absolute pressure, then by phase rule, for three phases and two components,

$$F = C - P + 2 = 2 - 3 + 2 = 1 \text{ (Degree of Freedom).}$$

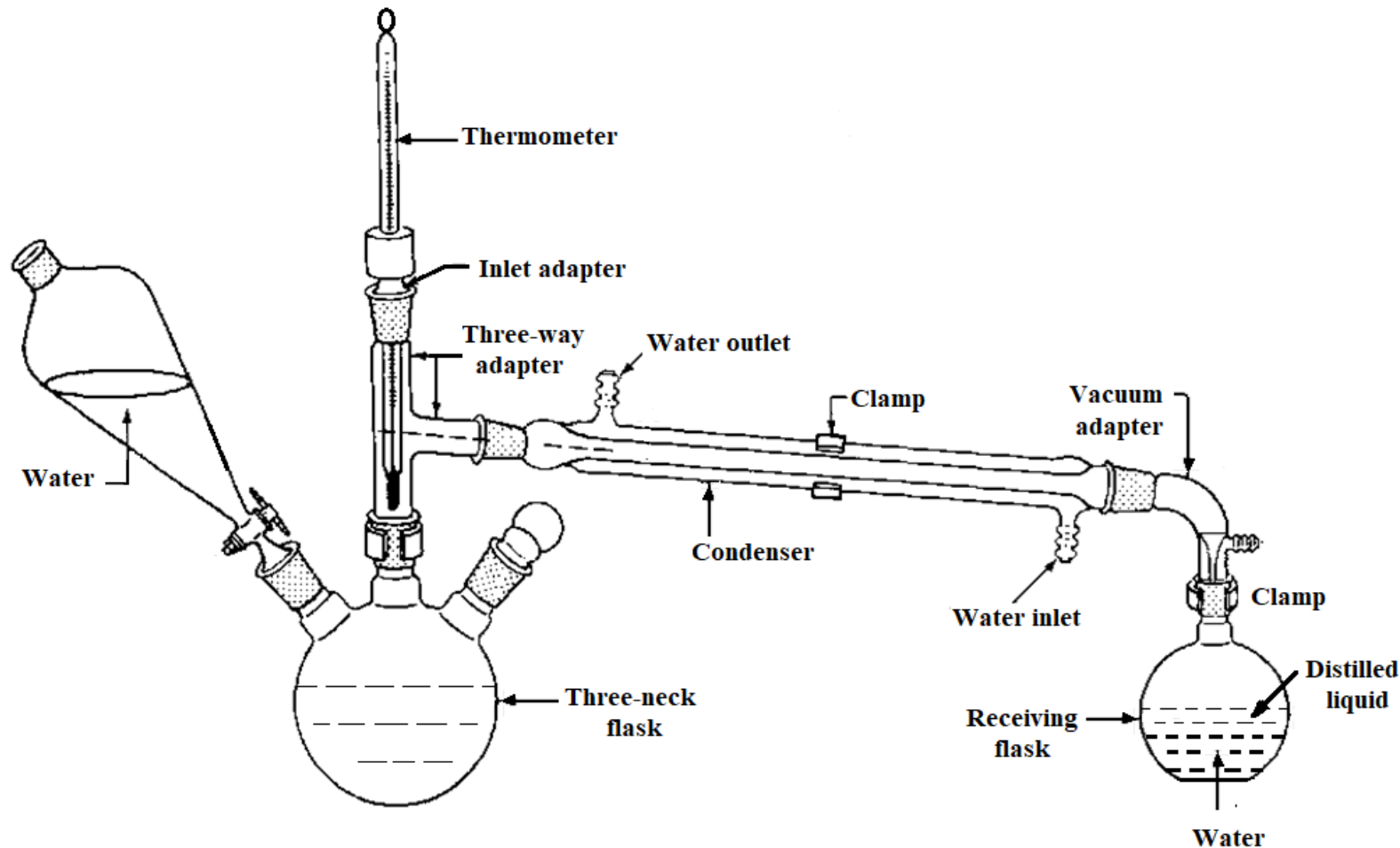
Hence, if the total pressure is fixed, then the system is fixed. Since there are two liquid phases, each will exert its own vapour pressure at the prevailing temperature and cannot be influenced by presence of the other. When the sum of the separate vapour pressures equals the total pressure, the mixture boils and

$$P_A + P_B = P_t$$

where  $P_A$  is the vapour pressure of pure water and  $P_B$  is that of pure *B*. Then the vapour composition is

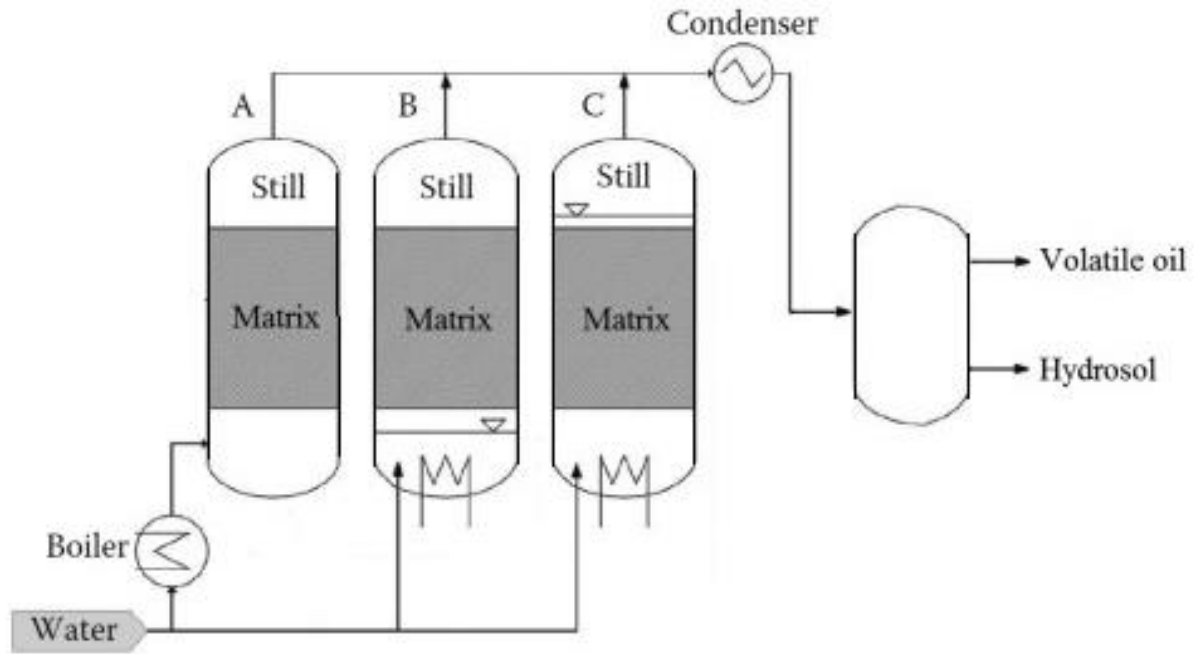
$$y_A = P_A/P_t \text{ and } y_B = P_B/P_t$$

As long as the two liquid phases are present, the mixture will boil at the same temperature, giving a vapour of constant composition,  $y_A$ . The temperature is found by using the vapour pressure curves of pure *A* and pure *B*.



**Steam Distillation Set-up**

In practice, the process uses water and/or steam as extracting agent to vaporize or liberate the volatile compounds from the raw material. The compounds are volatilized by absorbing heat from the steam, and are then transported to the steam where they are diffused. The resulting vapor phase is cooled and condensed prior to separating the water from the organic phase based on their immiscibility. In this process, two products are obtained: volatile oil and hydrosol. The volatile oil is in the upper phase and the hydrosol (water and some hydrolyzed compounds) is in the bottom phase of the decanter.



## Variants of steam distillation process

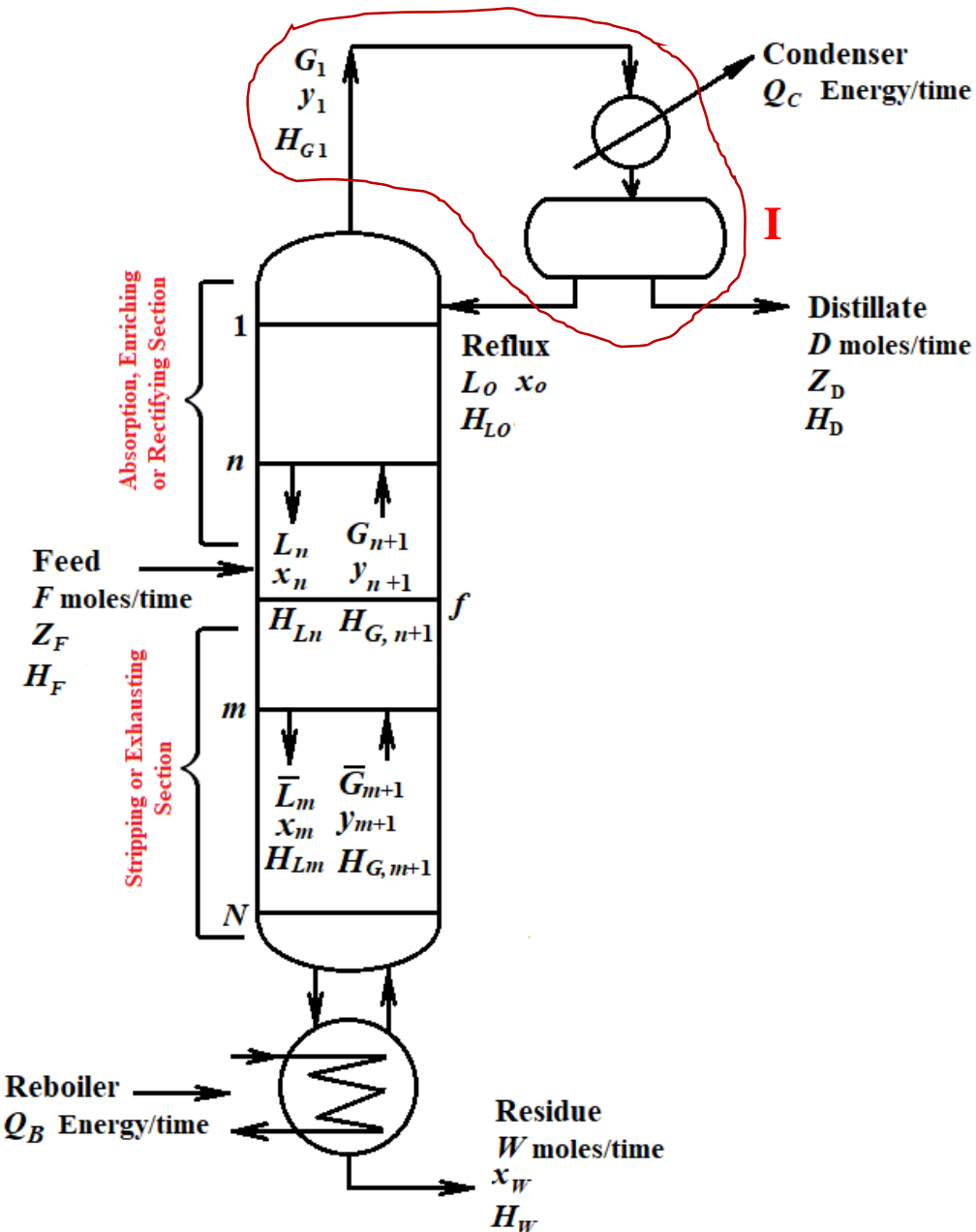
(A) dry steam distillation, (B) direct steam distillation, and (C) hydrodistillation (water distillation).

In direct steam distillation (B), the matrix is supported on a perforated grid or screen inserted slightly above the bottom of the still. This scheme does not allow direct contact with water, whereas the boiler can be inside or outside the still. The low-pressure saturated steam flows up through the matrix, collecting the evaporated compounds.

In hydrodistillation (C), the matrix is in direct contact with the boiling water either by floating or by being completely immersed depending on its density. The boiler is inside the still and agitation may be necessary to prevent agglutination.

In dry steam distillation (A), the matrix is supported and steam flows through it. The differences are due to the steam being generated outside the still and superheated at moderate pressures.

# Continuous Rectification or Fractionation



Reflux ratio: 
$$R = \frac{L_0}{D} \quad \dots (1)$$

Total material balance over envelope I:

$$G_1 = D + L_0 \quad \dots (2)$$

Or, 
$$G_1 = D + RD = D(R + 1) \quad \dots (3)$$

For substance A:

$$G_1 y_1 = D z_D + L_0 x_0 \quad \dots (4)$$

Enthalpy balance over envelope I provides the heat load of the condenser:

$$G_1 H_{G1} = Q_C + L_0 H_{L0} + D H_D \quad \dots (5)$$

$$\Rightarrow Q_C = D[(R + 1)H_{G1} - R H_{L0} - H_D] \quad \dots (6)$$

Reboiler heat load is obtained by complete enthalpy balance about the entire column:

$$Q_B = D H_D + W H_W + Q_C + Q_L - F H_F \quad \dots (7)$$

# **Design of Multistage Distillation Column (Tray Tower)**

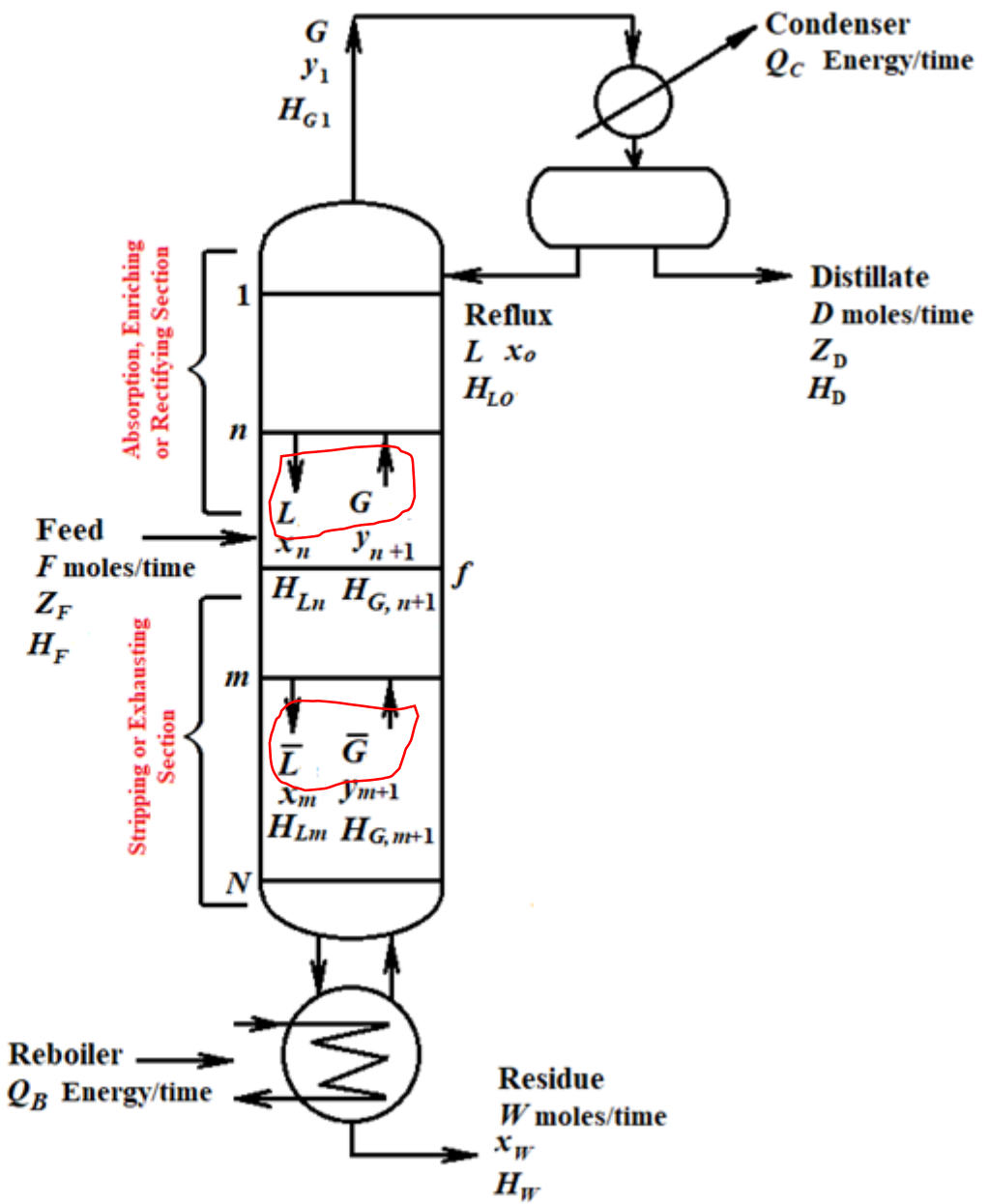
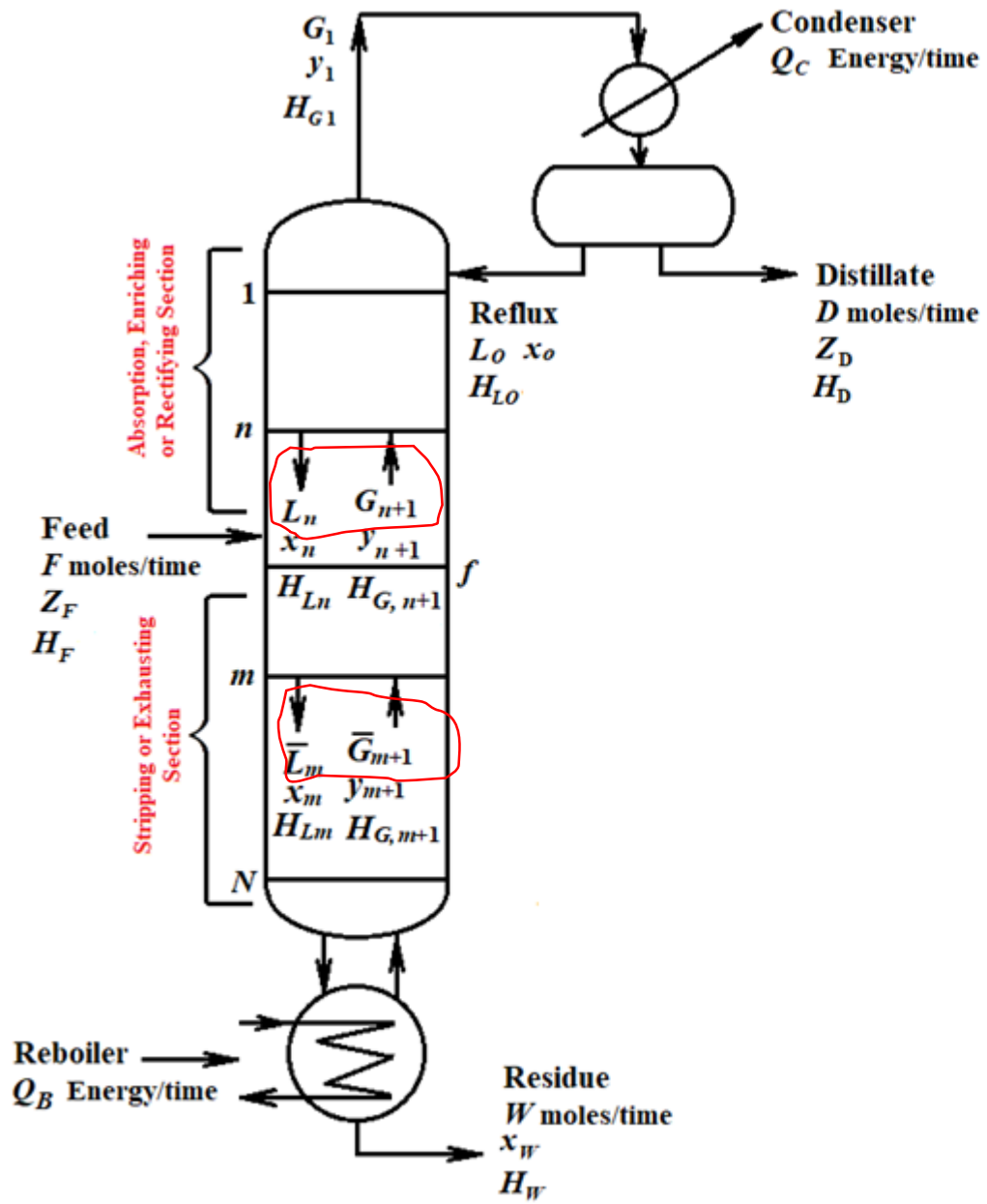
**Method of McCabe and Thiele**

**Method of Ponchon and Savarit**

## **Design of Tray Tower - Method of McCabe and Thiele**

**Principle of equimolal overflow and vaporization:**

**The rate of liquid flow from each tray in a section of the tower is constant on a molar basis.**





## Enriching Section: Total Condenser - Reflux at the Bubble Point

A total material balance over the envelope gives:

$$G = L + D = D(R + 1) \quad \dots (8)$$

For component A

$$G y_{n+1} = L x_n + D x_D \quad \dots (9)$$

From which the enriching section operating line is

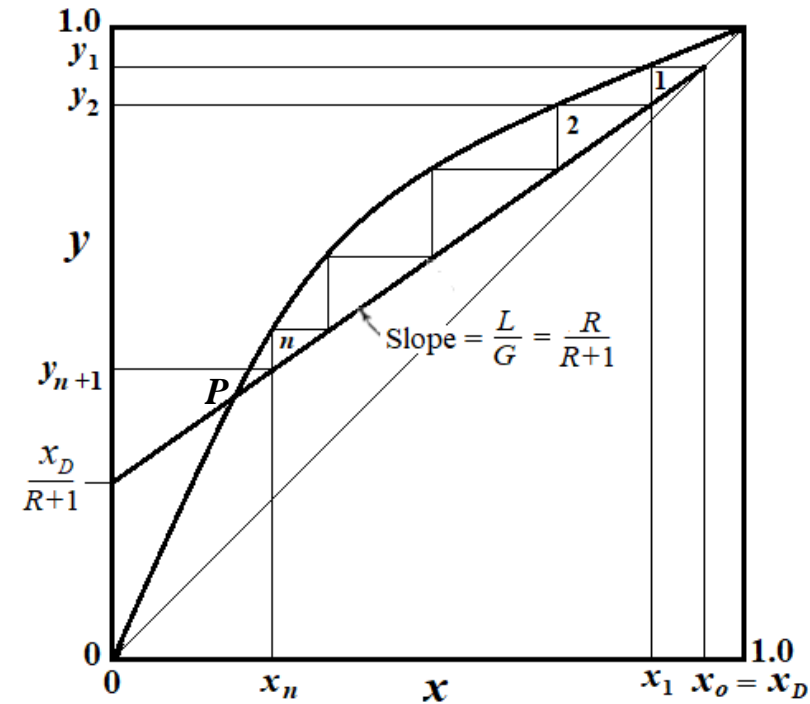
$$y_{n+1} = \frac{L}{G} x_n + \frac{D}{G} x_D \quad \dots (10)$$

Replacing  $G$  of Eqn. (10) by Eqn. (8) gives:

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \quad \dots (11)$$

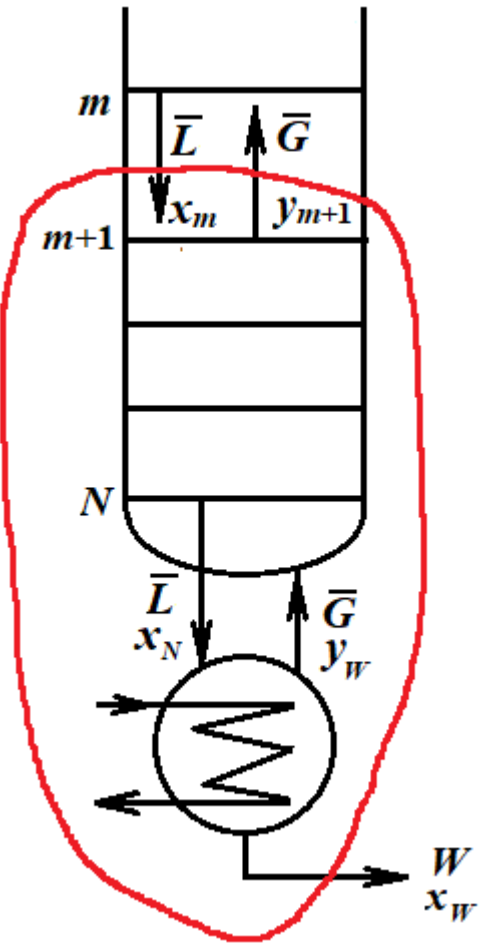
This is the equation of a straight line on  $x, y$  coordinates of slope  $L/G = R/(R+1)$  and with a  $y$ -intercept of  $x_D/(R+1)$ .

Setting  $x_n = x_D$ ,  $y_{n+1} = x_D$ , so that the line passes through the point  $x = y = x_D$  on the  $45^\circ$  diagonal. This point and the  $y$ -intercept permit easy construction of the operating line.



**The steps cannot be carried further than point P.**

## Stripping Section: Reboiled Vapour in Equilibrium with Residue



Total material balance over the envelope:

$$\bar{L} = \bar{G} + W \quad \dots (12)$$

Component (A) material balance:

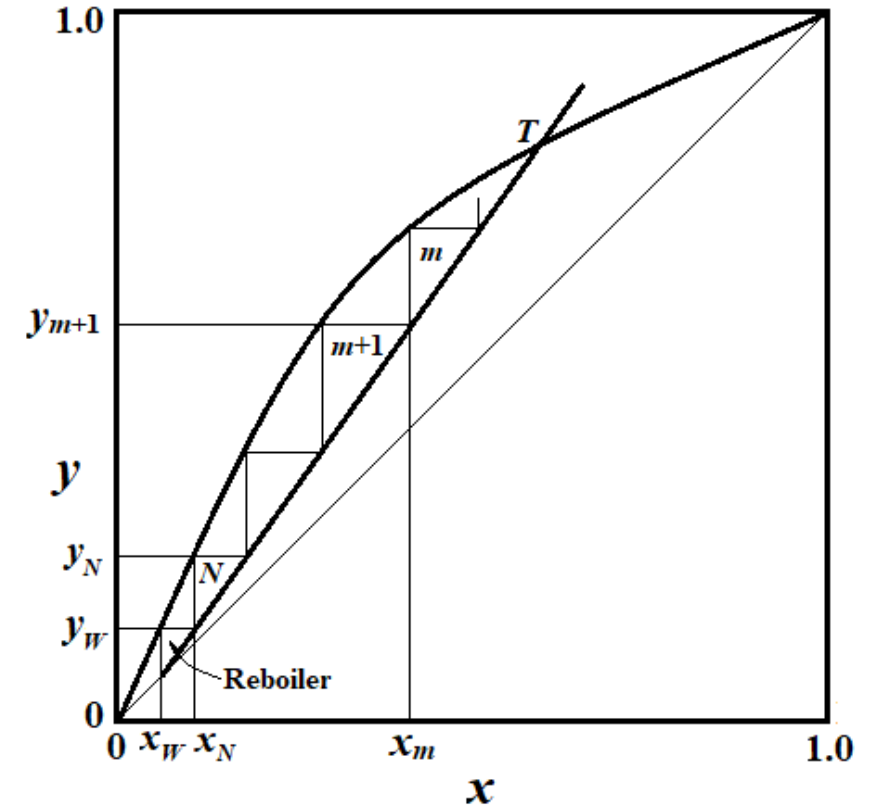
$$\bar{L} x_m = \bar{G} y_{m+1} + W x_W \quad \dots (13)$$

$$\Rightarrow y_{m+1} = \frac{\bar{L}}{\bar{G}} x_m - \frac{W}{\bar{G}} x_W \quad \dots (14)$$

Replacing  $G$  with the help of Eqn. (12) as  $\bar{G} = \bar{L} - W$

$$y_{m+1} = \frac{\bar{L}}{\bar{L} - W} x_m - \frac{W}{\bar{L} - W} x_W \quad \dots (15)$$

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 reboiled vapour  $y_W$  is in equilibrium with the residue  $x_W$ , the first step of the staircase construction represents the reboiler.



**The steps can be carrier no further than point T.**

## Introduction of Feed

Overall material balance near the feed tray:

$$F + L + \bar{G} = G + \bar{L} \quad \dots (16)$$

An enthalpy balance gives

$$F H_F + L H_{L_{f-1}} + \bar{G} H_{G_{f+1}} = G H_{G_f} + \bar{L} H_{L_f} \quad \dots (17)$$

The vapours and liquids inside the tower are all saturated, and the molal enthalpies of all saturated vapours 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  $H_{G_f} = H_{G_{f+1}} = H_G$  and  $H_{L_{f-1}} = H_{L_f} = H_L$ . Enthalpy balance Eqn. (17) then becomes

$$(\bar{L} - L)H_L = (\bar{G} - G)H_G + F H_F \quad \dots (18)$$

Combining this with Eqn. (16) gives

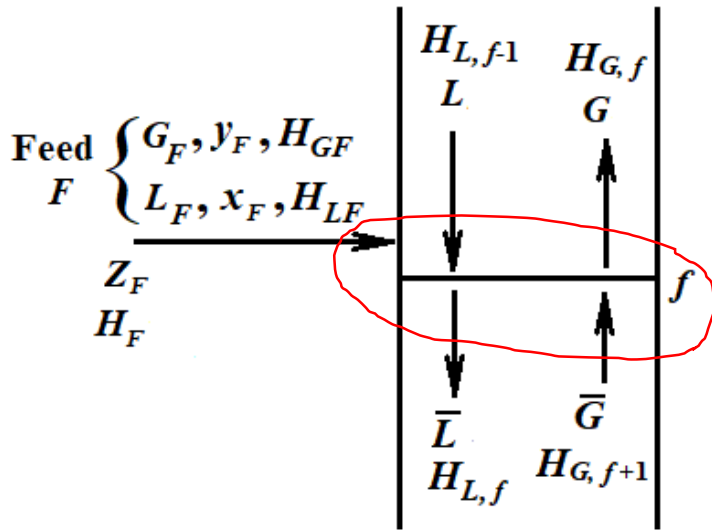
$$\frac{\bar{L} - L}{F} = \frac{H_G - H_F}{H_G - H_L} = q \quad \dots (19)$$

The quantity  **$q$**  is thus seen to be the **heat required to convert one mole of feed from its condition  $H_F$  to a saturated vapour, 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 vapour, for each of which the value of  **$q$**  will be different.

Combining Eqns. (16) and (19), we get

$$\bar{G} - G = F(q - 1) \quad \dots (20)$$

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



The point of intersection of the two operating lines will help locate the exhausting-section operating line. This can be established as follows. Rewriting Eqns. (9) and (13) without the tray subscripts, we have

$$G y_{n+1} = L x_n + D x_D \quad \dots (21)$$

$$\bar{L} x_m = \bar{G} y_{m+1} + W x_W \quad \dots (22)$$

Subtracting gives

$$(\bar{G} - G) y = (\bar{L} - L) x - (W x_W + D x_D) \quad \dots (23)$$

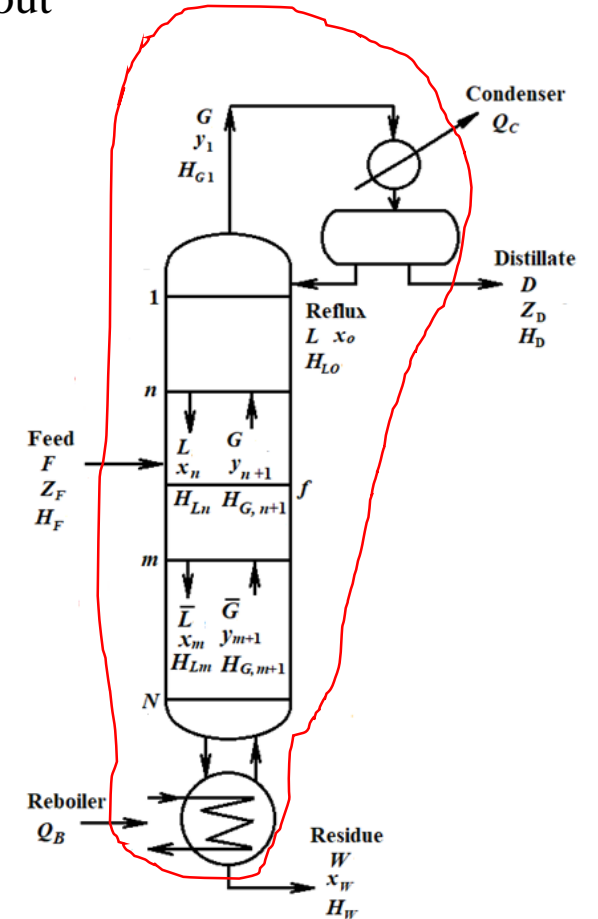
Further, by an overall material balance

$$F z_F = W x_W + D x_D \quad \dots (24)$$

Substituting this and Eqns. (19) and (20) in Eqn. (23) gives

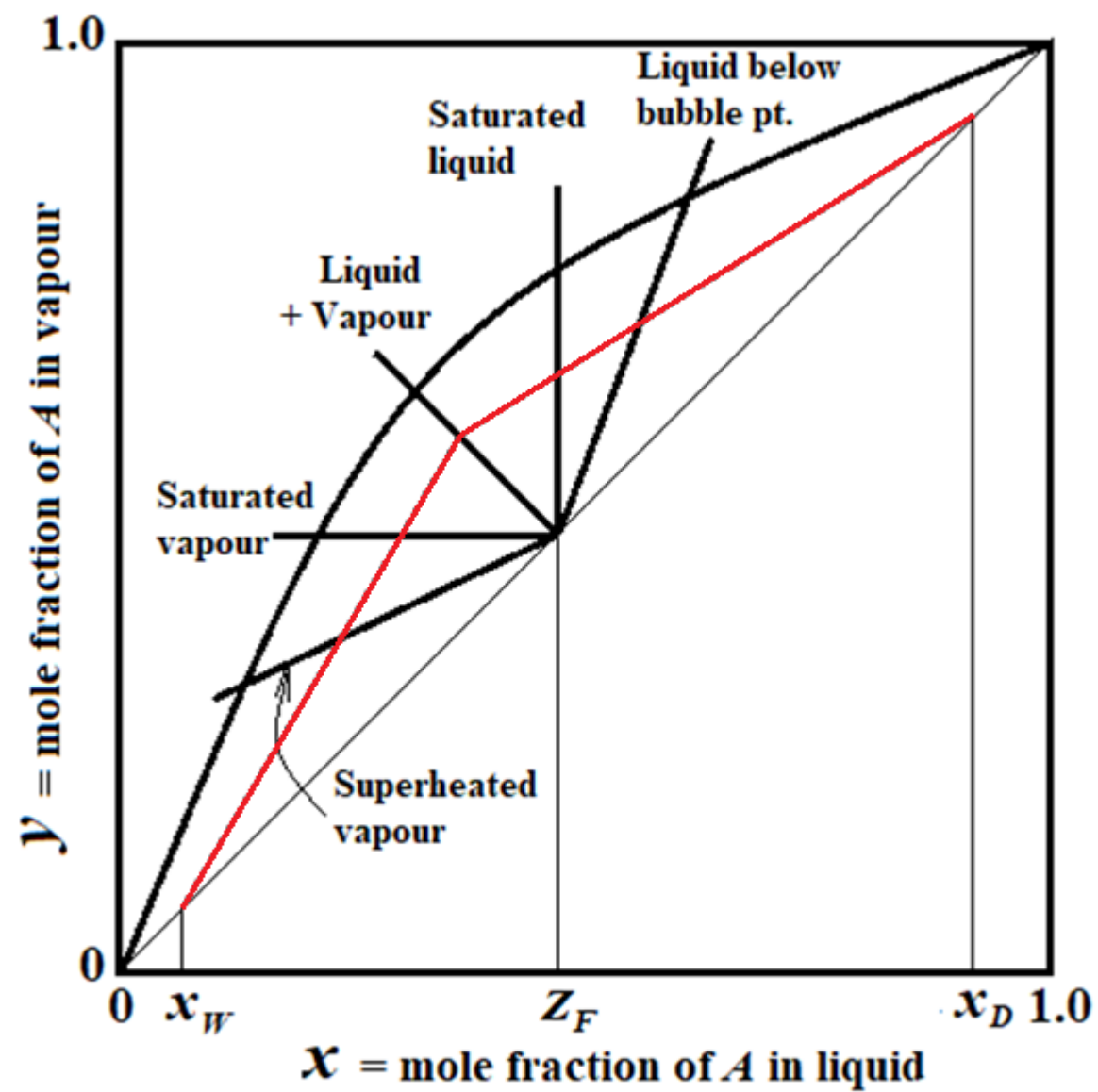
$$y = \frac{q}{q-1} x - \frac{z_F}{q-1} \quad \dots (25)$$

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  $45^\circ$  diagonal. It is clear that for a given feed condition, fixing the reflux ratio at the top of the column automatically establishes the liquid/vapour ratio in the exhausting section and the reboiler heat load as well.



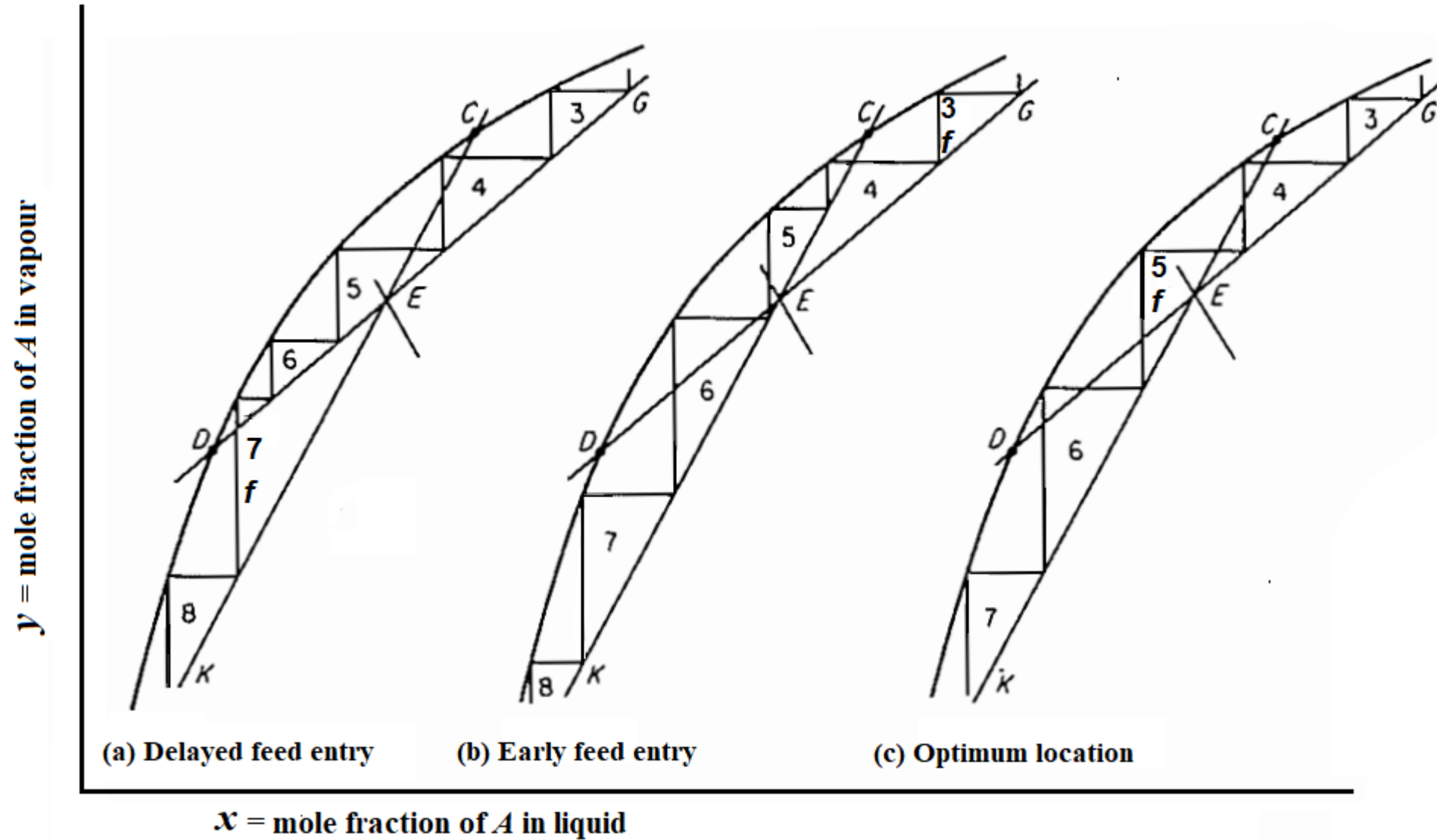
# Various Thermal Conditions of Feed

Feed Condition	$G_F$ mol/(time)	$L_F$ mol/(time)	$H_{GF}$ energy/mol	$H_{LF}$ energy/mol	$H_F$ energy/mol	$q = \frac{H_G - H_F}{H_G - H_L}$	$\frac{q}{q-1}$
Liquid below bubble point	0	$F$		$H_F$	$H_F < H_L$	$> 1.0$	$> 1.0$
Saturated liquid	0	$F$		$H_F$	$H_L$	1.0	$\infty$
Mixture of liquid and vapor	$G_F$ ( $F = G_F + L_F$ )	$L_F$ ( $F = G_F + L_F$ )	$H_G$	$H_L$	$H_G > H_F > H_L$	$L_F/F$ $1.0 > q > 0$	$\frac{L_F}{L_F - F}$
Saturated vapor	$F$	0	$H_F$		$H_G$	0	0
Superheated vapor	$F$	0	$H_F$		$H_F > H_G$	$< 0$	$1.0 > \frac{q}{q-1} > 0$

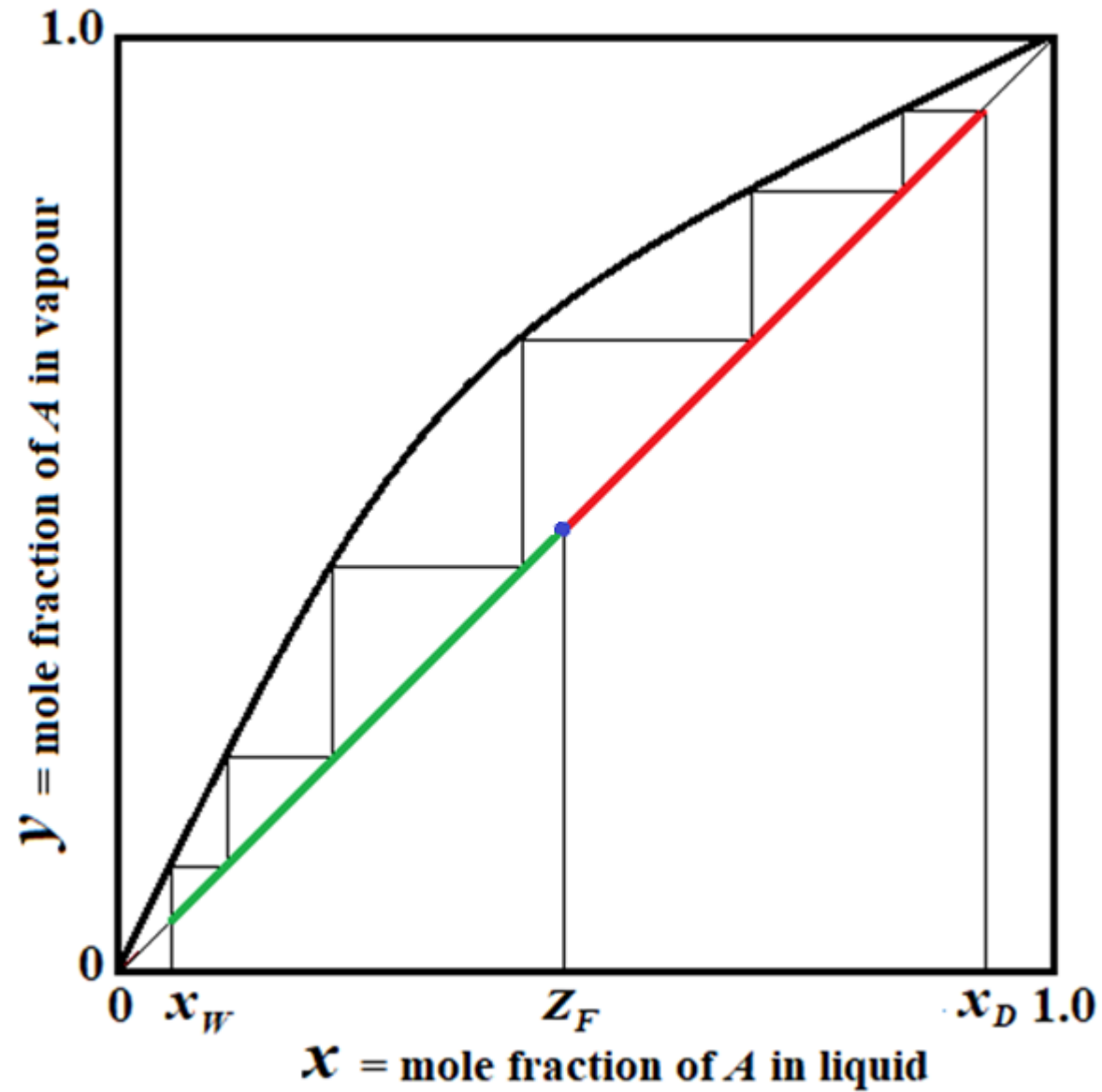


**Location of  $q$ -line for typical feed conditions**

## Determination of Optimum Location of Feed Tray



## Total Reflux, or Infinite Reflux Ratio





## Minimum Number of Trays for Constant Relative Volatility

A useful analytical expression for the minimum number of theoretical trays can be obtained for cases where the relative volatility is reasonably constant. Applying defining equation for relative volatility to the residue product gives:

$$\frac{y_W}{1 - y_W} = \alpha_W \frac{x_W}{1 - x_W} \quad \dots (26)$$

where  $\alpha_W$  is the relative volatility at the reboiler. At total reflux the operating line coincides with the 45° diagonal so that  $y_W = x_{N_m}$ . Therefore,

$$\frac{x_{N_m}}{1 - x_{N_m}} = \alpha_W \frac{x_W}{1 - x_W} \quad \dots (27)$$

Similarly, for the last tray of the column, where  $\alpha_{N_m}$  pertains,

$$\frac{y_{N_m}}{1 - y_{N_m}} = \alpha_{N_m} \frac{x_{N_m}}{1 - x_{N_m}} = \alpha_{N_m} \alpha_W \frac{x_W}{1 - x_W} \quad \dots (28)$$

This procedure can be continued up the column until ultimately

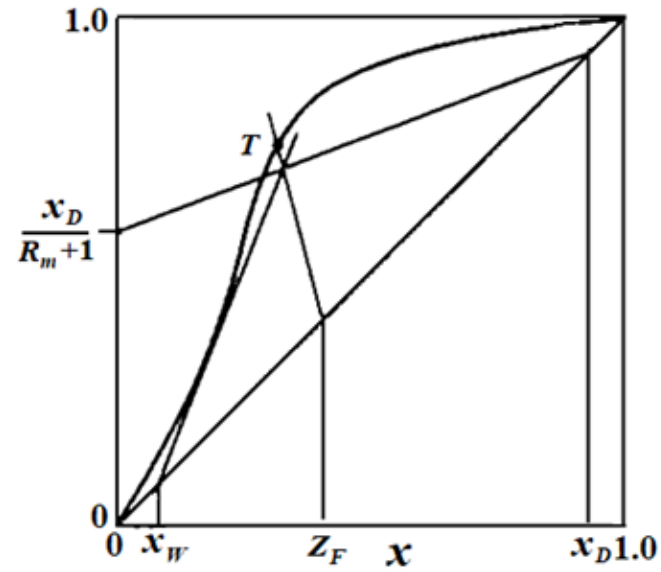
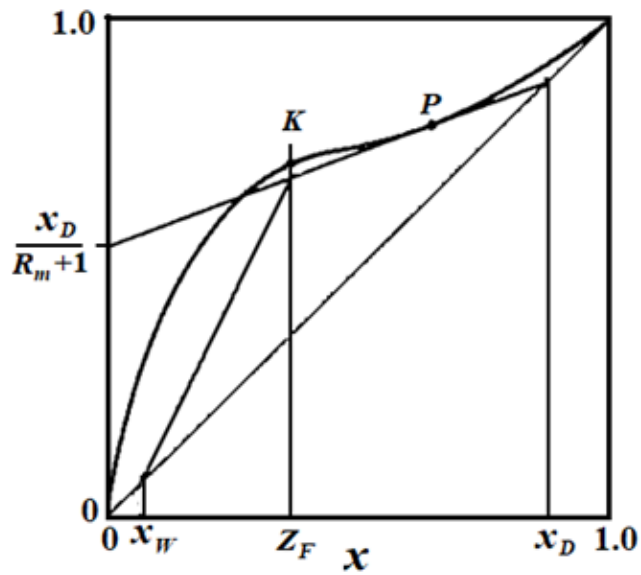
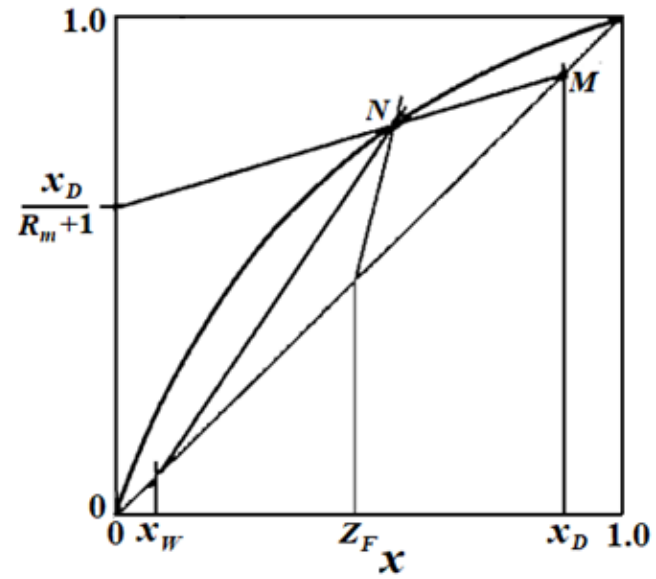
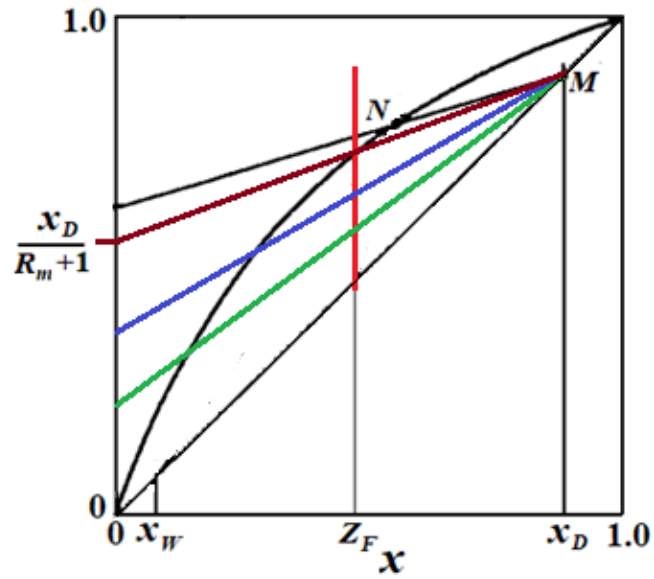
$$\frac{y_1}{1 - y_1} = \frac{x_D}{1 - x_D} = \alpha_1 \alpha_2 \dots \alpha_{N_m} \alpha_W \frac{x_W}{1 - x_W} \quad \dots (29)$$

If some average relative volatility  $\alpha_{av}$  can be used, then

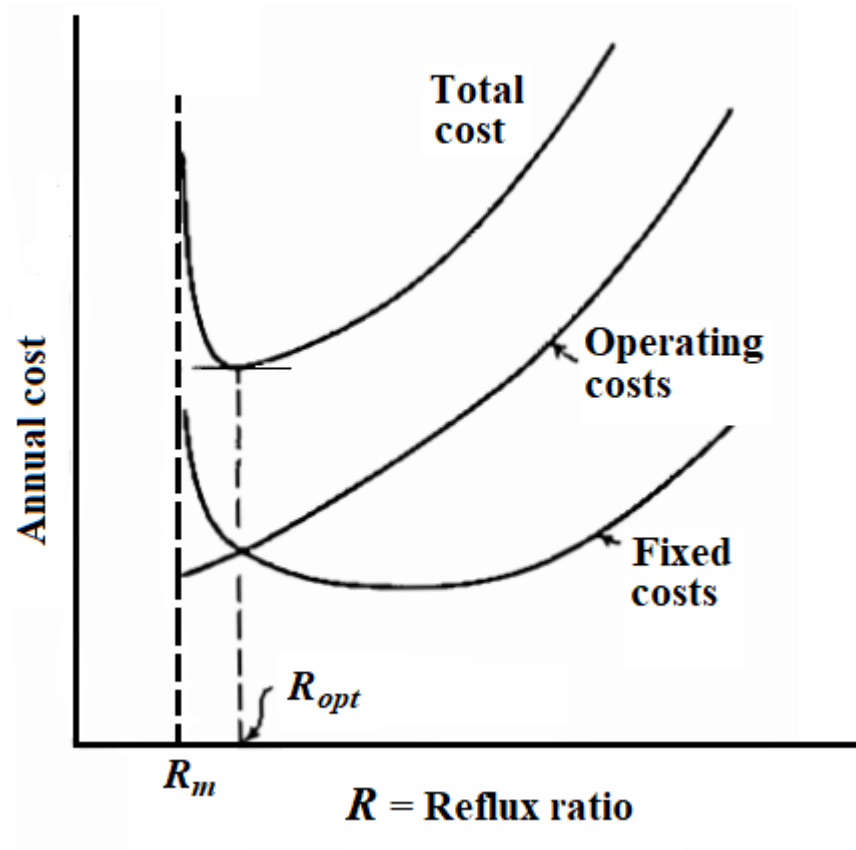
$$\frac{x_D}{1-x_D} = \alpha_{av}^{N_m+1} \frac{x_W}{1-x_W}$$
$$\Rightarrow N_m + 1 = \frac{\log \frac{x_D}{1-x_D} \frac{1-x_W}{x_W}}{\log \alpha_{av}} \quad \dots (30)$$

which is known as the *Fenske's equation*. The total number of theoretical stages to produce product  $x_D$  and  $x_W$  is  $N_m+1$ , which then includes the reboiler. For small variations in  $\alpha$ ,  $\alpha_{av}$  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  $\alpha$  is nearly constant.

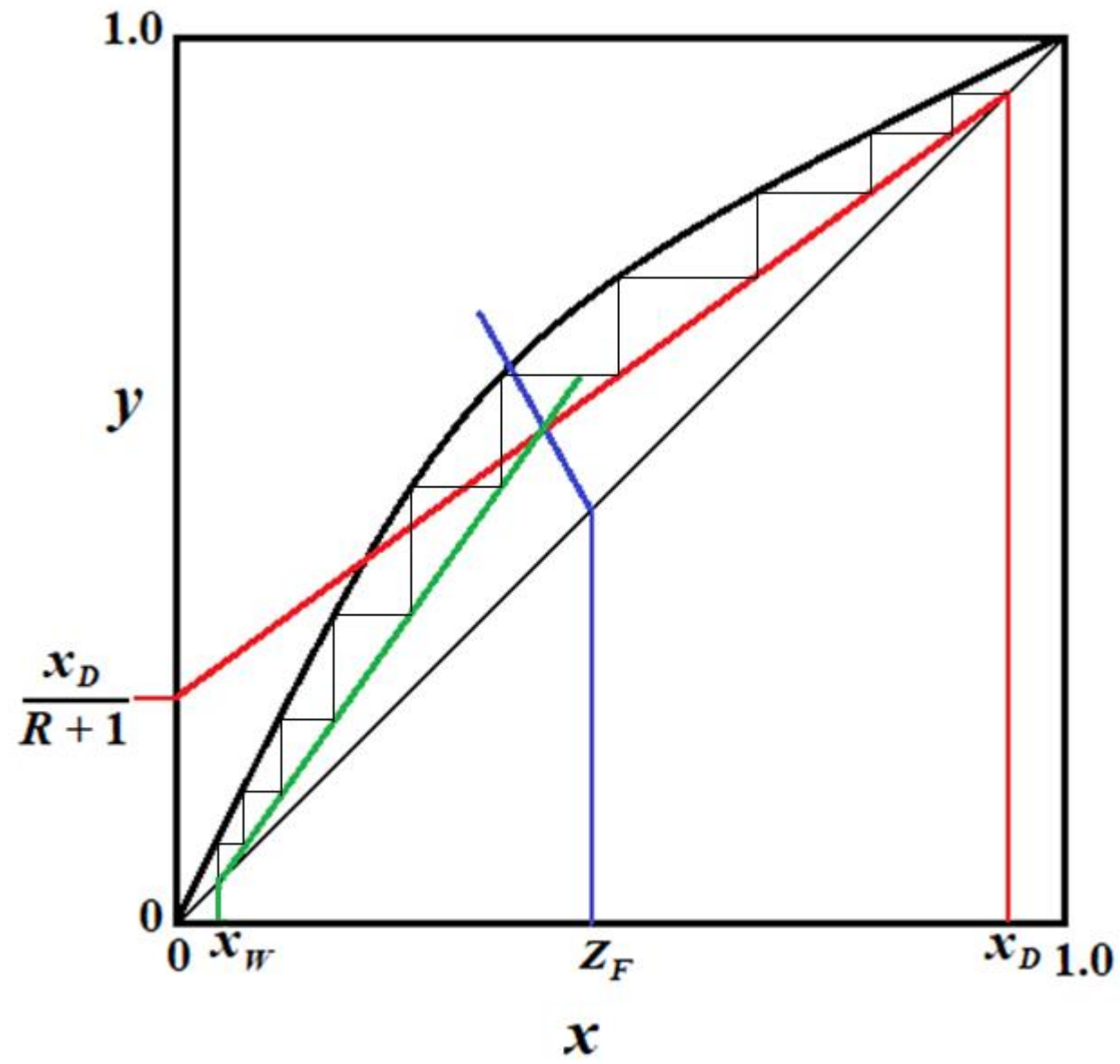
# Determination of Minimum Reflux Ratio



## Determination of Optimum or Operating Reflux Ratio



$$R_{opt} \Rightarrow 1.2 R_m \text{ to } 1.5 R_m$$



**Determination of number of ideal trays for continuous rectification**

## Cold Reflux

If the overhead vapour is condensed and cooled below its bubble point so that the reflux liquid is cold, vapour  $G_1$  rising from the top tray will be less in quantity than that for the rest of the enriching section since some will be required to condense and heat the reflux to its bubble point. External reflux  $L_o$  will require heat to the extent of  $L_o C_{Lo} M_{av} (t_{bp,R} - t_R)$ , where  $t_{bp,R}$  and  $t_R$  are the reflux bubble point and actual temperatures, respectively. An amount of vapour,  $L_o C_{Lo} M_{av} (t_{bp,R} - t_R) / (\lambda M)_{av}$ , will condense to provide the heat, and the condensed vapour adds to  $L_o$  to provide  $L$ , the liquid flow rate below the top tray. Therefore,

$$L = L_o + \frac{L_o C_{Lo} M_{av} (t_{bp,R} - t_R)}{(\lambda M)_{av}} = RD \left[ 1 + \frac{C_{Lo} M_{av} (t_{bp,R} - t_R)}{(\lambda M)_{av}} \right] \quad \dots (40)$$

where  $R$  is the usual external reflux ratio,  $L_o/D$ . Defining an apparent reflux ratio  $R'$  by

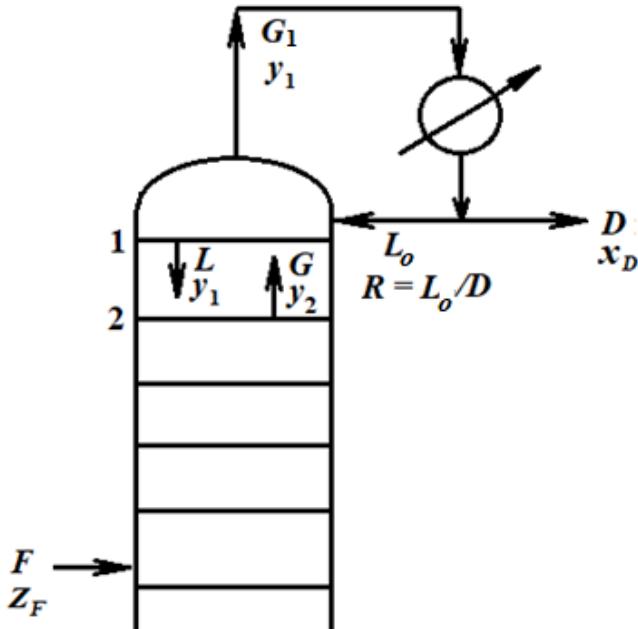
$$R' = \frac{L}{D} = \frac{L}{G - L} \quad \dots (41)$$

gives

$$R' = R \left[ 1 + \frac{C_{Lo} M_{av} (t_{bp,R} - t_R)}{(\lambda M)_{av}} \right] \quad \dots (42)$$

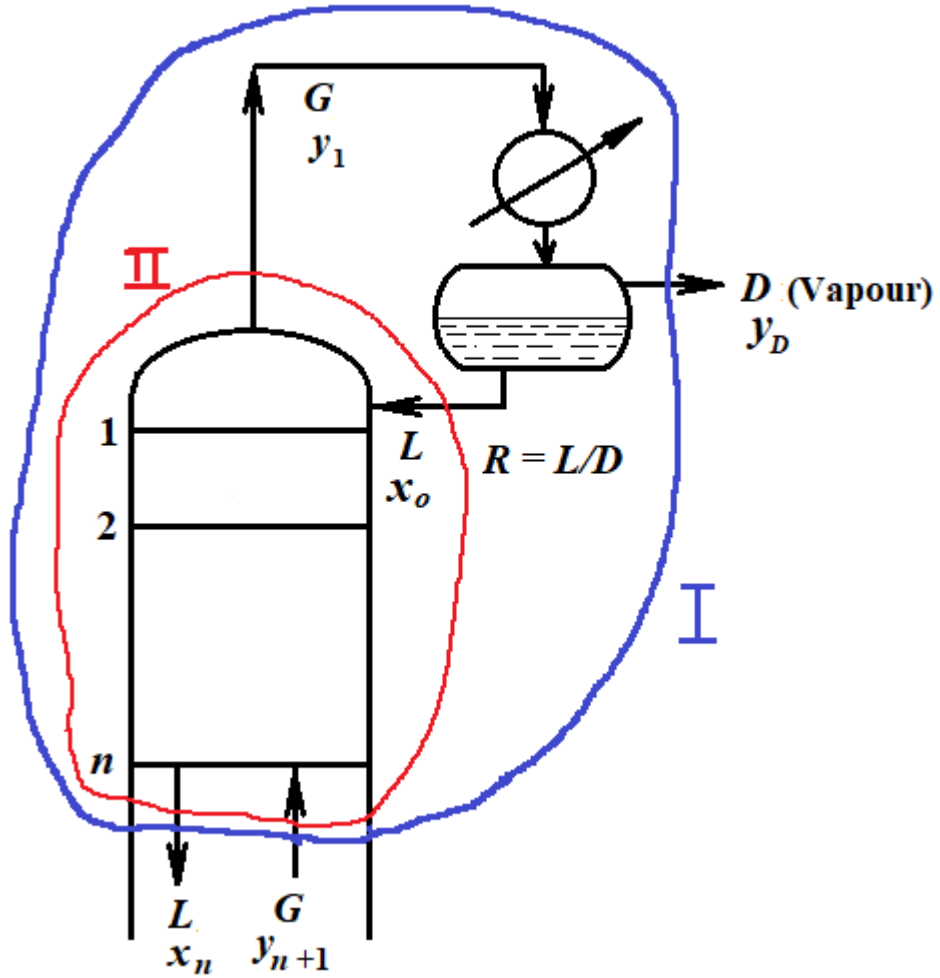
The enriching operating line becomes

$$y_{n+1} = \frac{R'}{R' + 1} x_n + \frac{x_D}{R' + 1} \quad \dots (43)$$



And it is plotted through  $y = x = x_D$ , with a y intercept at  $x_D/(R' + 1)$  and a slope of  $R'/(R' + 1)$ .

# Equilibrium Partial Condenser



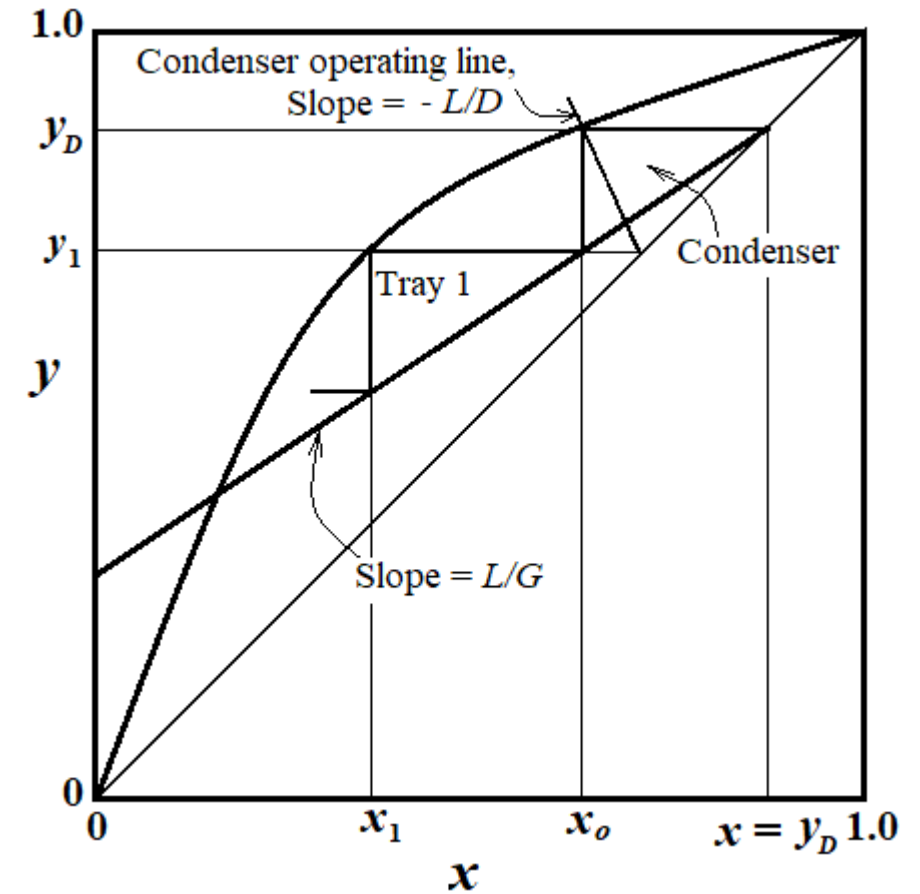
**Envelope – I:**

$$G = L + D \quad \dots (37)$$

$$G y_{n+1} = L x_n + D y_D \quad \dots (38)$$

**Envelope – II:**

$$G y_{n+1} + L x_0 = G y_1 + L x_n \quad \dots (39)$$



## Use of Open Steam

Overall material balance:

$$F + \bar{G} = D + W \quad \dots (31)$$

Component A balance:

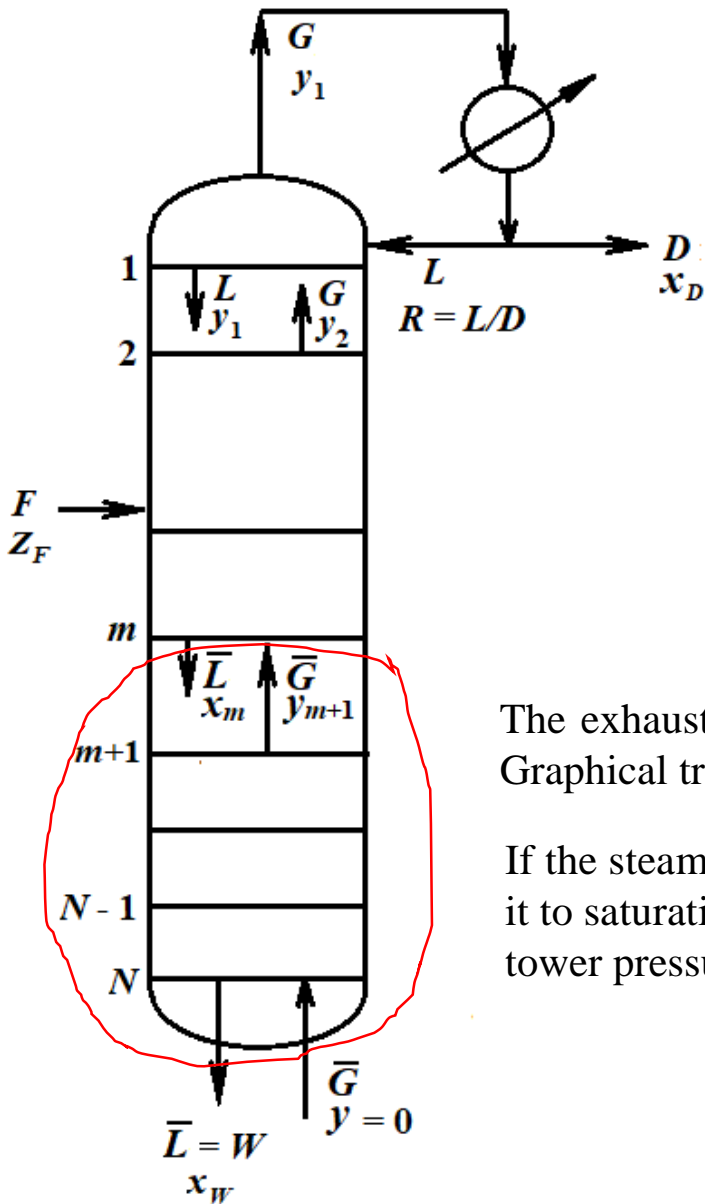
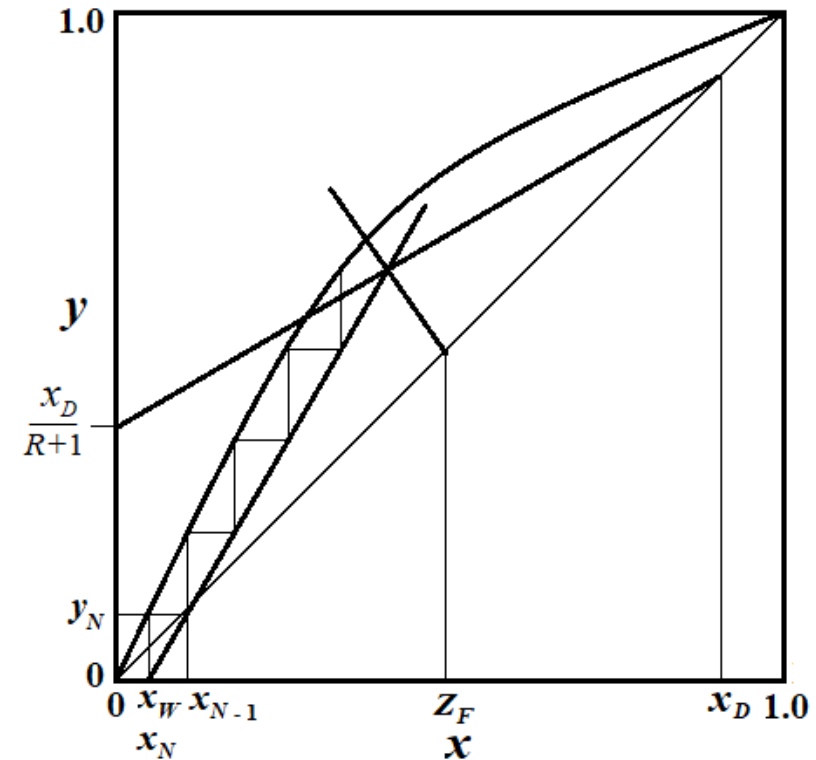
$$F z_F = D x_D + W x_W \quad \dots (32)$$

A material balance for component A below tray  $m$  in the exhausting section gives:

$$\bar{L} x_m + \bar{G} (0) = \bar{G} y_{m+1} + W x_W \quad \dots (33)$$

Since  $\bar{L} = W$  in this case,

$$\frac{\bar{L}}{\bar{G}} = \frac{y_{m+1}}{x_m - x_W} \quad \dots (34)$$



The exhausting section operating line, therefore, passes through the point  $(x = x_w, y = 0)$  as shown in the Figure. Graphical tray construction must, therefore, be continued to the  $x$  axis of the diagram.

If the steam entering the tower,  $\bar{G}_{N+1}$ , is superheated, it will vaporize liquid on tray  $N$  to the extent necessary to bring it to saturation,  $\bar{G}_{N+1}(H_{G,N+1} - H_{G,sat}) / \lambda M$ , where  $H_{G,sat}$  is the enthalpy of saturated steam and  $\lambda M$  the molar latent heat at the tower pressure.

$$\bar{G} = \bar{G}_{N+1} \left( 1 + \frac{H_{G,N+1} - H_{G,sat}}{\lambda M} \right) \quad \dots (35)$$

and 
$$\bar{L} = \bar{L}_N + (\bar{G} - \bar{G}_{N+1}) \quad \dots (36)$$

from which the internal  $\bar{L}/\bar{G}$  ratio can be computed.

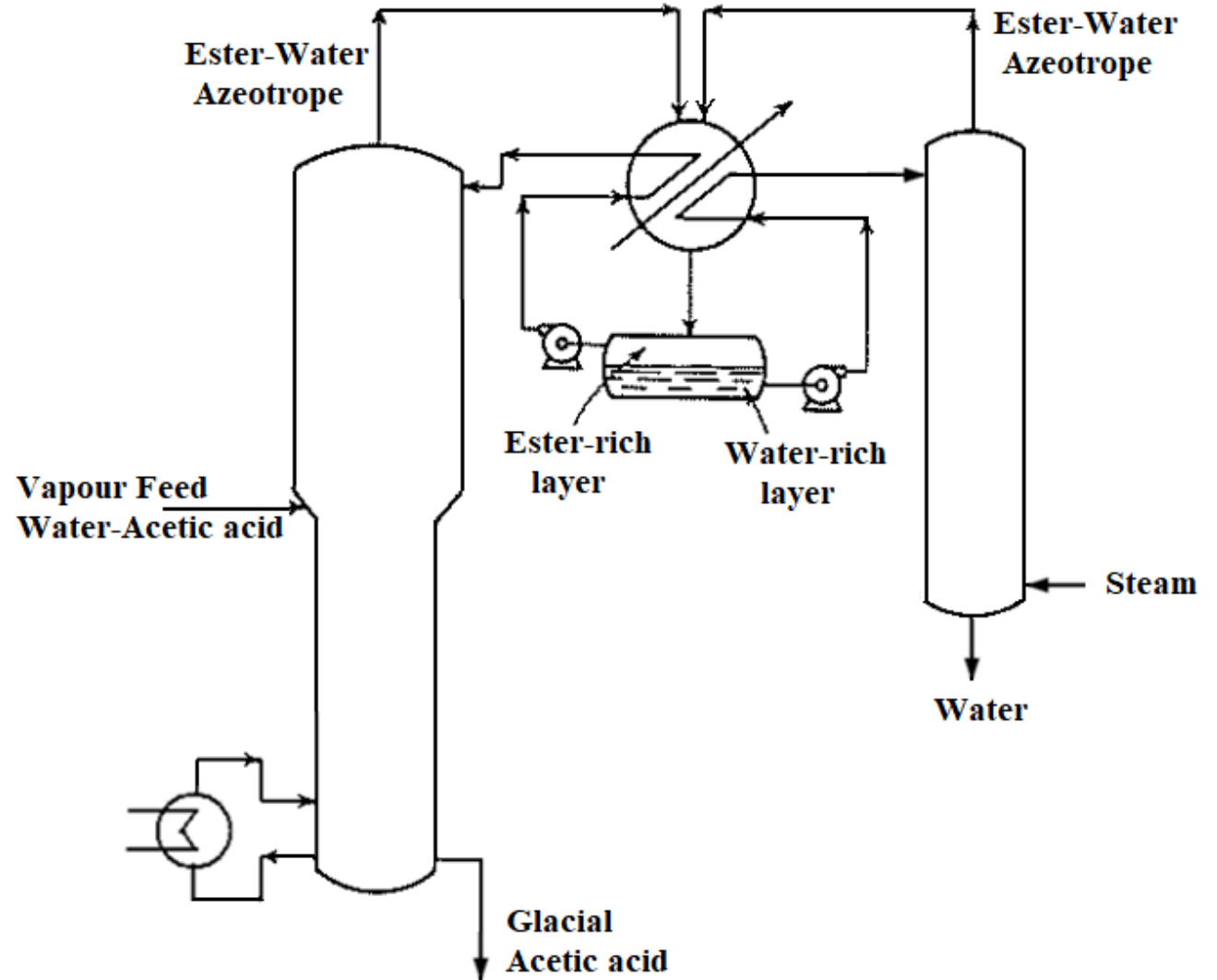
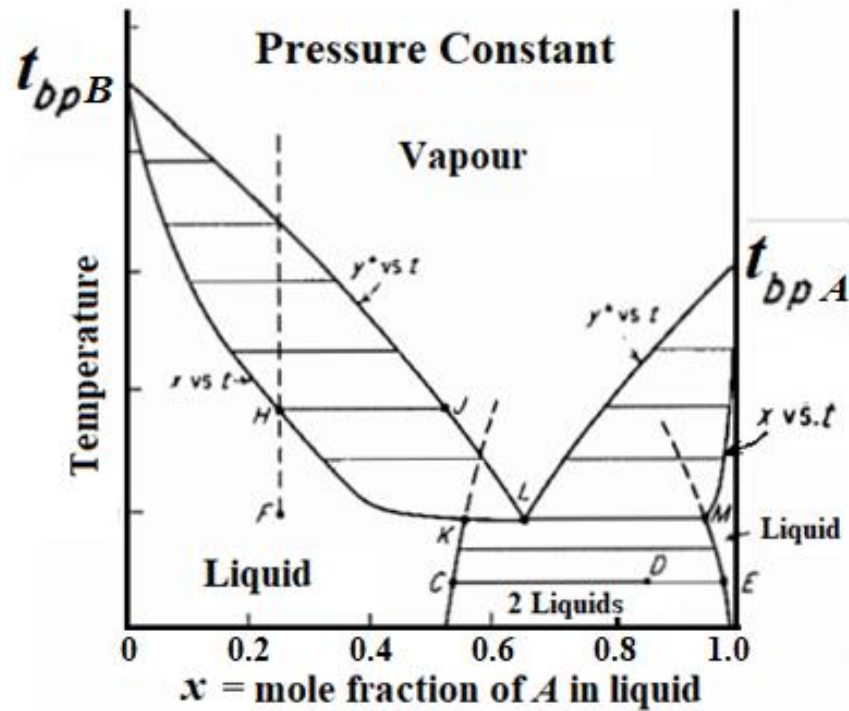


# Azeotropic Distillation

Water (bp = 100 °C) – Acetic acid (bp = 118.1 °C)

**Entrainer:** Butyl acetate (bp = 181.4 °C)

**Heteroazeotrope** (bp = 90.2 °C)



## Choice of Entrainer

The entrainer should **preferably form a low-boiling azeotrope** with only one of the constituents of the binary mixture it is desired to separate, preferably the constituent present in the minority so as to reduce the heat requirements of the process.

The new azeotrope **must be of sufficient volatility** to make it readily separable from the remaining constituent so that inappreciable amounts of the entrainer will appear in the residue product.

It should **preferably be lean in entrainer content**, to reduce the amount of vaporization necessary in the distillation. It should **preferably be of the heterogeneous – liquid type**, which then simplifies greatly the recovery of the entrainer.

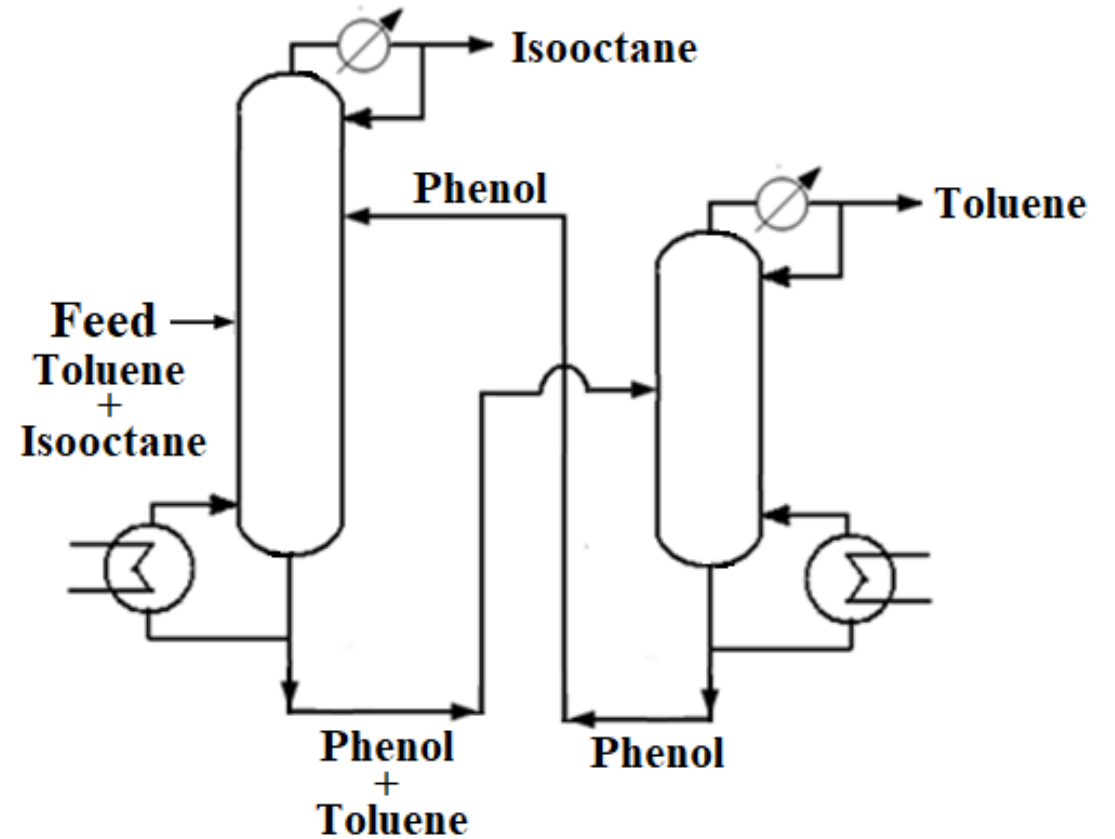
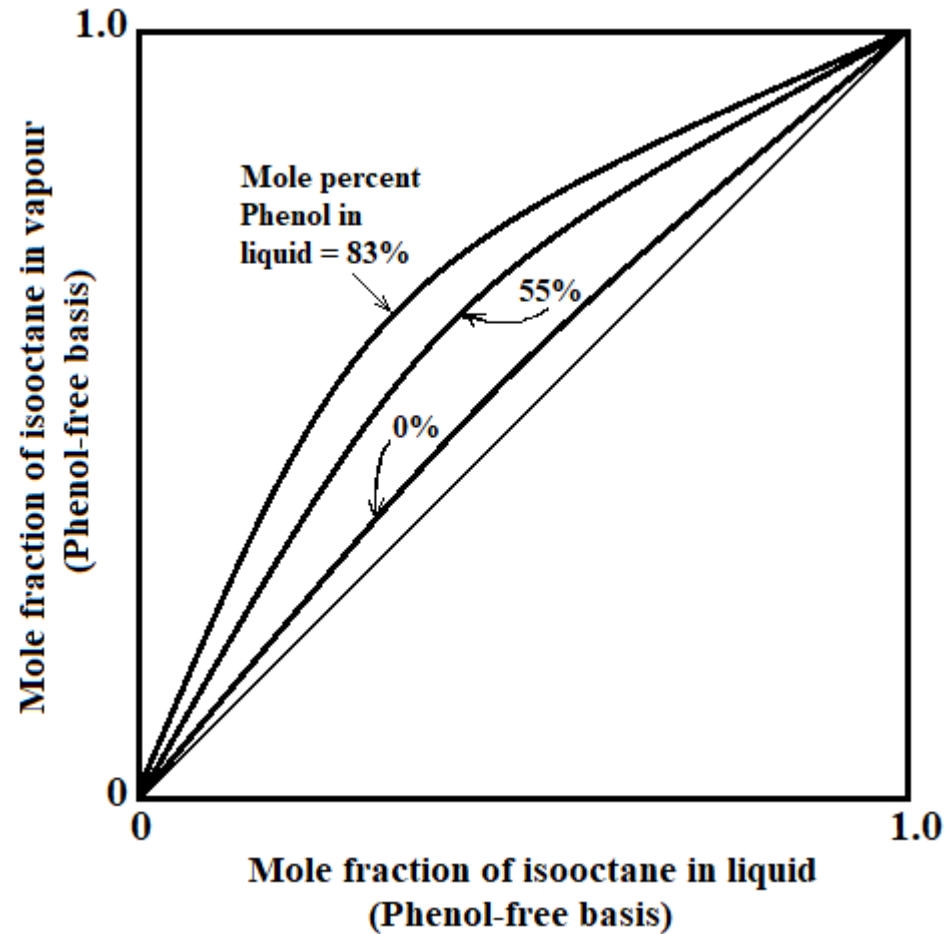
In addition, a satisfactory entrainer must be

- (1) **cheap and readily available**,
- (2) **chemically stable and inactive** toward the solution to be separated,
- (3) **noncorrosive** toward common construction materials,
- (4) **nontoxic**,
- (5) of **low latent heat of vaporization**,
- (6) of **low freezing point** to facilitate storage and outdoor handling, and
- (7) of **low viscosity** to provide high tray efficiencies.

# Extractive Distillation

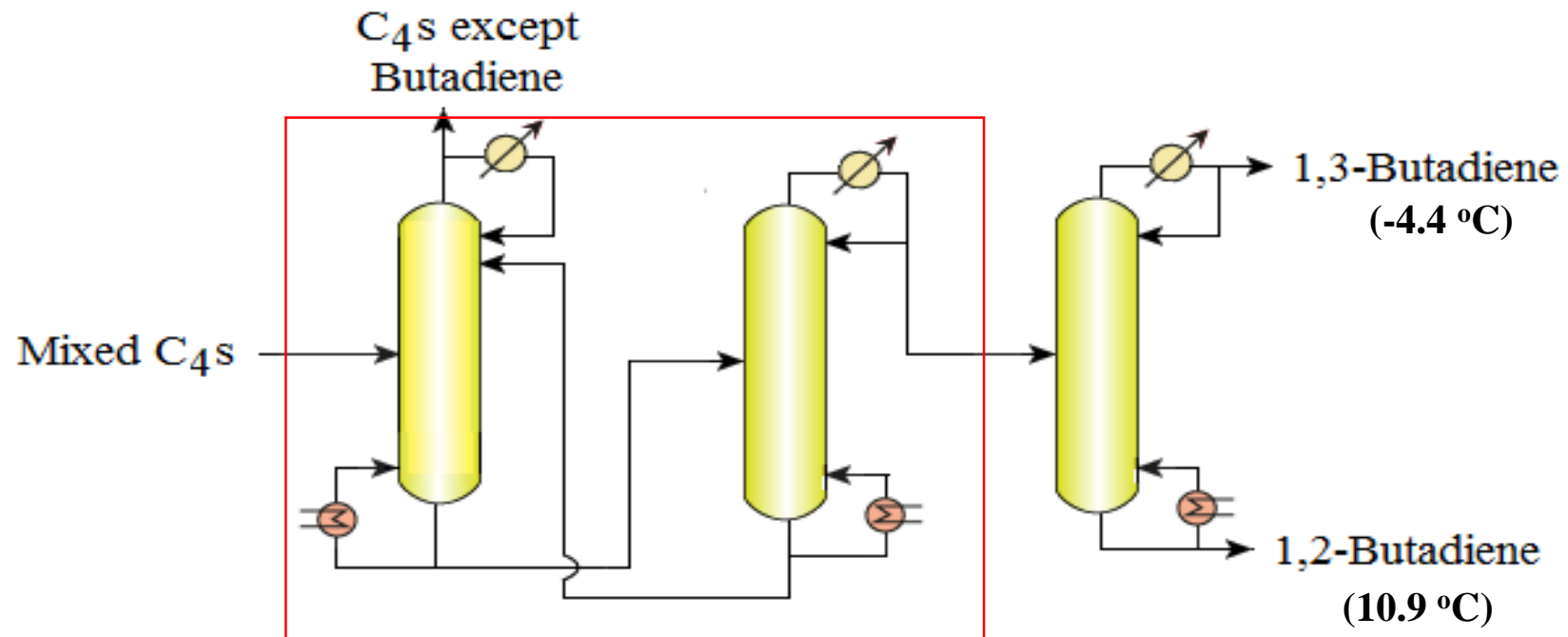
Toluene (bp = 110.8 °C) – *iso*-Octane (bp = 99.3 °C)

Solvent: Phenol (bp = 181.4 °C)



## Typical Composition of Mixed C<sub>4</sub>s Stream of Naphtha Cracker

Component	C <sub>3</sub>	n-C <sub>4</sub>	i-C <sub>4</sub>	i-C <sub>4</sub> =	1- C <sub>4</sub> =	2- C <sub>4</sub> =	Butadiene	C <sub>5</sub> <sup>+</sup>
Percentage	0.5	3.0	1.0	23.0	14.0	11.0	47.0	0.5



**Solvent: Acetonitrile (bp = 82 °C)**

**Separation of Butadiene from Mixed C<sub>4</sub>s by Extractive Distillation**

**Requirements of a satisfactory extractive distillation solvent** are:

- (1) **High selectivity**, or ability to alter the vapour-liquid equilibria of the original mixture sufficiently to permits its easy separation with, however, use of only small quantities of solvent.
- (2) **High capacity**, or ability to dissolve the components in the mixture to be separated. It frequently happens that substances which are incompletely miscible with the mixture are very selective; yet if sufficiently high concentrations of solvent cannot be obtained in the liquid phase, the separation ability cannot be fully developed.
- (3) **Low volatility** in order to prevent vaporization of the solvent with the overhead product and to maintain high concentration in the liquid phase. Nonvolatile salts can be especially useful.
- (4) **Separability**; the solvent must be readily separated from the mixture to which it is added, and particularly it must form no azeotropes with the original substances.
- (5) The same considerations of **cost, toxicity, corrosive character, chemical stability, freezing point, and viscosity** apply as for entrainers for azeotropic distillation.

## Comparison of Azeotropic and Extractive Distillations

It is generally true that adding an extraneous substance such as entrainer or solvent to a process is undesirable. Since it can never be completely removed, it adds an unexpected impurity to the products. There are inevitable losses (ordinarily of the order of 0.1% of the solvent circulation rate), and they may be large since the solvent/feed ratios must frequently be greater than 3 or 4 to be effective. An inventory and source of supply must be maintained. Solvent recovery costs can be large, and new problems in choices of materials of construction are introduced. It follows that these processes can be considered only if, despite these drawbacks, the resulting process is less costly than conventional distillation.

Extractive distillation is generally considered to be more desirable than azeotropic distillation since **(1) there is a greater choice of added component because the process does not depend upon the accident of azeotrope formation and (2) smaller quantities of solvent must be volatilized.** However, the latter advantage can disappear if the volatilized impurity is a minor constituent of the feed and the azeotrope composition is favourable, i.e., low in solvent composition. Thus in the dehydration of ethanol from an 85.6 mole% ethanol-water solution, azeotroping the water with n-pentane as entrainer is more economical than using ethylene glycol as an extractive distillation solvent. The reverse might be true for a more dilute alcohol feed.