7

CRYSTALLIZATION

7.1 INTRODUCTION

Crystallization is a process in which the solid particles are formed from a homogeneous phase. During the crystallization process, the crystals form from a saturated solution. The mixture of crystals and the associated mother liquor is known as *magma.* The advantages of crystals are given below:

(i) uniform size and shape
(ii) ease in filtering and washing
(iii) caking tendency is minimised
(iv) high purity
(v) they do not crumble easily

7.2 CRYSTAL GEOMETRY

A crystal is the most highly organised type of non-living matter. It is characterised by the fact that its constituent particles like atoms or molecules or ions are arranged in an orderly three-dimensional arrays called *space lattices*. The angles made by corresponding faces of all crystals of the same material are equal and characteristic of that material, although the size of the faces and edges may vary.

7.2.1 Classification of Crystals

The classification of crystals based on the interfacial angle and lengths of axes is as follows

Cubic: Three equal rectangular axes.

Hexagonal: Three equal coplanar axes inclined to 60° to each other and a fourth axis different in length from the other three and perpendicular to them.

Trigonal: Three equal and equally inclined axes.

Tetragonal: Three rectangular axes, two of which are equal and different in length from the third.

Orthorhombic: Three unequal rectangular axes.

Monoclinic: Three unequal axes, two of which are inclined but perpendicular to the third.

Triclinic: Three mutually inclined and unequal axes, all angles unequal and other than 30°, 60° and 90°.

Crystals can also be classified based on the type of bond needed to hold the particles in place in the crystal lattice. The crystals are classified as indicated below.

Metals: These are electropositive elements bonded together by coulomb electrostatic forces from positive ions. The mobility of electrons is responsible for their excellent thermal and electrical conductivity in metals. Metal alloys do not follow valence rules.

Ionic crystals: They are the combinations of highly electronegative and highly electropositive ions, such as the ordinary inorganic salts. They are held together by strong coulomb forces and obey valence rules. It can be thought of as a single giant molecule.

Valence crystals: They are formed from the lighter elements in the right half of the periodic table. The atomic particles are held together by sharing electrons. The forces are strong and valence crystals are extremely hard with high melting points. They follow valence rules. For example, diamond and silicon carbide.

Molecular crystals: They are bonded by weak Vander-waals forces. They are soft, weak and have low melting points. They do not follow valence rules and many organic crystals belong to this category.

Hydrogen bonded crystals: Substances such as ice and hydrogen are held together by special bonds originating in the electron spins of the orbital electrons of the hydrogen atom.

Semiconductors: Substances such as silicon and germanium, when they contain very small amounts of impurities, have lattice deficiencies with 'holes' where electrons are missing and positive charges are in excess or with extra electrons present.

7.3 INVARIANT CRYSTAL

Under ideal conditions, a growing crystal maintains its geometric similarity during growth and such a crystal is called invariant. A single dimension can be used as the measure of the size of an invariant crystal of any definite shape. The ratio of the total surface area of a crystal, S_P to the crystal volume, V_P is

$$\frac{S_P}{V_P} = \frac{6}{(\varphi_s d_p)} \tag{7.1}$$

where φ_s is the sphericity and d_p is particle size. If the characteristic length L of the crystal is defined as equal to $\varphi_s\, d_p$ then,

$$L = \varphi_s\, d_p = 6\left(\frac{V_P}{S_P}\right) \tag{7.2}$$

7.4 PRINCIPLES OF CRYSTALLIZATION

The following factors govern the principles of crystallization.

7.4.1 Purity of Product

Although a crystal is as such pure, it retains mother liquor when removed from the final magma. If the crop contains crystalline aggregates, considerable amount of mother liquor may be occluded within the solid mass. When the product dries under such conditions, the impurity of the mother liquor is retained by the crystals. Hence, in practice, the retained mother liquor is separated from the crystals by filtration or centrifuging and the balance is removed by washing with fresh solvent to improve the purity of product.

7.4.2 Equilibria and Yield

Equilibrium in crystallization process is reached when the solution is saturated and it is normally indicated by the solubility curve. The solubility is normally indicated as a function of temperature. The characteristics of the solubility curve changes with the solute involved as indicated below in Fig. 7.1.

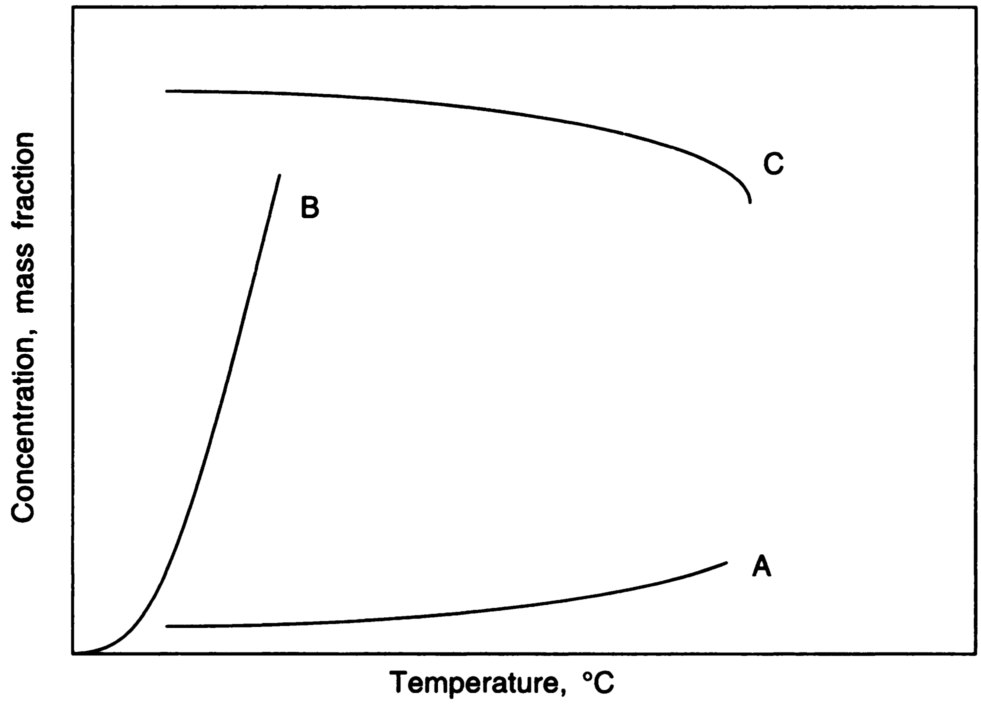
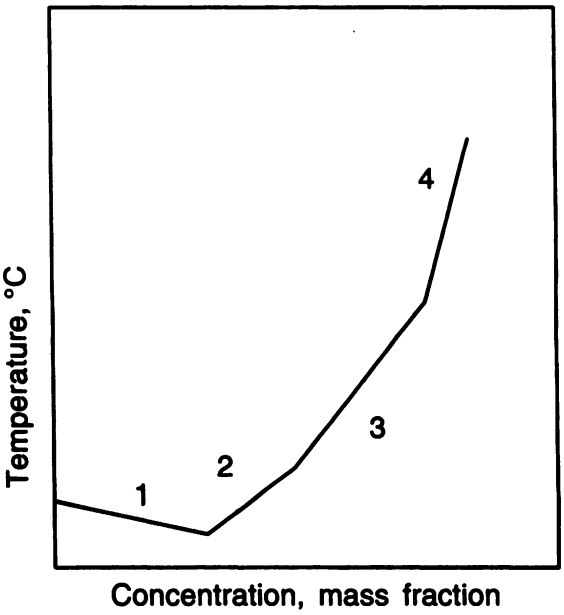


Fig. 7.1 Solubility curve.

In Fig. 7.1, A—flat solubility curve (NaCl), B—Steep solubility curve (KNO_3), and C—inverted solubility curve ($MnSO_4 \cdot H_2O$).

Substances like NaCl show a flat solubility curve (curve A) i.e. the increase in solubility with temperature is very less. The curve B is exhibited by most of the materials like KNO_3. In such systems the solubility increases very rapidly with temperature. Some of the substances like $MnSO_4 \cdot H_2O$ indicate an inverted solubility curve (curve C) in which solubility decreases with increase in temperature. Many important inorganic substances crystallise with water during crystallization. In some systems, as in the case of $MgSO_4 + H_2O$, several hydrates are formed depending on various levels of concentration and temperature. A typical phase diagram is shown in Fig. 7.2.



1: salt. a H_2O, 2: salt. b H_2O, 3: salt. c H_2O, 4: salt. d H_2O

Fig. 7.2 Phase diagram for hydrated salt.

7.4.3 Yield

The yield in the crystallization process is calculated by knowing the original concentration of solution and the solubility of solute at the final temperature. When the rate of crystal growth is slow, considerable time is required to reach equilibrium. This generally occurs in viscous solutions and when the crystals have a tendency to sink to the bottom. In such cases, there is little crystal surface exposed to the super-saturated solution and hence the actual yield is less than that calculated from solubility curve. Estimating the yield of anhydrous crystals is simple as the solid phase is free from solvent. However, when the crop contains water of crystallization, as in the case of hydrated salt, that must also be considered in estimating the yield.

7.4.4 Enthalpy Balance

In heat balance calculations for crystallizers, the heat of crystallization is important. This is the latent heat evolved when solid forms from solution. The heat of crystallization varies with both temperature and concentration. This is also equal to the heat absorbed by crystals dissolving in a saturated solution. This data is available in literature. The enthalpy balance enables us to determine the quantity of heat that should be removed from a solution during crystallization process.

7.5 SUPER-SATURATION

Crystallization from a solution is an example of the creation of a new phase within a homogeneous phase. It occurs in two stages, viz., nucleation and crystal growth. The driving force for these is super-saturation and without this crystallization does not occur. This is nothing but the concentration difference between that of the super-saturated solution in which the crystal is growing and that of a solution in equilibrium with the crystal. Super-saturation is generated by one or more of the following methods,

(i) by evaporation of solvent
(ii) by cooling
(iii) by adding a third component which may combine with the original solvent to form a mixed solvent, where the solubility of the solute is highly reduced is called *salting*. A new solute may be created chemically by the addition of third component by the reaction between the original solute and the new third component added is called *precipitation.*

The super-saturation is defined as follows

$$\Delta y = y - y_s$$
$$\Delta c = C - C_s$$

where

Δy = super-saturation, mole fraction of solute
y = mole fraction of solute in super-saturated solution
y_s = mole fraction of solute in saturated solution
Δc = molar super-saturation, moles per unit volume
C = molar concentration of solute in super-saturated solution
C_s = molar concentration of solute in saturated solution

The super-saturation ratio, s is defined as y/y_s.

Since the effect of super-saturation differs in nucleation process and crystal growth process, separate treatment of both the processes is necessary.

7.6 NUCLEATION

Crystal nuclei may form from molecules, atoms or ions. Due to their rapid motion, these particles are called *kinetic units*. These kinetic units join together and also break frequently. When they are held together, they can also be joined by a third particle. Combinations of this sort are called *clusters*. These clusters are also liable for break in their formation. When the number of kinetic units in a cluster is very large, it is called an *embryo*. However, they can also break into clusters or kinetic units. Depending on the level of super-saturation, the embryo grows and forms nucleus. The number of kinetic units in a nucleus is of the order of hundred and when the nuclei gains kinetic units, it results in the formation of a crystal. However, nuclei can also loose units and dissolve in solution. Hence, the stages of crystal growth may be indicated as,

Kinetic units → Cluster → Embryo → Nucleus → Crystal units

The factors which influence nucleation are,

(i) super-saturation
(ii) it is stimulated by an input of mechanical energy—by the action of agitators and pumps
(iii) the presence of solid particles—microscopic or macroscopic
(iv) the effect of particle size

7.6.1 Theory of Homogeneous Nucleation

The solubility data in literature applies only to large crystals. A small crystal can be in equilibrium with a super-saturated solution. Such an equilibrium is unstable, because if a large crystal is also present in the solution, the smaller crystal will dissolve and the larger one will grow until the smaller one disappears. The surface energy of a particle is given by

$$U_S = \gamma \cdot A_p \tag{7.3}$$

where U_S is surface energy in ergs, A_p is area of particle in cm^2 and γ is interfacial tension in ergs/cm^2.

The interfacial tension γ is the work required to increase the area of the particle by 1 cm^2 in the absence of other energy effects. Interfacial tension depends on temperature but not on the shape or size of the particle.

Although the crystals are polyhedra nuclei, the embryos are assumed to be spherical in shape. The particle diameter is taken as D cm. A nucleus has a definite size and it depends on super-saturation $(y - y_s)$ and the diameter of the nucleus is D_C. The volume of a particle is V_P in cm^3 and the mass is N_P in g-moles. Nucleation is assumed to take place at constant temperature and volume.

The formation of embryo is due to two kinds of work, viz., the one to form surface and the other to form volume. The surface work is given by Eq. (7.3). The work required to form the volume is $-(\mu - \mu_\alpha)\, N_P$, where μ is the chemical potential of the solute in the super-saturated solution and μ_α is the chemical potential of the solid, based on a crystal sufficiently large to reach equilibrium with a saturated solution. The unit of μ is ergs/g-mole.

The total work is equated to increase of work function, $\Delta\Omega$, and is shown below

$$\Delta\Omega = \gamma A_p - (\mu - \mu_\alpha)\, N_p \tag{7.4}$$

If V_m is the molal volume of the solid phase in cc/g mole then,

$$N_p = \frac{V_P}{V_m} \tag{7.5}$$

For spherical particles $$A_P = \pi D^2 \tag{7.6}$$

$$V_P = \left(\frac{\pi}{6}\right) D^3 \tag{7.7}$$

Substituting Eqs. (7.5), (7.6) and (7.7) in (7.4), we get

$$\Delta\Omega = \pi D^2 \left[\gamma - \left(\frac{D}{6V_M}\right) \cdot (\mu - \mu_\alpha)\right] \tag{7.8}$$

Under equilibrium for a definite value of $(\mu - \mu_\alpha)$, $\frac{d}{dD}[\Delta\Omega] = 0$

On differentiating Eq. (7.8) and equating to zero, we get

$$\frac{d}{dD}(\Delta\Omega) = 0 = 2\pi\gamma D - \left(\frac{\pi}{6V_m}\right)(\mu - \mu_\alpha)(3D^2) = 0$$

i.e. $$D = \frac{4\gamma V_m}{[\mu - \mu_\alpha]} \tag{7.9}$$

The diameter under the above equilibrium condition is the critical diameter D_C for nucleus and the work function becomes $(\mu - \mu_\alpha)_C$. Therefore,

$$D_C = \frac{4\gamma V_m}{[\mu - \mu_\alpha]_C} \tag{7.10}$$

The chemical potential difference is related to the concentrations of the saturated and super-saturated solutions by

$$(\mu - \mu_\alpha)_C = nR_oT \ln\left(\frac{y}{y_s}\right) = n\,R_oT \ln s \tag{7.11}$$

where n is the number of ions per molecule of solute and for molecular crystals, $n = 1$.

Substituting $(\mu - \mu_\alpha)_C$ from Eq. (7.11) in Eq. (7.10), we get

$$\ln s = \ln\left(\frac{y}{y_s}\right) = \frac{4\gamma V_m}{n\,R_oT \cdot D_C} \tag{7.12}$$

Equation (7.12) is the Kelvin equation which relates solubility of a substance to its particle size.

The work required for nucleation $\Delta\Omega_C$ is found by substituting for D_C from Eq. (7.10) and for D from Eq. (7.9) and then $(\mu - \mu_\alpha)_C$ from Eq. (7.11) into the resulting equation.

$$\begin{aligned}\Delta\Omega_C &= \gamma\pi\,D_C{}^2 - (\mu - \mu_\alpha)_C\left[\left(\frac{\pi}{6}\right)\left(\frac{D_C^3}{V_m}\right)\right]\\ &= \gamma\pi\,D_C{}^2 - \left(\frac{4\gamma V_m}{D_C}\right)\left[\left(\frac{\pi}{6}\right)\left(\frac{D_C^3}{V_m}\right)\right]\end{aligned}$$

$$= \frac{1}{3}\gamma\pi D_C^2 = \frac{1}{3}\gamma\pi\left[\frac{4\gamma V_m}{nR_oT\ln s}\right]^2$$

$$= \frac{16\pi\gamma^3 V_m^2}{3(nR_oT\ln s)^2} \tag{7.13}$$

The work of nucleation represents an energy barrier which controls the kinetics of embryo building. The rate of nucleation from the theory of chemical kinetics is

$$\tilde{N} = C\exp\left[-\frac{\Delta\Omega_C}{\mathcal{K}T}\right] = C\exp\left[\frac{-\Delta\Omega_C\cdot N_a}{R_oT}\right] \tag{7.14}$$

Substituting for $\Delta\Omega_C$ from Eq. (7.13) in Eq. (7.14)

$$\tilde{N} = C\exp\left[\frac{-16\pi\gamma^3 V_m^2 N_a}{3n^2(R_oT)^3(\ln s)^2}\right] \tag{7.15}$$

where $\tilde{N}$ is the nucleation rate, number/cm^3 s

$\mathcal{K}$ is Boltzmann constant, 1.3805×10^{-16} erg/(g mol K)

N_a is Avogadro number, 6.0225×10^{23} molecules/g mol

R_o is gas constant, 8.3143×10^{7} ergs/g mol °C

C is frequency factor

The frequency factor represents the rate at which individual particle strikes the surface of crystal. As far as the formation of water droplets from saturated vapour is concerned, it is of the order of 10^{25}. Its value from solutions is not known and the nucleation rate is dominated by ln s term in the exponent. Similarly, the numerical values for γ also are uncertain. They can be calculated from solid state theory and for ordinary salts, it is of the order of 80 to 100 ergs/cm^2. With these values of C and γ for a nucleation rate of one nucleus per sec, per cm^3, the value of s can be calculated and it is found to be very high and it is highly impossible for materials of usual solubility. Hence, homogeneous nucleation in ordinary crystallization from solution never occurs and that all actual nucleations in these situations are heterogeneous.

However, in precipitation reactions where y_s is very small and where large super-saturations can be generated rapidly, homogenous nucleation probably occurs.

7.6.2 Heterogeneous Nucleation

The catalytic effect of solid particles on nucleation rate is the reduction of energy barrier. Hence, the level of super-saturation needed is greatly reduced.

7.7 CRYSTAL GROWTH

Crystal growth is a diffusional process, modified by the effect of the solid surfaces on which the growth occurs. Solute diffuses through the liquid phase and reach the growing faces of a crystal and crystal starts growing.

7.7.1 ΔL—Law of Crystal Growth

If all crystals in magma grow in a uniform super-saturation field and at the same temperature and if all crystals grow from birth at a rate governed by the super-saturation, then all crystals are not only invariant but also have the same growth rate that is independent of size. Hence, growth rate is not a function of crystal size and it remains constant.

i.e.

$$\Delta L = G \cdot \Delta t \tag{7.16}$$

7.7.2 Growth Coefficients

By using the expression for overall coefficient K in terms of film coefficients, the overall coefficient is expressed in terms of film coefficient.

The overall coefficient K is defined as,

$$K = \frac{m'}{[S_P(y - y_s)]} \tag{7.17}$$

where m' is the rate of mass transfer in moles/hr, S_P is surface area of crystal and $(y - y_s)$ is the driving force.

For an invariant crystal of volume V_P, the volume is proportional to the cube of its characteristic length L

i.e. $V_P = aL^3$, where a is a constant (7.18)

If ρ_m is the molar density, the mass of the crystal m is then,

$$m = V_P\, \rho_m = aL^3\, \rho_m \tag{7.19}$$

Differentiating the above Eq. (7.19), we get

$$m' = \frac{dm}{dt} = 3aL^2\, \rho_m \left(\frac{dL}{dt}\right)$$

$$= 3a\, L^2\, \rho_m G \tag{7.20}$$

We have

$$\frac{S_P}{V_P} = \frac{6}{L} \text{ and } Vp = aL^3$$

$\therefore$

$$S_P = 6aL^2 \tag{7.21}$$

Substituting the above Eq. (7.20) and (7.21) in Eq. (7.17), we get

$$K = \frac{3aL^2 \rho_m G}{6aL^2\, (y - y_s)} = \frac{(\rho_m G)}{2(y - y_s)}$$

$\therefore$

$$G = 2\frac{(y - y_s)\, K}{\rho_m} \tag{7.22}$$

7.8 APPLICATION TO DESIGN

Once the yield is estimated, then it is desirable to solve the problem of estimating the crystal size distribution of the product. An idealised model, called the Mixed Suspension–Mixed Product Removal (MSMPR) model has served well as a basis for identifying the kinetic parameters and hence the evaluation of the performance of such a crystallizer. The assumptions of the MSMPR model is as follows,

(i) steady state operation
(ii) no product classification
(iii) uniform super-saturation exists throughout the magma
(iv) ΔL—law of crystal growth applies
(v) no size classified withdrawal system is used
(vi) no crystals in feed
(vii) mother liquor in product magma is saturated
(viii) no disintegration of crystals

Due to the above assumptions, nucleation rate is constant at all points in the magma. The particle size distribution is independent of location in the crystallization and is identical to that of the distribution in the product.

7.8.1 Population Density Function

The crystal number density is defined as the number of crystals of size L and smaller in the magma per unit volume of mother liquor. Hence, if N is the number of crystal of size L and less in the magma, V is the volume of mother liquor in the magma and L is the size of crystals, then N/V is the crystal number density. A plot of crystal density vs crystal size is shown below in Fig. 7.3. At $L = 0$; $N = 0$ and at $L = L_T$, the largest of the crystal in the magma, then $N = N_T$. The population density n, is defined as the slope of the cumulative distribution curve at size L or it can be expressed as

$$n = \frac{d\left(\frac{N}{V}\right)}{dL} = \left(\frac{1}{V}\right)\left(\frac{dN}{dL}\right) \tag{7.23}$$

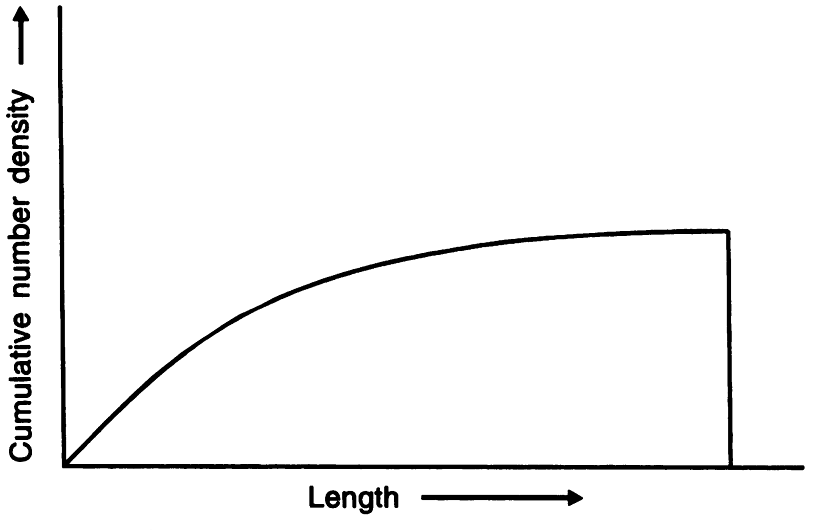


Fig. 7.3 Population density function.

At $L = 0$, the population density is the maximum, i.e. $n = n^0$ and at $L = L_T$, the population density is zero. In MSMPR model, both n and N/V are invariant with time and location.

Consider $N\,dL$ crystals between sizes L and $L + dL$ per unit volume of magma in the crystallizer. In the MSMPR model, each crystal of length L has same age t_m.

$$\therefore \qquad L = G\, t_m \tag{7.24}$$

Let $(\Delta n)\, dL$ be the amount of product withdrawn from the above magma during a time interval of Δt. Since the operation is in steady state, withdrawal of product does not affect size distribution in the product. If Q is the volumetric flow rate of liquid in the product and V_C is the total volume of liquid in the crystallizer, then

$$\frac{-\Delta n\, dL}{n\, dL} = -\left(\frac{\Delta n}{n}\right) = \left(\frac{Q\Delta t}{V_C}\right) \tag{7.25}$$

where the negative sign indicates the withdrawn product. The growth of each crystal is given by,

$$\Delta L = G\Delta t \tag{7.26}$$

Combining Eqs. (7.25) and (7.26) for eliminating Δt,

$$-\Delta n = Q\ \Delta t \cdot \frac{n}{V_C}$$

$$-\frac{\Delta n}{\Delta L} = \frac{Qn}{V_C G} \tag{7.26a}$$

Letting $\Delta L \to 0$; $-\dfrac{\Delta n}{\Delta L} = -\dfrac{dn}{dL}$

$$\Delta L \to 0$$

i.e.

$$-\left(\frac{dn}{dL}\right) = \frac{Qn}{V_C G} \tag{7.27}$$

The retention time τ of the magma in the crystallizer is defined by

$$\tau = V_C/Q$$

Hence

$$\frac{-dn}{n} = \left(\frac{1}{G\tau}\right) dL \tag{7.28}$$

Integrating Eq. (7.28), we get

$$\int_{n^0}^{n} \frac{dn}{n} = \left(-\frac{1}{G\tau}\int_0^L dL\right)$$

$$\ln\left(\frac{n^o}{n}\right) = \left(\frac{L}{G\tau}\right) \tag{7.29}$$

i.e. $$n = n^o e^{-z} \tag{7.30}$$

The quantity $L/G\tau$ is the dimensionless length and is denoted as Z.

7.8.2 Number of Crystals per Unit Mass

The number of crystals n_c in a unit volume of liquid in either magma or product is,

$$n_c = \int_0^\infty n\,dL \tag{7.31}$$

$$= \int_0^\infty G\tau\, n^o \cdot e^{-z} dz = n_c = n^o\, G\tau \tag{7.32}$$

The total mass of product crystals in a unit volume of liquid is,

$$m_c = \int_0^\infty mn \cdot dL \tag{7.33}$$

$$= a\rho_c n^o (G\tau)^3 \int_0^\infty Z^3 e^{-z} \cdot dZ = 6a\rho_c n^o (G\tau)^4 \tag{7.34}$$

where ρ_c is the density of crystals.

∴ The number of crystals per unit mass is

$$\frac{n_c}{m_c} = \frac{n^o G\tau}{6a\rho_c n^o (G\tau)^4} = \frac{1}{6a\rho_c (G\tau)^3} \tag{7.35}$$

The predominant crystal size L_{pr} in the product occurs when $L_{pr} = 3G\tau$

$$\therefore \quad \frac{n_c}{m_c} = \frac{1}{\left[6a\rho_c \left(\frac{L^3{}_{pr}}{27}\right)\right]} = \frac{9}{2a\rho_c L^3_{pr}} \tag{7.36}$$

7.9 CRYSTALLIZERS

The classification of crystallizers is generally based on the method by which super-saturation is achieved.

7.9.1 Super-saturation by Cooling

This is done on batch basis in a (i) tank crystallizer and in an (ii) agitated tank crystallizer and on continuous basis in Swenson–Walker crystallizer.

7.9.1.1 Tank crystallizer

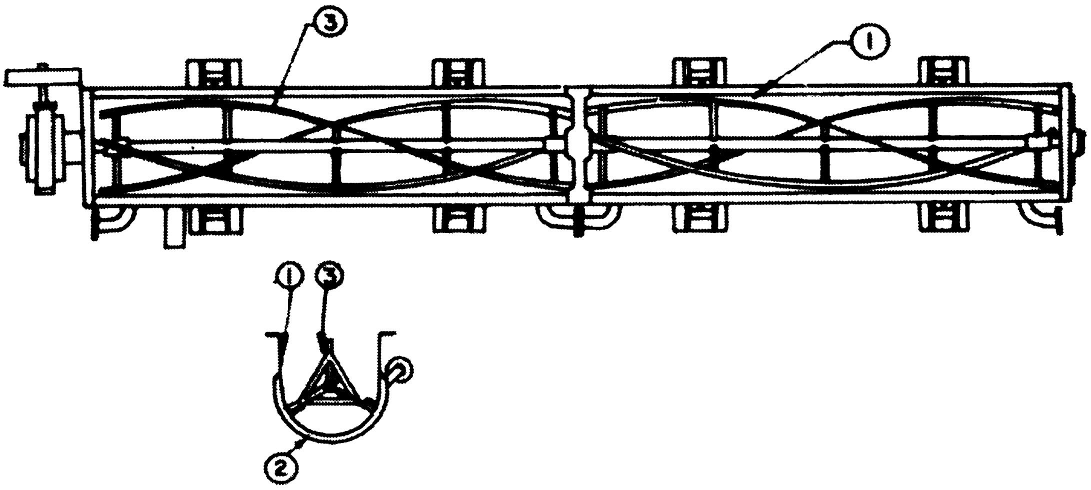
A simple tank crystallizer is an open tank containing the solution from which the crystal grows without any agitation. In this crystallizer, the crystal growth is very slow, irregular and interlocking of crystals occur. The mother liquor is also occluded due to interlocking of crystals which leads to impurities in the crystals.

7.9.1.2 Agitated tank crystallizer

This is a modified form of tank crystallizer with provisions of cooling coil and agitation. The agitation not only helps in a uniform transfer of heat but also enables a uniform growth of crystals. However, the major disadvantage is the build up of crystals on cooling coil which decreases the rate of heat transfer.

7.9.1.3 Swenson–Walker crystallizer

It is a continuous crystallizer which makes use of cooling to achieve supersaturation. A sketch of the equipment is shown in Fig. 7.4. It generally consists of an open trough, *A* which is approximately 0.6 m wide with a semi-cylindrical bottom and an external water jacket, *B*. Through the water jacket, cooling water is circulated. A slow speed, long pitch spiral agitator rotating at about 5–7 rpm, and set as close to the bottom of the trough as possible is provided inside the trough. The crystallizer comprises of several units for handling higher amount of feed. Each unit will be generally 3 m in length. The maximum length that could be driven by one shaft is around 12 m. If it is desired to have higher lengths, then the units are arranged one above the other and the solution transferred from one set of unit to the other in the cascade.



1. Trough 2. Jackets 3. Agitator

Fig. 7.4 Swenson–Walker crystalliser.

The hot concentrated solution is fed into the trough and cooling water flows through jackets in countercurrent direction. If necessary to control crystal size, an extra amount of water can also be let into certain sections. The objective of providing the spiral stirrer is primarily to prevent the accumulation of crystals on the cooling surface and subsequently to lift the formed crystals and shower them down through the solution. This enables a uniform size of crystals which is free from inclusions or aggregations. The rotation of stirrer also helps to transfer the crystals towards the crystal discharge point for subsequent processing.

7.9.2 Super-saturation by Evaporation

Super-saturation occurs by evaporation in a Krystal crystallizer.

7.9.2.1 Krystal crystallizer

The schematic diagram of Krystal crystallizer is shown in Fig. 7.5. This consists of a vapour head, '1' and crystal growth chamber, '2'. Solution is pumped from chamber '2' by using a pump, '6' to chamber '1' through a heater '3'. Vapour from '1' discharges into a condenser and vacuum pump. The operation is so effectively controlled that crystals do not form in '1'. The section '1' is connected to almost the bottom of chamber '2' through a tube '4'. The lower part of '2' contains a bed of crystals suspended in an upward flowing stream of liquid caused by the discharge from '4'. The super-saturated liquid formed in '1' flows over the surface of the crystals in '2'. The liquid from '2' after contributing to crystallization process leaves through '7' and recirculated. Periodically the coarse crystals are drawn out from the bottom of the vessel through '5'. There is a gradual variation in size of crystals in '2' with the coarser ones at the bottom and the finer ones at the top. Feed is usually introduced into the suction of pump '6'.

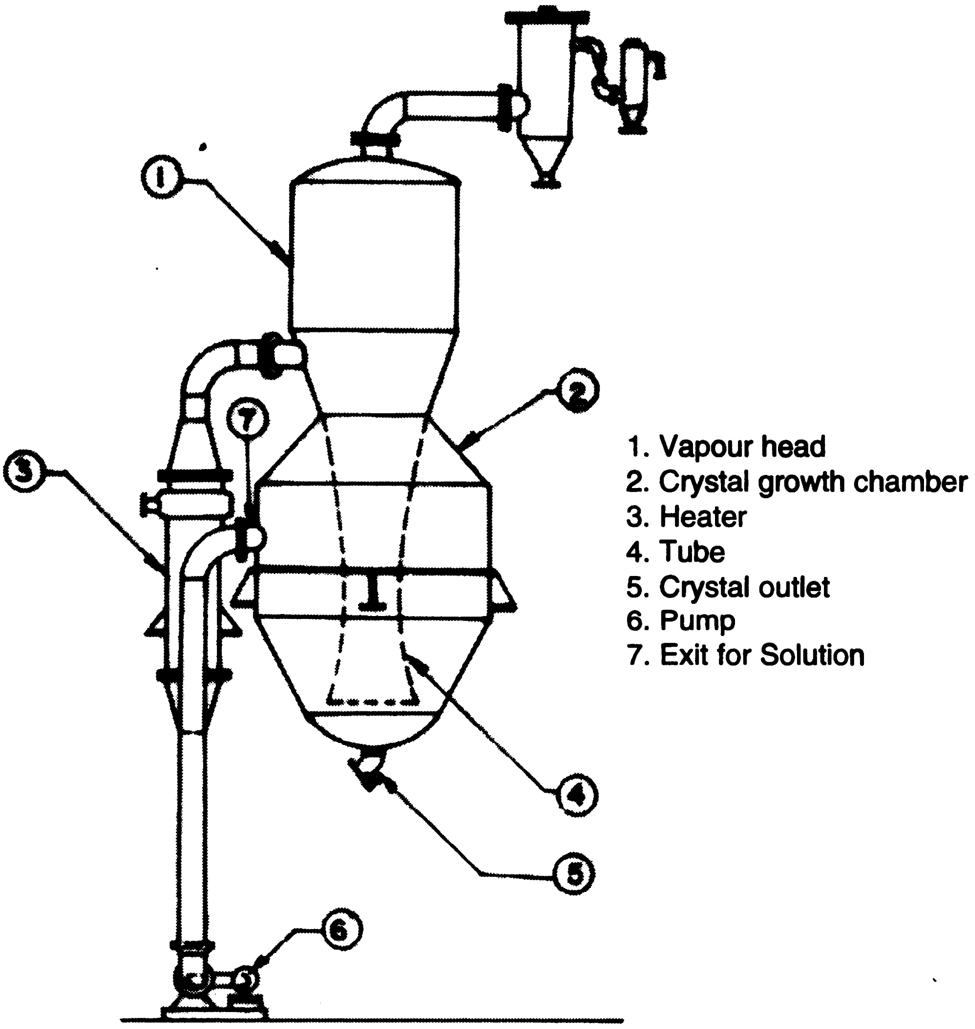


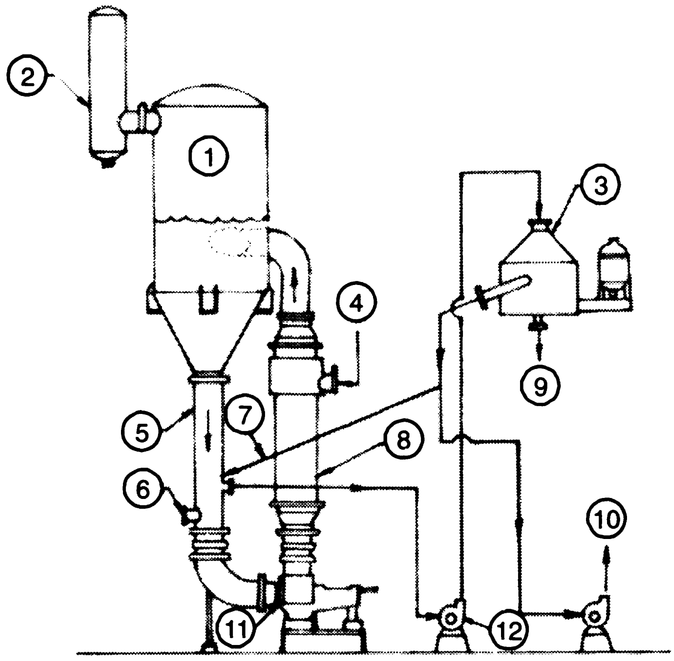
Fig. 7.5 Krystal crystallizer.

7.9.3 Super-saturation by Evaporation and Cooling

Most of the modern crystallizers achieve super-saturation by adiabatic evaporative cooling. In such crystallizers vacuum is maintained and a warm saturated solution at a temperature well above the boiling point of solution (corresponding to the pressure in crystallizer and concentration of solute) is fed in. The feed solution cools spontaneously to the equilibrium temperature, since both the enthalpy of cooling and the enthalpy of crystallization appear as enthalpy of vapourisation, a portion of the solvent evaporates. The super-saturation thus generated by both cooling and evaporation causes nucleation and crystal growth. The yield of crystals is proportional to the difference between the concentration of the feed and the solubility of the solute at equilibrium temperature.

7.9.3.1 Vacuum crystallizer

A typical continuous vacuum crystallizer using the above principle is shown in Fig. 7.6. The crystallizer consists of a body maintained under vacuum and is similar to that of single effect evaporator. From the conical bottom of the body, magma flows down through a down-pipe. It is mixed with the fresh feed from the feed inlet point located before the suction of the circulating pump. The mixture is sent up through a vertical tubular heater by the pump. The heated mixture enters the crystallizer body through a tangential inlet just below the level of magma surface. The swirling motion to the magma facilitates flash evaporation and cooling. The super-saturation thus generated provides the driving potential for nucleation and crystal growth.



1. Body 2. Barometric condenser 3. Centrifuge 4. Steam 5. Down-pipe
6. Feed 7. Mother liquor recycle 8. Heater 9. Product 10. Bleed
11. Circulating pump 12. Slurry pump

Fig. 7.6 Continuous vacuum crystallizer.

Mother liquor is separated from the crystals in a centrifuge. Crystals are taken off as a product for further processing and the mother liquor is recycled back to the down-pipe. Some portion of the mother liquor bleeds from the system to prevent accumulation of impurities.

The drawbacks of vacuum crystallizer are as follows:

(i) The crystals tend to settle at the bottom of the crystallizer where there may be little or no super saturation.

(ii) The crystallizer will not be effective in the absence of agitation to magma.

7.9.3.2 Draft tube baffle (DTB) crystallizer

A more versatile and effective crystallizer shown in Fig. 7.7 is draft tube baffle crystallizer. In this the crystallizer body is equipped with a draft tube which also acts as a baffle to control the circulation of magma and a downward directed propeller agitator to provide a controllable circulation within the crystallizer. The DTB crystallizer is provided with an elutriation leg below the body to classify the crystals by size and may also be equipped with a baffled settling zone for fines removal. There is an additional circulating pump outside the crystallizer body which circulates the recycle liquid and fresh feed through a heater. Part of the circulating liquid is pumped to the bottom of the leg and used as a hydraulic sorting fluid to carry small crystals back into crystallising zone for further growth.

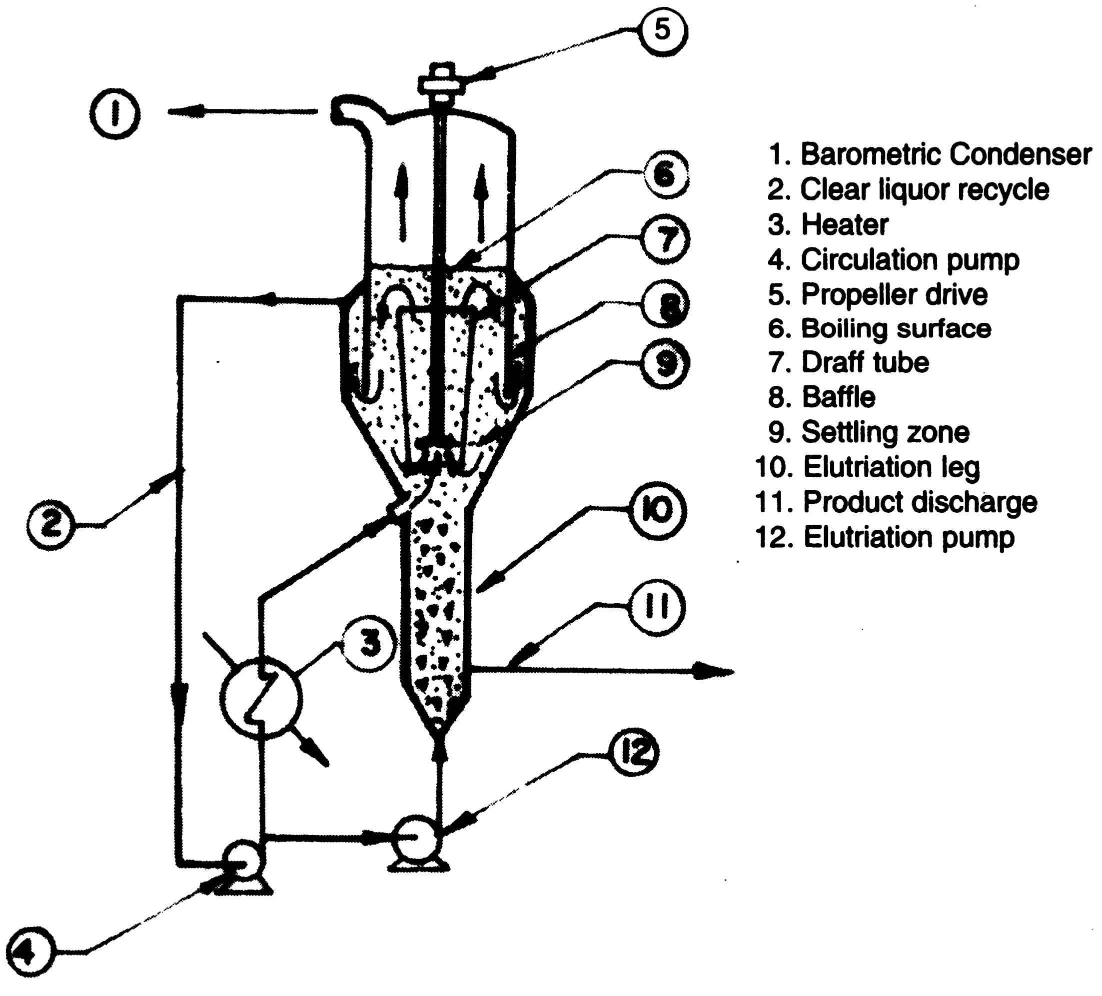


Fig. 7.7 Draft tube baffle crystalliser.

Discharge slurry is withdrawn from the lower part of the elutriation leg and sent to a filter or centrifuge, and the mother liquor is returned to the crystallizer. Unwanted nuclei is removed by providing an annular space or jacket by enlarging the conical bottom and using the lower wall of the crystallizer body as a baffle. In the annular space, fines are separated from the larger ones and they float due to upward flowing stream of mother liquor. This stream of liquor along with fines of size 60 mesh and smaller, also called clean liquor, is mixed with fresh feed and sent through a heater. In the heater these tiny crystals get dissolved. The liquor is now clear and mixes with the slurry in the main body of the crystallizer.

WORKED EXAMPLES

1. Mother liquor after crystallization has a solute content of 49.8 kg of $CaCl_2$ per 100 kg of water. Find out the weight of this solution needed to dissolve 100 kg of $CaCl_2 \cdot 6H_2O$ at 25°C. Solubility at 25°C is 81.9 kg of $CaCl_2$/100 kg of water.

Solution.

Let x be the weight of water in the quantity of solution needed.

$$\text{Molecular weight of } CaCl_2 = 111,$$

$$\text{Molecular weight of } CaCl_2 \cdot 6H_2O = 219$$

$$\text{Water present in 100 kg of } CaCl_2 \cdot 6H_2O = \left(\frac{108}{219}\right) \times 100 = 49.3 \text{ kg}$$

$$CaCl_2 \text{ present in 100 kg of } CaCl_2 \cdot 6H_2O = \left(\frac{111}{219}\right) \times 100 = 50.68$$

$$\text{Total } CaCl_2 \text{ entering for solubility} = 50.68 + 0.498x$$

$$\text{Total water used for solubility} = x + 49.3$$

$$\text{Total } CaCl_2 \text{ after solubility} = \frac{[81.9 \times (x + 49.3)]}{100}$$

$$\text{Making material balance for } CaCl_2 = 50.68 + 0.498x = \left(\frac{81.9}{100}\right)(x + 49.3)$$

$$50.68 + 0.498x = 0.819x + 40.37$$

$$0.819x - 0.498x = 50.68 - 40.37$$

$$0.321x = 10.30$$

$$\therefore x = 32.09$$

Weight of $CaCl_2$ in mother liquor corresponding to the weight water is 32.09 kg

$$= \left(\frac{49.8}{100}\right) \times 32.09$$

$$= 15.98 \text{ kg}$$

Total weight of solution needed = 15.98 + 32.09

= 48.07 kg. **Ans.**

2. Sodium nitrate solution at 50°C contains 45% by weight of sodium nitrate.
   (i) Find out the percentage saturation of this solution
   (ii) Find out the weight of sodium nitrate crystal formed if 1000 kg of this solution is cooled to 10°C
   (iii) Find out the percentage yield of this process.

   Data: Solubility at 50°C = 104.1 kg of $NaNO_3$/100 kg of water
   Solubility at 10°C = 78 kg of $NaNO_3$/100 kg of water

Solution.

(i) $NaNO_3$ weight percentage of saturated solution at 50°C

$$= \left(\frac{104.1}{204.1}\right) \times 100 = 51\%$$

$$\text{Percentage saturation at 50°C} = \left[\frac{(45/55)}{(51/49)}\right]$$

$$= \left[\frac{(45 \times 49)}{(55 \times 51)}\right] \times 100 = 78.6\%$$ **Ans.**

(ii) Let x be the weight of $NaNO_3$ crystal formed after crystallization
By writing material balance for $NaNO_3$

$1000 \times 0.45 = x + (1000 - x) \times (78/178)$

$450 = x + 438.2 - 0.438x$

$x = 20.99$ kg. **Ans.**

(iii) Yield = weight of $NaNO_3$ crystal formed/weight of $NaNO_3$ in original solution

$$= \frac{20.99}{450} = 0.0466$$

% Yield = 4.66% **Ans.**

3. A saturated solution, of potassium sulphate is available at a temperature of 70°C. Calculate the temperature to which this should be cooled to crystallise 50% of potassium sulphate.

   Data: Solubility at 70°C = 19.75/100 g of water
   Solubility at 50°C = 16.5/100 g of water
   Solubility at 30°C = 12.97/100 g of water
   Solubility at 10°C = 9.22/100 g of water
   Solubility at 0°C = 7.34/100 g of water
   Basis: 1000 kg of saturated solution

Solution.

Weight of K_2SO_4 in original solution $= 1000 \times \left(\frac{19.75}{119.75}\right) = 164.92$ kg

$$\text{Weight of water} = 1000 - 164.92 = 835.08 \text{ kg}$$

After crystallisation, the weight of K_2SO_4 in solution is $= 164.92 \times 0.5$
$= 82.46$ kg

Weight percentage of K_2SO_4 in solution after crystallization

$$= \left[\frac{82.46}{(835.08 + 82.46)}\right] \times 100 = 8.98\%$$

From the solubility data, it is found that temperature corresponding to 8.98% of K_2SO_4 is 15°C (by linear interpolation between 10 to 30°C). **Ans.**

4. Sodium acetate solution is available at a temperature of 70°C with a solute content of 58%. Find out (i) percentage saturation (ii) yield of crystal if 2000 kg of this solution is cooled to 10°C (iii) percentage yield.
Data: Solubility at 70°C = 146 gms of sodium acetate/100 gms of water
Solubility at 10°C = 121 gms of sodium acetate/100 gms of water

Solution.

(i) Weight percentage of solute at 70°C at saturation condition

$$= \left(\frac{146}{246}\right) \times 100 = 59.34\%$$

$$\text{Percentage saturation} = \left[\frac{(58/42)}{(59.34/40.66)}\right]$$

$$= \left[\frac{(58 \times 40.66)}{(42 \times 59.34)}\right] \times 100 = 94.62\% \quad \textbf{Ans.}$$

(ii) Weight of solute in 2000 kg of solution $= 2000 \times 0.58 = 1160$ kg
Let x be the weight of crystal formed making solute balance

$$1160 = x + (2000 - x)\frac{121}{221}$$

$$1160 = x + 1055.02 - 0.547x$$

$$x = 231.74 \text{ kg} \quad \textbf{Ans.}$$

(iii) % Yield $= \left(\frac{231.74}{1160}\right) \times 100 = 19.97\%$ **Ans.**

5. A saturated solution of sodium sulphate solution is available at a temperature of 30°C. Find out the weight of $Na_2SO_4 \cdot 10H_2O$ formed, if 1000 kg of this solution cooled to 10°C.
Data: Solubility at 30°C = 40.8 g of Na_2SO_4/100 g of water
Solubility at 10°C = 9.0 g of Na_2SO_4/100 g of water

Solution.

$$\text{Weight percent of solute in } Na_2SO_4 \cdot 10H_2O = \frac{142}{322} = 44.2\%$$

Let x be the quantity of crystal formed, by making material balance for solute

$$1000 \times \left(\frac{40.8}{140.8}\right) = 0.442x + (1000 - x) \times \frac{9}{109}$$

$$x = 576.07 \text{ kg}$$

Weight of crystals formed = 576.07 kg **Ans.**

6. A solution of sodium carbonate available at a temperature of 40°C with a solute content of 30%. Find out the weight of $Na_2CO_3 \cdot 10H_2O$ crystal formed if 2000 kg of this solution is cooled to 10°C. Also find out the yield.

Data: Solubility at 10°C = 12.5 gms of Na_2CO_3/100 gms of water

Solution.

$$\text{Molecular weight of } Na_2CO_3 \cdot 10H_2O = 286$$

$$\text{Weight percent of solute in } Na_2CO_3 \cdot 10H_2O = \frac{106}{286} = 0.3706$$

Let x be the quantity of $Na_2CO_3 \cdot 10H_2O$ crystal formed

$$2000 \times 0.3 = 0.3706x + (2000 - x) \times \frac{12.5}{112.5}$$

$x = 1455.86$ kg **Ans.**

Weight of crystals present in the original solution

$$= \left(\frac{286}{106}\right) \times 2000 \times 0.3 = 1618.87$$

$$\%\ \text{Yield} = \left(\frac{1455.87}{1618.87}\right) \times 100 = 89.93\%$$ **Ans.**

7. A saturated solution of K_2CO_3 is available at a temperature of 80°C. If it is cooled to 20°C, find the weight of crystal ($K_2CO_3 \cdot 2H_2O$) formed and yield for 500 kg of solution.

Data: Solubility of K_2CO_3 at 80°C = 139.8 g of K_2CO_3/100 g of water
Solubility of K_2CO_3 at 20°C = 110.5 g of K_2CO_3/100 g of water

Solution.

$$\text{Molecular weight of } K_2CO_3 \cdot 2H_2O = 174.2$$

$$\text{Percentage solute in } K_2CO_3 \cdot 2H_2O = \left(\frac{138}{174.2}\right) \times 100 = 79.21\%$$

Let x be the quantity of crystal formed, making material balance for solute

$$500 \times \left(\frac{139.8}{239.8}\right) = (0.7921x) + (500 - x) \times \left[\frac{110.5}{210.5}\right]$$

$$x = 108.62 \text{ kg}$$

Weight of crystals formed = 108.62 kg **Ans.**

Weight of K_2CO_3 present in the original solution

$$= \left(\frac{174.7}{138}\right) \times 500 \times \left(\frac{139.8}{239.8}\right) = 369.013$$

$$\text{Percentage yield} = \left(\frac{108.62}{369.01}\right) \times 100 = 29.4\% \quad \textbf{Ans.}$$

8. 900 kg of ferrous sulphate solution with a solute content of 40% is available. If it is cooled to 10°C, find out the weight of crystal formed and yield of the crystal with the crystal of the form $FeSO_4 \cdot 7H_2O$.

Data: Solubility of $FeSO_4$ at 10°C = 20.51 g of $FeSO_4$/100 g of water

Solution.

Molecular weight of $FeSO_4 \cdot 7H_2O$ = 277.85

Percentage solute in $FeSO_4 \cdot 7H_2O$ = 151.85/277.85 = 0.5465

Let x be the quantity of $FeSO_4 \cdot 7H_2O$ crystal formed by making material balance for solute

$$900 \times 0.4 = 0.5465x + (900 - x) \times \left(\frac{20.51}{120.51}\right)$$

$x = 549.34$ kg **Ans.**

Weight of $FeSO_4 \cdot 7H_2O$ in original solution

$$= \left(\frac{277.85}{151.85}\right) \times 900 \times 0.4 = 658.71 \text{ kg}$$

$$\text{Percentage yield} = \left(\frac{549.34}{658.71}\right) \times 100 = 83.39\% \quad \textbf{Ans.}$$

9. Cesium chloride solution with a solute content of 68% is at 60°C. Find out (i) percentage saturation (ii) weight $CsCl_2$ crystal formed if 1000 kg of solution is cooled (iii) percent yield of solution if cooled to 10°C.

Data: Solubility at 60°C = 229.7 g of $CsCl_2$/100 g of water
Solubility at 10°C = 174.7 g of $CsCl_2$/100 g of water

Solution.

(i) Weight percent of solute at saturation condition at 60°C

$$= \left(\frac{229.7}{329.7}\right) \times 100 = 69.66\%$$

$$\text{Percentage saturation} = \left[\frac{(68/32)}{(69.66/30.34)}\right] \times 100 = 92.5\% \quad \textbf{Ans.}$$

(ii) Let x be the weight of $CsCl_2$ formed
Making material balance gives,

$$1000 \times 0.68 = x + (1000 - x) \times \left(\frac{174.7}{274.7}\right)$$

$$x = 120.97 \text{ kg}$$

Weight of crystal formed = 120.97 kg **Ans.**

(iii) Percentage yield $= \left(\frac{120.97}{680}\right) \times 100 = 17.8\%$ **Ans.**

10. A solution of sodium carbonate in water is saturated at a temperature of 10°C. Calculate the weight of $Na_2CO_3 \cdot 10H_2O$ needed to dissolve in 200 kg of original solution at 30°C.

Data: Solubility at 30°C = 38.8 gms of Na_2CO_3/100 g of water
Solubility at 10°C = 12.5 gms of Na_2CO_3/100 g of water

Solution.

Molecular weight of $Na_2CO_3 \cdot 10H_2O = 286$

$$\text{Percentage solute in } Na_2CO_3 \cdot 10H_2O = \left(\frac{106}{286}\right) \times 100 = 37.06\%$$

Let x be the weight of $Na_2CO_3 \cdot 10H_2O$ needed to dissolve
Weight of Na_2CO_3 originally present in 200 kg of solution

$$= 200 \times \left(\frac{12.5}{112.5}\right) = 22 \text{ kg}$$

Weight of water = 200 − 22 = 178 kg
Weight of Na_2CO_3 after dissolution = $22 + 0.3706x$
Weight fraction of solute after dissolution at 30°C

$$= \frac{38.8}{138.8} = 0.279$$

For the total solution after dissolution

$$= \frac{(22 + 0.3706x)}{[(22 + 0.3706x) + (178 + 0.6294x)]} = 0.279$$

Solving for x,
$x = 369$ kg **Ans.**

11. A 35% solution of Na_2CO_3 weighing 6000 kg is cooled to 20°C to yield crystals of $Na_2CO_3 \cdot 10H_2O$. During cooling 4% by weight of original solution is lost due to vapourisation. Find out the weight of crystal formed.

Data: Solubility at 20°C = 21.5 g of Na_2CO_3/100 g of water

Solution.

Molecular weight of $Na_2CO_3.10H_2O = 286$

$$\text{Percentage of solute in hydrated salt} = \left(\frac{106}{286}\right) \times 100 = 37.06\%$$

Weight of solute = 6000 × 0.35 = 2100 kg

Weight of solution lost by vapourisation = 6000 × 0.04 = 240 kg

Let x be the weight of $Na_2CO_3 \cdot 10H_2O$ formed

Making material balance on solute

$$2100 = 0.3706x + (6000 - 240 - x) \times \left(\frac{21.5}{121.5}\right)$$

$$x = 5580 \text{ kg} \qquad \textbf{Ans.}$$

12. How much feed is required when 10,000 kg of crystal as $FeSO_4 \cdot 7H_2O$ is produced per hour by a simple vacuum crystallizer. The feed containing 40 parts of $FeSO_4$ per 100 parts of total water, enters the crystallizer at 80°C. The crystallizer vacuum is such that crystallizer temperature of 30°C can be produced.

Data: Saturated solution at 30°C contains 30 parts of $FeSO_4$ per 100 parts of total water vapour enthalpy is 612 cal/g (neglect superheat). The enthalpies of saturated solution, the crystals leaving the crystallizer and feed are: –1.33, –50.56 and 26.002 cal/g.

Solution.

$FeSO_4 \cdot 7H_2O$

Crystals formed = 10000 kg

Enthalpy of feed h_F at 80°C = 26.002 cal/g

Enthalpy of saturated solution at 30°C = h_L = –1.33 cal/g

Enthalpy of crystals h_C = – 50.56

$$x_F = \frac{40}{(100+40)} = 0.286$$

$$x_M = \frac{30}{(100+30)} = 0.231$$

$$x_C = \frac{151.85}{277.85} = 0.547$$

Component balance,

$$F(x_F) = (M)\,(x_M) + C(x_C)$$

$$0.286F = (M)\,(0.231) + (10000)\,(0.547)$$

$$F = M + 10000 + V$$

$$F \cdot H_F = V \cdot H_V + M \cdot H_M + C \cdot H_C$$

$$H_F = 26.002 \text{ cal/g}$$

$$H_V = 612 \text{ cal/g}$$

$$H_M = -1.33 \text{ cal/g}$$

$$H_C = -\,50.56 \text{ cal/g}$$

$$F = M + V + 10000 \quad (1)$$

$$0.286\ F = 0.231\ M + 5470 \quad (2)$$

$$(26.002)\ (F) = (612)\ V + (-1.33)\ (M) + (-50.56)\ (10000) \quad (3)$$

Solving Eq. (1) × 0.286

$$0.286\ F = 0.286\ M + 0.286\ V + 2860 \quad (4)$$

$$0 = 0.055\ M + 0.286\ V - 2610$$

$$2610 = 0.055\ M + 0.286\ V \quad (5)$$

Equation (1) × 26.002

$$26.002\ F = 26.002\ M + 26.002\ V + 260200 \quad (6)$$

Equation (6) – Eq. (3)

$$0 = 27.332\ M - 585.998\ V + 765800 \quad (7)$$

$$765800 = -\ 27.33\ M + 585.998\ V$$

Equation (5) × 496.9 gives

$$1296909 = +\ 27.33\ M + 142.113\ V \quad (8)$$

Equation (7) + Eq. (8) $2062709 = 728.111\ V$

$$\therefore\ V = 2832.96 \text{ kg/h}$$

$$M = 32723.16 \text{ kg/h}$$

$$F = 45556.12 \text{ kg/h} \qquad \textbf{Ans.}$$

13. A Swenson–Walker crystallizer has to produce 800 kg per hour of $FeSO_4 \cdot 7H_2O$ crystals. The saturated solution enters the crystallizer at 49°C and the slurry leaves at 27°C. Cooling water enters the crystallizer jacket at 15°C and leaves at 21°C. The overall heat transfer co-efficient has been estimated to be 175 kcal/(hr)(m^2)(°C). There are 1.3 m^2 of cooling surface per metre of crystallizer length.

    (i) Estimate the cooling water requirement in kg/h.

    (ii) Determine the number of crystallizer sections, each section being 3 metre long.

    Data: Saturated solutions of $FeSO_4$ at 49°C and 27°C contain 140 parts and 74 parts of $FeSO_4 \cdot 7H_2O$ per 100 parts of free water respectively. Average specific heat of the initial solution is 0.70 and the heat of crystallization is 15.8 kcal/kg.

Solution.

Crystals produced = 800 kg/h

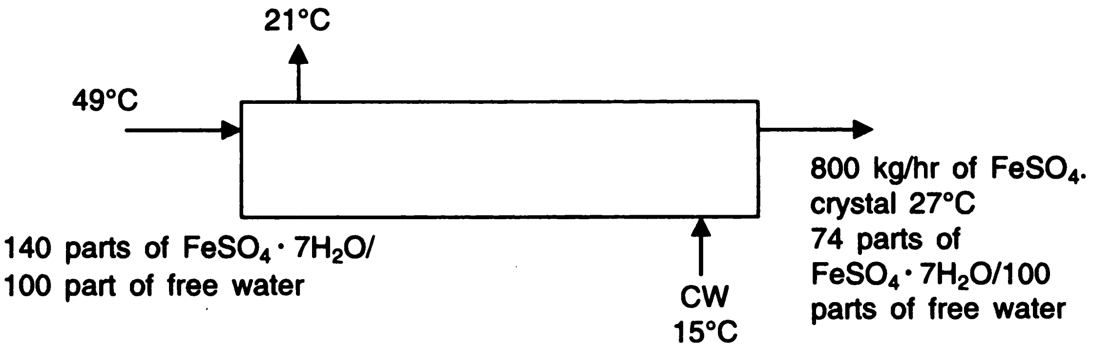


Fig. 7.8 Example 13 Material and energy balance schematic diagram.

$$U = 175 \text{ kcal/(h)(m}^2\text{)(°C)}$$

Feed concentration = 140 parts of $FeSO_4 \cdot 7H_2O$/100 parts of free water

$$140 \times \frac{151.85}{277.85} FeSO_4$$

i.e., 140 kg of $FeSO_4 \cdot 7H_2O$ = 76.51 kg of $FeSO_4$

$$\text{Concentration in feed solution} = \frac{76.51}{240} = 0.319$$

Product concentration in leaving solution/100 parts of free water =

$$74 \times \frac{151.85}{277.85} = 40.44$$

$$\text{Concentration of } FeSO_4 \text{ in product} = \frac{40.44}{174} = 0.2324$$

$$x_L = \frac{151.85}{277.85} = 0.547$$

∴ Total feed solution, F entering by mass balance is

$$\text{Feed} = \text{Mother liquor} + \text{Crystals}$$

$$F = M + C$$

Making a solute balance

$$F \cdot x_F = M \cdot x_M + C \cdot x_C$$

$$\begin{aligned}(F)(0.319) &= (M)(0.2324) + (C)\,(0.5465)\\ &= (F - C)\,(0.2324) + (C)\,(0.5465)\\ F\,(0.0866) &= C\,(0.3141)\\ F &= \frac{800 \times 0.3141}{0.0866} = 2901.62 \text{ kg/h}\\ M &= 2101.616 \text{ kg/h}\\ F &= 2901.62 \text{ kg/h}\\ M &= 2101.62 \text{ kg/h}\\ C &= 800.00 \text{ kg/h}\end{aligned}$$

Making an energy balance,

Heat to be removed by cooling water 'Q' = (Heat to be removed from solution + Heat of Crystillisation) = $F \,.\, C_p \,.\, (\Delta T) + (\Delta H_C)_C$

$$\begin{aligned}Q &= (2901.62)\,(0.7)\,(49 - 27) + (15.8)(800)\\ &= 57324.95 \text{ kcal/h}\end{aligned}$$

Cooling water needed = $m_W\, C_p\, \Delta T$

$$= \frac{57324.95}{(1)(6)} = 9554.16 \text{ kg/h}$$

$$Q = UA\,(\Delta T)\,l_m$$

$$(\Delta T)\ l_m = \frac{(49-21)-(27-15)}{\ln\left[\dfrac{49-21}{27-15}\right]} = \frac{(28-12)}{\ln\left(\dfrac{28}{12}\right)} = \frac{16}{0.847} = 18.88$$

$$A = \frac{57324.94}{175(18.88)} = 17.35\ \text{m}^2$$

$$\text{Length needed} = \frac{17.35}{1.3} = 13.35\ \text{m} \qquad \textbf{Ans.}$$

EXERCISES

1. A solution of sodium nitrate in water at a temperature of 40°C contains 45% $NaNO_3$ by weight.
   (a) Calculate the percentage saturation of this solution
   (b) Calculate the weight of $NaNO_3$ that may be crystallised from 500 kg of solution by reducing the temperature to 10°C
   (c) Calculate the percentage yield of the process.
   Solubility of $NaNO_3$ at 40°C = 51.4% by weight.
   Solubility of $NaNO_3$ at 10°C = 44.5% by weight.

   (**Ans:** (a) 87.55%, (b) 4.5 kg, (c) 2%)

2. A solution of $K_2Cr_2O_7$ in water contains 10% by weight. From 1000 kg of this solution are evaporated 600 kg of water. The remaining solution is cooled to 20°C. Calculate the amount and the percentage yield of $K_2Cr_2O_7$ crystals formed.

   Solubility at 20°C = 0.39 kmole/1000 kg H_2O.

   (**Ans:** 65.58 kg, 65.58%)

3. 1000 kg of a 25% aqueous solution of Na_2CO_3 is slowly cooled to 20°C. During cooling 10% water originally present evaporates. The crystal is $Na_2CO_3 \cdot 10H_2O$. If the solubility of anhydrous Na_2CO_3 at 20°C is 21.5 kg/100 kg of water, what weight of salt crystallises out?

   (**Ans:** 445.64 kg)

4. A batch of saturated Na_2CO_3 solution of 100 kg is to be prepared at 50°C. The solubility is 4.48 g moles/1000 g H_2O at 50°C.

   (i) If the monohydrate were available, how many kg of water would be required to form the solution?

   (ii) If the decahydrate is available how many kg of salt will be required?

   (**Ans:** 62.33 kg, 54.68 kg)

5. A crystallizer is charged with 10000 kg of aqueous solution at 104°C containing 30% by weight of anhydrous Na_2SO_4. The solution is then cooled

to 20°C. During this operation 4% of water is lost by evaporation. Glauber salt crystallises out. Find the yield of crystals.

Solubility at 20°C = 19.4 g Na_2SO_4/100 g water.

(**Ans:** 74.98%)

6. 2500 kg of KCl are present in a saturated solution at 80°C. The solution is cooled to 20°C in an open tank. The solubilities of KCl at 80°C and 20°C are 55 and 35 parts per 100 parts of water.
   (a) Assuming water equal to 5% by weight of solution is lost by evaporation, calculate the weight of crystals obtained.
   (b) Calculate the yield of crystals neglecting loss of water by evaporation KCl crystallises without any water of crystals.

(**Ans:** 908.755 kg and 36.37%)

7. A crystallizer is charged with 6400 kg of an aqueous solution containing 29.6% of anhydrous sodium sulphate. The solution is cooled and 10% of the initial water is lost by evaporation. $Na_2SO_4 \cdot 10H_2O$ crystallises out. If the mother liquor (after crystallization) is found to contain 18.3% Na_2SO_4, calculate the weight of the mother liquor.

(**Ans:** 2826.7 kg)

8. A hot solution containing 2000 kg of $MgSO_4$ and water at 330 K and with a concentration of 30 wt% $MgSO_4$ is cooled to 293 K and $MgSO_4 \cdot 7H_2O$ crystals are removed. The solubility at 293 K is 35.5 kg $MgSO_4$ per 100 kg total water. The average heat capacity of feed solution is 2.93 kJ/kg K. The heat of solution at 293 K is—13.31×10^3 kJ/K · mol $MgSO_4 \cdot 7H_2O$. Calculate the yield of crystals and make a heat balance. Assume no water is vaporised. Molecular weight of $MgSO_4$ = 120.35.

(**Ans:** 27.29%)

9. A hot solution containing 5000 kg of Na_2CO_3 and water with a concentration of 25 wt% Na_2CO_3 is cooled to 293 K and crystals of $Na_2CO_3 \cdot 10H_2O$ are precipitated. At 293 K, the solubility is 21.5 kg anhydrous Na_2CO_3/100 kg of water. Calculate the yield of crystals obtained if 5% of the original water in the system evaporates on cooling. Molecular weight of Na_2CO_3 = 106.

(**Ans:** 60.98%)

9

DISTILLATION

9.1 INTRODUCTION

The method of separating the components from a solution depending on its distribution between a liquid phase and vapour phase is termed distillation. This is applied to mixtures which distribute in both the phases.

This can also be defined as an operation in which a liquid or vapour mixture of two or more components is separated into its component fractions of desired purity, by the application of heat. Thus, in this process, a vapour is obtained from a boiling mixture which will be richer in components that have lower boiling points.

9.2 VAPOUR LIQUID EQUILIBRIA (VLE)

The vapour liquid equilibrium data is the basis for design of distillation operation equipments.

9.2.1 Constant Pressure Equilibria

A typical VLE at constant pressure is shown in Fig. 9.1.

The upper curve is the dew point curve which provides the relationship between temperature and mole fraction of the more volatile component in vapour phase (y) and the lower curve is the bubble point curve which gives the relationship between the temperature and mole fraction of the more volatile component in liquid phase (x) at a particular pressure. The horizontal tie lines CD, EF and GH at different temperatures provide equilibrium compositions of liquid and vapour phase at each temperature. Any mixture lying on the lower (bubble point) curve will be a saturated liquid and the mixture lying on the upper (dew point) curve will be a saturated vapour. A mixture located in between the two

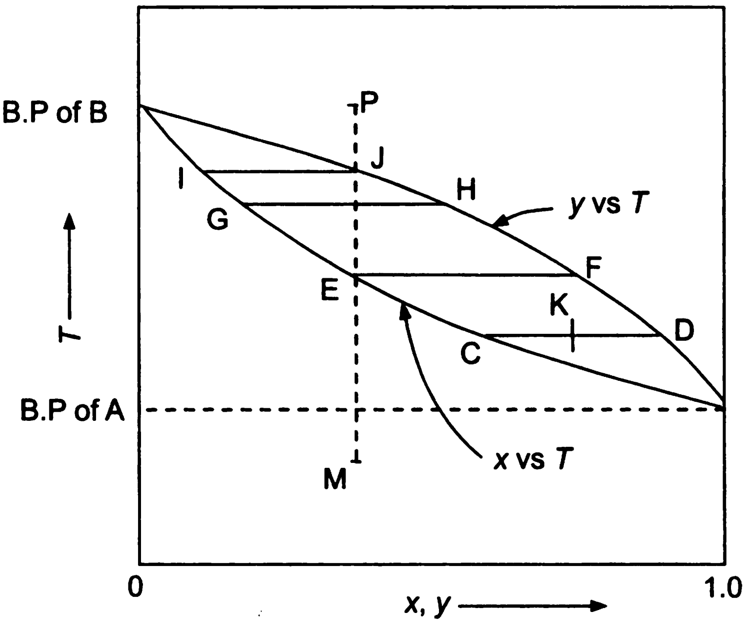


Fig. 9.1 VLE diagram at constant pressure.

curves, say K, will be a two-phase mixture of liquid and vapour with compositions C and D in liquid phase and vapour phase respectively. Their relative amounts are given by

$$\frac{\text{moles of } C}{\text{moles of } D} = \frac{\text{Length of line } KD}{\text{Length of line } KC}$$

Consider a mixture at point M. It is only a liquid. If it is kept inside a cylinder fitted with a frictionless piston and heated, its temperature will increase till it reaches 'E' when it will become a saturated liquid. The vapour in equilibrium with it will have a composition of F. As heating is further continued, more vapourization takes place, the liquid phase composition will move towards G and the associated vapour will have a composition of H. The effective composition of the entire mass comprising both liquid and vapour continues to remain at M. Finally, when the last droplet of liquid as indicated at point 'I' is vapourized, the vapour generated would have a composition of 'J'. Further application of heat results in superheating of the vapour. During the entire operation, the pressure is kept constant.

9.2.2 Effect of Pressure

As pressure is increased, the boiling points of components increase and the looped curves become more and more narrow. As the critical pressure is exceeded for one of the components, there is no longer a distinction between vapour and liquid for that component, and for mixtures the looped curves are, therefore, shorter as depicted in Fig. 9.2, for case (C). Distillation is possible only in the region where a looped curve exists. It is also clear that relative volatility, α, also changes in such cases.

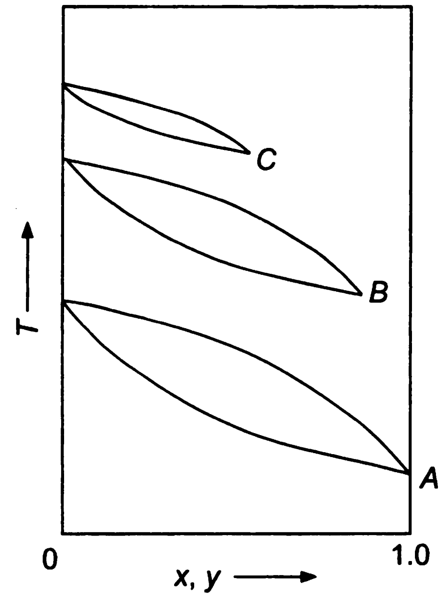


Fig. 9.2 Effect of pressure on VLE.

9.2.3 Constant Temperature Equilibria

A typical VLE at constant temperature is shown in Fig. 9.3.

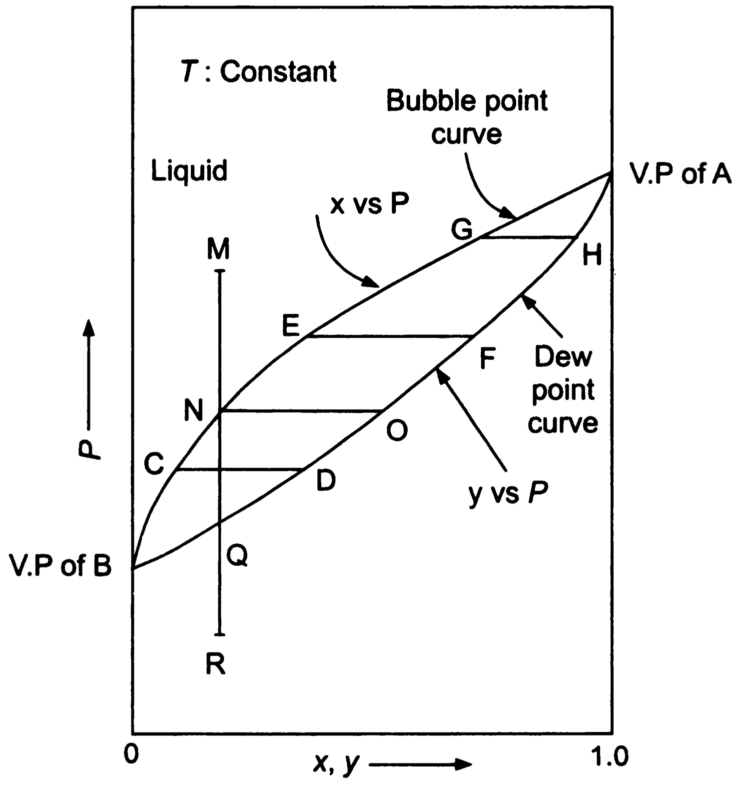


Fig. 9.3 VLE at constant temperature.

As in the case of constant temperature equilibria, lines CD, EF and GH are tie lines indicating the equilibrium compositions of liquid and vapour phase at various pressures. A liquid defined at point M is a liquid below its bubble point and as the pressure is reduced at constant temperature, at point 'N' on the upper (bubble point) curve, a saturated liquid is obtained. As the pressure is brought down further, at point Q on the lower (dew point) curve, a saturated vapour forms and a further reduction in pressure gives a fully superheated vapour as defined by R.

9.3 RELATIVE VOLATILITY (α)

This is defined as the ratio of vapour pressure of more volatile component to that of less volatile component. If P_A and P_B are the vapour pressures of A and B respectively, the relative volatility of A with respect to B, α_{AB} is defined as the ratio of vapour pressure of A to that of B.

i.e.
$$\alpha_{\mathrm{AB}} = \frac{P_A}{P_B} \tag{9.1}$$

Raoult's law states that when a gas and a liquid are in equilibrium, the partial pressure of A, p_A is equal to the product of its vapour pressure, P_A at that temperature and its mole fraction x_A in the liquid.

i.e.
$$p_A = P_A \cdot x_A \tag{9.2}$$

Similarly,
$$p_B = P_B \cdot x_B \tag{9.3}$$

When the gas and liquid behave ideally, Raoult's law holds good.

We know that sum of the partial pressures of components in a gas mixture is equal to the total pressure, P_T. The composition of a component y, in gas phase is given by Dalton's law,

$$y_A = \frac{p_A}{P_T} \quad \text{and} \quad y_B = \frac{p_B}{P_T} \tag{9.4}$$

$$\therefore \qquad \alpha_{AB} = \frac{P_A}{P_B} = \frac{\left(\dfrac{p_A}{x_A}\right)}{\left(\dfrac{p_B}{x_B}\right)} = \frac{\left(\dfrac{P_T y_A}{x_A}\right)}{\left(\dfrac{P_T y_B}{x_B}\right)} = \frac{\left(\dfrac{y_A}{y_B}\right)}{\left(\dfrac{x_A}{x_B}\right)}$$

$$\alpha_{AB} = \frac{\left(\dfrac{y_A}{1-y_A}\right)}{\left(\dfrac{x_A}{1-x_A}\right)} \tag{9.5}$$

Rearranging, we get

$$y_A = \frac{\alpha_{AB} x_A}{1 + x_A(\alpha_{AB} - 1)} \tag{9.6}$$

and more simply as

$$y = \frac{\alpha x}{1 + x(\alpha - 1)} \tag{9.7}$$

9.4 COMPUTATION OF VLE DATA (EQUILIBRIUM DATA)

The vapour pressure of the components involved is the basis for the computation of VLE data.

From Eqs. (9.2) and (9.3), $p_A = x_A P_A$

$$p_B = x_B P_B = (1 - x_A) P_B \tag{9.8}$$

For a binary system,

$$p_A + p_B = P_T = x_A P_A + (1 - x_A) P_B = P_B + x_A (P_A - P_B) \tag{9.9}$$

$$\therefore \qquad x_A = \frac{(P_T - P_B)}{(P_A - P_B)} \tag{9.10}$$

From the vapour pressure data at each temperature, x_A can be computed using Eq. (9.10). After computing x_A, the partial pressure p_A can be estimated by using Eq. (9.2). The mole fraction of A in gas phase, y_A is then determined by using Eq. (9.4). Thus, for the whole range of boiling points of components involved, the VLE data can be computed.

Whenever α lies in a narrow range, y can be computed by assuming various values of x using Eq. (9.7).

9.5 DEVIATION FROM IDEALITY

A mixture whose total pressure is either greater or lesser than that computed using Raoult's law is said to exhibit either a positive deviation or a negative deviation from ideality.

9.5.1 Positive Deviation from Ideality

When the total pressure of a mixture is greater than that for ideal mixtures computed using Raoult's law, the mixture is said to exhibit positive deviations from ideality and such mixtures are called minimum boiling azeotropes, i.e. at some composition the mixture shows minimum boiling point (at constant pressure) and maximum pressure (at constant temperature) as shown in Figs. 9.4 and 9.5. A typical x-y diagram is also shown in Fig. 9.6. Most of the azeotropic mixtures fall under this category.

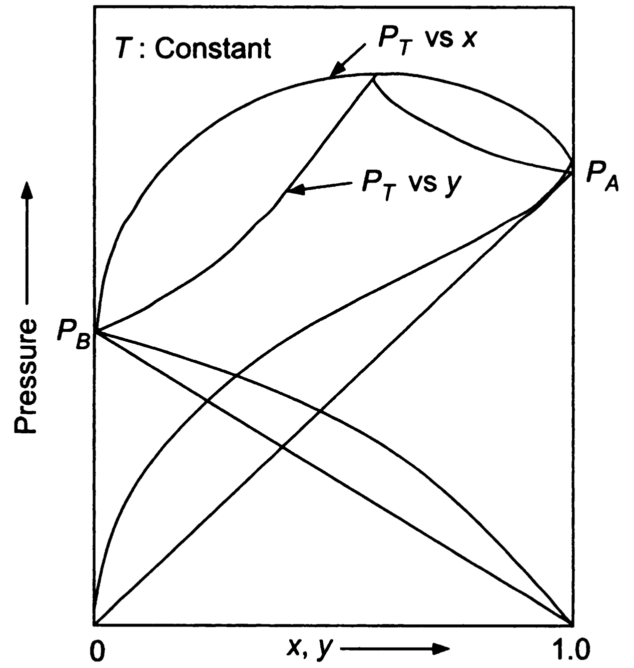


Fig. 9.4 Minimum boiling azeotrope at constant temperature.

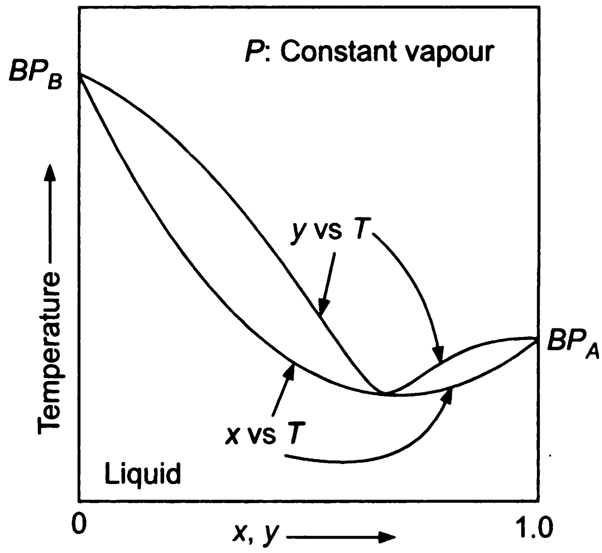


Fig. 9.5 Minimum boiling azeotrope at constant pressure.

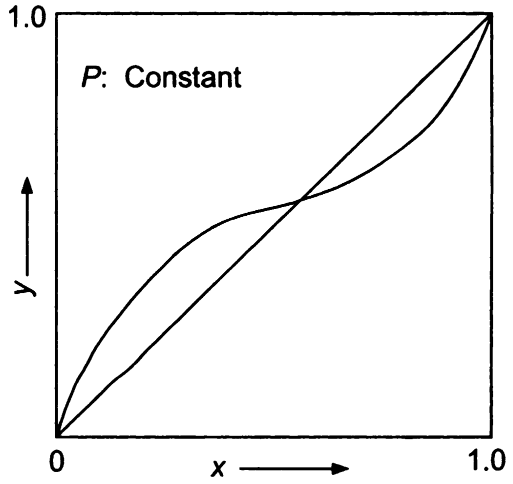


Fig. 9.6 VLE of minimum boiling azeotrope.

9.5.2 Negative Deviations from Ideality

When the total pressure of a system is less than the ideal value as computed using Raoult's law, the system is said to deviate negatively. Such systems are very rare and they are also called maximum boiling azeotropes, i.e. at some composition the mixture shows maximum boiling point. Typical *P*–*x*–*y*, *T*–*x*–*y* and *x*–*y* diagrams are shown in Figs. 9.7, 9.8 and 9.9.

9.6 TYPES OF DISTILLATION COLUMNS

Based on the nature of operation, distillation columns have been classified as batch and continuous columns as shown in Fig. 9.10.

9.6.1 Batch Columns

In batch columns, the feed to the column is introduced batchwise and the distillation is carried. When the desired quality is reached or when the desired quantity is distilled out, the operation is stopped and next batch of feed is introduced.

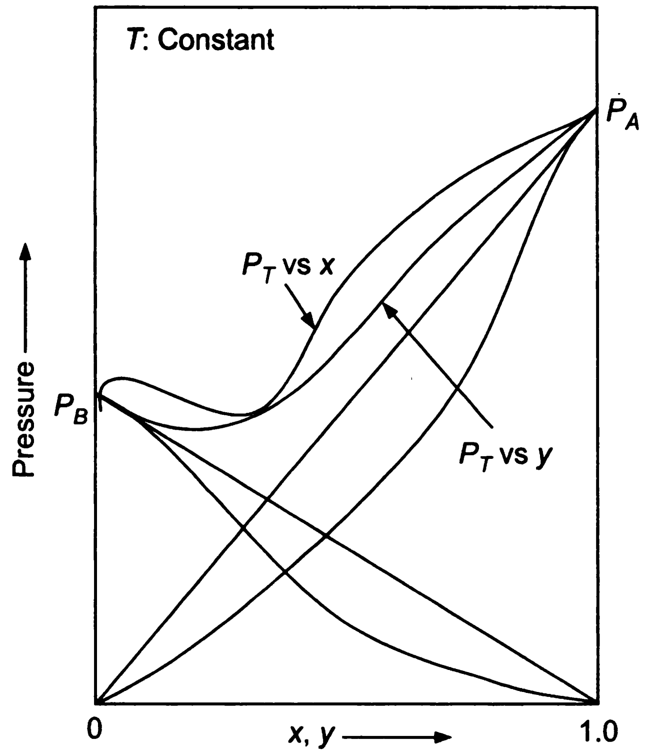


Fig. 9.7 Maximum boiling azeotrope at constant temperature.

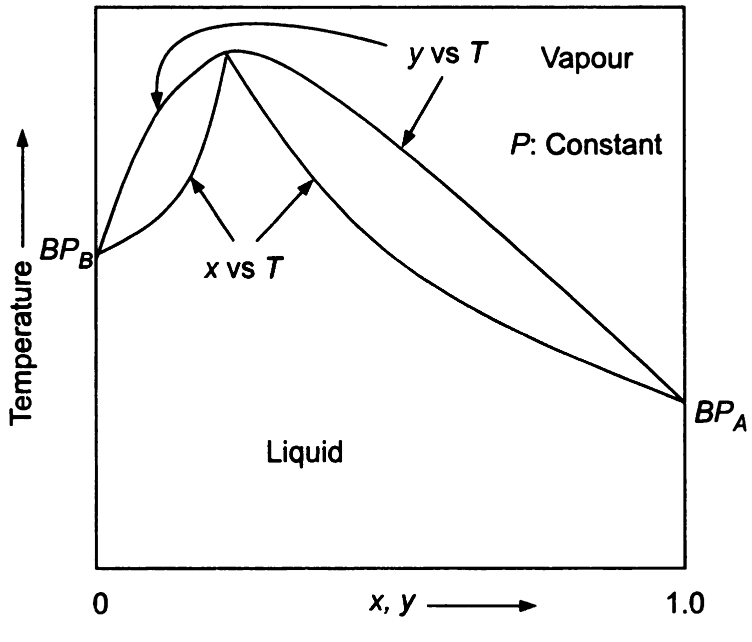


Fig. 9.8 Maximum boiling azeotrope at constant pressure.

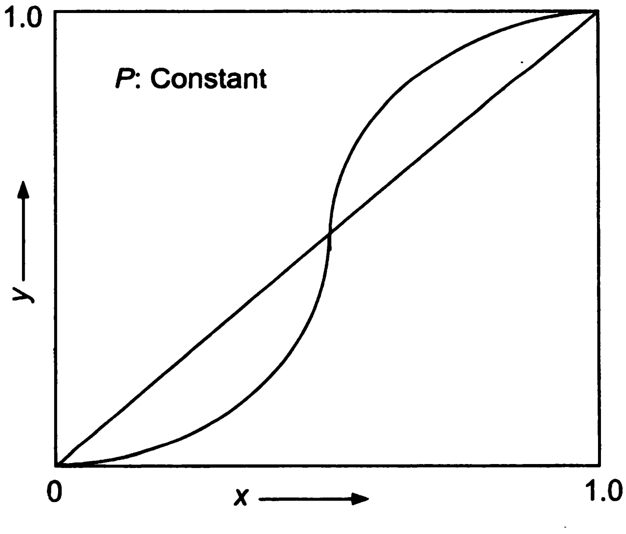


Fig. 9.9 VLE of maximum boiling azeotrope.

9.6.2 Continuous Columns

These columns have a continuous feed stream and are capable of handling high throughputs. These are further classified on the basis of,

- *The nature of the feed they are further processing*
    - Binary columns—Feed has only two components
    - Multicomponent column—Feed has more than two components
- *The number of product streams they have*
    - Two product streams
    - Multi product streams
- *The use of additional components in distillation*
    - Extractive distillation—use of solvent
    - Azeotropic distillation—use of entrainer
- *The type of columns*:
    - Tray columns—use of sieve plate columns/Bubble cap trays/Valve trays for better vapour–liquid contacting
    - Packed towers—use of packings in columns for better vapour—liquid contacting.

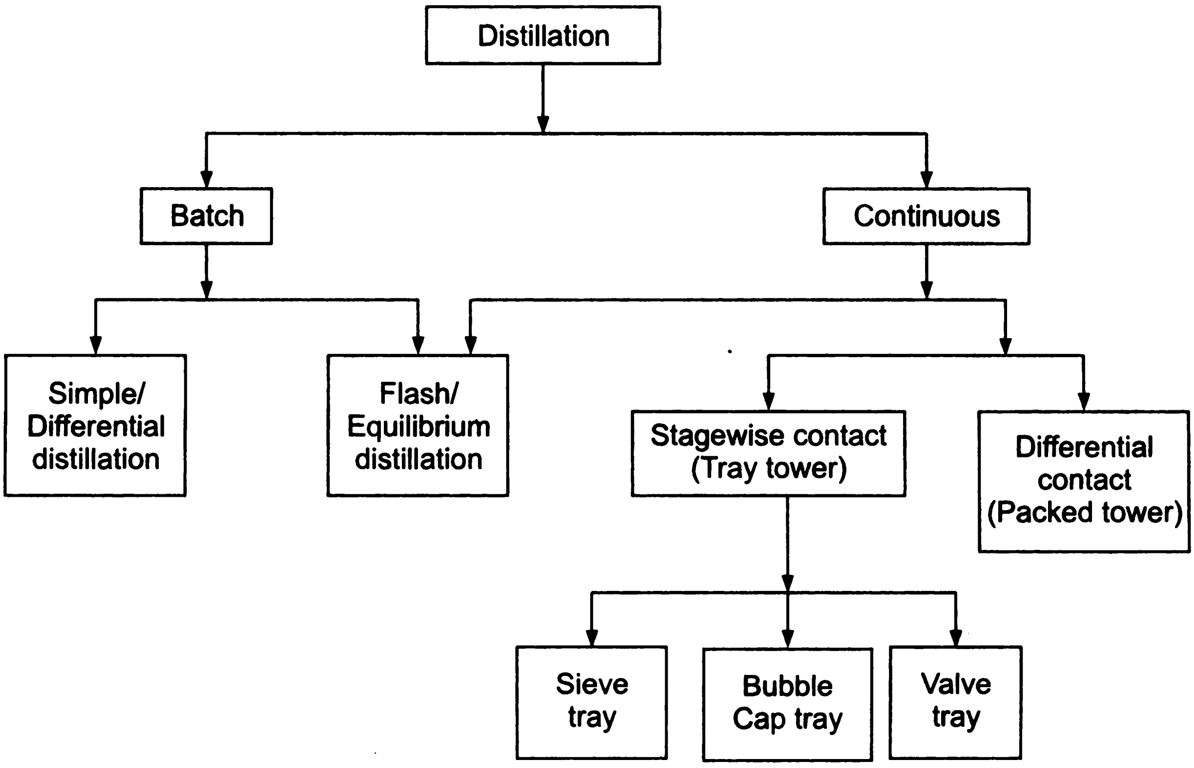


Fig. 9.10 Types of distillation and equipments.

9.7 STEAM DISTILLATION

Some systems have very high boiling points and some of these substances are unstable at high temperatures. Especially when such systems are completely insoluble with each other, steam distillation can be a useful method of separating such mixtures.

For example, consider a mixture of hydrocarbon and water which are immiscible. The vapour pressure of either component cannot be influenced by the presence of the other component and each exerts its own vapour pressure at the prevailing temperature. When the sum of the vapour pressures is equal to the total pressure, the mixture boils. With vapour pressure data of the individual components, one can also estimate the temperature at which such distillations take place.

$$P_T = P_A + P_B \tag{9.11}$$

It is clear from Fig. 9.11, that this type of distillation takes place at a temperature which will be even less than that of the boiling point water. This method suffers from poor efficiency in its operation, as large quantity of water has to be evaporated. However, one can introduce the effectiveness in such operations by

- Operating at different total pressures in which case the ratio of vapour pressure of the substances may be more favourable.
- Sparging the mixture with superheated steam or other insoluble gas.

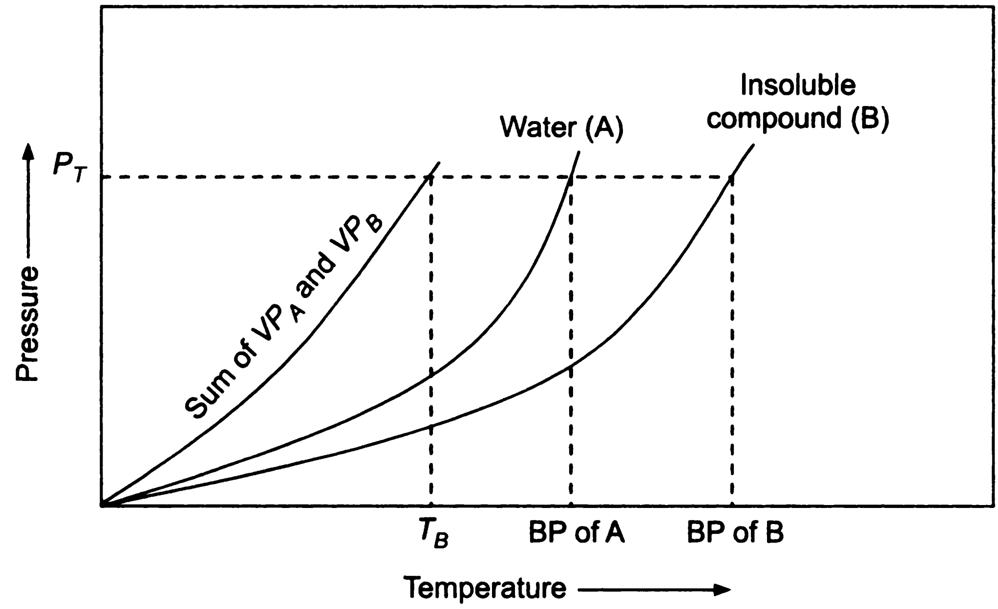


Fig. 9.11 Steam distillation.

9.8 DIFFERENTIAL OR SIMPLE DISTILLATION

Consider a feed F containing x_F mole fraction of more volatile component fed into a batch still as shown in Fig. 9.12. Let L be the total moles present in the still at any instant, t and x be the mole fraction of more volatile component. Let dL be the moles distilled out. The concentration of vapour in the leaving stream is y^*. The moles left behind in the still is $(L - dL)$. During this process the concentration of more volatile component left behind in the still is $(x - dx)$.

Total moles of more volatile component present initially is Lx

Total moles of more volatile component in distillate is $y^* dL$

Total moles of more volatile component in residue is $(L - dL)\,(x - dx)$

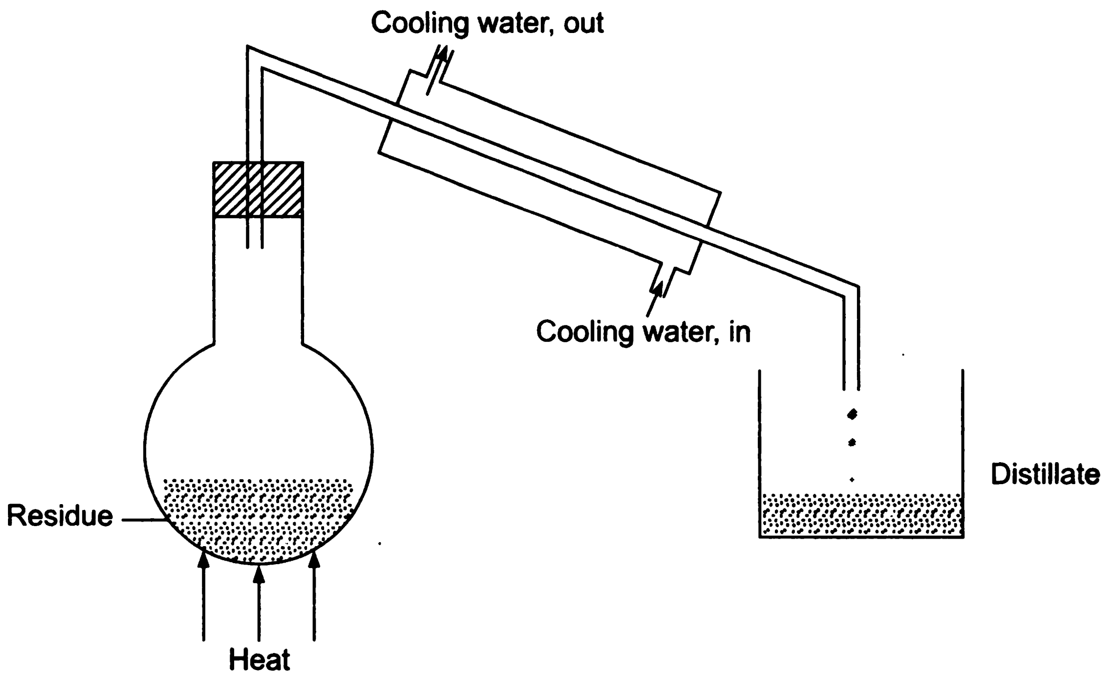


Fig. 9.12 Differential distillation.

Making a component balance, we get

$$Lx = y^*\,dL + (L - dL)\,(x - dx) \tag{9.12}$$

$$Lx = y^*\,dL + Lx - Ldx - x\cdot dL + \cancelto{0}{dx\,dL} \tag{9.13}$$

($\because$ Product of two very small quantities)

Then,
$$dL(y^* - x) = Ldx \tag{9.14}$$

$\therefore$
$$\frac{dL}{L} = \frac{dx}{(y^* - x)} \tag{9.15}$$

Integrating between limits $\quad x = x_F \quad L = F$

$\quad x = x_W \quad L = W$

$\therefore$
$$\int_W^F \frac{dL}{L} = \int_{x_w}^{x_F} \frac{dx}{(y^* - x)} \tag{9.16}$$

$$\ln \frac{F}{W} = \int_{x_w}^{x_F} \frac{dx}{(y^* - x)} \tag{9.17}$$

Equation (9.17) is called *Rayleigh's equation.*

The right-hand side cannot be integrated as y* is a function of x.

Hence, the right-hand side of Eq. (9.17) can be evaluated either graphically or numerically with the help of x-y or VLE data.

For systems where the relative volatility lies in a narrow range, we can use Eq. (9.7) which states that

$$y = \frac{\alpha x}{[1 + (\alpha - 1)x]}$$

Hence, replacing y in terms of Eq. (9.7), we get

$$\ln\frac{F}{W}=\int_{x_w}^{x_F}\left[\frac{dx}{\dfrac{\alpha x}{\left[1+(\alpha-1)x\right]}-x}\right] \tag{9.18}$$

$$\text{RHS of Eq. (9.18)} = \int\left[\frac{dx}{\dfrac{\alpha x}{\left[1+(\alpha-1)x\right]}-x}\right]. \tag{9.19}$$

On simplification,

$$=\int\frac{[1+(\alpha-1)x]dx}{[\alpha x-x-\alpha x^2+x^2]}=\int\frac{[1+(\alpha-1)x]dx}{x[\alpha-1-\alpha x+x]}$$

$$=\int\frac{[1+(\alpha-1)x]dx}{x[1(\alpha-1)-x(\alpha-1)]}=\int\frac{[1+(\alpha-1)x]dx}{[x(1-x)(\alpha-1)]}$$

$$=\int\frac{dx}{[x(1-x)(\alpha-1)]}+\int\frac{dx}{(1-x)}=\frac{1}{(\alpha-1)}\int\left[\left(\frac{A}{x}\right)+\left(\frac{B}{1-x}\right)\right]dx-\ln(1-x)$$

$$=\frac{1}{(\alpha-1)}\int\frac{A(1-x)+B(x)}{x(1-x)}dx-\ln(1-x)$$

$$=\frac{1}{(\alpha-1)}\left[\int\frac{dx}{x}+\int\frac{dx}{(1-x)}\right]-\ln(1-x)$$

Substituting the limits for x as x_F and x_W, we get

$$=\frac{1}{(\alpha-1)}\left[\ln x-\ln(1-x)\right]-\ln(1-x)$$

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

i.e.

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

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

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

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

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

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

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

i.e.

$$\frac{Fx_F}{Wx_W}=\left[\frac{F(1-x_F)}{W(1-x_W)}\right]^{\alpha} \tag{9.20}$$

Equation (9.20) is very useful in the estimation of the amount of residue (alternatively, the estimation of the quantity to be distilled) in case of systems of constant relative volatility. This is also used in the estimation of relative volatility for such systems.

9.9 EQUILIBRIUM OR FLASH DISTILLATION

Consider a feed at a flow rate of F (moles per hour), containing the more volatile component with a composition of Z_F and an enthalpy of H_F (per mole of feed) entering a preheater. Let the heat added in the preheater be Q. The mixture then enters a flash chamber where a distillate leaves at a rate of D (moles per hour) with a composition of y_D and an enthalpy of H_D (per mole of distillate). The bottoms (residue) leave at a rate of W, with a composition of x_W and an enthalpy of H_W (per mole of residue). The entire process is shown in Fig. 9.13

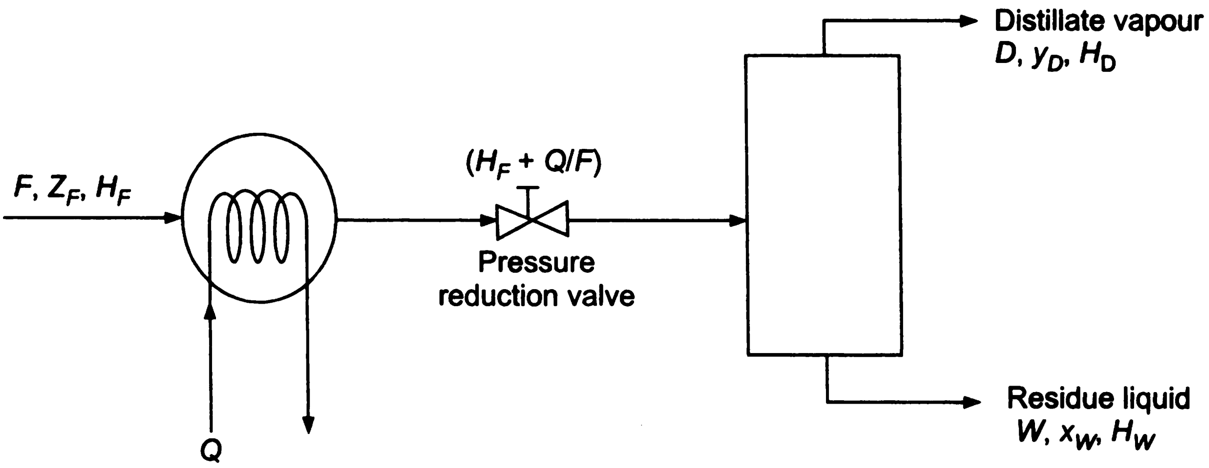


Fig. 9.13 Flash distillation.

A total material balance, gives,

$$F = W + D \tag{9.21}$$

A component balance gives,

$$FZ_F = Wx_W + Dy_D \tag{9.22}$$

An enthalpy balance gives,

$$FH_F + Q = WH_W + DH_D$$

i.e.

$$F\left(H_F + \frac{Q}{F}\right) = WH_W + DH_D \tag{9.23}$$

From Eqs. (9.21) and (9.22), we get

$$(W + D)Z_F = Wx_W + Dy_D \tag{9.24}$$

$$\therefore \quad W\,[Z_F - x_W] = -D[Z_F - y_D] \tag{9.25}$$

$$\therefore \quad -\frac{W}{D} = \frac{(Z_F - y_D)}{(Z_F - x_W)} \tag{9.26}$$

Similarly from Eqs. (9.21) and (9.23), we get

$$-\frac{W}{D} = \frac{\left[\left(H_F + \frac{Q}{F}\right) - H_D\right]}{\left[\left(H_F + \frac{Q}{F}\right) - H_W\right]} \tag{9.27}$$

Dividing Eq. (9.25) by F, we get

$$\frac{W}{F}(Z_F - x_W) = -\frac{D}{F}(Z_F - y_D) \tag{9.28}$$

Let f be the fraction of feed vaporised and subsequently condensed and removed. Hence, $(1 - f)$ is the fraction of feed left behind as residue.

$$\therefore \quad (1 - f)\,(Z_F - x_W) = f\,(y_D - Z_F) \tag{9.29}$$

$$Z_F - x_W - fZ_F + f\,x_W = fy_D - fZ_F$$

$$\therefore \quad Z_F - x_W = f\,(y_D - x_W)$$

$$Z_F + x_W\,(f - 1) = fy_D$$

$$\therefore \quad y_D = \frac{Z_F}{f} + x_W\,\frac{(f - 1)}{f} \tag{9.30}$$

So Eq. (9.30) can be called an operating line drawn with a slope of $[(f - 1)/f]$ and simplified as,

$$y = \left(\frac{Z_F}{f}\right) + x\left(\frac{f - 1}{f}\right) \tag{9.31}$$

The feed point is $x = y = Z_F$

Having seen the principles involved in flash distillation, let us now see how compositions are estimated in a flash distillation operation.

9.9.1 Steps

There are two methods available to estimate the composition of products. They are explained in detail below.

Case I

When the equilibrium data and the quantity of either the distillate or the residue and feed are available, the following procedure shall be adopted:

- Draw the equilibrium curve
- Draw the diagonal ($x = y$ line)
- Locate feed point corresponding to x_F on the diagonal ($x_F = y_F = Z_F$)
- Draw the operating line with a slope of $\left[-\dfrac{W}{D}\right]$
- The intersection of this line with equilibrium curve gives x_W and y_D as shown in Fig. 9.14.

Case II

When the enthalpy–concentration data (H_L vs x and H_G vs y) and heat added Q are available, the following procedure shall be adopted.

- Plot the enthalpy concentration data and also equilibrium curve below it.
- Locate the feed point corresponding to $F(Z_F, H_F + Q/F)$
- Draw a line by trial and error, passing through F such that it will be a tie line.
- The points of intersection of this line (drawn by trial and error) with enthalpy–concentration curves gives the enthalpy and concentration of both the distillate and the residue.

Figures (9.14) and (9.15) represent the procedures followed to determine the product concentrations for case I and case II respectively.

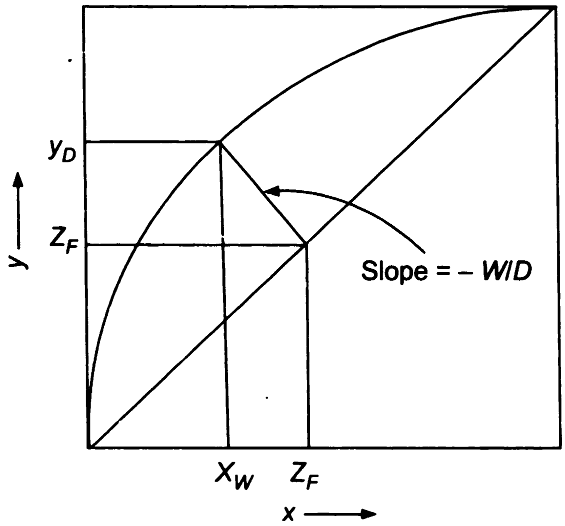


Fig. 9.14 Estimation of composition of products in flash distillation.

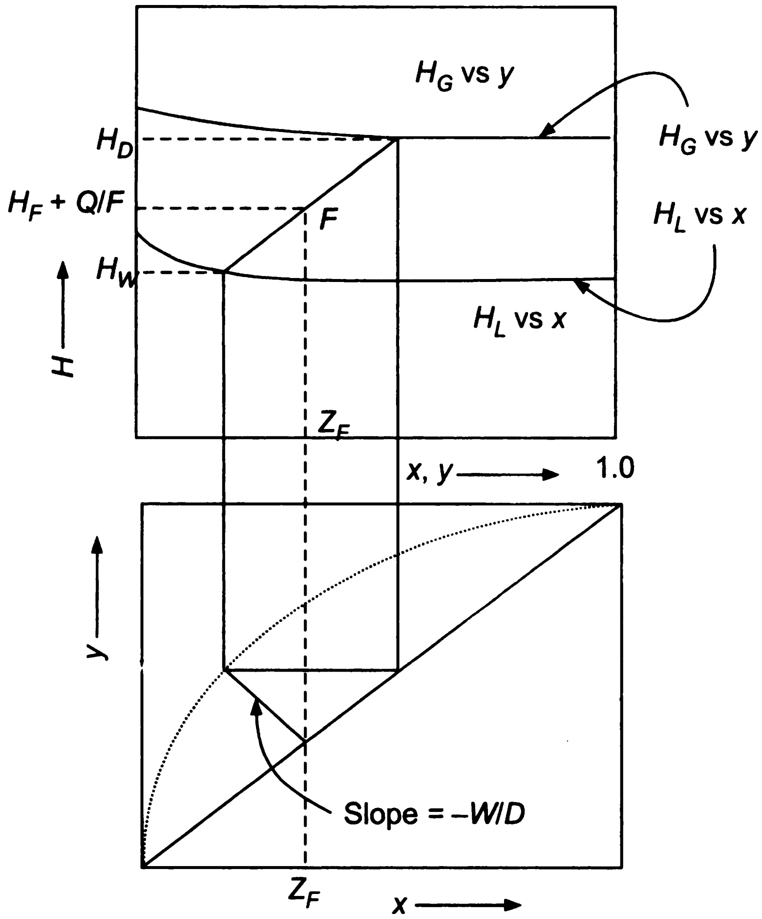


Fig. 9.15 Enthalpy–concentration diagram.

9.10 MULTICOMPONENT SIMPLE DISTILLATION

Let us consider a multicomponent mixture fed to a still. The distillate and the residue left behind will also be multicomponent mixtures. For our analysis, let us consider a three-component system wherein α remains fairly constant. Modified Rayleigh's equation can be applied for material balance,

$$\ln\left[\frac{Fx_{F,A}}{Wx_{W,A}}\right] = \ln\left[\frac{Fx_{F,B}}{Wx_{W,B}}\right]^{\alpha_{AB}} \tag{9.32}$$

$$\ln\left[\frac{Fx_{F,A}}{Wx_{W,A}}\right] = \ln\left[\frac{Fx_{F,C}}{Wx_{W,C}}\right]^{\alpha_{AC}} \tag{9.33}$$

Similarly,

$$\ln\left[\frac{Fx_{F,B}}{Wx_{W,B}}\right] = \ln\left[\frac{Fx_{F,C}}{Wx_{W,C}}\right]^{\alpha_{BC}} \tag{9.34}$$

Here, $BP_A < BP_B < BP_C$, where BP is the boiling point. We also know that

$$x_{WA} + x_{WB} + x_{WC} = 1.0 \tag{9.35}$$

In a typical feed mixture, the values of F, x_{FA}, x_{FB} and x_{FC} are known. The unknown quantities will be W, D, x_{WA}, x_{WB} and x_{WC}. To solve such problems one has to assume W. By substituting in the first three equations, a relationship between x_{WA}, x_{WB} and x_{WC} is obtained. Then it can be solved and checked for the validity of assumed value of W using Eq. (9.35). If Eq. (9.35) is satisfied, the assumed value of W is correct. If not, a new value for W is assumed and the above calculations are repeated till Eq. (9.35) is satisfied.

Subsequently using the total material balance equation, D can be calculated and then the mole fraction of each component in the distillate phase (vapour phase) can be evaluated by making a component balance.

However, in cases where α varies significantly, the Rayleigh's equation of the form $\ln\frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{(y-x)}$ has to be used taking two components at a time. Here also one has to assume W and suitably estimate x_W. The values of x_W will have to be determined for all the components and finally checked using Eq. (9.35). If Eq. (9.35) is not satisfied, one has to make a fresh assumption of W and has to proceed till Eq. (9.35) is satisfied.

9.11 MULTICOMPONENT FLASH DISTILLATION

At low pressures almost all systems behave ideally. As flash distillation occurs generally at low pressures, ideal behaviour can be expected and Raoult's law is applicable. Hence, the equilibrium relationship for any component may be expressed as

$$y_i = m_i x_i \tag{9.36}$$

where m_i = vapour pressure of component/total pressure. The suffix i denotes the component.

i.e.

$$y_{i,D} = m_i\,(x_{i,W}) \tag{9.37}$$

We know that $-\frac{W}{D} = \frac{(y_D - Z_F)}{(x_W - Z_F)}$ [from Eq. (9.26)]

∴

$$\frac{W}{D} = \frac{(y_{i,D} - Z_{i,F})}{(Z_{i,F} - x_{i,W})} \tag{9.38}$$

$$= \frac{\left[y_{i,D} - Z_{i,F}\right]}{\left[Z_{i,F} - \frac{y_{i,D}}{m_i}\right]} \tag{9.39}$$

or

$$\frac{W}{D}\left[Z_{i,F} - \frac{y_{i,D}}{m_i}\right] = [y_{i,D} - Z_{i,F}] \tag{9.40}$$

i.e.

$$Z_{i,F}\left[\frac{W}{D} + 1\right] = y_{i,D}\left[1 + \left(\frac{1}{m_i}\right)\left(\frac{W}{D}\right)\right] \tag{9.41}$$

∴ $$y_{i,D} = Z_{i,F}\frac{\left[\frac{W}{D}+1\right]}{\left[1+\left(\frac{1}{m_i}\right)\left(\frac{W}{D}\right)\right]} \tag{9.42}$$

and $$x_{i,W} = Z_{i,F}\frac{\left[\frac{W}{D}+1\right]}{\left[m_i+\frac{W}{D}\right]} \tag{9.43}$$

$y_{i,D}$ is evaluated using Eq. (9.42) and $x_{i,W}$ is evaluated using Eq. (9.43) by assuming (W/D) value and finally checked for its validity by using

$$\Sigma x_{i,W} = 1.0; \qquad \Sigma y_{i,D} = 1.0$$

9.11.1 Steps Involved

- From vapour pressure, determine m for each component.
- Assume W/D value and determine $x_{i,W}$ and $y_{i,D}$
- Check whether $\Sigma x_{i,W}$ and $\Sigma y_{i,D}$ are 1.0.
- If they are 1.0, then the assumed W/D ratio is correct.
- If not, assume a new value for W/D and ensure that $\Sigma x_{i,W} = 1.0$; $\Sigma y_{i,D} = 1.0$ are satisfied.

9.12 CONTINUOUS RECTIFICATION

A schematic sketch of a typical distillation column with a feed stream and a distillate and residue stream is shown in Fig. 9.16 along with its main accessories.

9.12.1 Ponchon–Savarit Method

There are two methods by which the design of the continuous fractionator can be established. Let us first consider Ponchon–Savarit method where it requires both enthalpy and concentration data.

Envelope I: Condenser section
Envelope II: Full distillation unit
Envelope III: Enriching/Rectifying section
Envelope IV: Stripping/Exhausting section

The numbering of plates or trays is accounted from the top to bottom. Suffix denotes the properties of streams leaving a particular plate or tray. Let n and m, denote general plates in the enriching section and stripping section respectively.

Let G be the molar flow rate of vapour in enriching section, $\bar{G}$ the molar flow rate of vapour in stripping section, L the molar flow rate of liquid in enriching

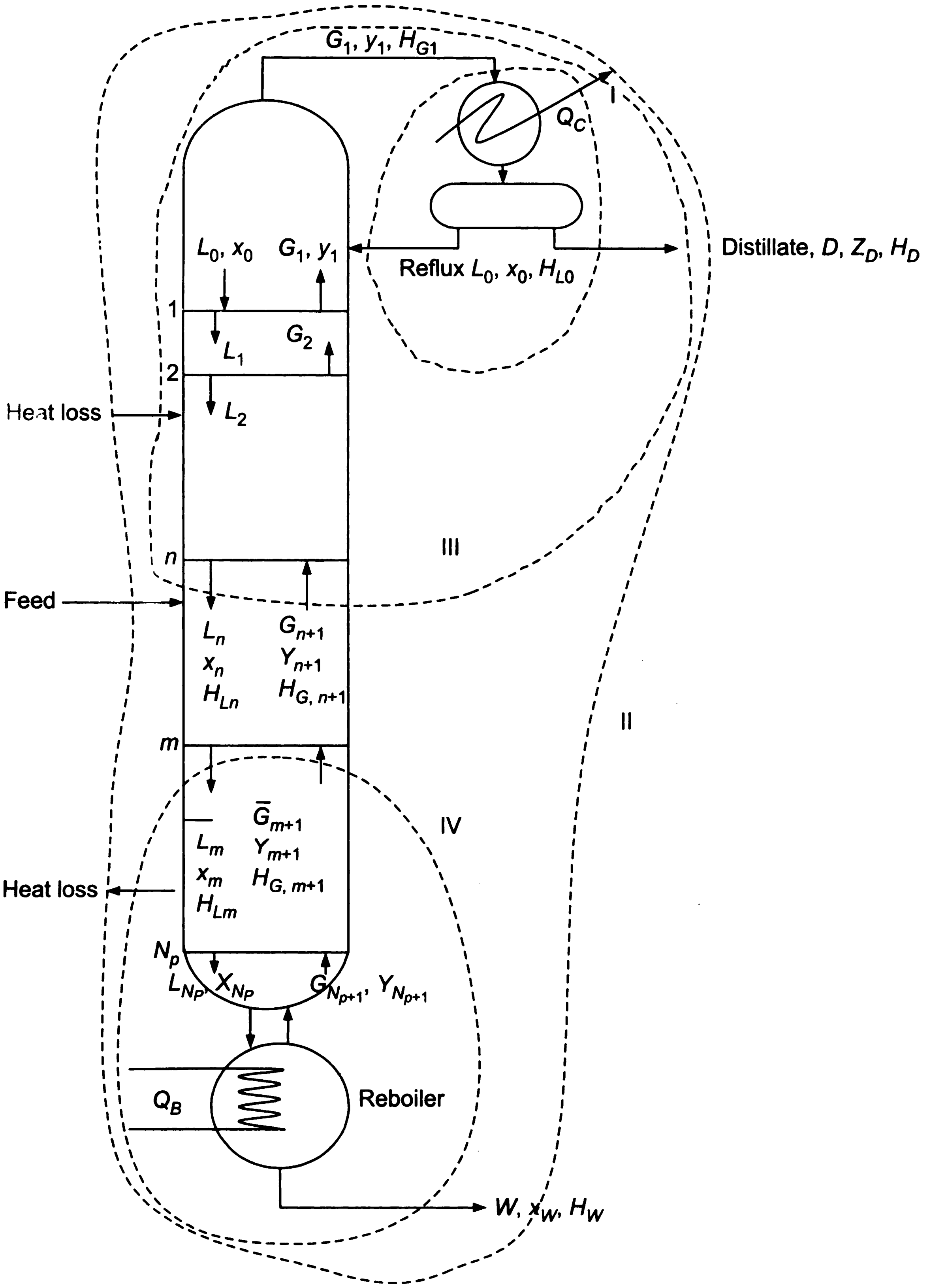


Fig. 9.16 Continuous fractionator.

section, $\bar{L}$ the molar flow rate of liquid in stripping section, H_G the Enthalpy of vapour, H_L the Enthalpy of liquid, y the mole fraction of more volatile component in vapour and x the mole fraction of more volatile component in liquid.

Let R be the *external reflux ratio* L_0/D, Q_C the load on condenser, Q_B the heat supplied in reboiler and Q_L the total heat loss.

Considering envelope I and making a mass balance,

$$G_1 = D + L_0 \tag{9.44}$$

$$G_1 = D + RD = D(R + 1) \tag{9.45}$$

A component balance gives

$$G_1 y_1 = DZ_D + L_0 x_0 \tag{9.46}$$

Making an energy balance, we get

$$G_1 H_{G_1} = L_0 H_{L_0} + DH_D + Q_C \tag{9.47}$$

$$\therefore \quad Q_C = G_1 H_{G_1} - L_0 H_{L_0} - DH_D \tag{9.48}$$

Substituting for G_1 from Eq. (9.45), we get

$$Q_C = [D(R + 1)\, H_{G_1}] - RDH_{L_0} - DH_D$$

$$= D[(R + 1)H_{G_1} - RH_{L_0} - H_D] \tag{9.49}$$

Considering envelope II and making an energy balance, we have
Heat in = Heat out

$$Q_B + FH_F = DH_D + WH_W + Q_C + Q_L \tag{9.50}$$

$\therefore$ Heat added in reboiler $Q_B = DH_D + WH_W + Q_C + Q_L - FH_F$ (9.51)

Now, let us consider envelope III, the enriching section and make mass and energy balance.
A total mass balance yields,

$$G_{n+1} = L_n + D \tag{9.52}$$

A component balance gives,

$$G_{n+1} y_{n+1} = L_n x_n + DZ_D \tag{9.53}$$

An energy balance gives,

$$G_{n+1} H_{G_{n+1}} = L_n \cdot H_{L_n} + DH_D + Q_C \tag{9.54}$$

Let Q' = (Net heat out/Net moles out) = $\left[\dfrac{(Q_C + DH_D)}{D}\right]$ (9.55)

Then, Eq. (9.54) becomes

$$G_{n+1}\, H_{G_{n+1}} = L_n \cdot H_{L_n} + DQ' \tag{9.56}$$

Eliminating D from Eq. (9.53) using Eq. (9.52), we get

$$(G_{n+1})(y_{n+1}) - L_n x_n = (G_{n+1} - L_n) Z_D \tag{9.57}$$

$$(G_{n+1})[Z_D - y_{n+1}] = L_n(Z_D - x_n)$$

$$\frac{L_n}{G_{n+1}} = \frac{(Z_D - y_{n+1})}{(Z_D - x_n)} \tag{9.58}$$

where (L_n/G_{n+1}) is defined as *internal reflux ratio.*

Similarly, Eqs. (9.52) and (9.56) yield

$$\frac{L_n}{G_{n+1}} = \frac{(Q' - H_{G_{n+1}})}{(Q' - H_{L_n})} \tag{9.59}$$

Equating Eq. (9.58) with Eq. (9.59), we get

$$\frac{L_n}{G_{n+1}} = \frac{(Z_D - y_{n+1})}{(Z_D - x_n)} = \frac{(Q' - H_{G_{n+1}})}{(Q' - H_{L_n})} \tag{9.60}$$

Equation (9.60) represents a straight line passing through

$(H_{G_{n+1}}, y_{n+1})$ at G_{n+1}, (H_{L_n}, x_n) at L_n and (Q', Z_D) at Δ_D

where Δ_D is called the difference point and it represents

Q': Net heat, out/Net moles, out and

Z_D: Net moles of more volatile component, out/Net moles, out

Let us consider Eq. (9.59).

$$\frac{L_n}{G_{n+1}} = \frac{(Q' - H_{G_{n+1}})}{(Q' - H_{L_n})}$$

Substituting for G_{n+1} in the above expression from Eq. (9.52), we have

$$\frac{L_n}{(L_{n+D})} = \frac{(Q' - H_{G_{n+1}})}{(Q' - H_{L_n})} \tag{9.61}$$

i.e.
$$\frac{(L_{n+D})}{L_n} = \frac{(Q' - H_{L_n})}{(Q' - H_{G_{n+1}})}$$

i.e.
$$1 + \left[\frac{D}{L_n}\right] = \frac{(Q' - H_{L_n})}{(Q' - H_{G_{n+1}})}$$

∴
$$\frac{D}{L_n} = \frac{(H_{G_{n+1}} - H_{L_n})}{(Q' - H_{G_{n+1}})} \tag{9.62}$$

∴
$$\frac{L_n}{D} = \frac{(Q' - H_{G_{n+1}})}{(H_{G_{n+1}} - H_{L_n})} \tag{9.63}$$

When $n = 0$, it indicates the condenser and for $n = 0$, we get

$$\frac{L_0}{D} = \frac{(Q' - H_{G_1})}{H_{G_1} - H_{L_0}} \tag{9.64}$$

i.e. R, the external reflux ratio $= \frac{L_0}{D} = \frac{\text{Length of line } \Delta_D G_1}{\text{Length of line } G_1 L_0}$ (9.65)

as indicated in Fig. 9.17(a).

Hence, if the reflux ratio R is known, then it will be easy for us to locate Δ_D point (Z_D, Q').

Also, $$\frac{L_n}{D} = \frac{(Z_D - y_{n+1})}{(y_{n+1} - x_n)} \quad \text{[from Eq. (9.58)]}$$

Let us consider envelope IV in the stripping section.
A mass balance yields

$$\therefore \quad \bar{L}_m = \bar{G}_{m+1} + W \tag{9.66}$$

A component balance yields

$$\bar{L}_m x_m = \bar{G}_{m+1} y_{m+1} + W x_W \tag{9.67}$$

$$\therefore \quad L_m\, x_m - \bar{G}_{m+1} y_{m+1} = W x_W \tag{9.68}$$

An energy balance yields

$$L_m \cdot H_{L_m} + Q_B = \bar{G}_{m+1} H_{G_{m+1}} + W H_W \tag{9.69}$$

Let $$Q'' = \frac{(W H_W - Q_B)}{W} \tag{9.70}$$

$$\therefore \quad \bar{L}_m \cdot H_{L_m} - \bar{G}_{m+1} H_{G_{m+1}} = W Q'' \tag{9.71}$$

Eliminating W from Eqs. (9.66) and (9.68), we get

$$\frac{\bar{L}_m}{G_{m+1}} = \frac{(y_{m+1} - x_W)}{(x_m - x_W)} \tag{9.72}$$

Similarly eliminating W from Eqs. (9.66) and (9.71), we have

$$\frac{\bar{L}_m}{\bar{G}_{m+1}} = \frac{(H_{G_{m+1}} - Q'')}{(H_{L_m} - Q'')} \tag{9.73}$$

Hence from Eqs. (9.72) and (9.73), we get

$$\frac{\bar{L}_m}{\bar{G}_{m+1}} = \frac{(y_{m+1} - x_W)}{(x_m - x_W)} = \frac{(H_{G_{m+1}} - Q'')}{(H_{L_m} - Q'')} \tag{9.74}$$

From Eq. (9.66), we have

$$\frac{\bar{L}_m}{\bar{G}_{m+1}} = 1 + \left(\frac{W}{\bar{G}_{m+1}} \right)$$

Hence, rearrangement of Eq. (9.74) using Eq. (9.66) gives

$$\frac{W}{\bar{G}_{m+1}} = \frac{(y_{m+1} - x_W)}{(x_m - x_W)} \tag{9.75}$$

$$\therefore \qquad \frac{\bar{L}_m}{W} = \frac{(H_{G_{m+1}} - Q'')}{(H_{G_{m+1}} - H_{L_m})} = \frac{y_{m+1} - x_W}{(y_{m+1} - x_m)} \tag{9.76}$$

Equation (9.76) represents a line passing through (x_W, Q''), (x_m, H_{L_m}) and (y_{m+1}, $H_{G_{m+1}}$) where Q'' represents net heat out /Net moles out and x_W denotes moles of A out/net moles out. Now let us consider the fractionator as single unit and make mass and energy balances;
Total mass balance gives

$$F = D + W \tag{9.77}$$

A component balance gives

$$FZ_F = Dy_D + Wx_W \tag{9.78}$$

An enthalpy balance gives

$$F \cdot H_F = (DQ' + WQ'') \tag{9.79}$$

(Neglecting Q_L, the heat loss)
Eliminating F from Eqs. (9.77), (9.78) and (9.79) we get

$$\frac{D}{W} = \frac{(Z_F - x_W)}{(Z_D - Z_F)} = \frac{(H_F - Q'')}{(Q' - H_F)} \tag{9.80}$$

Equation (9.80) represents a line passing through (Z_D, Q'), (Z_F, H_F) and (x_W, Q'')
In other words,

$$F = \Delta_D + \Delta_W \tag{9.81}$$

The schematic representation of enthalpy concentration and distribution diagrams for determination of number of stages for a total condensation of distillate vapour is shown in Fig. 9.17(a).

Steps involved

1. Draw H vs x, y diagram and the equilibrium curve.
2. Locate z_D, y_D and x_W in both the diagrams and draw vertical lines from z_D in positive y-axis direction and from x_W in the negative y-axis direction.
3. Locate $F(x_F, H_F)$ in the H–x, y diagram.
4. Obtain Q' using the given reflux ratio, $R = \dfrac{(Q' - H_{G_1})}{(H_{G_1} - H_{L_0})}$

   where H_{G_1}, H_{L_0} indicate the enthalpy of vapour and liquid correspond to the distillate composition for a total condensation.
5. In cases where the reflux ratio is not given, an optimum reflux ranging from 1.5 to 2 times the minimum reflux can be chosen.
6. To determine the *minimum reflux*, several lines can be drawn through the feed point F in the entire range of x and projected downwards from both H vs x and H vs y curves to the x-y diagram as shown in Fig. 9.17(b) and one such horizontal line in x-y diagram will be a tie line. This line is extended to cut the vertical line drawn at z_D and this intersection point corresponds to the value of Q' at minimum reflux and the value of R estimated is R_{min}.

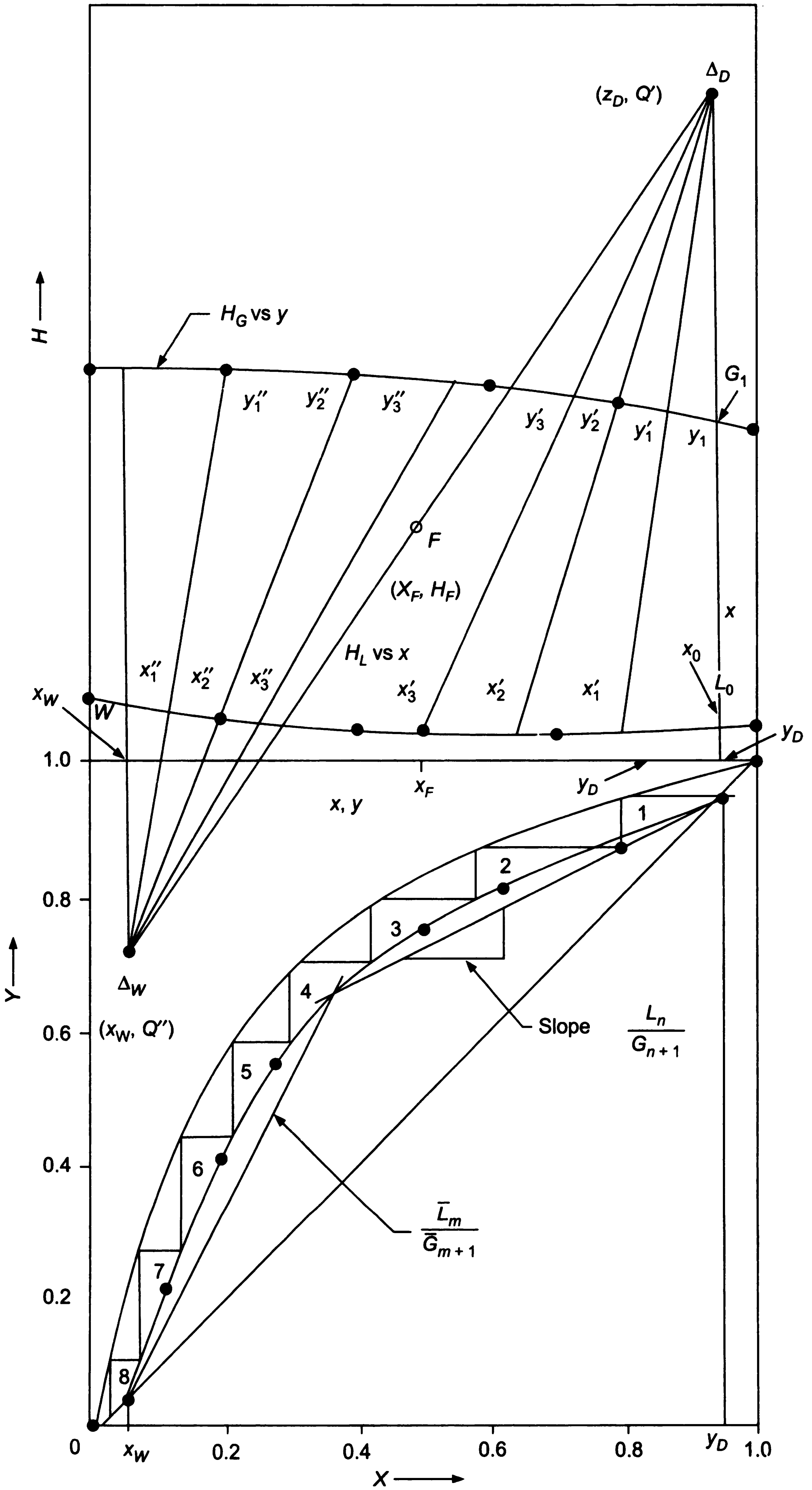


Fig. 9.17(a) Determination of number of stages by Ponchon–Savarit method.

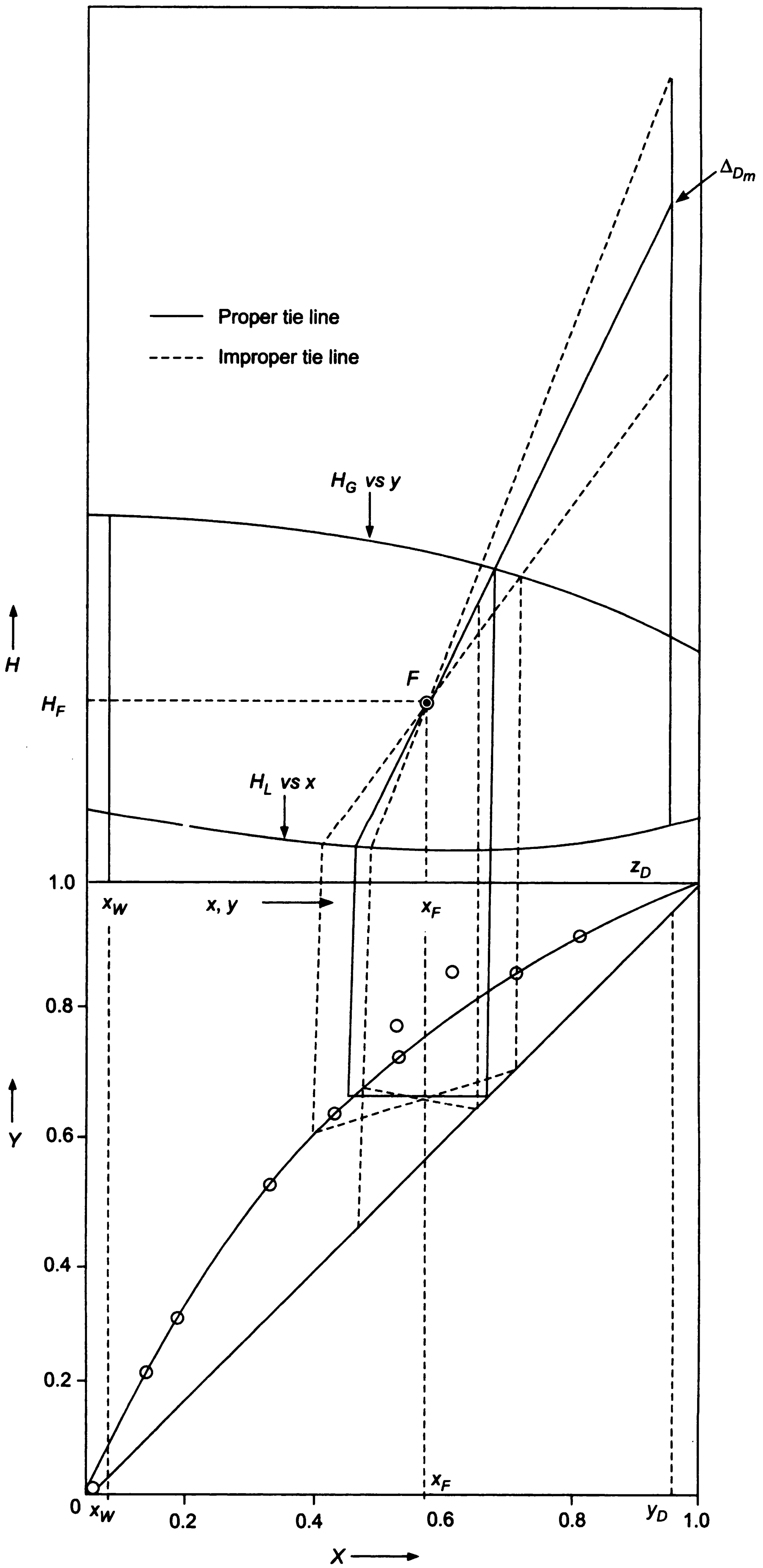


Fig. 9.17(b) Determination of minimum reflux in Ponchon–Savarit method.

7. Locate Δ_D (y_D, Q') using the H_{G_1}, H_{L_0} and reflux ratio.
8. Join Δ_D with F and project it to cut the vertical line at x_W and that point is Δ_W.
9. Draw arbitrarily several lines both from Δ_D and Δ_W to cut both the curves. The values taken from H vs y give y' and the line from H vs x gives x'. For each line drawn we will have a set of x' and y' values with which we can construct the operating line in the distribution diagram for both enriching and stripping sections.
10. Draw the equilibrium curve and plot x', y' data obtained from step (9).
11. By stepwise construction starting from point D, between the equilibrium curve and operating line up to W, the number of stages for the desired separation is determined.

9.12.2 McCabe–Thiele Method

When systems exhibit ideal behaviour, the time-consuming Ponchon–Savarit method of determining the number of ideal stages, can be replaced with the following technique. Let us begin our analysis by considering enriching section for total condensation of distillate as shown in Fig. 9.18.

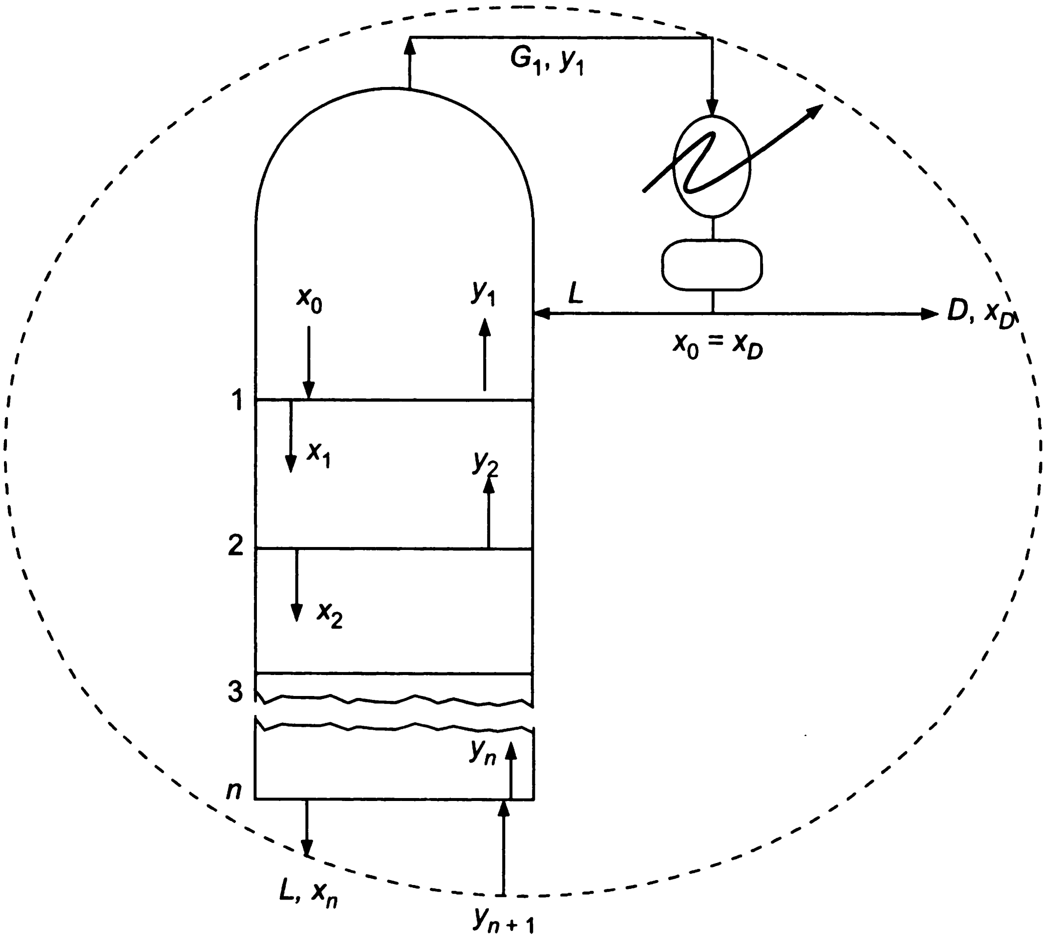


Fig. 9.18 Enriching section of a fractionator.

Assuming the application of equimolar counter diffusion, i.e. the molar flow rates are assumed to be constant for both the vapour and liquid steams irrespective of the stages, we get

$$G_1 \approx G_2 \approx G_{n+1} \approx G$$

A total material balance gives

$$G = L + D \tag{9.82}$$

Let the external reflux ratio R be given by

$$R = \frac{L_0}{D} \approx \frac{L}{D}$$

then,
$$G = DR + D = D(R + 1) \tag{9.83}$$

A component balance for A in enriching section gives

$$Gy_{n+1} = Lx_n + Dy_D \tag{9.84}$$

i.e.
$$y_{n+1} = \left[\frac{L}{G}\right]x_n + \left[\frac{D}{G}\right]x_D \tag{9.85}$$

$$\frac{L}{G} = \frac{L}{L+D} = \frac{\left(\frac{L}{D}\right)}{\left(\frac{L}{D}\right)+\left(\frac{D}{D}\right)} = \frac{R}{R+1} \tag{9.86}$$

$$\frac{D}{G} = \frac{D}{L+D} = \frac{1}{R+1} \tag{9.87}$$

$\therefore$
$$y_{n+1} = \left[\frac{R}{R+1}\right]x_n + \left[\frac{1}{R+1}\right]x_D \tag{9.88}$$

Equation (9.88) represents the operating line for enriching section, which has a slope of $\left[\dfrac{R}{R+1}\right]$ and an intercept of $\left[\dfrac{x_D}{R+1}\right]$. If $x_n = x_D$, then substituting in Eq. (9.88), we get

$$y_{n+1} = \left(\frac{1}{R+1}\right)(Rx_D + x_D) = y_D \tag{9.89}$$

i.e. when $x_n = x_D$, $y_{n+1} = x_D$.

Hence, this line passes through $x = y = x_D$, i.e. it lies on the diagonal. This point on the diagonal and the y-intercept $\left[\dfrac{x_D}{R+1}\right]$ permit us the construction of operating line for enriching section.

Let us consider the stripping section as shown in Fig. 9.19.

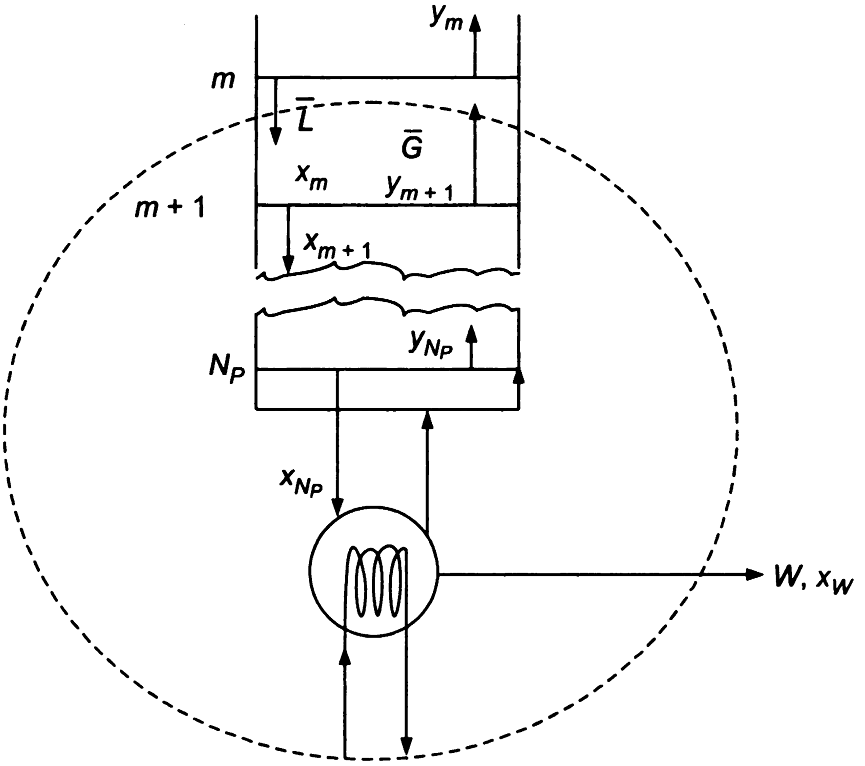


Fig. 9.19 Stripping section.

Material balance gives

$$\bar{L} = \bar{G} + W \tag{9.90}$$

A component balance for A gives,

$$\bar{L}x_m = \bar{G}y_{m+1} + Wx_W \tag{9.91}$$

$$\therefore \qquad y_{m+1} = \left(\frac{\bar{L}}{\bar{G}}\right)x_m - \left(\frac{W}{\bar{G}}\right)x_W \tag{9.92}$$

$$\text{i.e.} \qquad y_{m+1} = \left(\frac{\bar{L}}{\bar{L}-W}\right)x_m - \left(\frac{W}{\bar{L}-W}\right)x_W \tag{9.93}$$

Equation (9.93) describes the operating line for stripping section. The operating line has a slope of $\left(\frac{\bar{L}}{\bar{L}-W}\right)$ and an intercept of $-\left(\frac{W}{\bar{L}-W}\right)$.

Let us assume that $x_m = x_W$ (Reboiler)

$$\therefore \qquad y_{m+1} = \left(\frac{\bar{L}}{\bar{L}-W}\right)x_W - \left(\frac{W}{\bar{L}-W}\right)x_W = x_W \tag{9.94}$$

$$\text{i.e.} \qquad x_m = y_{m+1} = x_W$$

Hence, the operating line passes through the point $x = y = x_W$ (i.e. it lies on the diagonal). Having seen the analysis of enriching section and stripping section separately, let us analyze the feed plate, f, shown in Fig. 9.20.

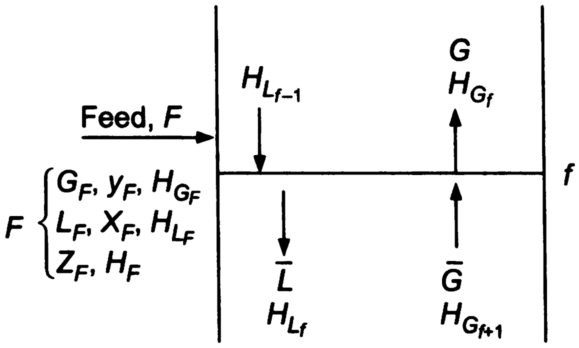


Fig. 9.20 Feed plate section.

A mass balance on feed plate gives

$$F + L + \bar{G} = G + \bar{L} \tag{9.95}$$

$$(L - \bar{L}) = (G - \bar{G}) - F \tag{9.96}$$

i.e.

$$(\bar{L} - L) = (\bar{G} - G) + F \tag{9.97}$$

Enthalpy balance on feed plate gives

$$F \cdot H_F + L \cdot H_{L_{f-1}} + \bar{G} \cdot H_{G_{f+1}} = G \cdot H_{G_f} + \bar{L} \cdot H_{L_f} \tag{9.98}$$

As an approximation, $H_{G_f} \approx H_{G_{f+1}} = H_G$ and $H_{L_{f-1}} = H_{L_f} = H_L$ (9.99)

∴

$$(\bar{L} - L)H_L = (\bar{G} - G)H_G + FH_F \tag{9.100}$$

i.e.

$$\frac{(\bar{L} - L)}{F} H_L = \frac{(\bar{G} - G)}{F} H_G + H_F \tag{9.101}$$

Substituting for $(\bar{L} - L)$ from Eq. (9.97) we get

$$\left[\frac{(\bar{G} - G) + F}{F}\right] HL = \frac{(\bar{G} - G)}{F} H_G + H_F \tag{9.102}$$

i.e.

$$\frac{(\bar{G} - G)}{F} H_L + H_L = \frac{(\bar{G} - G)}{F} H_G + H_F \tag{9.103}$$

$$\frac{(\bar{G} - G)}{F}(H_L - H_G) = (H_F - H_L) \tag{9.104}$$

$$\left[\frac{(\bar{G} - G)}{F}\right] = \frac{(H_F - H_L)}{(H_L - H_G)} \tag{9.105}$$

Substituting for $(\bar{G} - G)$ from Eq. (9.97), we get

$$\frac{(\bar{L} - L) - F}{F} = \frac{(H_F - H_L)}{(H_L - H_G)} \tag{9.106}$$

i.e.
$$\frac{(\bar{L}-L)}{F} = \frac{(H_F - H_L)}{(H_L - H_G)} + 1 \tag{9.107}$$

$$= \frac{(H_G - H_F)}{(H_G - H_L)} \tag{9.108}$$

Let us now define $\frac{(H_G - H_F)}{(H_G - H_L)}$ as q, where q is the quantity of heat required to convert one mole of feed at its thermal condition to a saturated vapour, to the molal latent heat of vaporization.

∴
$$q = \frac{(\bar{L}-L)}{F} = \frac{(H_G - H_F)}{(H_G - H_L)} \tag{9.109}$$

Similarly,
$$\frac{(\bar{G}-G)}{F} = \frac{(\bar{L}-L)}{F} - 1 = (q-1) \tag{9.110}$$

i.e.
$$(\bar{G}-G) = F(q-1) \tag{9.111}$$

A solute balance above feed plate gives

$$Gy = Lx + Dx_D \tag{9.112}$$

A solute balance below feed plate gives

$$\bar{G}y = \bar{L}x - Wx_W \tag{9.113}$$

Subtracting Eq. (9.112) from Eq. (9.113), we have

$$(\bar{G}-G)y = (\bar{L}-L)x - (Dx_D + Wx_W) \tag{9.114}$$

Total component balance for the distillation column gives

$$FZ_F = Dx_D + Wx_W \tag{9.115}$$

Substituting Eqs. (9.109), (9.111) and (9.115) in Eq. (9.114), we get

$$\cancel{F}(q-1)y = \cancel{F}q \cdot x - \cancel{F}Z_F$$

∴
$$y = \frac{q}{(q-1)}x - \frac{Z_F}{(q-1)} \tag{9.116}$$

Equation (9.116) is the equation for feed line. It has a slope of $q/q - 1$ and passes through $y = x = Z_F$.

The various values of slope obtained under different thermal conditions of feed are given below and shown in Fig. 9.21.

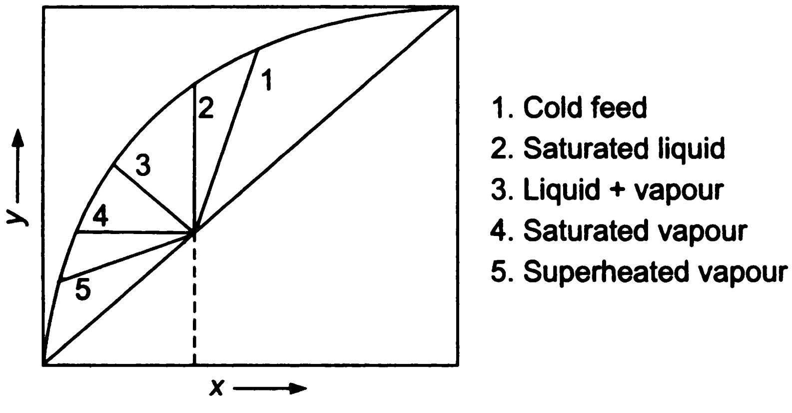


Fig. 9.21 Feed line for different thermal conditions of feed.

Feed condition	G_F	L_F	H_{G_F}	H_{L_F}	Enthalpy of feed, H_F	$q=\left[\frac{(H_G-H_F)}{(H_G-H_L)}\right]$	$\frac{q}{q-1}$
Liquid below boiling point	0	F	–	H_F	$H_F < H_L$	> 1.0	>1.0
Saturated liquid	0	F	–	H_F	$H_F = H_L$	1.0	∞
Liquid + vapour	G_F	L_F	H_G^*	H_L^*	$H_G^* > H_F > H_L^*$	1.0 to 0	$\frac{L_F}{L_F - F}$
Saturated vapour	F	0	H_F	–	$H_F = H_G$	0	0
Superheated vapour	F	0	H_F	–	$H_F > H_G$	< 0	1.0 to 0

* indicates H_G and H_L are enthalpies per mole of individual phases.

Determination of q is as follows:

(i) *Cold feed*

From Eq. (9.109), we have

$$q = \frac{(H_G - H_F)}{(H_G - H_L)}$$

Let T_b be the boiling point of mixture and T_F be the feed temperature. Let H_G and H_L be the enthalpies of saturated vapour and liquid respectively. If λ is the latent heat of vaporization, $C_{P,L}$ is the specific heat of feed liquid and T_0 is the reference temperature, then

$$H_G = C_{P,L}(T_b - T_0) + \lambda$$

$$H_F = C_{P,L}(T_F - T_0) \text{ and } (H_G - H_L) = \lambda \tag{9.117}$$

$$q = \frac{[C_{P,L}(T_b - T_0) + \lambda] - [C_{P,L}(T_F - T_0)]}{\lambda} = \frac{[C_{P,L}(T_b - \cancel{T_0} - T_F - \cancel{T_0}) + \lambda]}{\lambda} \tag{9.118}$$

i.e.

$$q = 1 + \frac{C_{P,L}(T_b - T_F)}{\lambda} \tag{9.119}$$

(ii) *Saturated liquid*

$$q = \frac{(H_G - H_F)}{(H_G - H_L)} \tag{9.120}$$

For saturated liquid $H_F = H_L$, $\therefore$ $q = 1.0$

(iii) *Mixture of liquid and vapour*

Let x be the mole fraction of liquid in feed in the case of liquid + vapour mixture. Then,

$$H_F = xH_L + (1 - x)H_G \tag{9.121}$$

Therefore,
$$q = \frac{\left[\cancel{H_G} - xH_L - \cancel{H_G} + xH_G\right]}{\left(H_G - H_L\right)}$$

$$= \overset{1.0}{\frac{x\cancel{(H_G - H_L)}}{\cancel{(H_G - H_L)}}} = x \tag{9.122}$$

(iv) *Saturated vapour*

$$q = \frac{(H_G - H_F)}{(H_G - H_L)} \tag{9.123}$$

For saturated vapour $H_F = H_G$, $\therefore$ $q = 0$

(v) *Superheated vapour*

Let $C_{P,V}$ be the specific heat of feed vapour

$$H_G = H_G$$

$$H_F = H_G + C_{P,V}\,(T_F - T_b) \tag{9.124}$$

$$q = \frac{\cancel{H_G} - [\cancel{H_G} + C_{P,V}(T_F - T_b)]}{\lambda} = -\frac{C_{P,V}(T_F - T_b)}{\lambda} \tag{9.125}$$

Steps involved in the determination of number of trays

The equilibrium curve along with the operating lines for both enriching and stripping sections to determine the number of stages is shown in Fig. 9.22.

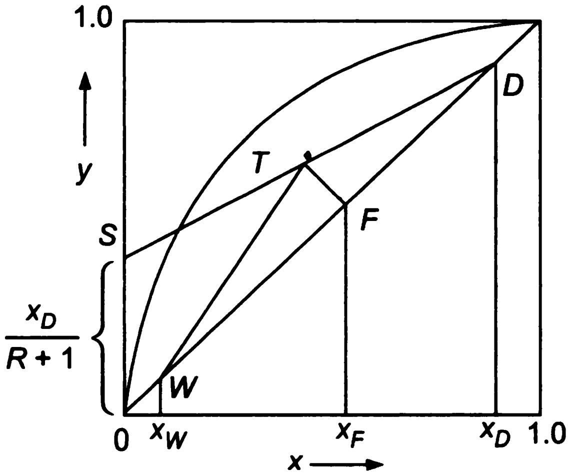


Fig. 9.22 Determination of number of stages by McCabe–Thiele method.

1. Draw the equilibrium curve and diagonal.
2. Locate F, D and W corresponding to feed, distillate and residue compositions based on more volatile component.
3. Estimate $x_D/(R + 1)$ and locate it on y-axis as S.
4. Join SD, this is the operating line for enriching section.
5. From F draw q-line depending on feed condition. Let it cut the operating line for enriching section at T.

6. Join *TW*-operating line for stripping section.
7. Construct stepwise from *D* to *W* and the steps so constructed will give the number of stages.

9.13 LOCATION OF FEED TRAY

For an optimal design or when a column is designed first (wherein one goes for optimal design) the feed tray is located at the intersection of operating lines of enriching and exhausting sections of the tower.

However, we may at times use a column which has been designed with some other objectives. Whenever the quality and condition of feed is fixed along with reflux ratio, x_D and x_W, the operating lines are fixed. It may so happen that in an existing column, the location of feed nozzle is fixed and it may not really lie at the optimal point as shown in Figs. 9.23(a), (b) and (c).

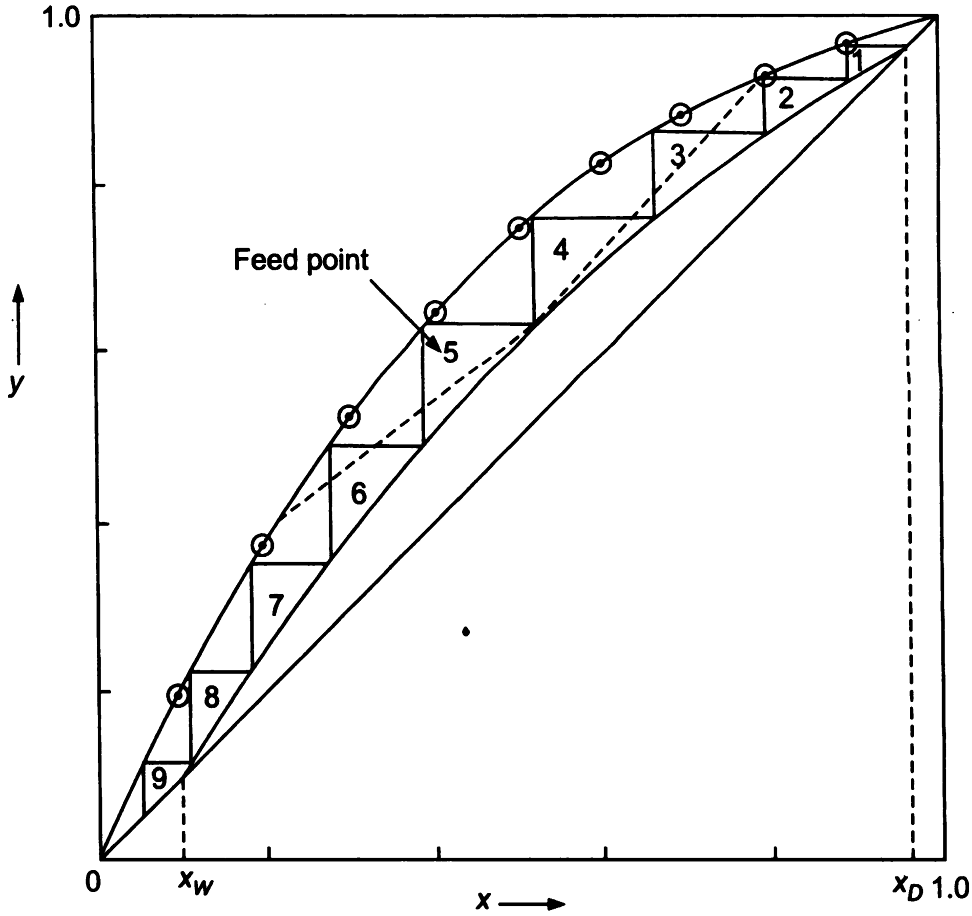


Fig. 9.23(a) Optimal feed location.

The point of intersection of the two operating lines is generally believed to be the point that demarcates enriching and exhausting sections. This normally occurs in the newly designed columns from a specific x_w, x_D, x_F and condition of feed. However, in an existing column, designed for a different utility, the feed point location is fixed and may not be at the optimum location. Further, the feed entry point will not demarcate the enriching and exhausting sections.

Generally when the reflux ratio and the x_D values are fixed, the operating line for enriching section is fixed. Further, when the x_w and the condition of the feed are fixed the operating line for exhausting section is fixed.

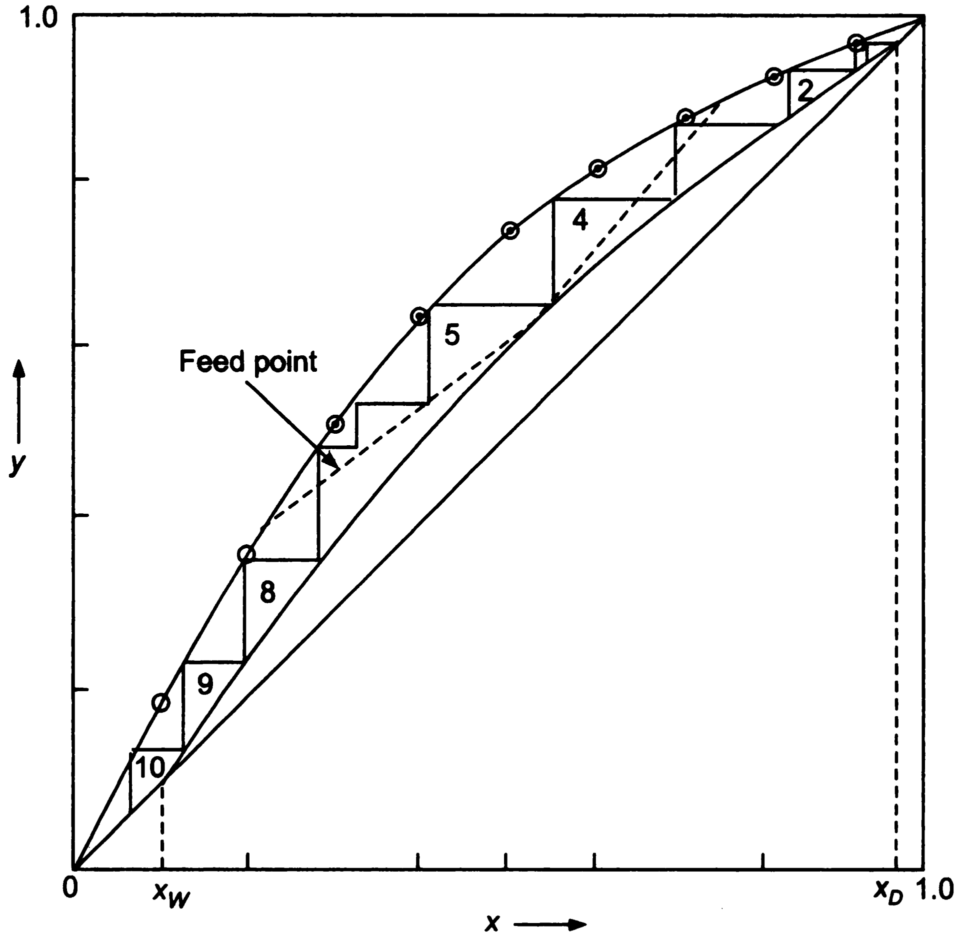


Fig. 9.23(b) Delayed feed entry.

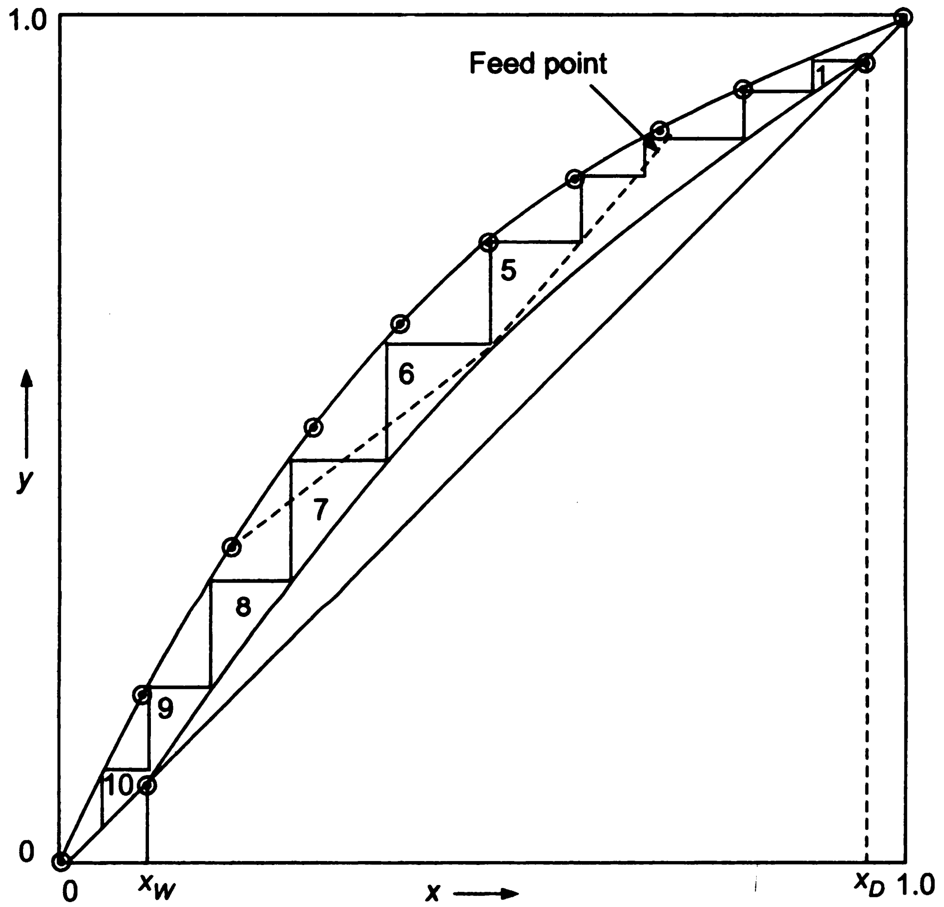


Fig. 9.23(c) Early feed entry.

Once a feed enters a specific plate, below the point of intersection of operating lines and q-line (in an existing column), from the top plate to feed entry point, the operating line for enriching section is to be used and subsequently the operating line for exhausting section. Such an arrangement indicates a *delayed feed entry.* If the feed enters at a specific plate, above the point of intersection of operating lines and q-line (in an existing column), from the top plate to feed entry point, the operating line for enriching section is to be used and subsequently the operating line for exhausting section. This arrangement indicates an *early feed entry.* In both the cases the number of stages estimated will always be more compared to the number of stages estimated with feed entering exactly at the point of intersection of operating lines and q-line.

Consider the above three figures,

Figure 23(a): Optimal design with 9 plates and the 5th plate is feed plate.

Figure 23(b): An existing column with 10 plates and feed enters at 7th plate.

Figure 23(c): An existing column with 10 plates and feed is introduced at 3rd plate.

9.14 REFLUX RATIO

It is one of the important operating parameters in distillation, by which the quality of the products can be changed. Let us deal with the relationship between reflux ratio and the number of trays in the tower.

9.14.1 Determination of Minimum Reflux Ratio

To determine the minimum reflux ratio, draw the q-line from F to cut the equilibrium curve at T'. Join DT' and extend it to intersect on y-axis and indicate it as S'. OS' gives $\left[\dfrac{x_D}{R_{\min}+1}\right]$ from which $R_{\min}$ is estimated as shown in Fig. 9.24.

Normally at $R_{\min}$ condition, the number of stages will be infinity as the equilibrium curve and operating line get pinched.

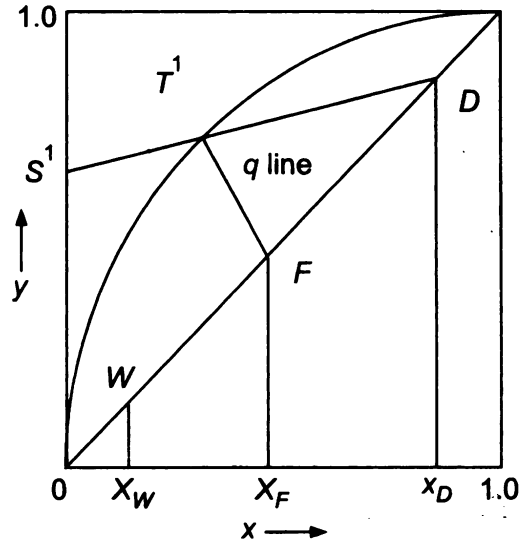


Fig. 9.24 Determination of minimum reflux ratio.

Steps involved in the determination of minimum reflux

1. Draw the equilibrium curve and diagonal.
2. Locate F, D and W corresponding to feed, distillate and residue compositions based on more volatile component.
3. Draw the q-line from F and allow it to intersect the equilibrium curve at T'.
4. Join $T'D$ and allow it to intersect the y-axis at S'.
5. OS' corresponds to $\left[\dfrac{y_D}{R_{\min}+1}\right]$ from which $R_{\min}$, the minimum reflux ratio is estimated.

9.14.2 Total Reflux

At total reflux, all the distillate is returned to the column and no product is taken out as distillate.

i.e.
$$D = 0$$

$$\therefore \quad R = \frac{L}{D} = \infty$$

Hence, the operating line [Eq. (9.88)] for enriching section is

$$y_{n+1} = \left[\frac{R}{R+1}\right]x_n + \left[\frac{1}{R+1}\right]x_D$$

becomes,
$$y_{n+1} = x_n \tag{9.126}$$

i.e. it merges with the diagonal ($x = y$ line) for both enriching and stripping sections. Under such circumstances, the minimum number of theoretical stages can be estimated by the same graphical procedure described in the Section of 9.12.2. For systems where the relative volatility is constant and under total reflux conditions the theoretical number of stages needed could be estimated analytically.

We know that for a binary system, $\alpha_{AB} = \left[\dfrac{\left[\dfrac{y_A}{x_A}\right]}{\left[\dfrac{y_B}{x_B}\right]}\right] = \left[\dfrac{\left[\dfrac{y_A}{y_B}\right]}{\left[\dfrac{x_A}{x_B}\right]}\right]$

$$\therefore \quad \frac{y_A}{y_B} = \alpha_{AB}\frac{x_A}{x_B}$$

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

Let us apply this relationship to $(n + 1)$th plate

$$\therefore \qquad \frac{y_{n+1}}{(1-y_{n+1})} = \alpha \frac{x_{n+1}}{(1-x_{n+1})} \tag{9.127}$$

At total reflux $D = 0$ and $\frac{L}{G} = \frac{R}{R+1} = 1.0$

Hence, from Eq. (9.126), we get

$$(y_{n+1}) = x_n \tag{9.128}$$

When $n = 0$, i.e. at the top of the column, $x_n = x_0$
$y_1 = x_0 = x_D$, when total condenser is used.
Substituting for y_{n+1} in terms of x_n in Eq. (9.128), we get

$$\therefore \qquad \frac{x_n}{(1-x_n)} = \alpha_{AB} \frac{x_{n+1}}{(1-x_{n+1})} \tag{9.129}$$

When $n = 0$,

$$\frac{x_0}{(1-x_0)} = \alpha_{AB} \frac{x_1}{(1-x_1)} \tag{9.130}$$

When $n = 1$,

$$\frac{x_1}{(1-x_1)} = \alpha_{AB} \frac{x_2}{(1-x_2)} \tag{9.131}$$

When $n = n - 1$,

$$\frac{x_{n-1}}{(1-x_{n-1})} = \alpha_{AB} \frac{x_n}{(1-x_n)} \tag{9.132}$$

Substituting for $x_1, x_2, \ldots, x_{n-1}$ from Eqs. (9.131) and (9.132), we get

$$\frac{x_0}{(1-x_0)} = (\alpha_{AB})^n \frac{x_n}{(1-x_n)} \tag{9.133}$$

Substituting $n = N_P + 1$ (last stage, i.e. reboiler), we get

$$\frac{x_0}{(1-x_0)} = (\alpha)^{N_p+1} \frac{x_{N_p+1}}{(1-x_{N_p+1})} \tag{9.134}$$

As $(N_P + 1)$th stage accounts for reboiler, $x_{N_P+1} = x_w$

i.e.

$$\frac{y_D}{(1-y_D)} = (\alpha)^{N_p+1} \frac{x_W}{(1-x_W)} \tag{9.135}$$

Equation (9.135) is called *Fenske equation.* To apply this equation, α, the relative volatility must be fairly constant and the column has to be operated under total reflux conditions. This may not be possible in industries, but has theoretical importance.

9.14.3 Optimum Reflux Ratio

At minimum reflux ratio the column requires infinite number of stages or trays. However, as reflux ratio increases from minimum, for a given feed and specified quality of distillate and residue, the number of stages or trays decrease. At minimum reflux ratio when the stages or trays are infinite, the fixed cost and the maintenance cost are also infinite. However, the operating cost for operating condenser, reboiler etc. is the least. When the reflux increases, the trays or stages reduce but the column diameter has to be increased to handle larger capacities of liquid being recycled. The size of other accessories like condenser and reboiler increase which will result in a higher requirement of cooling water or heating. Ultimately this will result in a higher operating cost. Thus, the total cost which includes both operating cost and fixed cost, vary with reflux ratio and reach a minimum value for a certain reflux ratio which is called the *optimum or economic reflux ratio*. This value is normally in the range of 1.2 $R_{\min}$ to 1.5 $R_{\min}$. This is shown in Fig. 9.25.

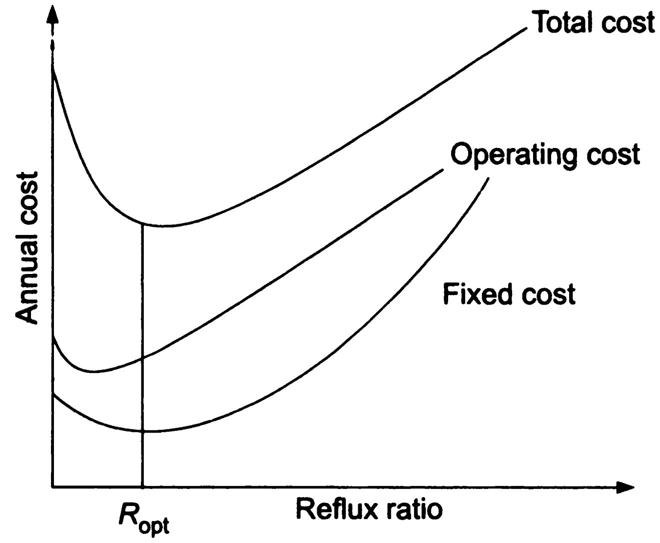


Fig. 9.25 Effect of Reflux ratio on cost.

9.15 REBOILERS

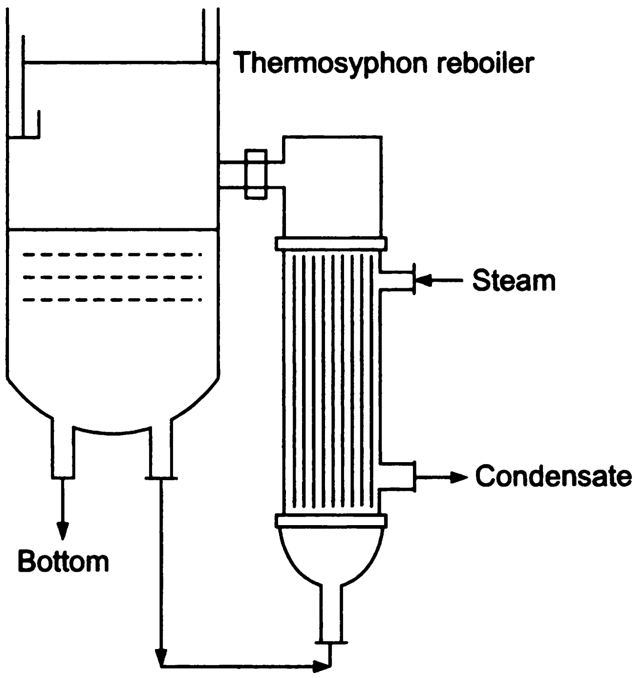


Fig. 9.26(a) Thermosyphon reboiler.

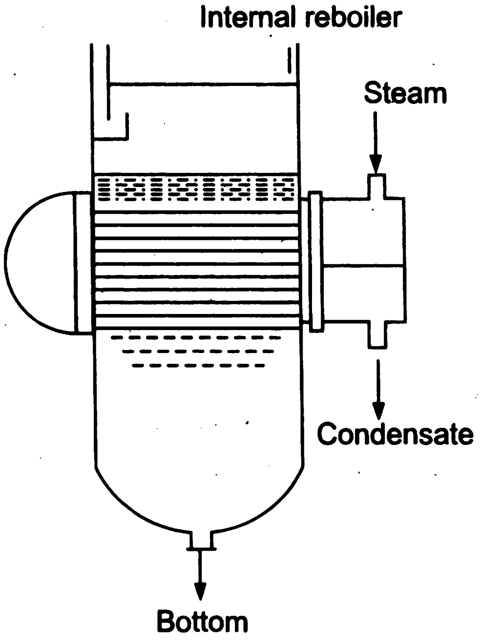


Fig. 9.26(b) Internal reboiler.

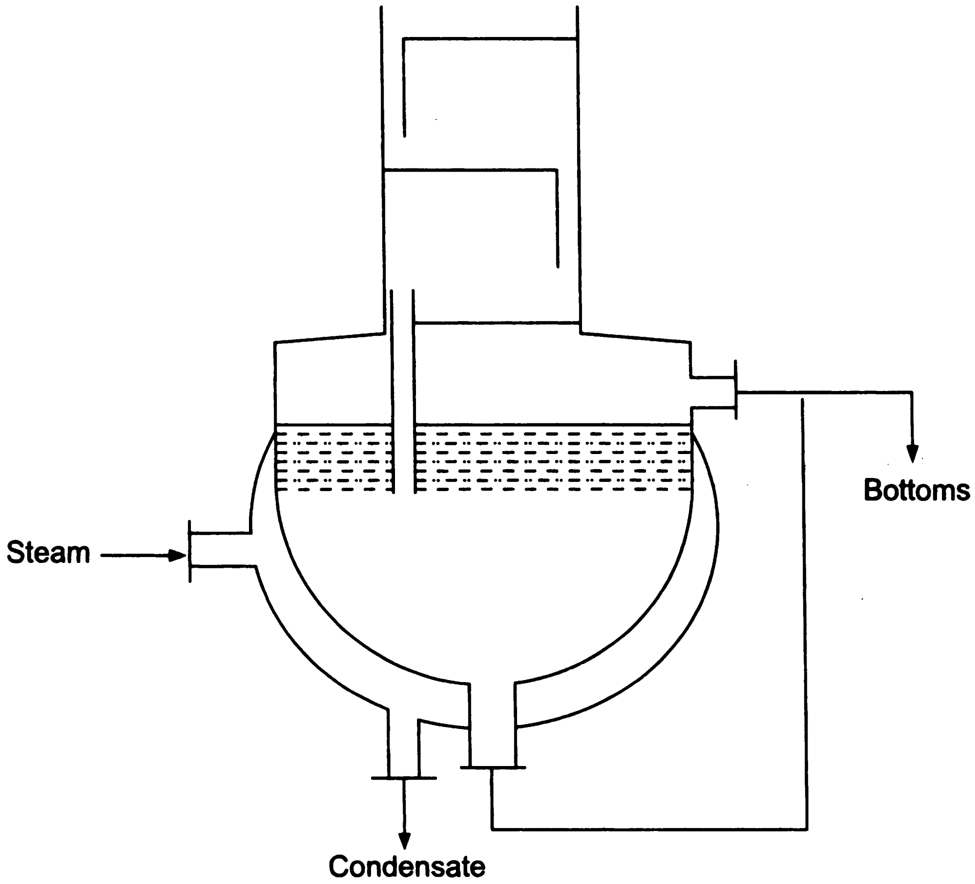


Fig. 9.26(c) Jacketed kettle reboiler.

They are heat exchangers of different configurations used to supply the heat to the liquid at the bottom of the column to vaporize them. In effect all the heat needed is basically supplied at the reboiler only.

A simple Jacketed kettle is one such reboiler which has a low heat transfer area and hence vapour generation capacity will also be poor.

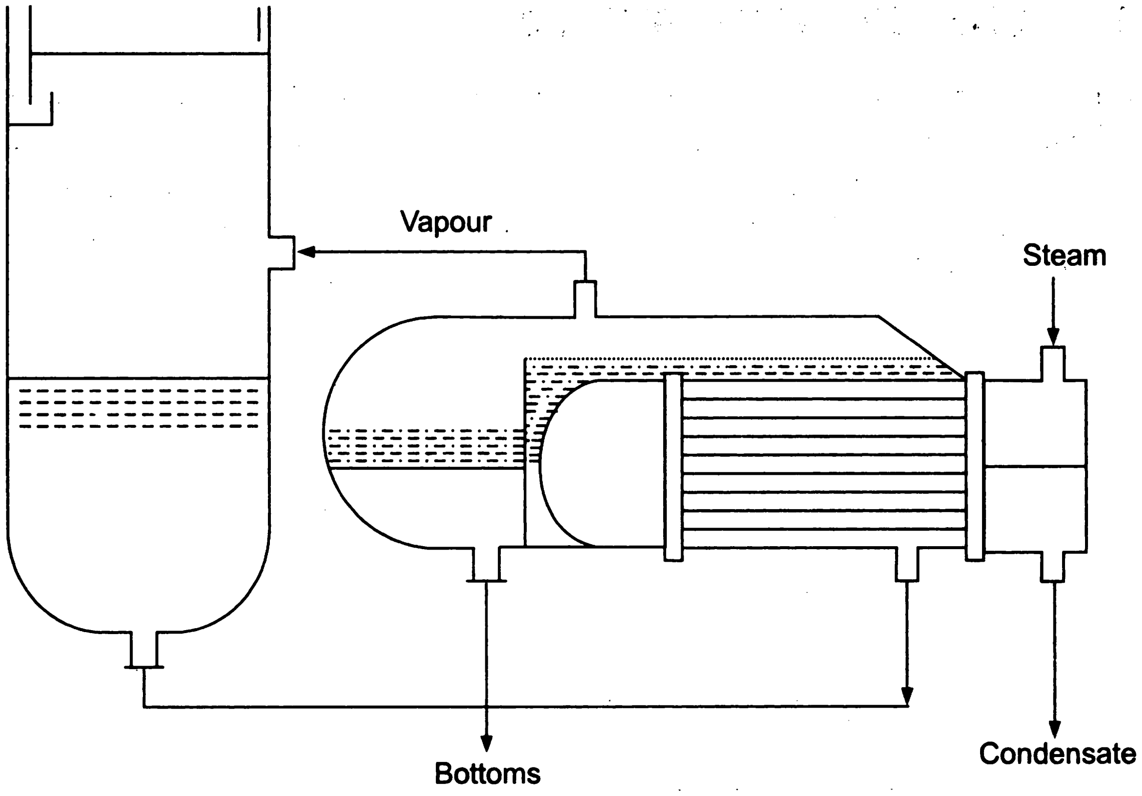


Fig. 9.26(d) External reboiler

Tubular heat exchangers (both of vertical and horizontal configurations) provide larger area of heat transfer. They can be placed inside the column or outside the column. When they are located inside, during cleaning of the exchanger, the distillation operation has to be stopped. However, when external reboilers are used, a standby exchanger is always kept which can be used during cleaning of the exchanger attached to the column. Thus, the distillation operation will proceed without any interruption. The liquid can flow either through the tube side or shell side. Reboilers can be heated by steam, oil or other hot fluids. Different types of reboilers are shown in Figs. 9.26(a)–(d).

9.16 CONDENSERS

The condensers are generally heat exchangers of horizontal orientation with coolant flowing through the tube side. However, in rare instances vertical condensers are used with the coolant flowing on either side of the tubes. They are placed above the tower in the case of laboratory scale units for gravity flow of the condensed reflux to the topmost tray. Sometimes they are placed at ground level for easy maintenance, in which case the liquid is pumped from accumulator to the top tray. The coolant is normally water. The condensers may either be a total condenser or a partial condenser. Whenever a partial condenser is used, the condensate is returned as reflux and the vapour from condenser is the main distillate product. The partial condenser itself acts as one stage for separation. In an existing distillation column, if one desires to have a highly enriched distillate (richer than the designed value) then one can resort to partial condensation and obtain an enriched product. However, when a column is being designed fresh it is always preferable to go for additional trays compared to partial condensation technique for enrichment.

9.17 USE OF OPEN STEAM

Normally the heat needed for distillation is supplied through (by heat exchangers) reboilers. However, when an aqueous solution is fractionated to give non-aqueous solute as distillate and water as residue, the heat required may be supplied by open steam in which case the reboiler is not required. The schematic arrangement is shown in Fig. 9.27 and the overall material balance is given below.

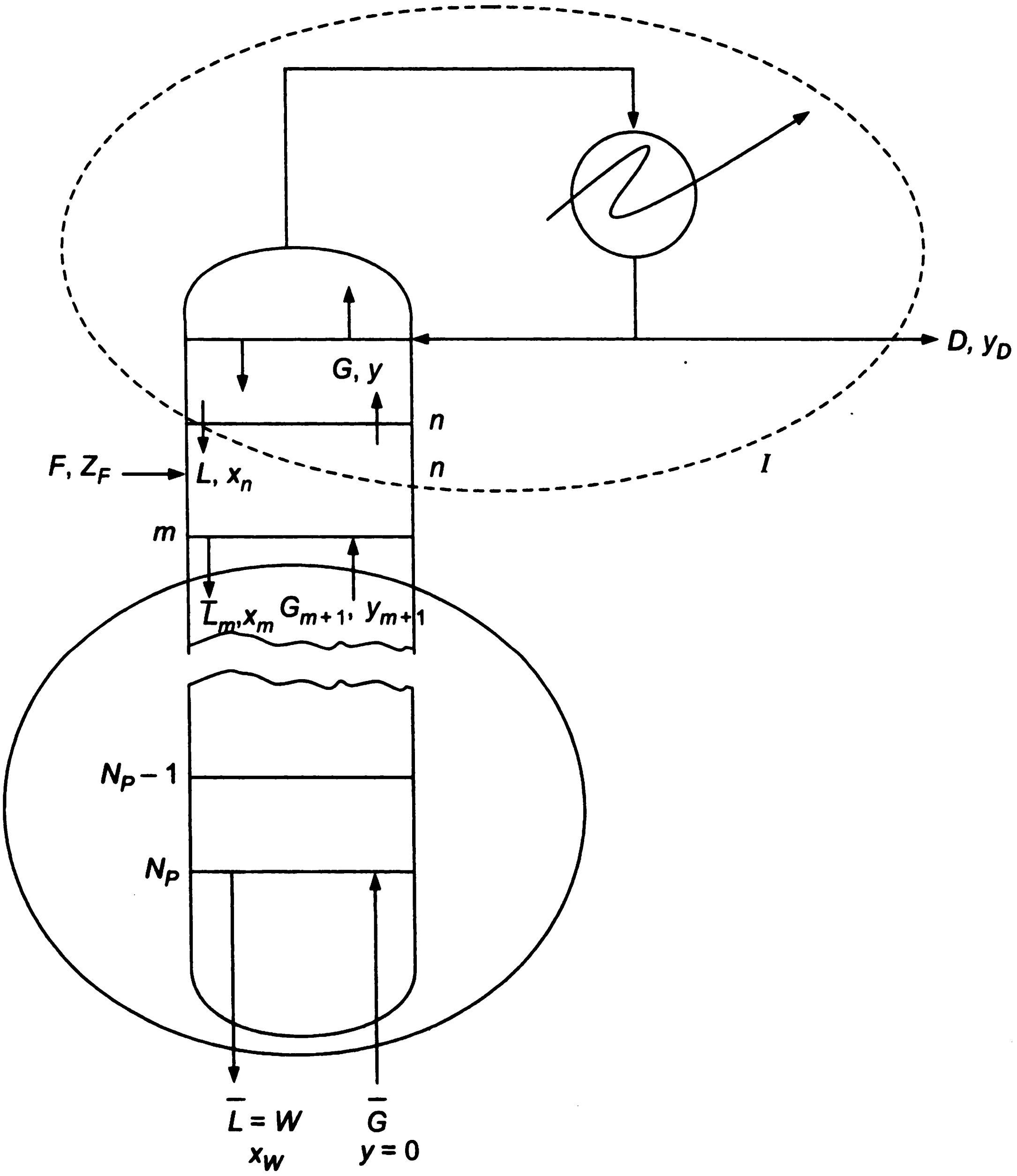


Fig. 9.27 Open steam distillation.

The equation for the operating line in enriching section is obtained as in the case of McCabe–Thiele method.

i.e.
$$\text{Slope} = \frac{L}{G} = \frac{R}{R+1} \text{ and intercept} = \frac{x_D}{R+1} \tag{9.136}$$

However, let us analyze the exhausting section.

A component balance gives

$$\bar{L}x_m + \bar{G}(0) = \bar{G}y_{m+1} + \bar{L}x_W \tag{9.137}$$

$$\bar{L}x_m + \bar{G}(0) = \bar{G}y_{m+1} + Wx_w \tag{9.138}$$

i.e.

$$\frac{\bar{L}}{\bar{G}} = \frac{(y_{m+1} - 0)}{(x_m - x_W)} \tag{9.139}$$

The operating line for exhausting section passes through ($x = x_W$ and $y = 0$) and (x_m, y_{m+1}). Thus, the line passes through x_W, the point in x-axis as shown in Fig. 9.28. After constructing the equilibrium curve and operating lines, by step-wise construction the number of stages are determined as in the case of McCabe-Thiele method.

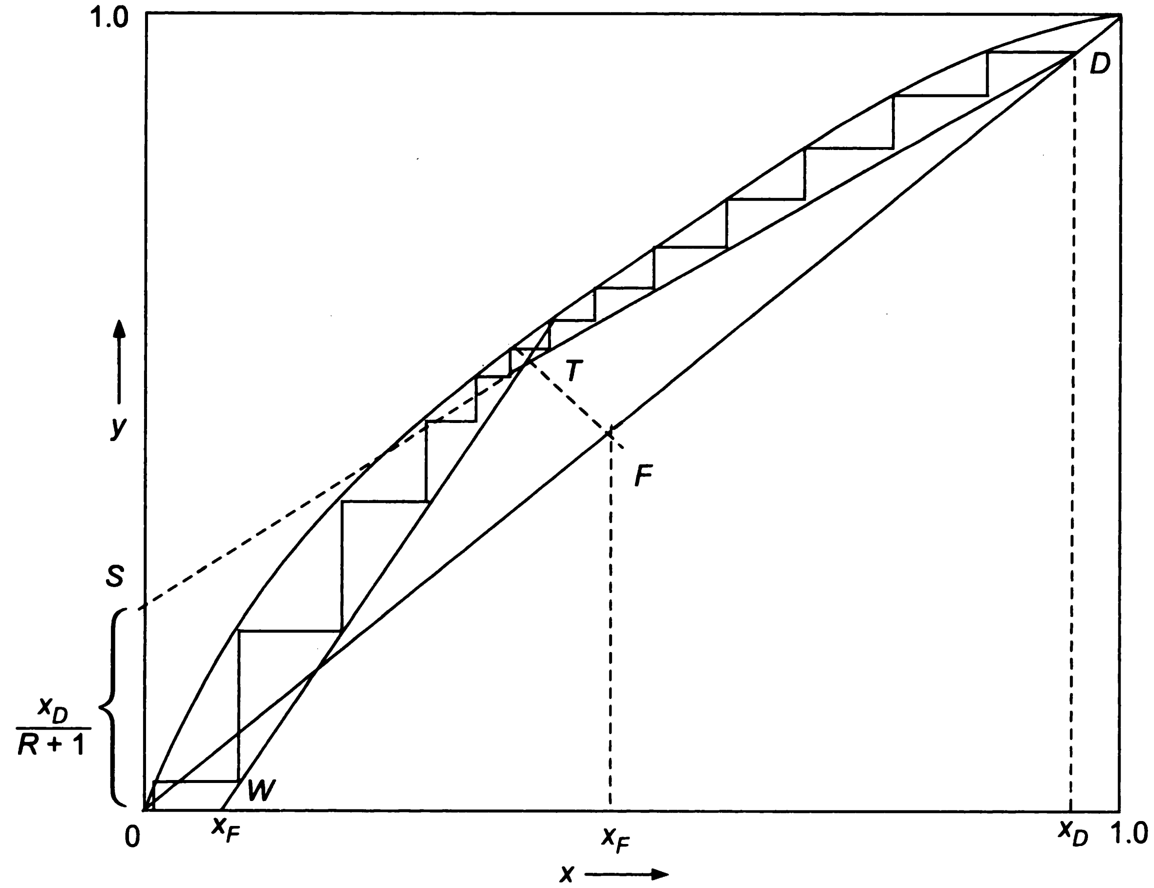


Fig. 9.28 Determination of number of stages in open steam distillation.

If the steam entering the tower is superheated ($H_{G,\,N_{P+1}}$), it will vaporize liquid on tray N_P to the extent such that the steam will reach saturation ($H_{G,\,\mathrm{Sat}}$). An energy balance yields,

$$\bar{G} = \bar{G}_{N_{P+1}}\left[1 + \frac{\left(H_{G,N_{P+1}} - H_{G,Sat}\right)}{\lambda M}\right] \tag{9.140}$$

where λM is the molar latent heat of vaporization, and

$$\bar{L} = \bar{G} - \bar{G}_{N_{P+1}} + \bar{L}_{N_P} \tag{9.141}$$

Using Eqs. (9.140) and (9.141), the $\bar{L}/\bar{G}$ ratio is computed.

9.17.1 Determination of Number of Trays

1. Draw the equilibrium curve and diagonal.
2. Locate F and D corresponding to the composition of feed and distillate respectively on diagonal.
3. Locate W corresponding to the composition of x_W on x-axis.
4. Based on the reflux ratio and distillate composition, estimate $\frac{x_D}{R+1}$ and locate it on y-axis as S.
5. Join SD, this is the operating line for enriching section.
6. From F draw q-line depending on feed condition and allow it to cut the operating line for enriching section SD, and locate the point of intersection as T.
7. Join TW. TW is the operating line for stripping section.
8. By stepwise construction starting from D up to W, the number of stages can be determined.
9. The minimum reflux ratio needed is estimated in the same manner as in the case of McCabe–Thiele method.

9.18 CONTINUOUS DIFFERENTIAL CONTACT–PACKED TOWER DISTILLATION

Whenever we have heat sensitive materials to be distilled which require less contact time, packed towers are preferred. The pressure drop is also low and hence it is suitable for low pressure distillation operations.

The height of column can be determined in the same way as for other mass transfer operations using packed towers by making a material balance across a differential section and integrating as indicated in Fig. 9.29.

The material balance across the elemental section in enriching zone gives

$$N_A = \frac{d(Gy)}{adZ} = k_y'(y_i - y) = \frac{d(Lx)}{adZ} = k_x'(x - x_i) \qquad (9.142)$$

$$\therefore \qquad Z_e = \int_0^{Z_e} dZ = \int_{(Gy)_a}^{(Gy)_2} \frac{d(Gy)}{k_y'a(y_i - y)} = \int_{(Lx)a}^{(Lx)_2} \frac{d(Lx)}{k_x'a(x - x_i)} \qquad (9.143)$$

Assuming that G, L, k_y' and k_x' are constants.

(However, this has to be checked before using as k_x and k_y depending on the flow rates)

$$Z_e = \frac{G}{k_y'a} \int_{y_a}^{y_2} \frac{dy}{(y_i - y)} = (H_{tG})(N_{tG}) \text{ (By definition)} \qquad (9.144)$$

(Suffix a indicates the point of intersection of operating lines)

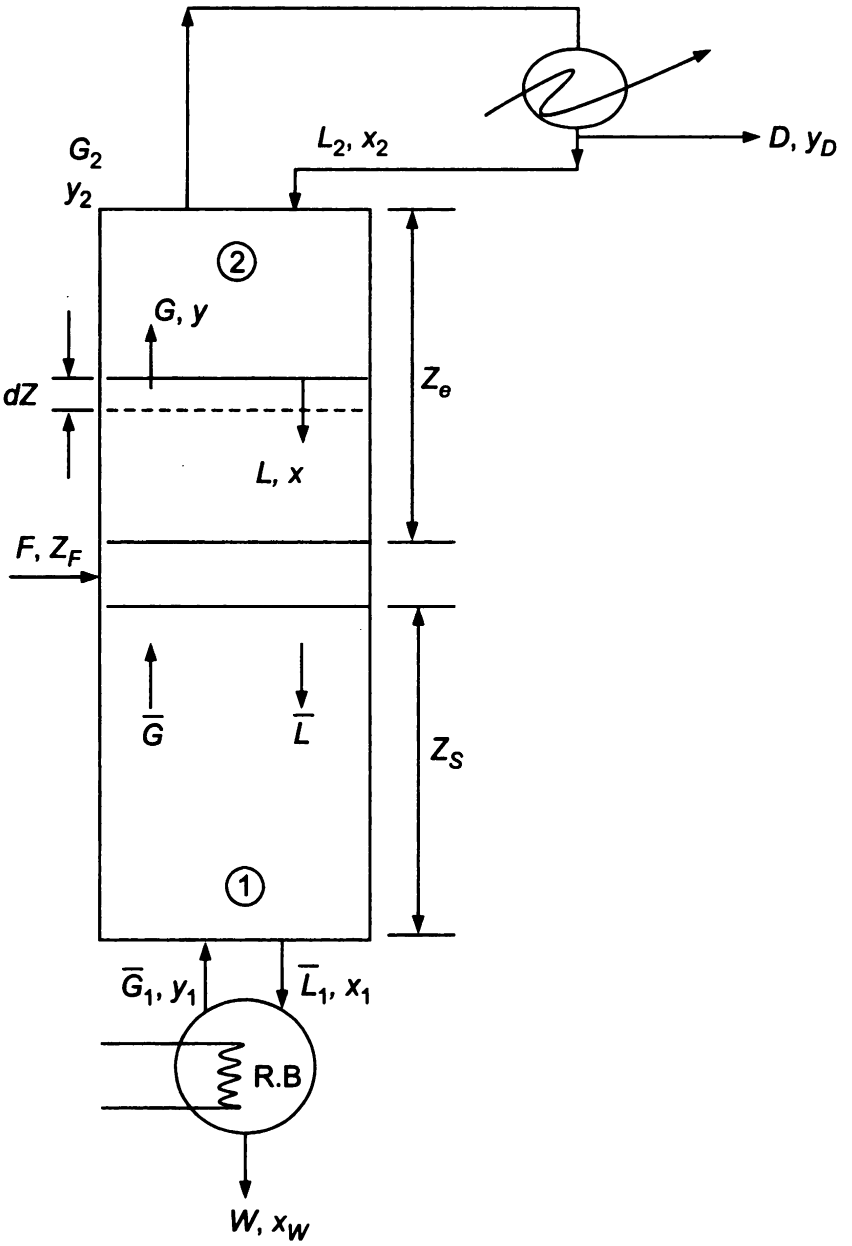


Fig. 9.29 Analysis of packed distillation column.

Based on liquid phase, Z_e can be expressed as

$$Z_e = \frac{L}{k_x'a} \int_{x_a}^{x_2} \frac{dx}{(x - x_i)} = (H_{tL})(N_{tL}) \text{ (By definition)} \tag{9.145}$$

Similarly, the stripping section can also be analysed and it can be shown that,

$$Z_S = (H_{tG})\,(N_{tG}) = (H_{tL})\,(N_{tL}) \tag{9.146}$$

$$\text{Total height } Z = Z_e + Z_S \tag{9.147}$$

The determination of H_{tG} or H_{tL} can be done using the flow rates of vapour or liquid and vapour or liquid mass transfer coefficients. However, to determine N_{tG} or N_{tL} one needs to find interfacial compositions. If the film coefficients are known, the interfacial concentrations can be determined from the operating line and equilibrium curve. These values are given by a line drawn with a slope of

$\left[-\frac{k'_x}{k'_y}\right]$ from the operating line to the equilibrium curve. The point at which this line cuts operating line gives x and y values and the point of intersection with the equilibrium curve gives the interfacial compositions x_i and y_i. A number of such lines can be drawn which will give various sets of $(x - x_i)$ and $(y_i - y)$ values as shown in Fig. 9.30. Using these values, N_{tL} or N_{tG} can be determined. One should use N_{tL} or N_{tG} (corresponding to H_{tL} or H_{tG}) to determine the height depending on the resistance which is controlling the mass transfer.

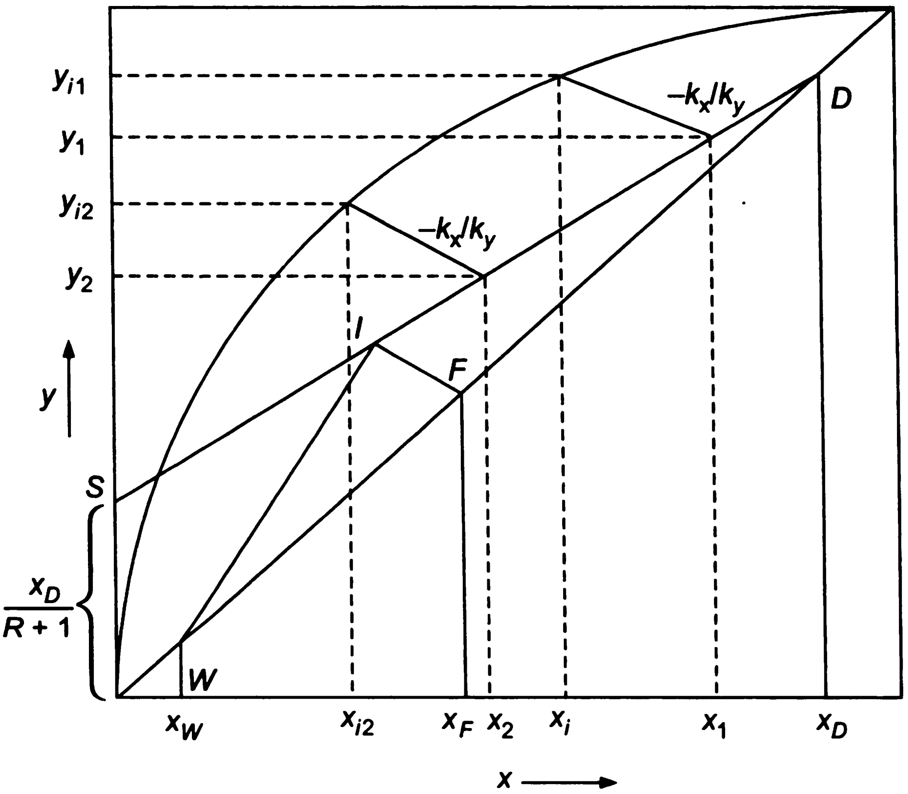


Fig. 9.30 Determination of interfacial conditions for packed distillation column.

Further, if the equilibrium curve is essentially straight in the range of our application, then the expressions are simplified as

$$Z_e = H_{t_0G}\int_{y_a}^{y_2}\frac{dy}{(y^* - y)} = (H_{t_0G})(N_{t_0G}) \tag{9.148}$$

when gas phase is controlling and

$$Z_e = H_{t_0L}\int_{x_a}^{x_2}\frac{dx}{(x - x^*)} = (H_{t_0L})(N_{t_0L}) \tag{9.149}$$

when liquid phase is controlling.

In Eqs. (9.148) and (9.149) , $(y^* - y)$ and $(x - x^*)$ are the overall driving forces in terms of vapour and liquid phase composition respectively.

Here, $H_{t_0G} = \frac{G}{K'_y a}$ and $H_{t_0L} = \frac{L}{K'_x a}$

We know that, $$\frac{1}{K'_y} = \frac{1}{k'_y} + \frac{m}{k'_x}$$

$$\frac{1}{K'_x} = \frac{1}{k'_x} + \frac{1}{mk'_y}$$

Similarly, H_{t_0G} and H_{t_0L} can also be written as

$$H_{t_0G} = H_{tG} + \left(\frac{mG}{L}\right)H_{tL} \tag{9.150}$$

$$H_{t_0L} = H_{tL} + \left(\frac{L}{mG}\right)H_{tG} \tag{9.151}$$

where m is the slope of the equilibrium curve.

9.18.1 Steps Involved in the Determination of the Height of Tower

1. Draw the equilibrium curve and diagonal.
2. Locate S, corresponding to $\frac{x_D}{R+1}$ in y-axis.
3. Locate F, D and W on diagonal corresponding to x_F, x_D and x_W
4. Join DS. This is the operating line for enriching section.
5. From F draw q-line. Let the point of intersection on operating line DS for enriching section be T.
6. Join TW. This is the operating line for stripping section.
7. From D to T and T to W draw lines of slope $\left[-\frac{k'_x}{k'_y}\right]$ or $\left[-\frac{K'_x}{K'_y}\right]$ (as the case may be) to obtain (x_i and y_i) or (x^* and y^*) and (x and y) values.
8. x and y values are read from operating lines and (x_i, y_i) or (x^*, y^*) values are read from equilibrium curve.
9. Evaluate $\int \frac{dx}{(x - x_i)}$ or $\int \frac{dy}{(y_i - y)}$ or $\int \frac{dx}{(x - x^*)}$ or $\int \frac{dy}{(y^* - y)}$ graphically to determine N_{tL} or N_{tG} or N_{toL} or N_{toG}.
10. H_{tL}, H_{tG}, H_{toG} or H_{toL} are determined with the help of liquid and vapour flow rates and mass transfer coefficients.
11. Height is then estimated based on the values from steps (9) and (10).
12. The tower diameter is normally set by the conditions at the top of stripping section because of large liquid flow rate at that point.

9.19 AZEOTROPIC DISTILLATION

This is a technique which is used for the separation of binary mixtures which are either difficult or impossible to separate by ordinary fractionation. This happens when either the mixture to be separated has a very low relative volatility, in which case one may require high reflux ratio and more number of trays, or when the mixture forms an azeotrope. Under such circumstances, a third component called an 'entrainer' is added to the binary mixture to form a new low boiling hetero-azeotrope with one of the components in the original mixture whose volatility is such that it can be separated from the other original constituent.

A typical example for this operation is presented in the flow diagram of Fig. 9.31 where the separation of acetic acid (BP: 118.1°C) and water (BP: 100°C) mixture is demonstrated. This mixture has a low relative volatility and hence separation by conventional methods is not economical. Here Butyl acetate, which is slightly soluble in water, is added to the mixture from the top of the column as an entrainer. It forms a 'hetero-azeotrope' with all the water in the feed and readily distills out from the high boiling acetic acid and the acetic acid leaves as a residue product. The hetero-azeotrope on condensation forms two insoluble layers which can easily be separated. The water layer obtained is saturated with ester and vice versa. The ester layer saturated with water is returned back to the column as a source of entrainer for further separation. The aqueous layer is also sent to another column to separate water and ester. The separated ester is also sent back as entrainer.

Sometimes the new azeotrope formed contains all the three constituents. In the dehydration of ethanol water mixture, benzene is added as an entrainer which gives a ternary azeotrope containing benzene (53.9 mole %), water (3.3 mole %) and ethanol (22.8 mole %) boiling at 64.9°C as distillate and ethanol (BP: 78.4°C) as residue. Benzene is separated and sent back to the top of the column as entrainer. Since water – ethanol are equally present in distillate, the mixture should be given a preliminary rectification to produce an alcohol rich binary azeotrope. Azeotropic distillation is shown in Fig. 9.31.

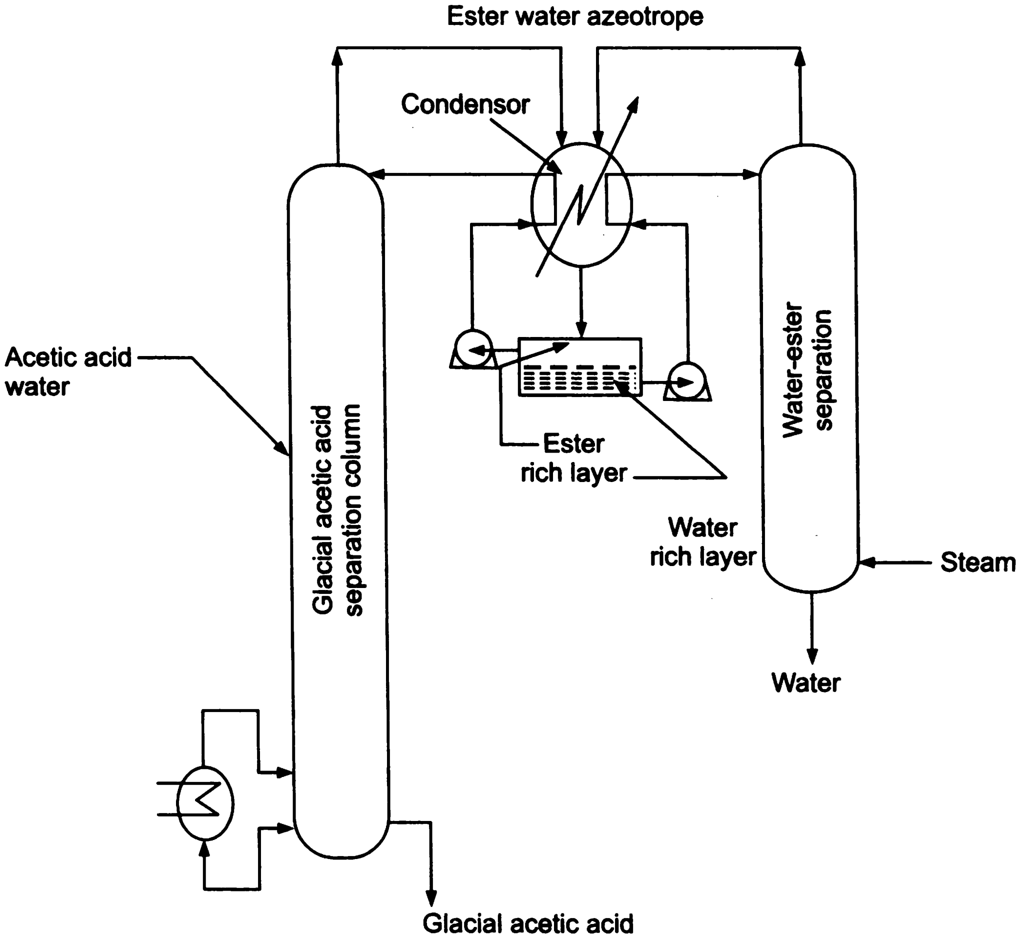


Fig. 9.31 Azeotropic distillation.

9.19.1 Desired Properties of an Entrainer for Azeotropic Distillation

(i) Should be cheap and easily available.
(ii) Chemically stable and inactive towards the solution to be separated.
(iii) Non-corrosive.
(iv) Non-toxic.
(v) Low latent heat of vaporization.
(vi) Low freezing point to facilitate storage and easy handling.
(vii) Low viscosity to provide high tray efficiency and minimum pumping cost.

9.20 EXTRACTIVE DISTILLATION

This method is also used under similar circumstances as in the case of azeotropic distillation. Here a third component called solvent is added, instead of entrainer, which alters the relative volatility of the original constituents, thus permitting the separation. The added solvent should have low volatility and not vaporized in the fractionator.

One such example is the separation of toluene (BP: 110.8°C) from isooctane (BP: 99.3°C). Their separation is relatively difficult. In the presence of Phenol (BP: 181.4°C), the relative volatility of isooctane increases, so that with an increase in phenol content, the separation becomes more and more easy. A typical flow diagram of the process is shown in Fig. 9.32.

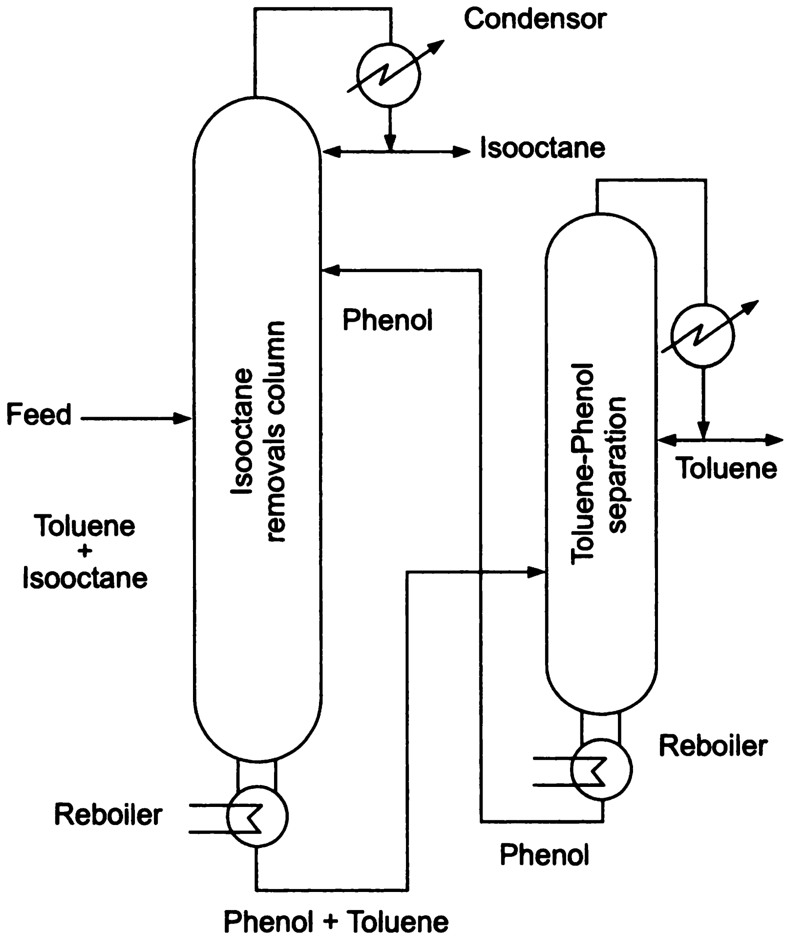


Fig. 9.32 Extractive distillation.

Here, the toluene–isooctane binary mixture is introduced in the middle of the column and phenol near the top of the column. Isooctane is readily distilled as an overhead product, while toluene and phenol are collected as residue. The residue from the tower is rectified in the auxiliary tower to separate toluene and phenol as distillate and residue respectively. Phenol is returned to the main column as solvent. Similarly a mixture of acetone (BP: 56.4°C) and methanol (BP: 64.7°C) can be separated by using Butanol (BP: 117.8°C) solvent.

9.20.1 Desired Properties of Solvent for Extractive Distillation

(i) High selectivity and capability to alter VLE for easy separation.
(ii) Ability to dissolve the components in the mixture.
(iii) Low volatility in order to prevent vaporization of solvent.
(iv) Easy separability, for easier removal of solvent.
(v) Non-corrosive.
(vi) Non-toxic.
(vii) Cheap and easily available.
(viii) Low freezing point.
(ix) Low viscosity.
(x) Chemical stability and inertness towards the components to be separated.

9.21 COMPARISON OF AZEOTROPIC AND EXTRACTIVE DISTILLATION

In both the processes an additional external agent is added, which is undesirable. Solvent to feed ratio in extractive distillation greater than 3 or 4 is found to be effective. Proper choice of material of construction and recovery technique are to be examined. However, of the two, extractive distillation is said to be more favoured than azeotropic distillation since (i) there is a greater choice of solvent, (ii) the smaller quantity of solvent to be volatilized. In spite of the above advantages, the azeotropic distillation is said to be more effective in the dehydration of ethanol from an 85.6 mole % Ethanol–water solution. In this case water is azeotroped with *n*–pentane and then separated rather than using extractive distillation with ethylene glycol as solvent.

9.22 LOW PRESSURE DISTILLATION

Whenever the heat sensitive materials are to be separated, as in the case of many organic mixtures, low pressure distillation will be effective. In this case the time of exposure of the substances to high temperature is kept minimum. Packed towers can be used for distillation under pressures of 50 to 250 mm Hg. Bubble cap and sieve trays can be used for pressure drops around 2.6 mm Hg and shower trays for pressure drops around 0.75 mm Hg. This is used in the separation of vitamins from animal and fish oils as well as the separation of plasticizers.

9.22.1 Molecular Distillation

This is a very low pressure distillation where the absolute pressure is in the range of 0.003 mm Hg to 0.03 mm Hg. On reducing the absolute pressure, the mean free path of the molecules becomes large. If the condensing surface is placed at a distance from the vaporizing liquid, surface not exceeding few cms, only a few molecules will return to the liquid. The composition of the distillate will now be different from that given by normal vaporization and the ratio of the constituents is given by

$$\frac{N_A}{N_B} = \frac{\text{moles of } A}{\text{moles of } B} = \left[\frac{\left(\dfrac{\bar{p}_A}{M_A{}^{0.5}}\right)}{\left(\dfrac{\bar{p}_B}{M_B{}^{0.5}}\right)}\right] \tag{9.152}$$

In molecular distillation this ratio is maintained by allowing the liquid to flow in a thin film over a solid surface thus renewing the surface continually and at the same time maintaining low hold-up of liquid.

A schematic arrangement of a device used for this type of distillation is shown in Fig. 9.33. The degassed liquid to be distilled is introduced at the bottom of the inner surface of the rotor, rotating at 400 to 500 rpm. A thin layer of liquid 0.05 to 0.1 mm spreads over the inner surface and travels rapidly to the upper periphery under centrifugal force. Heat is supplied to the liquid through the rotor from radiant electrical heaters. Vapors generated are condensed and collected in the collection troughs. The residue liquid is collected in the collection gutter and removed. The entire unit is maintained at low pressure, good enough for molecular distillation to occur. Normal residence time is of the order of 1 second and hence decomposition of mixture does not take place. Multiple units can be used to have multistage separation effects.

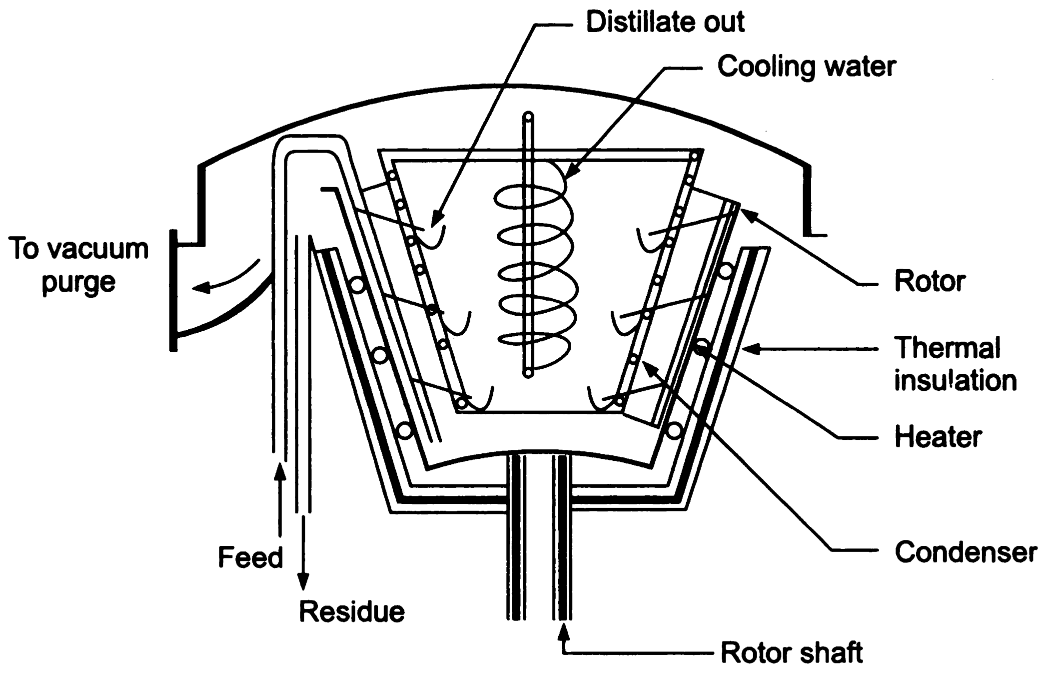


Fig. 9.33 Molecular distillation.

WORKED EXAMPLES

1. Compute the equilibrium data from the following data at 760 mm Hg pressure and calculate the relative volatility.

VP of A, mm Hg	760	830	920	1060	1200	1360
VP of B, mm Hg	200	350	420	550	690	760

P_T = 760 mm Hg

Solution.

P_A, mm Hg	760	830	920	1060	1200	1360
P_B, mm Hg	200	350	420	550	690	760

We know that $x_A = \left[\dfrac{(P_T - P_B)}{(P_A - P_B)}\right]$ and $y_A = \left[\dfrac{(P_A x_A)}{P_T}\right]$

$x_A = \left[\dfrac{(P_T - P_B)}{(P_A - P_B)}\right]$	1.0	0.854	0.68	0.412	0.137	0
$y_A = \left[\dfrac{(P_A x_A)}{P_T}\right]$	1.0	0.933	0.823	0.575	0.216	0
α_{AB} = VP of A/VP of B	3.80	2.37	2.19	1.93	1.74	1.79

Average relative volatility: 2.303

2. The vapour pressure data for *n*–Hexane –*n*–Octane system is given below. Compute the equilibrium data and relative volatility for the system at a total pressure of 101.32 kPa.

T°C	*n*-Hexane P_A, kPa (*A*)	*n*-Octane P_B, kPa (B)
68.7	101.32	16.1
79.4	136.7	23.1
93.3	197.3	37.1
107.2	284.0	57.9
125.7	456.0	101.32

Solution.

T°C	n-Hexane P_A,kPa (A)	n – Octane P_B,kPa (B)	$\alpha_{cal} = P_A/P_B$	$x_A = \frac{P_t - P_B}{(P_A - P_B)}$	$y_A = \frac{P_A x_A}{P_t}$	$y = \frac{\alpha x}{[1+(\alpha-1)x]}$
68.7	101.32	16.1	6.29	1.000	1.00	1.000
79.4	136.7	23.1	5.92	0.689	0.930	0.923
93.3	197.3	37.1	5.32	0.401	0.781	0.783
107.2	284.0	57.9	4.91	0.192	0.538	0.562
125.7	456.0	101.32	4.50	0	0	0

3. Compute x–y data at 1 atm. Pressure from the following data:

T	80.1	85	90	95	100	105	110.6
VP_A	760	877	1016	1168	1344	1532	1800
VP_B	–	345	405	475	577	645	760

Solution.

T	80.1	85	90	95	100	105	110.6
VP_A	760	877	1016	1168	1344	1532	1800
VP_B	—	345	405	475	577	645	760
$\alpha = \frac{VP_A}{VP_B}$	—	2.54	2.51	2.46	2.33	2.38	2.37

(**Ans:** $\alpha_{\text{average}} = 2.43$)

$x_A = \left[\frac{(P_T - P_B)}{(P_A - P_B)}\right]$	1.0	0.78	0.58	0.411	0.239	0.13	0
$y_A = \left[\frac{(P_A x_A)}{P_T}\right]$	1.0	0.9	0.777	0.632	0.423	0.26	0

4. A solution of methanol and ethanol are substantially ideal. Compute the VLE for this system at 1 atm pressure and relative volatility.

$$\log\,[P,\ \text{mm}]_{\text{Methanol}} = 7.84863 - \frac{1473.11}{(230 + t°\text{C})}$$

$$\log\,[P,\ \text{mm}]_{\text{Ethanol}} = 8.04494 - \frac{1554.3}{(222.65 + t°\text{C})}$$

Solution.

In this problem one has to compute the vapour pressure values at different temperatures. The temperature range is fixed by keeping the pressure as

760 mm Hg for each component. Thus, in the following equation for Methanol,

$$\log\,[P,\ \text{mm}]_{\text{Methanol}} = 7.84863 - \frac{1473.11}{(230 + t°\text{C})}$$

Setting the vapour pressure as 760 mm Hg (at BP, vapour pressure equals the prevailing pressure), we get the temperature as 66.53°C, which is the boiling point of Methanol. Similarly, by setting P as 760 mm Hg in the equation for ethanol,

$$\log\,[P,\ \text{mm}]_{\text{Ethanol}} = 8.04494 - \frac{1554.3}{(222.65 + t°\text{C})}$$

we get the boiling point of Ethanol as 78.33°C. This fixes the range of temperature.

t°C	66.53	70	72	74	76	78	78.33
V.P. of Methanol, P_A, mm	760	867.5	934.94	1006.6	1082.79	1163.6	1177.4
V.P. of Ethanol, P_B, mm	467.8	541.77	588.66	638.9	692.66	750.14	760
Relative volatility, $\alpha = \frac{P_A}{P_B}$	1.625	1.601	1.588	1.576	1.563	1.551	1.549
$x_A = \frac{P_t - P_B}{(P_A - P_B)}$	1.0	0.67	0.495	0.329	0.173	0.024	0.0
$y_A = \frac{P_A x_A}{P_t}$	1.0	0.765	0.609	0.436	0.246	0.0365	0.0

Average relative volatility = 1.579

5. Methanol and Ethanol form an ideal solution. Compute the VLE data at 760 mm Hg pressure,
Vapour pressure Data:

Vapour pressure, mm Hg	200	400	760	1520
Temperature,°C, Ethanol	48.4	62.5	78.4	97.5
Temperature,°C, Methanol	34.8	49.9	64.7	84.0

Plot vapour pressure vs temperature for both the components and compute T vs. VP for Methanol and T vs. VP for Ethanol as shown in Fig. 9.34.

Solution.

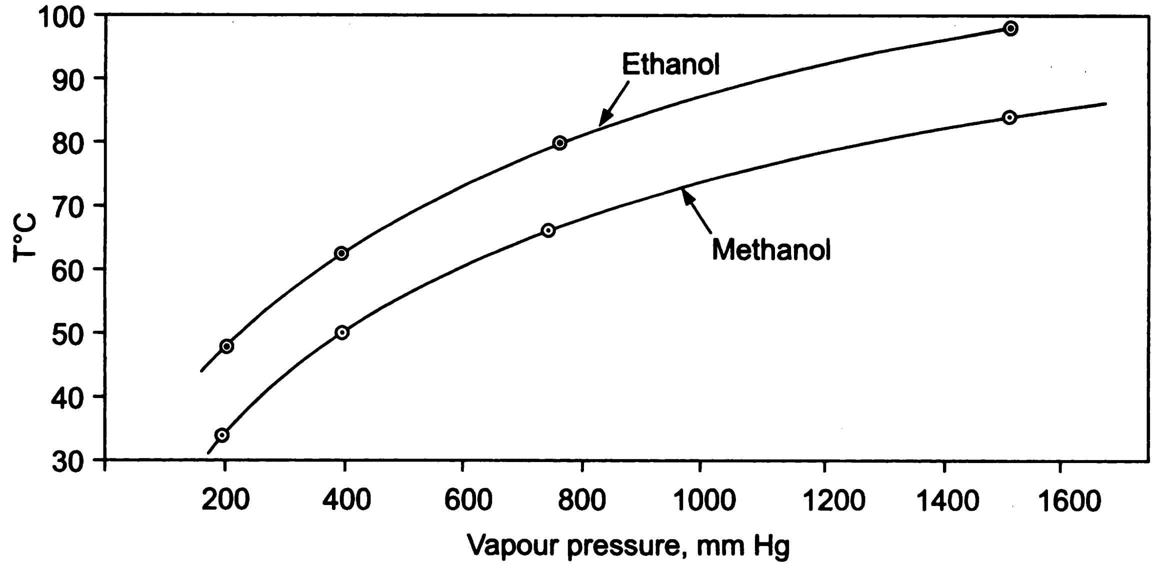


Fig. 9.34 Example 5 Vapour Pressure–temperature plot.

Temperature, °C	*V.P. of Ethanol,* mm Hg (*B*)	*V.P. of Methanol,* mm Hg (*A*)	$x_A = \frac{P_t - P_B}{(P_A - P_B)}$	$y_A = \frac{P_A x_A}{P_t}$
64.7	430	760	1.0	1.0
67.0	470	830	0.806	0.880
70.0	540	950	0.537	0.671
73.0	620	1080	0.304	0.432
76.0	700	1200	0.120	0.189
78.4	760	1300	0.0	0.0

6. It is desired to separate a feed mixture containing 40% heptane and 60% ethyl benzene, such that 60% of the feed is distilled out. Estimate the composition of the residue and distillate when the distillation process is (i) equilibrium distillation, and (ii) differential distillation.

Equilibrium Data:

x	0	0.08	0.185	0.251	0.335	0.489	0.651	0.79	0.914	1.0
y	0	0.233	0.428	0.514	0.608	0.729	0.814	0.910	0.963	1.0

x, *y*: Mole fraction of heptane in liquid and vapour phase respectively.

Solution.

(i) Plot the equilibrium data and draw the diagonal.

Draw a line with a slope of $-W/D = -0.4/0.6 = -0.667$ from a point on the diagonal corresponding to $x_F = 0.4$ and its intersection on the equilibrium curve and read them as x_w and y_D as shown in Fig. 9.35.

$$x_w = 0.24 \text{ and } y_D = 0.5$$

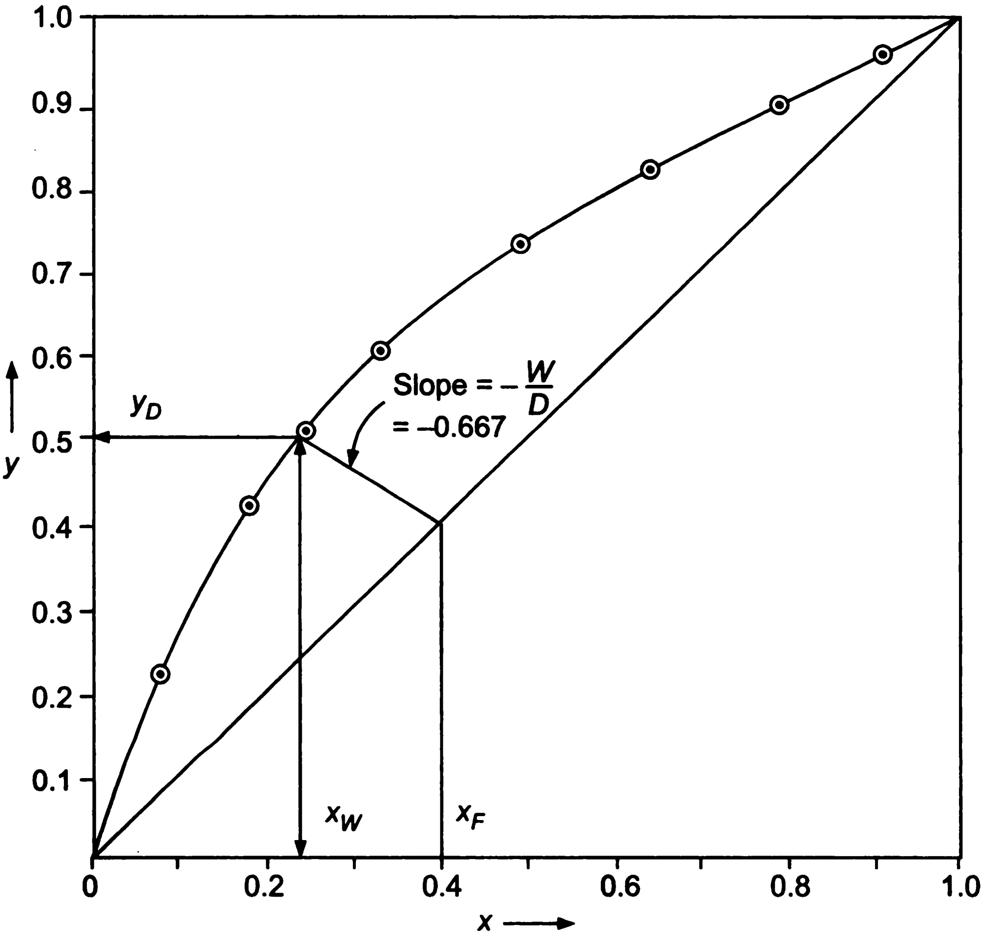


Fig. 9.35 Example 6 Solution for flash distillation.

(ii) Compute $\frac{1}{y-x}$ and plot it against x as shown in Fig. 9.36

x	0	0.08	0.185	0.251	0.335	0.489	0.651	0.79	0.914	1.0
y	0	0.233	0.428	0.514	0.608	0.729	0.814	0.91	0.963	1.0
$y-x$	0	0.153	0.243	0.263	0.273	0.240	0.163	0.12	0.049	0
$\frac{1}{y-x}$	α	6.54	4.12	3.80	3.66	4.17	6.13	8.33	20.41	α

We know that

$$\int_{x_w}^{x_F} \frac{dx}{(y-x)} = \ln\left[\frac{F}{W}\right] = \ln\left[\frac{1}{0.4}\right] = 0.916$$

By trial and error, find the x-co-ordinate which will give the area under the curve as 0.916 from $x_F = 0.4$. $x_w = 0.2$. By making component balance, $y_D = 0.533$.

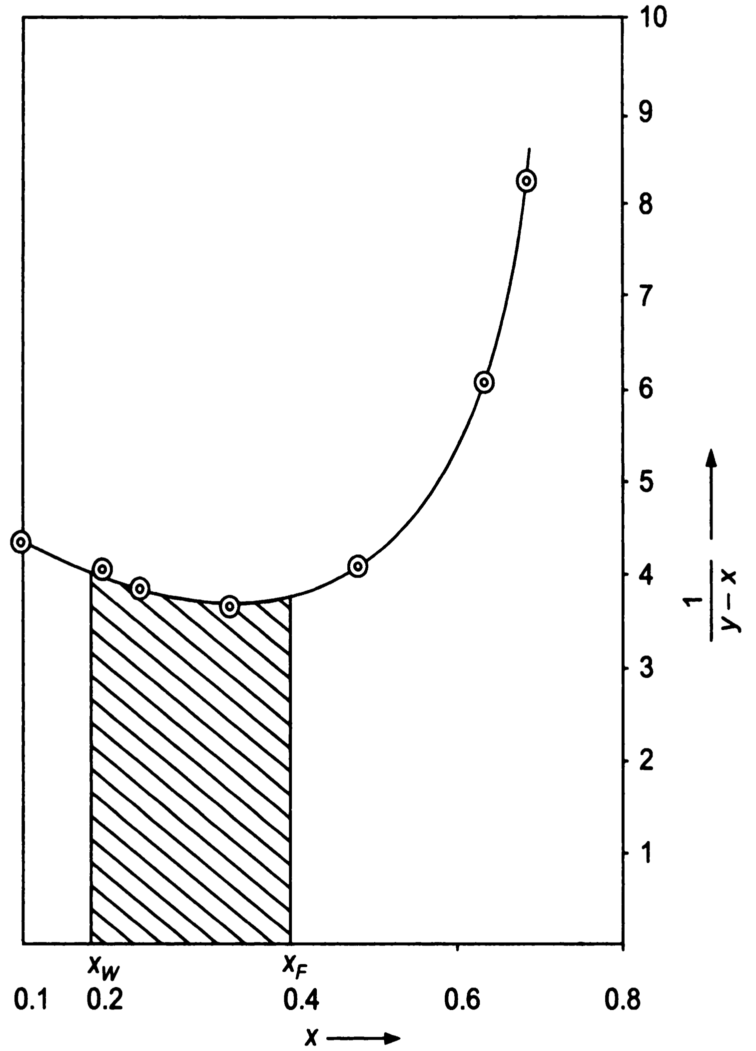


Fig. 9.36 Example 6 Solution for differential distillation.

7. A feed mixture containing 50 mole % Hexane and 50 mole % Octane is fed into a pipe still through a pressure reducing valve and flashed into a chamber. The fraction of feed converted to vapour is 0.6. Find the composition of the distillate and residue

x	0	4.5	19.2	40	69	100
y	0	17.8	53.8	78	93.2	100

x, y mole percent of Hexane in liquid and vapour phase respectively

Solution.

Draw the equilibrium curve and diagonal. From the feed point draw a line with a slope of

$$\left[-\frac{W}{D}\right] = -\frac{0.4}{0.6} = -0.667$$

From graph shown in Fig. 9.37, we get

$$x_W = 0.275, \quad y_D = 0.65$$

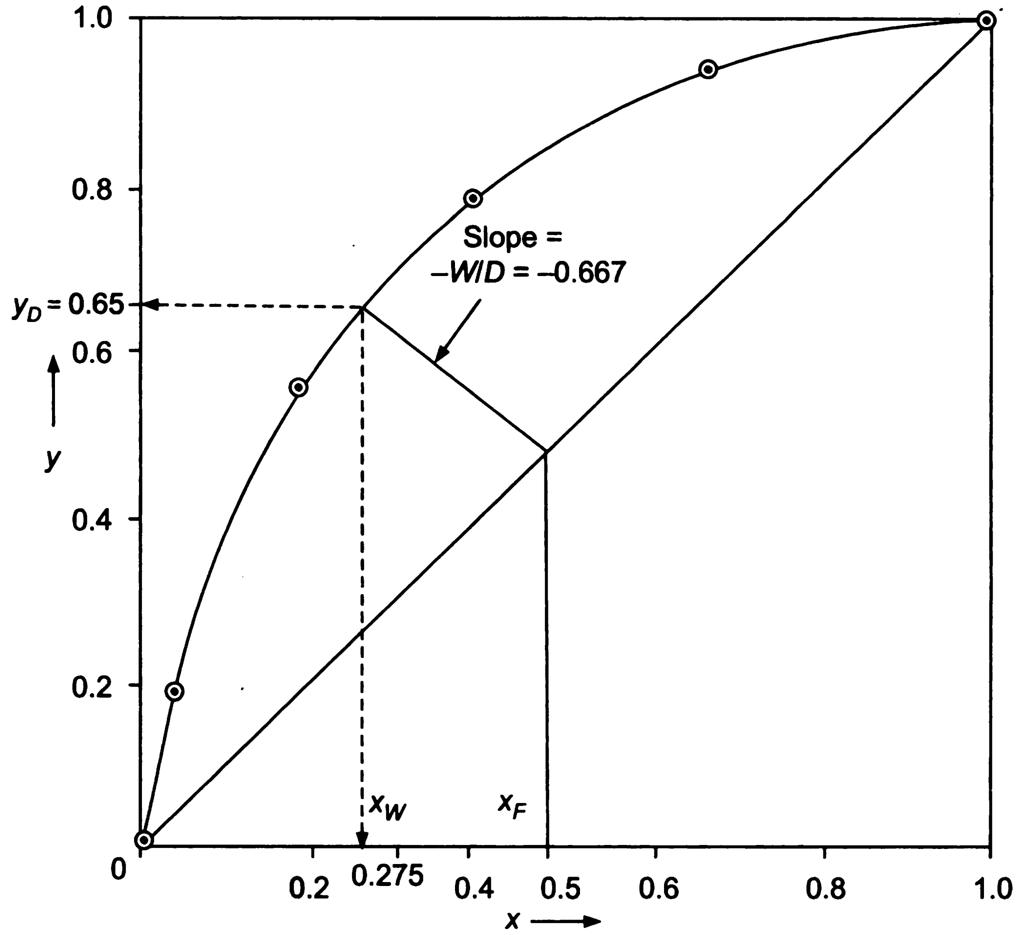


Fig. 9.37 Example 7 Flash distillation.

8. A equimolar feed mixture containing A and B is differentially distilled such that 70% of the feed is distilled out. Estimate the composition of the distillate and residue.

Equilibrium data

x	0	1	8	14	21	29	37	46	56	66	97	100
y	0	3	16	28	39	50	59	65	76	83	99	100

x, y: mole fraction of benzene in liquid and vapour phase respectively.

Solution.

x	0	0.01	0.08	0.14	0.21	0.29	0.37	0.46	0.56	0.66	0.97	1.0
y	0	0.03	0.16	0.28	0.39	0.50	0.59	0.65	0.76	0.83	0.99	1.0
$y–x$	0	0.02	0.08	0.14	0.18	0.21	0.22	0.19	0.20	0.17	0.02	0
$\frac{1}{y-x}$	α	50	12.5	7.14	5.56	4.76	4.55	5.26	5.0	5.88	50	α

Plot $\dfrac{1}{y-x}$ against x as shown in Fig. 9.38

We know that,

$$\int_{x_w}^{x_F} \frac{dx}{(y-x)} = \ln\left[\frac{F}{W}\right]$$

Let the feed be 100 moles

Therefore, $D = 70$ moles and $W = 30$ moles

$$\therefore \qquad \ln\left[\frac{F}{W}\right] = \ln\left[\frac{100}{30}\right] = 1.204$$

By trial and error, locate x_w such that $\displaystyle\int_{x_w}^{x_F} \frac{dx}{(y-x)} = 1.204$

We get, $\qquad x_w = 0.23$

Making material balance, we get

$$F = W + D$$

$$Fx_F = W\,x_W + Dy_D$$

Substituting for various quantities, we get

$$100 \times 0.5 = 30 \times 0.23 + 70 \times y_D$$

Solving, we get,

$$y_D = 0.616$$

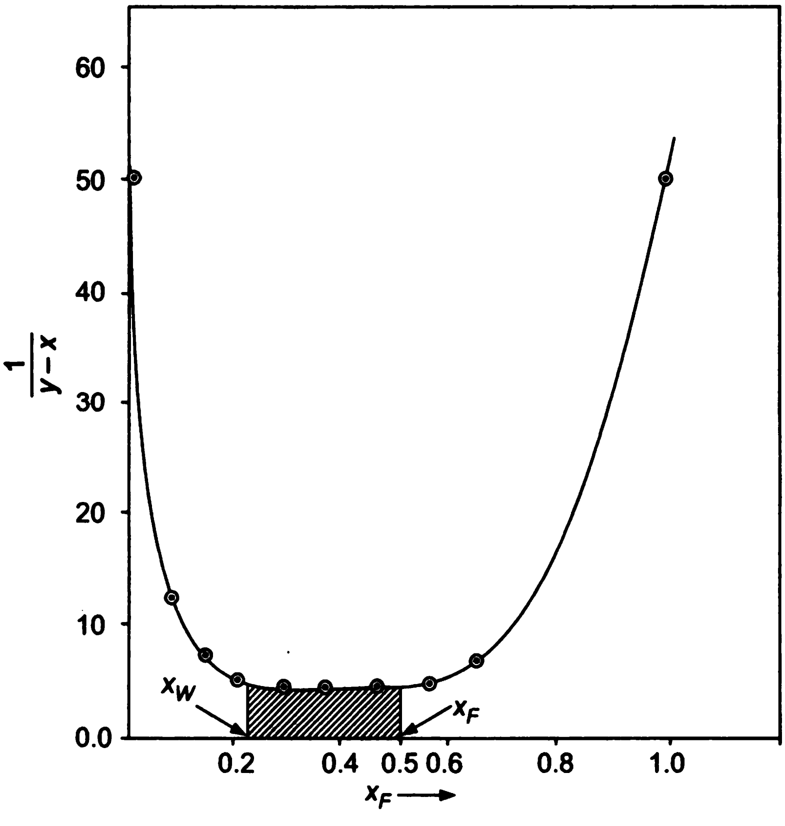


Fig. 9.38 Example 8 Solution for differential distillation.

9. A liquid mixture of components A and B containing 30 mole percent A is subjected to differential distillation. What percentage of the original mixture must be distilled off in order to increase the concentration of A in the residue to 65 mole percent?

The relative volatility of B in respect of A is 2.15.

Solution.

$$\ln\left[\frac{Fx_{F,B}}{WX_{W,B}}\right] = \alpha_{BA}\ln\left[\frac{Fx_{F,A}}{WX_{W,A}}\right]$$

$$\ln\left[\frac{F\times 0.7}{W\times 0.35}\right] = 2.15\ln\left[\frac{F\times 0.3}{W\times 0.65}\right]$$

$$2\left[\frac{F}{W}\right] = \left[\frac{F\times 0.4615}{W}\right]^{2.15}$$

Solving, we get $\left[\frac{F}{W}\right] = 7.75$

Therefore, if F = 100 kmol, W = 12.91 kmol.
Hence, 87.09% of feed has to be distilled.

10. Nitrobenzene (NB) has to be steam distilled. If the vaporization efficiency is 85%, estimate the amount of nitrobenzene in the distillate if 100 kg of steam is present in distillate. The distillation takes place at a total pressure of 760 mm Hg.

Vapour pressure data for nitrobenzene:

T°, C	44.4	71.6	84.9	99.3	115.4	125.8	139.9	185.8	210.6
VP of NB mm Hg	1	5	10	20	40	60	100	400	760

Vapour pressure of water:

T°C	20	40	60	80	100
VP of water, mm Hg	17.5	55.3	149.4	355.1	760

T (°C)	71	78	80	82	90	96	100
p_B	5	7.5	9	10	14	17.5	21
p_A	242.5	340	355	412.5	515	605	760

Solution.

From total vapour pressure curve: Boiling point of mixture = 99.0°C

At 99°C, vapour pressure of nitrobenzene = 20 mm Hg
vapour pressure of water = 740 mm Hg

Vaporization η = [(Actual NB/Actual water)]

$$0.85 = \left[\frac{\left[\dfrac{\text{Actual NB}}{\text{Actual water}}\right]}{\left[\dfrac{\text{Theoretical NB}}{\text{Theoretical water}}\right]}\right] \text{ (all in moles)}$$

$$\frac{\text{Actual NB}}{\text{Actual water}} = 0.85 \times \left[\frac{\text{Theoretical NB}}{\text{Theoretical water}}\right]$$

$$= \frac{0.85 \times 20 \times 123}{740 \times 18} \text{ kg of NB/kg of steam}$$

$$= 0.85 \times 0.1847 = 0.157 \text{ kg of NB/kg of steam}$$

Mass of NB per 100 kg of steam = 15.7 kg

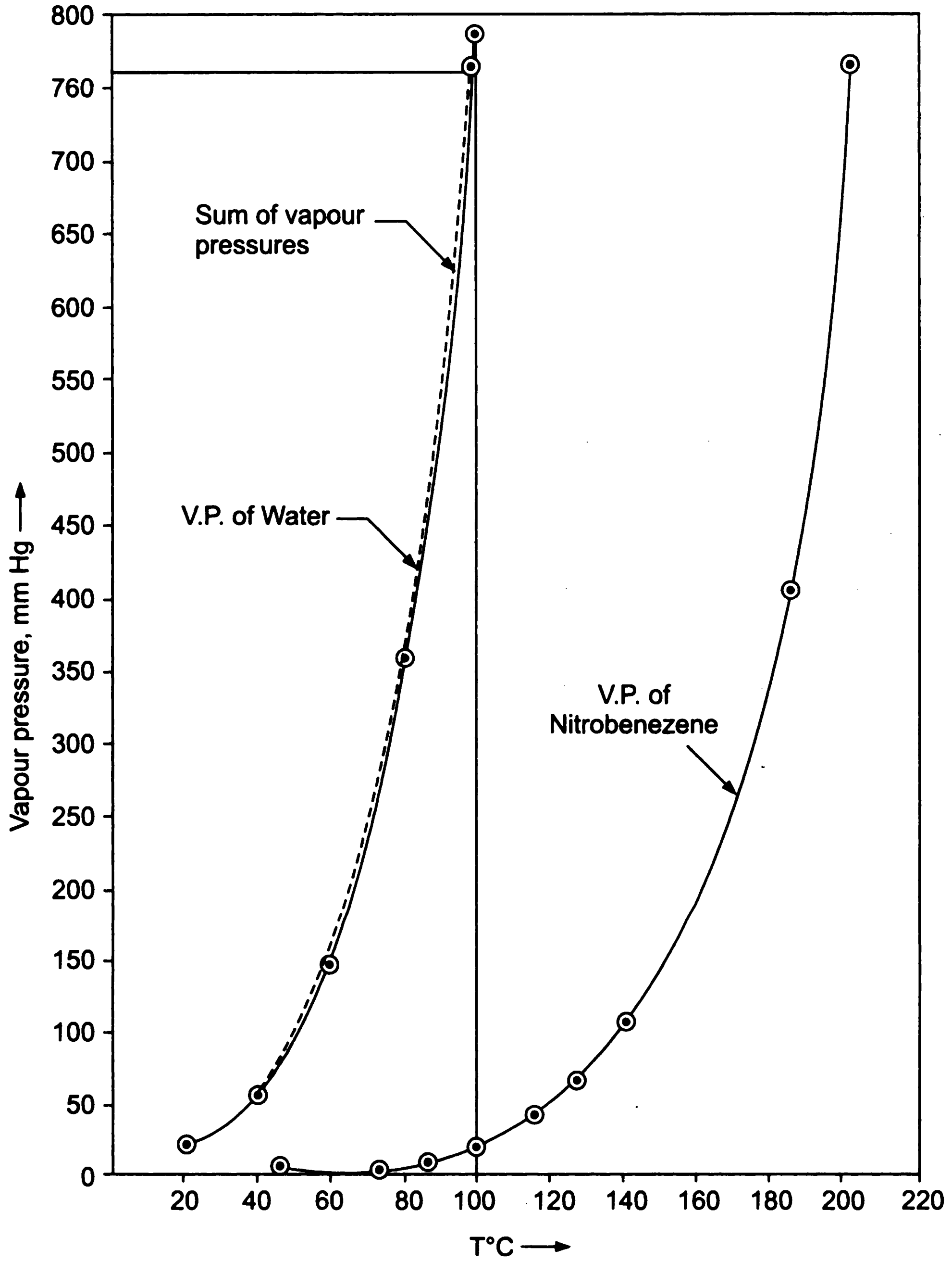


Fig. 9.39 Example 10 Determination of boiling point for steam distillation.

11. A methanol–water solution containing 36 mole % methanol at 26.7°C is continuously distilled to yield a distillate containing 91.5 mole % methanol and a residue containing 99 mole % water. The feed enters at its bubble point. Distillate is totally condensed and refluxed at its bubble point. (i) Find the minimum reflux ratio. (ii) For a reflux ratio of 3, estimate the number of plates by Ponchon–Savarit method.

Enthalpy data:

x or y mole fraction of methanol	*Enthalpies of saturated liquid* kJ/kmol	*Enthalpies of saturated vapour* kJ/kmol
0	8000	48000
1	7500	39000

Equilibrium data:

x, %	4	10	20	30	50	70	90	95
y, %	23	42	58	66	78	87	96	98.15

x, y are mole fractions of methanol in liquid and vapour phase respectively.

Solution.

(i) $x_F = 0.36$, $x_w = (1 - 0.99) = 0.01$, $x_D = 0.915$

Both feed and Reflux are at bubble point.

Plot H-x-y diagram and xy diagram as shown in Fig. 9.40.

By intrapolation, $H_{G1} = 39765$ kJ/kmol

Locate F corresponding to $x_F = 0.36$ on the bubble point curve.

Through F draw a tie line and extend it to intersect the vertical line drawn at $x_D = 0.915$

$$Q'_{\min} \text{ (from graph)} = 62500 \text{ kJ/kmol}$$

$$R_{\min} = \frac{(Q'_{\min} - H_{G_1})}{(H_{G_1} - H_{L_0})} = \frac{(62500 - 39765)}{(39765 - 7542.5)} = 0.7056$$

Minimum reflux ratio = 0.7056

(ii) For $R = 3$

$$R = \frac{(Q' - H_{G_1})}{(H_{G_1} - H_{L_0})} = \frac{(Q' - 39765)}{(39765 - 7542.5)} = 3$$

$$Q' = 136432.5 \text{ kJ/kmol}$$

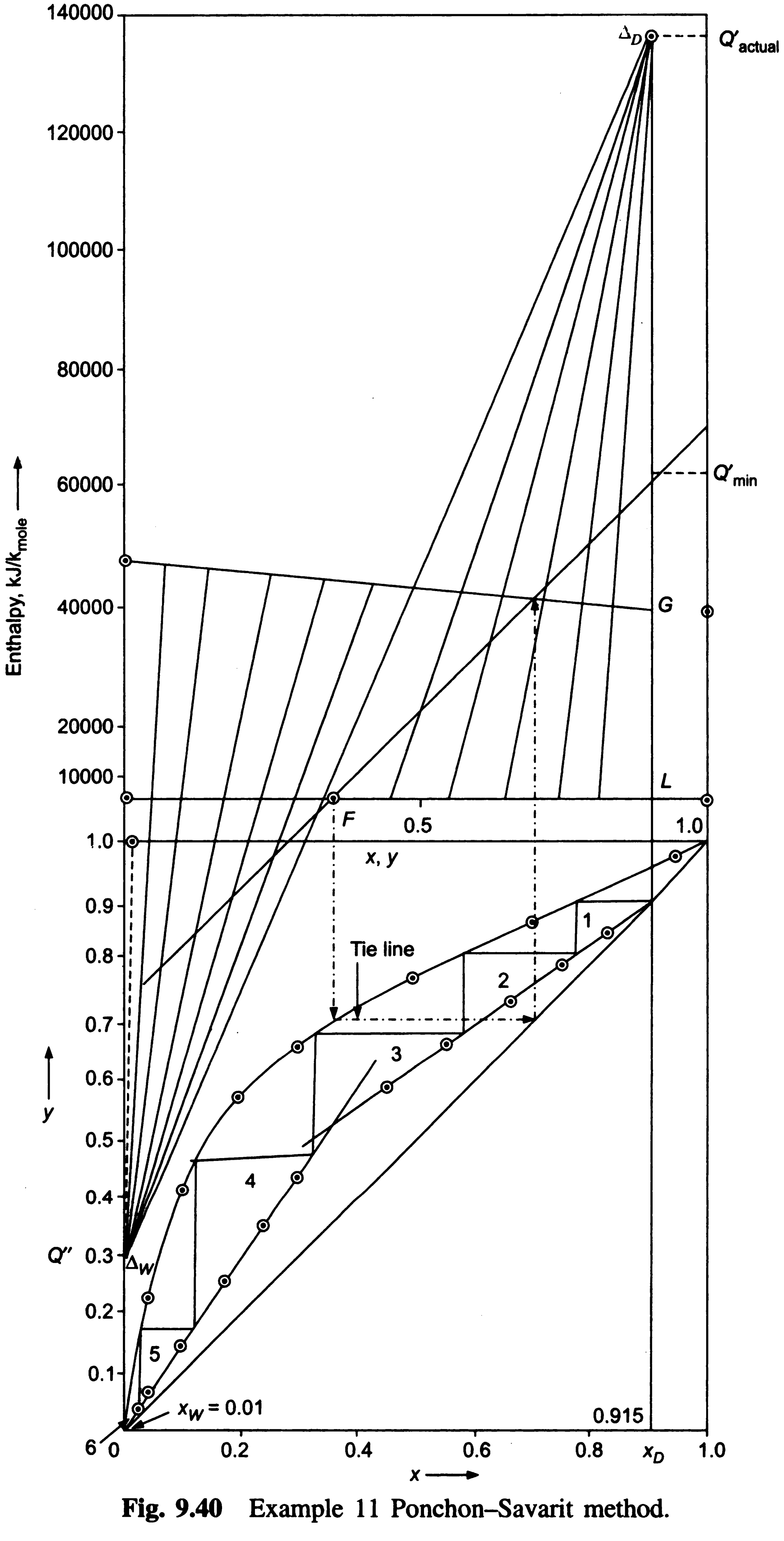


Fig. 9.40 Example 11 Ponchon–Savarit method.

We know that Δ_D, Δ_W and $F(Z_F, H_F)$ lie on a straight line

$$\frac{(Z_F - Z_w)}{(x_D - x_F)} = \frac{(H_F - Q'')}{(Q' - H_F)}$$

$$Q'' = -73004.5 \text{ kJ/kmol}$$

Locate $\Delta_D(Q', x_D)$ and $\Delta_w(Q'', x_w)$ on H_{xy} diagram. Randomly draw construction lines starting from Δ_D and Δ_w and obtain the operating curves for both sections on *xy*-diagram. Stepwise construction between equilibrium curve and operating curve will give the number of stages.

Number of stages (including reboiler) = 6

Number of plates in tower = 6 − 1 = 5

12. A continuous distillation column is used to separate a feed mixture at its boiling point, containing 24 mole % acetone and 76 mole % methanol into a distillate product containing 77 mole % acetone and a residue product containing 5 mole % acetone. A reflux ratio of twice the minimum is to be used. The overall plate efficiency is 60%. Determine the number of plates required for the separation.

Equilibrium data:

x	0.0	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
y	0.0	0.102	0.186	0.322	0.428	0.513	0.586	0.656	0.725	0.82	0.9	1.0

Solution.

x, *y* Mole fraction of acetone in liquid and vapour phase respectively.

$$x_F = 0.24, \qquad x_D = 0.77, \qquad x_w = 0.05$$

$R_{\text{actual}} = 2R_{\min}$

$\eta_{\text{overall}} = 60\%$

Plot *xy* diagram and draw the feed line with its corresponding slope of infinity to equilibrium curve and let it be *F*. Let the point *D* on the diagonal corresponds to x_D. Join *DF* and extend it to *y*-axis. The point of intersection is

$$\frac{x_D}{R_{\min} + 1} = 0.19 \text{ (from Fig. 9.41)}$$

$$\therefore \quad R_{\min} = 3.053$$

$$\therefore \quad R_{\text{actual}} = 6.106$$

$$\frac{x_D}{R_{\text{actual}} + 1} = \frac{0.77}{7.106} = 0.108$$

Locate 0.108 on *y*-axis and let it be *A*. Join *AD*. The point of intersection of *AD* with feed line is *Q*. *DQ* is the operating line for enriching section. Locate *W* on diagonal corresponding to x_W = 0.05. Join *W* and *Q*. *WQ* is the operating line for stripping section. By stepwise construction the number of stages = 14 (including reboiler)

∴ Number of plates is 13 (Theoretical)

$$\text{Actual number of plates} = \frac{13}{0.6} = 21.7, \text{ i.e. 22 plates}$$

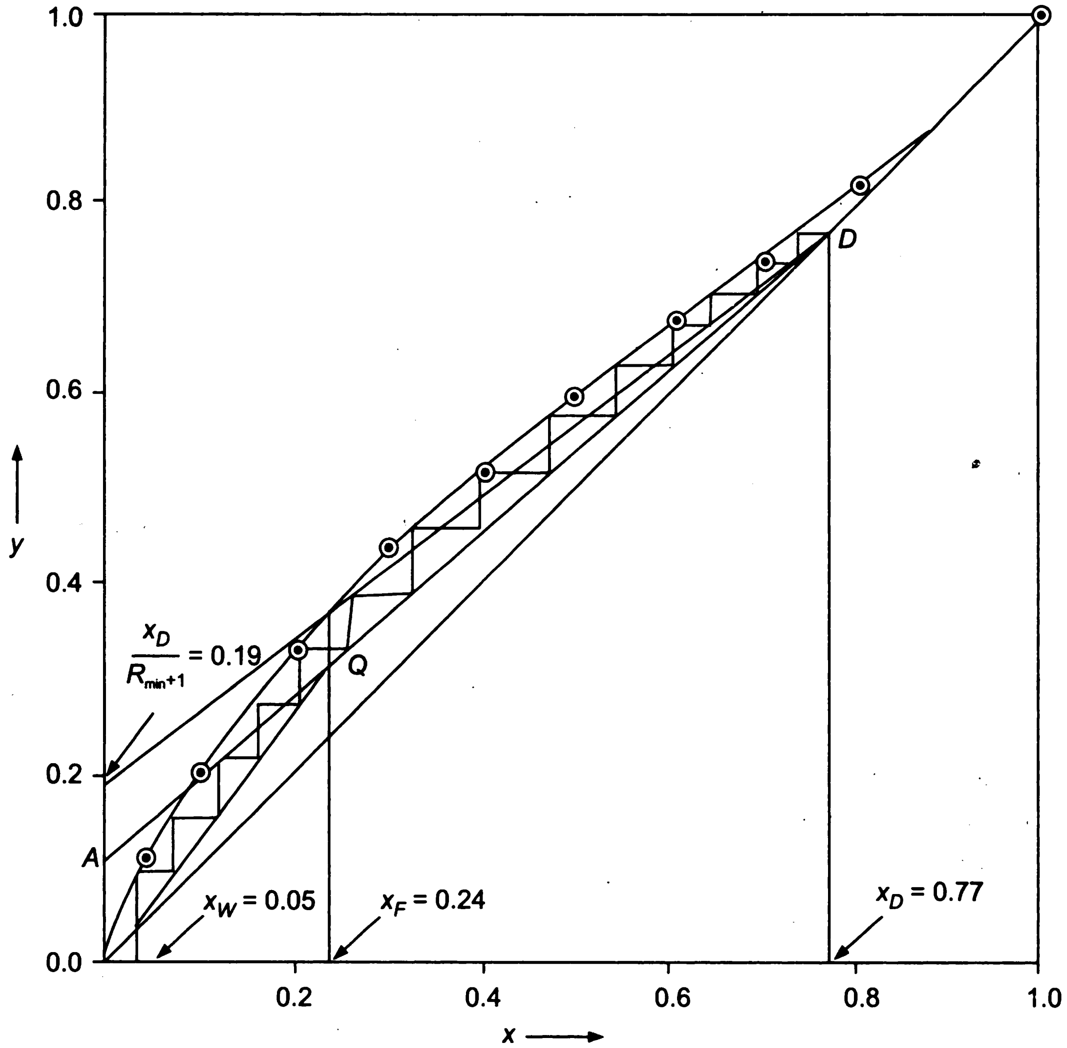


Fig. 9.41 Example 12 McCabe–Thiele method.

13. A fractionating column separates a liquid mixture entering at 5000 kmol/h containing 50 mole % A and 50 mole % B into an overhead product of 95 mole % A and a bottom product of 96 mole % B. A reflux ratio of twice the minimum will be used and the feed enters at its boiling point. Determine the number of theoretical stages required and the location of feed point.

Equilibrium data:

x	0.03	0.06	0.11	0.14	0.26	0.39	0.53	0.66	0.76	0.86	1.0
y	0.08	0.16	0.27	0.33	0.50	0.63	0.71	0.83	0.88	0.93	1.0

x, y mole fraction of A in liquid and vapour phase respectively.

Solution.

$$x_F = 0.5, \qquad x_D = 0.95, \qquad x_w = 0.04$$

Feed-saturated liquid

$$F = 5000 \text{ kmol/h}$$

Total condenser

(i) Total material balance

$$F = D + W$$

Component balance

$$Fx_F = Dx_D + Wx_W$$

$$5000 = D + W \tag{1}$$

$$(5000 \times 0.5) = (D \times 0.95) + (W \times 0.04) \qquad (2)$$

$$5000 = D + W$$

Distillate $D = 2527.5$ kmol/h

Residue $W = 2472.5$ kmol/h

(ii) $R_{\text{min}} = [(x_D - y')/(y' - x')]$

$$R_{\text{min}} = \left[\frac{(0.95 - 0.720)}{(0.720 - 0.5)}\right] = 1.045$$

Also, by graphical $x_D/(R_{\text{min}} + 1) = 0.46$ and $R_{\text{min}} = 1.065$

(iii) $R_{\text{actual}} = 2 \times R_{\text{min}}$

$R_{\text{actual}} = 2 \times R_{\text{min}} = 2 \times 1.045 = 2.09$ (Taking R_{min} value as 1.045)

$$\frac{x_D}{(R + 1)} = \frac{0.95}{(2.09 + 1)} = 0.307$$

With the above intercept, draw both enriching and stripping operating curves.
By McCabe–Thiele method,
Number of plates (including reboiler) = 11
Number of plates in tower = 11 − 1 = 10
The location of feed tray is 6th tray.

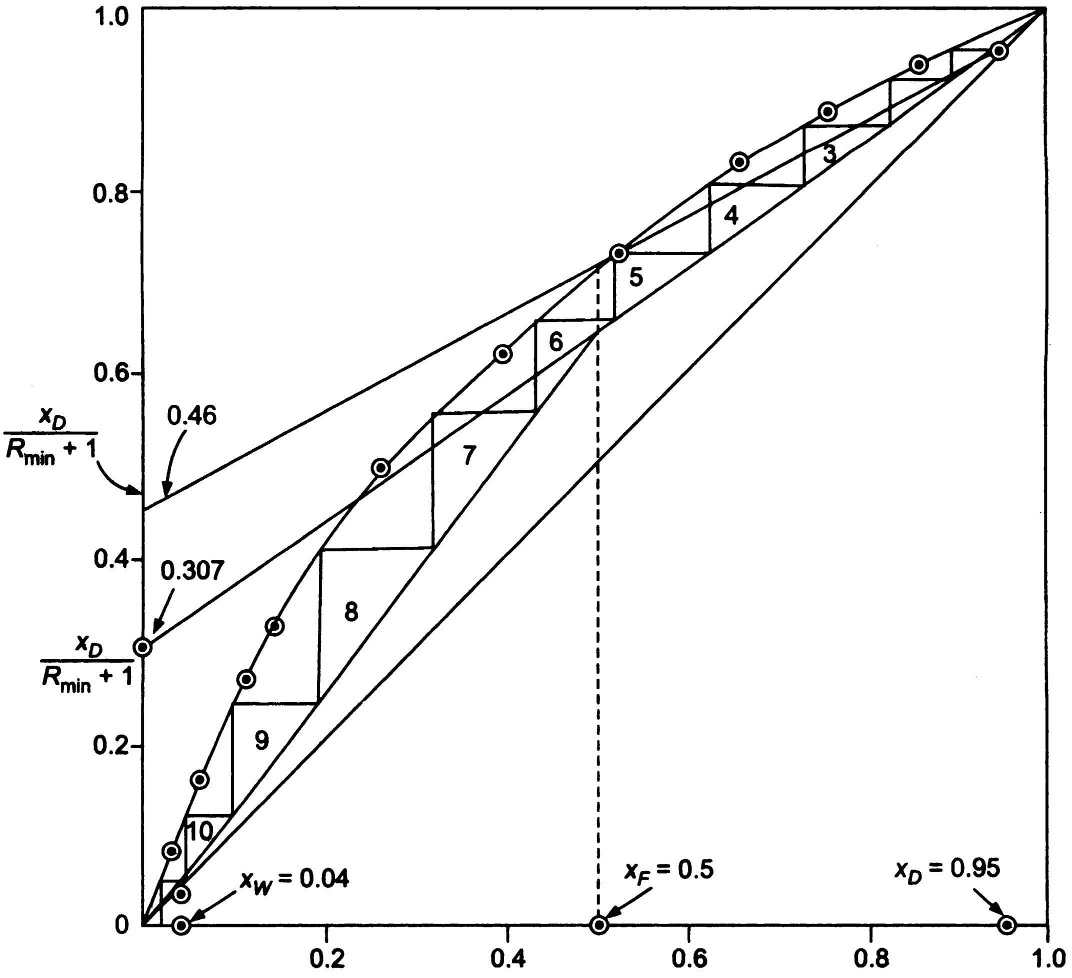


Fig. 9.42 Example 13 McCabe–Thiele method.

14. A mixture of benzene and toluene containing 38 mole % of benzene is to be separated to give a product of 90 mole % benzene at the top, and the bottom product with 4 mole % benzene. The feed enters the column at its

boiling point and vapour leaving the column is simply condensed and provide product and reflux. It is proposed to operate the unit with a reflux ratio of 3.0. Locate the feed plate and number of plates. The vapour pressures of pure benzene and toluene are 1460 and 584 mm Hg respectively. Total pressure is 750 mm Hg.

Solution.

$$\alpha = \frac{\text{vapour pressure of pure benzene}}{\text{vapour pressure of pure toluene}} = \frac{1460}{584} = 2.5$$

$$y = \frac{\alpha x}{[1 + (\alpha - 1)x]}$$

Compute equilibrium data.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
y	0	0.22	0.38	0.52	0.63	0.71	0.79	0.85	0.91	0.96	1.0

Draw the equilibrium curve, diagonal and locate feed, distillate and residue points as shown in Fig. 9.43.

Locate the intercept $\frac{x_D}{[R+1]} = \frac{0.9}{3+1} = 2.25$ and by stepwise construction we can get the number of stages.

No. of stages = 8 (including reboiler) and feed plate is 4

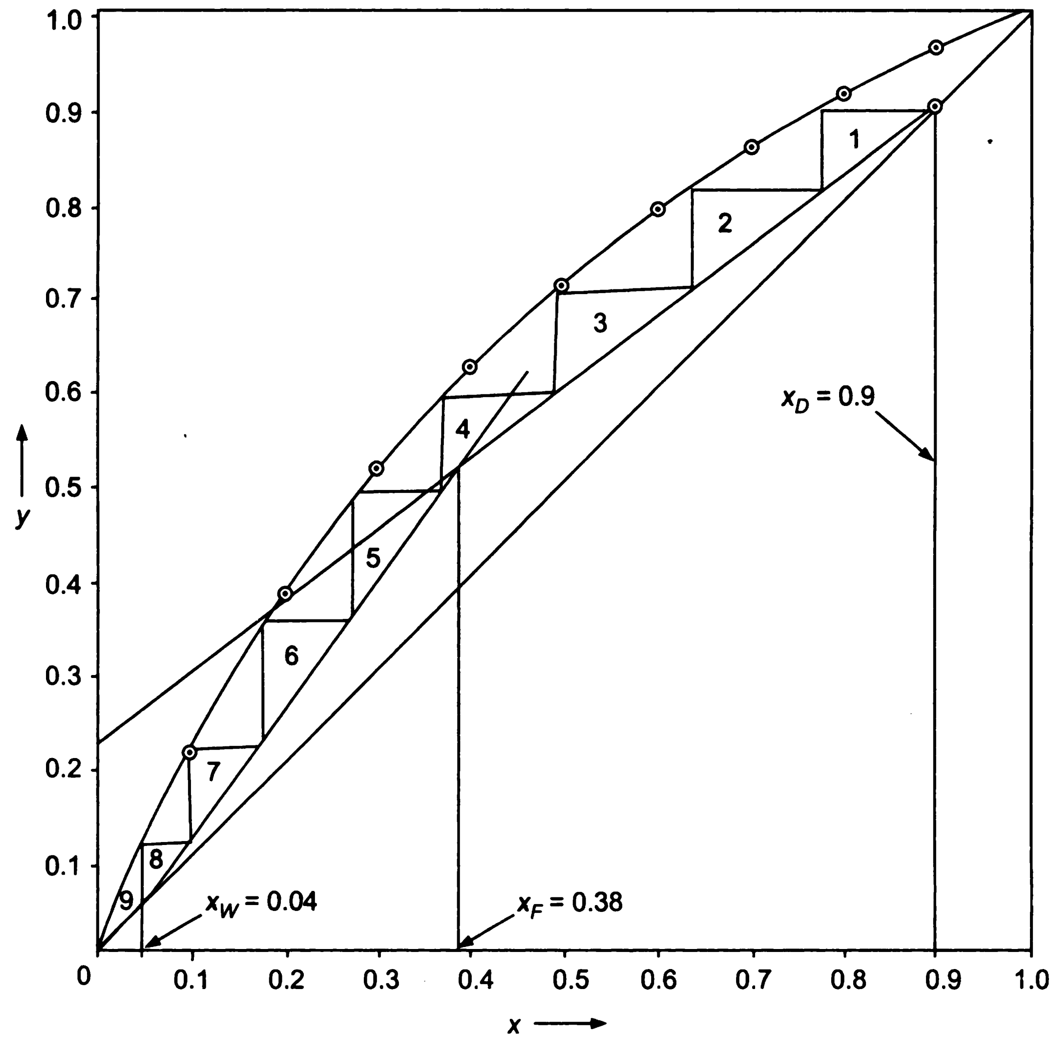


Fig. 9.43 Example 14 McCabe–Thiele method.

15. It is desired to separate a mixture of 50% vapour and 50% saturated liquid in a plate type distillation column. The feed contains 45 mole % A and the top product is to contain 96 mole % A. The bottom product is to contain 5 mole % A. Determine the minimum reflux ratio and the number of theoretical plates needed if a reflux ratio of twice the minimum is used.
Eq. data:

x	0	0.1	0.16	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
y	0	0.215	0.30	0.52	0.625	0.725	0.78	0.89	0.89	0.95	1.0

x, y : mole fraction of A in liquid and vapour phase respectively.

Solution.

$$\left[\frac{x_D}{R_{\min}+1}\right] = 0.33$$

$$R_{\min}+1 = \frac{0.96}{0.33}$$

$$R_{\min} = 1.909$$

$$q = 0.5 \text{ (Fraction of liquid)}$$

$$\text{Slope of } q\text{-line } \left[\frac{q}{q-1}\right] = \frac{0.5}{0.5-1} = -1.0$$

$$R_{\text{actual}} = 2.0 \times R_{\min} = 2.0 \times 1.909 = 3.818$$

$$\left[\frac{y_D}{R_{\text{actual}}+1}\right] = \frac{0.96}{3.818+1} = 0.199$$

Number of stages = 10

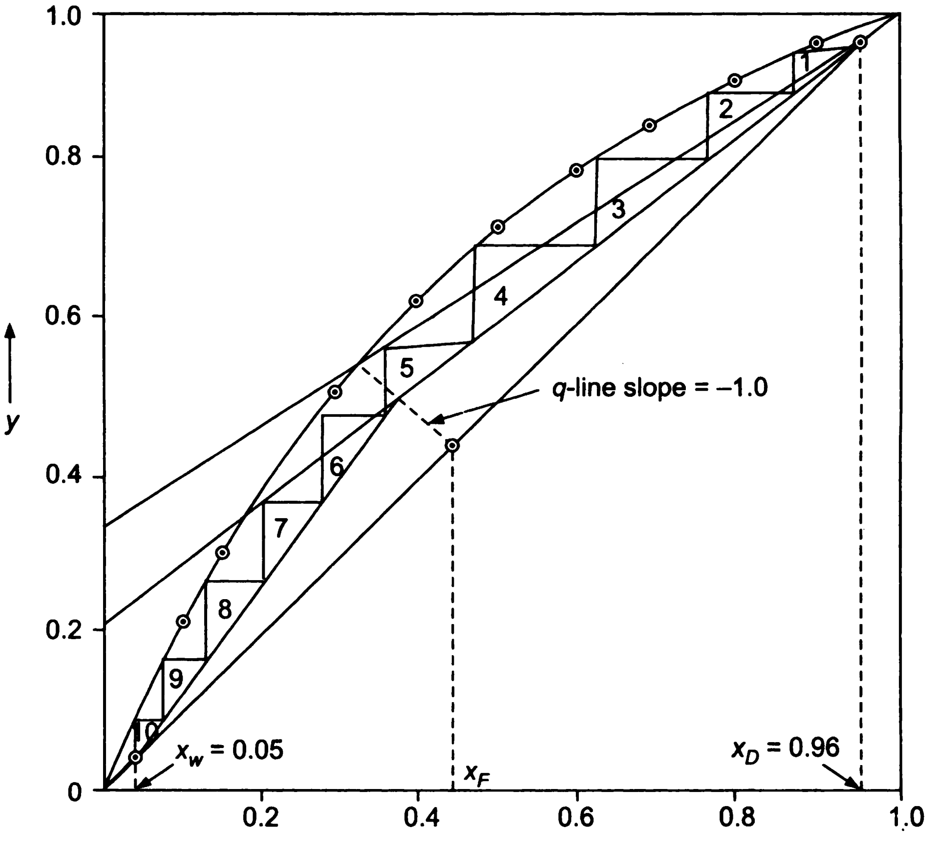


Fig. 9.44 Example 15 McCabe–Thiele method.

16. A fractionating column separates a liquid mixture containing 50 weight % chloroform and 50 weight % carbon disulphide into an overhead product of 94 weight % CS_2 and a bottom product of 95 weight % chloroform. A reflux ratio of twice the minimum will be used and the feed enters at its boiling point. Determine the number of theoretical stages required.
Equilibrium data:

x	0.03	0.06	0.11	0.14	0.26	0.39	0.53	0.66	0.76	0.86	1.0
y	0.08	0.16	0.27	0.33	0.50	0.63	0.71	0.83	0.88	0.93	1.0

x, y mole fraction of carbon disulphide in liquid and vapour phase respectively.

Solution.

Molecular weight of carbon disulphide = 76

Molecular weight of chloroform = 119.5

50 weight % of carbon disulphide,

$$x_F = \frac{\left(\frac{50}{76}\right)}{\left[\frac{50}{76} + \frac{50}{119.5}\right]} = 0.611 \text{ (in mole fraction)}$$

Similarly, the distillate and residue compositions in terms of mole fraction of carbon disulphide are $y_D = 0.961$ and $x_w = 0.076$ respectively.

From graph (Fig. 9.45), $\left(\frac{y_D}{R_{\min} + 1}\right) = 0.49$

$$R_{\min} = 0.96$$

$$R_{\text{act}} = 2 \times R_{\min} = 1.92$$

Therefore, $\left(\frac{y_D}{R_{\text{actual}} + 1}\right) = 0.329 \simeq 0.33$

Number of theoretical stages (from Fig. 9.45) including reboiler = 9

17. A laboratory rectification column is operated at atmospheric pressure and at total reflux, for benzene–chlorobenzene mixture. Samples of liquid from the condenser and reboiler analyze 95 mole percent benzene and 98 mole percent chlorobenzene respectively. Assuming a perfect reboiler, a total condenser, constant molal overflow and no heat loss from the tower, calculate the actual number of plates in the column. The average plate efficiency is 70%. The relative volatility of benzene to chlorobenzene is 4.13.

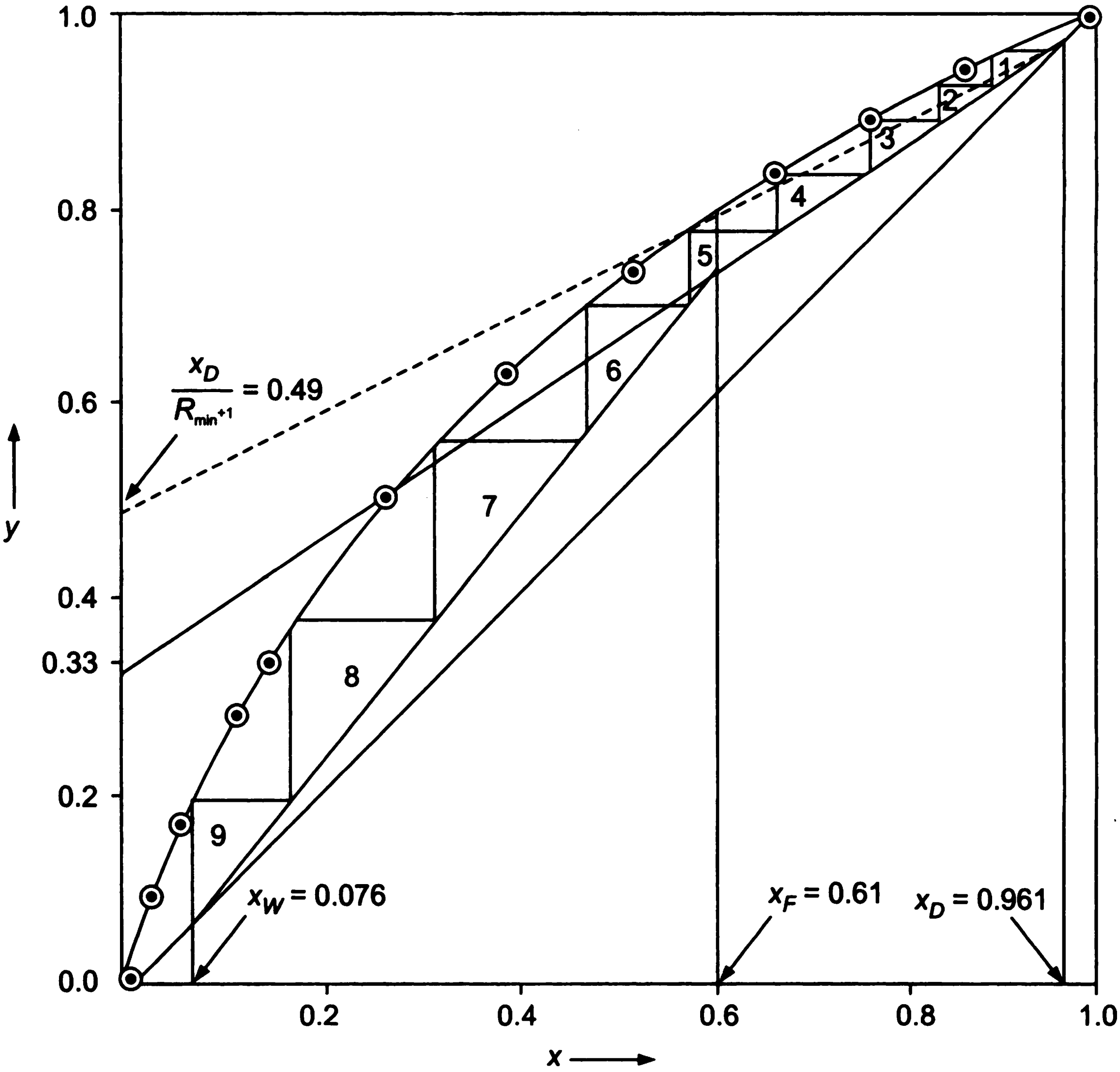


Fig. 9.45 Example 16 McCabe–Thiele method.

Solution.

$$y = \frac{\alpha x}{[1 + (\alpha - 1)x]}$$

Compute equilibrium data.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
y	0	0.31	0.51	0.64	0.73	0.81	0.86	0.91	0.94	0.97	1.0

Draw the equilibrium curve, diagonal and locate feed, distillate and residue points.

By stepwise construction, the number of stages determined is 5.

Hence, the theoretical plates required is 4.

Actual plates required will be $\frac{4}{0.7} = 5.71 \approx 6.$

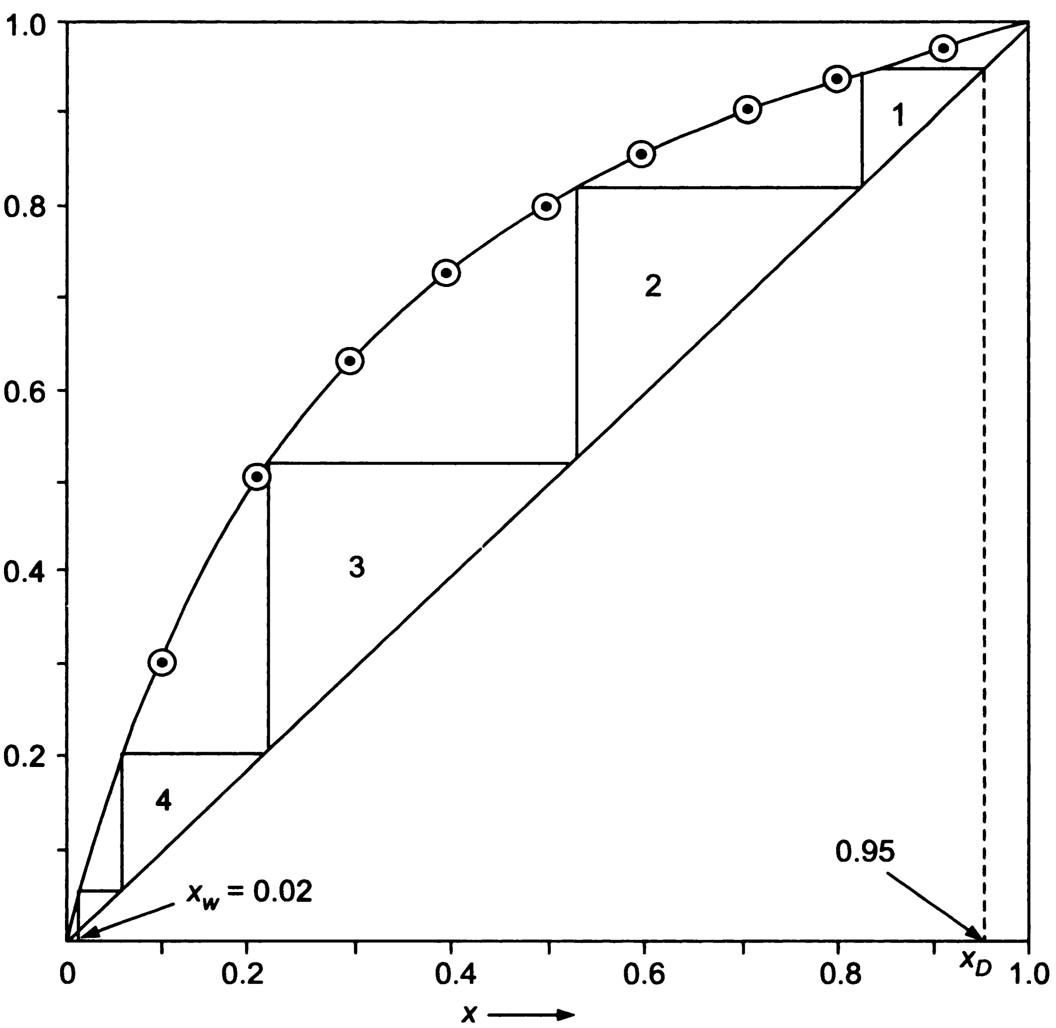


Fig. 9.46 Example 17 McCabe–Thiele method.

Alternatively, we can use the Fenske equation and determine the number of stages.

$$\frac{y_D}{(1-y_D)} = (\alpha)^{N_{P+1}} \frac{x_W}{(1-x_W)}$$

$$\frac{0.95}{(1-0.95)} = (4.13)^{N_{P+1}} \frac{0.02}{(1-0.02)}$$

$$19 = (4.13)^{N_{P+1}} \times 0.02041$$

Hence, $N_P + 1 = 4.82$ stages ≈ 5 stages
Therefore, the theoretical number of plates = 4

Actual plates required will be $\frac{4}{0.7} = 5.71 \approx 6$

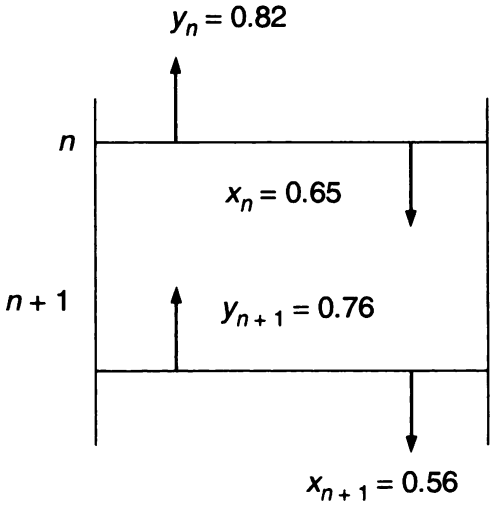
(Same as obtained from the graphical procedure)

18. A continuous rectification column is used to separate a binary mixture of A and B. Distillate is produced at a rate of 100 kmol/hr and contains 98 mole % A. The mole fractions of A in the liquid (x) and in the vapour (y) respectively from the two adjacent ideal plates in the enriching section are as follows:

x	y
0.65	0.82
0.56	0.76

The latent heat of vaporization is the same for all compositions. Feed is a saturated liquid. Calculate the reflux ratio and the vapour rate in the stripping section.

Solution.



$$\therefore \qquad y_{n+1} = \left[\frac{R}{R+1}\right] x_n + \left[\frac{1}{R+1}\right] y_D$$

$$0.76 = \left[\frac{R}{R+1}\right] 0.65 + \left[\frac{1}{R+1}\right] 0.98$$

Solving, we get

$$0.76R + 0.76 = 0.65R + 0.98$$

Reflux ratio, $R = 2$

In the stripping section,

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

$$\therefore \qquad q = \frac{(\bar{L} - L)}{F}$$

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

For a saturated feed $q = 1.0$

$$\therefore \qquad q = 1.0 = \frac{(\bar{G} - G)}{F}$$

i.e. $\bar{G} = G = L + D$

$= D(R + 1) = 100(2 + 1) = 300$ kmol/h

19. A continuous rectifying column treats a mixture containing 40% benzene and 60% toluene and separates into a distillate product containing 98% benzene and a bottom product containing 98% toluene. The feed enters as a liquid at its boiling point. If a reflux ratio of 3.5 is used, estimate height of the tower. The average height of a transfer unit is 0.7 m. The overall resistance to mass transfers lies in vapour phase.

Equilibrium data:

x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
y	0.22	0.38	0.51	0.63	0.70	0.78	0.85	0.91	0.96

x, y: mole fraction of benzene in liquid and vapour phase respectively.

Solution.

y	0.98	0.92	0.81	0.74	0.655	0.57	0.44	0.318	0.2	0.1	0.02
y'	0.995	0.96	0.89	0.83	0.75	0.655	0.543	0.43	0.30	0.183	0.05
$\frac{1}{(y'-y)}$	66.67	25	12.5	11.11	10.53	11.76	9.71	8.93	10	12.05	33.33

y is from operating line and y' is obtained from equilibrium curve for a specific x value.

$x_F = 0.4$, $x_w = (1 - 0.98) = 0.02$, $R = 3.5$, $HTU = 0.7$

$[x_D/(R + 1)] = [0.98/ (3.5 + 1)] = 0.218$

Overall mass transfer lies in vapour phase. So the slope $-[(1/kx)/(1/ky)]$ becomes vertical, y and y' values are obtained at the intersection of operating and equilibrium curves.

$$\int \left[\frac{dy}{(y' - y)}\right] = 13.175$$

$$Z = \text{HTU} \times \text{NTU} = 0.7 \times 13.175 = 9.22 \text{ m}$$

20. Feed rate to a distillation column is 400 kmol/hr. The overhead product rate is 160 kmol/h. The mole fraction of more volatile component in distillate is 94%. The residue contains 5% of more volatile component. The reflux ratio is 4. The mole fraction of vapour leaving a plate is 0.4, whereas the mole fraction of liquid coming to the same plate is 0.3. Assuming constant molal overflow, determine the condition of feed.

Solution.

Feed rate: 400 kmol/h

Distillate, D: 160 kmol/h

Therefore, flow rate of residue, W: 240 kmol/h

The composition of distillate $x_D = 0.94$

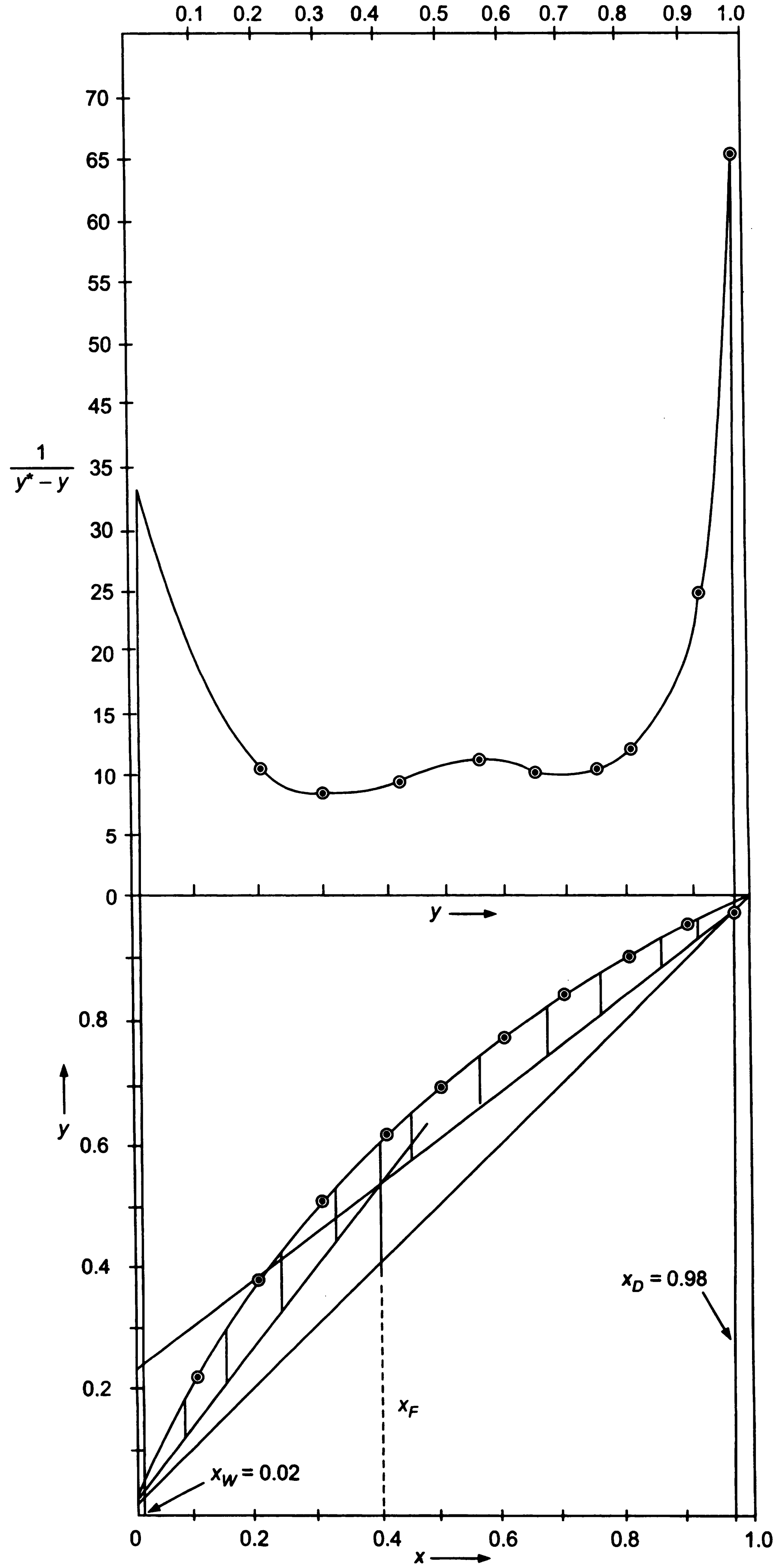


Fig. 9.47 Example 19 packed distillation.

The composition of residue $x_w = 0.05$
Reflux ratio: 4

$$y_{m+1} = 0.94$$

$$x_m = 0.05$$

We know that

$$\bar{L}_m = \bar{G}_{m+1} + W \qquad \text{[Eq. 9.67]}$$

Since, the molal overflow rate is constant, $\bar{L}_m = \bar{L}_{m+1} = \bar{L}$

$$y_{m+1} = \left(\frac{\bar{L}}{\bar{L} - W}\right)x_m - \left(\frac{W}{\bar{L} - W}\right)x_W \qquad \text{[Eq. 9.94]}$$

Substituting, we get,

$$0.4 = \left(\frac{\bar{L}}{\bar{L} - 240}\right)0.3 - \left(\frac{240}{\bar{L} - 240}\right)0.05$$

Solving, we get

$$\bar{L} = 880 \text{ kmol/h}$$

From Eq. (9.67) we get

$\bar{G}_{m+1} = L_m - W = 880 - 240 = 640$ kmol/h $= G_m = G$ (Due to constant molal flow rate).

Feed rate = 400 kmol/h

Reflux ratio $= \dfrac{L}{D} = 4$

Hence, $L = 4D = 640$ kmol/h.

$\bar{L} = 880$ kmol/h

We also know that

$$q = \frac{(\bar{L} - L)}{F} = \frac{(H_G - H_F)}{(H_G - H_L)} \qquad \text{(Eq. 9.110)}$$

$$\therefore \qquad \bar{L} = L + qF$$

Substituting, we get

$$q = \frac{880 - 640}{400} = 0.6 \text{ (Fraction of liquid)}$$

Hence, the feed is a mixture of 60% liquid and 40% vapour.

21. The feed rate to a binary distillation column is 200 kmol/hr and 75% of it is vaporized. Distillate flow rate is 120 kmol/h with 95% composition of more volatile component. Reboiler steam demand is 4000 kg/h. Latent heat of steam used in reboiler is 2304 kJ/kg. Latent heat of liquid to be distilled is 32000 kJ/kmol. Determine the reflux ratio.

Solution.

We know that $\bar{L} = L + qF$ (from Eq. 9.110)

$$G = (R + 1)D \qquad \text{(from Eq. 9.84)}$$

From Eq. (9.111), we get

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

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

$$\therefore \quad \bar{G} = G + F(q - 1)$$

i.e. $$\bar{G} = (R + 1)D + F(q - 1)$$

Fraction of vapour = $(1 - q) = 0.75$

Fraction of liquid = $q = 0.25$

$$\therefore \quad \bar{G} = (R + 1)120 + 200(0.25 - 1)$$

$$= (R + 1)120 - 150 = 120R - 30$$

Steam needed for the reboiler $m_s = \dfrac{\bar{G}\lambda_{\text{feed}}}{\lambda_{\text{steam}}}$

$$m_s\, \lambda_{\text{steam}} = \bar{G}\lambda_{\text{feed}} = (120R - 30)\lambda_{\text{feed}}$$

$$m_s\, \lambda_{\text{steam}} = 4000 \times 2304 = 9.216 \times 10^6 \text{ kJ/hr}$$

$$= (120R - 30)\lambda_{\text{feed}}$$

i.e. $$9.216 \times 10^6 = (120R - 30)32000$$

Solving, we get

$$R = 2.65.$$

EXERCISES

1. Compute the VLE data from the following vapour pressure data at 760 mm Hg. Pressure assuming ideal solution.

Temperature,°C	98.4	105	110	120	125.6
Vapour pressure of *A*, mm Hg	760	940	1050	1350	1540
Vapour pressure of *B*, mm Hg	333	417	484	650	760

Ans:

x_A	1.0	0.655	0.487	0.157	0.0
y_A	1.0	0.810	0.674	0.279	0.0

2. A mixture containing benzene and toluene with 50 mole % benzene is flash distilled such that 70% of the feed is distilled out. Estimate the composition of the distillate and residue. If the same quantity of distillate is obtained by simple distillation, estimate the composition of the residue and distillate.

   Equilibrium data:

x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
y	0.22	0.38	0.51	0.63	0.70	0.78	0.85	0.91	0.96

   x, y: mole fraction of benzene in liquid and vapour phase respectively.

   (**Ans:** (i) $-W/D = -0.3/0.7 = -0.429$

   $y_D = 0.56$ and $x_w = 0.35$ (From graph)

   (ii) $x_w = 0.245$ and $y_D = 0.61$)

3. A simple batch still is used to distill 1000 kg of a mixture containing 60 mass % ethyl alcohol and 40 mass % water after distillation, the bottom product contains 5 mass % alcohol. Determine the composition of the overhead product, its mass and mass of the bottom product.

   The equilibrium data:

x	5	10	20	30	40	50	60
y	36	51.6	65.5	71	74	76.7	78.9

   where x and y are weight percent of ethyl alcohol in liquid phase and vapour phase respectively.

   (**Ans:** Residue = 192.28 kg; Distillate 807.72 kg;
   $y_D = 0.731$ mass % alcohol)

4. A liquid mixture containing 50 mole % acetone and rest water is differentially distilled at 1 atm. pressure to vaporize 25% of the feed. Compute the composition of the composited distillate and residue. VLE data at 1 atm. pressure is given below.

x, mole fraction of acetone in liquid	0.1	0.2	0.3	0.4	0.6	0.7	0.9
y, mole fraction of acetone in vapour	0.76	0.82	0.83	0.84	0.86	0.87	0.94

5. A solution of 40 mole % of acetic acid in water is flash distilled at atmospheric pressure, until 60 mole % of the feed was distilled. Compute the compositions of the distillate and residue.

Equilibrium data:
Mole fraction of acetic acid in

Liquid, x	0.07	0.15	0.27	0.37	0.50	0.62	0.72	0.82	0.90	1.0
Vapour, y	0.05	0.11	0.20	0.28	0.38	0.49	0.60	0.73	0.80	1.0

(**Ans:** $x_w = 0.53$ and $y_D = 0.65$ in terms of water)

6. Feed mixture containing equimolar quantities of 'A' and 'B' is differentially distilled such that 60 mole % of feed is distilled out. Estimate the composition of distillate and residue.

x	0	0.157	0.312	0.487	0.655	1.0
y	0	0.279	0.492	0.674	0.810	1.0

x, y are mole fractions of A in liquid and vapour phase respectively.

(**Ans:** $x_w = 0.335$ and $y_D = 0.61$)

7. A equimolar feed mixture containing Benzene and Toluene is distilled such that 60% of feed is distilled out. Estimate the composition of distillate and residue by taking the relative volatility as 2.5 for (i) Simple distillation, (ii) Equilibrium distillation.

(**Ans:** (i) $x_W = 0.29$, $y_D = 0.64$ and (ii) $x_W = 0.365$, $y_D = 0.59$)

8. It is desired to separate a feed mixture of 'A' and 'B' containing 50 mole % A to a product such that 60% feed is distilled out. Estimate the composition of residue and distillate if (i) simple distillation is carried out and (ii) equilibrium distillation is carried out. VLE data:

x	0	5	10	15	20	30	40	50	60	70	80	90	100
y	0	11	21	30	38	51	63	72	78	85	91	96	100

x, y are mole % of A in liquid and vapour phase respectively.

(**Ans:** (i) $x_W = 0.3$, $y_D = 0.63$, (ii) $x_W = 0.36$, $y_D = 0.59$)

9. It is desired to separate a feed mixture of 100 kmol containing 60% heptane and 40% ethyl benzene such that 60 kmol of the feed is distilled out. Determine the composition of residue and distillate if the distillation is (i) Flash distillation and (ii) Differential distillation.

x	0	0.08	0.185	0.251	0.335	0.489	0.651	0.79	0.914	1.0
y	0	0.233	0.428	0.514	0.608	0.729	0.814	0.91	0.963	1.0

x, y is the mole fraction of heptane in liquid and vapour phase respectively.

(**Ans:** (i) $x_W = 45\%$, $y_X = 70\%$; (ii) $x_W = 37.5$, $y_D = 75\%$)

10. A liquid mixture containing 50 mole % *n*-heptane and 50 mole % *n*-octane is differentially distilled until the residue contains 33% *n*-heptane. Calculate the % vaporization and the composition of the composited distillate. If the residue with the same composition is achieved in an equilibrium still, estimate the composition of the distillate and total moles distilled assuming $\alpha = 2.17$.

(**Ans:** y_D *n*-heptane = 0.617, total moles distilled = 60 ml/h; vaporization: 60%; (ii) y_D = 0.52% vaporization: 89.47%)

11. A mixture of 30 mole % Naphthalene and 70 mole % Dipropylene glycol is differentially distilled at 100 mm Hg until a final distillate containing 55 mole % Naphthalene is obtained. Determine the amount of residue and the composition of residue.

VLE data:

x	5.4	11.1	28.0	50.6	68.7	80.6	84.8	88
y	22.3	41.1	62.9	74.8	80.2	84.4	86.4	88

12. A mixture containing 30 mole % Hexane, 45 mole % Heptane and 25 mole % Octane is subjected to flash distillation. If 60 mole % of the feed is vaporized and condensed, calculate the composition of vapour leaving the separator.

(*m* values for Hexane, Heptane and Octane: 2.18, 0.99 and 0.46 respectively)

13. A binary mixture containing 55 mole % *n*-heptane and 45 mole % *n*-octane at 27°C is subjected to differential distillation at atmospheric pressure with 60 mole % of the feed liquid is distilled. Assuming a relative volatility of *n*-heptane with respect to *n*-octane is 2.17, determine the composition of the charge in still and that of distillate.

(**Ans:** composition of *n*-heptane $x_W = 0.38$, $y_D = 0.665$)

14. Continuous fractionating column operating at 1 atm is designed to separate 13600 kg/hr of a solution of benzene and toluene. Feed is 0.4-mole fraction benzene. Distillate contains 0.97 mole fraction benzene and residue contains 0.98 mole fraction toluene. A reflux ratio of twice the minimum is used. Feed is liquid at its saturation temperature and reflux is returned at saturation.

Determine:

(i) Quantities of products in kg/hr
(ii) Minimum reflux ratio
(iii) Number of theoretical plates

The average relative volatility for the given system is 2.56.

(**Ans:** (i) D = 5524.2 kg/h w = 8075.8 kg/h; (ii) R_m = 1.487; (iii) 13)

15. A solution of carbon tetra chloride and carbon disulfide containing 50 mole % of each is to be fractionated to get a top and a bottom product of 95% and 6% carbon disulfide respectively. The feed is a saturated liquid at its boiling point and is fed at the rate of 5000 kg/hr. A total condenser is used and reflux returned to the top plate as a saturated liquid. The equilibrium data at 1 atm pressure is given below:

x	0	0.06	0.11	0.26	0.39	0.53	0.66	0.76	0.86	1.0
y	0	0.16	0.27	0.50	0.63	0.75	0.83	0.88	0.93	1.0

where x, y are mole fractions of carbon disulfide in liquid and vapour phase respectively.

(i) Determine the product rate in kg/hr.
(ii) What is the minimum reflux ratio?
(iii) Determine the theoretical number of plates required and the feed plate location if the tower is operated at twice the minimum reflux ratio.

16. A mixture of 35 mole % A and 65 mole % B is to be separated in the fractionating column. The concentration of A in the distillate is 93 mole % and 96% A in the feed is recovered in the distillate. The feed is half vapour and reflux ratio is to be 4.0. The relative volatility of A to B is 2.0. Calculate the number of theoretical plates in the column and locate the feed plate.

17. A continuous fractionating column, operating at atmospheric pressure, is to be designed to separate a mixture containing 30% CS_2 and 70% CCl_4 into an overhead product of 96% CS_2 and a bottom product of 96% CCl_4 (all mole percent). A reflux ratio of twice the minimum will be used and the overall efficiency of the column is estimated to be 65%. Feed enters at its boiling point. Determine the number of plates to be provided and the correct location of the feed plate.

Equilibrium data:

x	0.0296	0.0615	0.258	0.390	0.532	0.663	0.758	0.860
y	0.0823	0.1555	0.495	0.634	0.747	0.830	0.880	0.932

18. A continuous fractionating column, operating at atmospheric pressure, is to separate a mixture containing 30 mole % CS_2 and 70 mole % CCl_4 into an overhead product of 95 mole % CS_2 and a bottom product of 95 mole % CCl_4. The feed enters the column as liquid at its boiling point.

Assuming an overall plate efficiency of 70% and a reflux ratio of 3.16, determine the number of plates to be provided.

Mole fractions of CS_2 in liquid (x) in equilibrium with mole fraction CS_2 in vapour (y) are given below.

Equilibrium data:

x	2.96	11.06	25.8	53.18	66.3	75.75	86.04
y	8.23	26.6	49.5	74.7	83.0	88.0	93.2

19. A feed containing 50 mole % heptane and 50 mole % octane is fed into a pipe still through a pressure reducing value and then into a flash discharging chamber. The vapour and liquid leaving the chamber are assumed to be in equilibrium. If the fraction of feed converted to vapour is 0.5, find the composition of the top and bottom plates. The following table gives VLE data:

x, mole fraction of heptane in vapour phase	1.0	0.69	0.4	0.192	0.045	0.0
y, mole fraction of heptane in vapour phase	1.0	0.932	0.78	0.538	0.178	0.0

(**Ans:** $x_w = 0.31$ $y_D = 0.69$)

20. A continuous distillation column is used to separate a feed mixture containing 24 mole % acetone and 76 mole % methanol into a distillate product containing 77 mole % acetone and a residue product containing 5 mole % acetone. The feed is A saturated liquid. A reflux ratio of twice the minimum is used. The overall stage efficiency is 60%. Determine the number of plates required for the separation.

Equilibrium data:

x	0.0	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0
y	0.0	0.102	0.186	0.322	0.428	0.513	0.586	0.656	0.725	0.80	1.0

(x, y mole fraction of acetone in liquid and vapour phase respectively)

(**Ans:** 24 stages)

21. The enthalpy-concentration data for a binary system is given below:

x, mole fraction of A	0.0	0.25	0.407	0.62	0.839	1.0
y, mole fraction of A	0.0	0.396	0.566	0.756	0.906	1.0
H_l, kcal/kmol	280	180	145	195	260	380
Hg, kcal/kmol	1000	1030	955	895	885	880

Rest of the data could be obtained by extrapolation. A feed mixture with an initial composition of 30 mole % A is to separate into an overhead product of 95 mole % A and a 4 mole % bottom product. Determine the ideal number of stages needed if the reflux ratio is twice the minimum reflux ratio. Feed enters as a saturated liquid.

$x_F = 0.3$, $x_D = 0.95$, $x_w = 0.04$, $R = 2.4$

22. A mixture containing 50 mole % A and 50 mole % B is distilled in a packed column to yield a top product containing 94 mole % A and a bottom product containing 95 mole % B. The feed enters a saturated vapour. Estimate the height of the packing needed if the height of a transfer unit is 0.5 m. A reflux ratio of 1.5 times the minimum is to be used. The relative volatility of A with respect to B is 2.5.

(**Ans:** NTU = 11.25, Ht = 5.625 m)

10

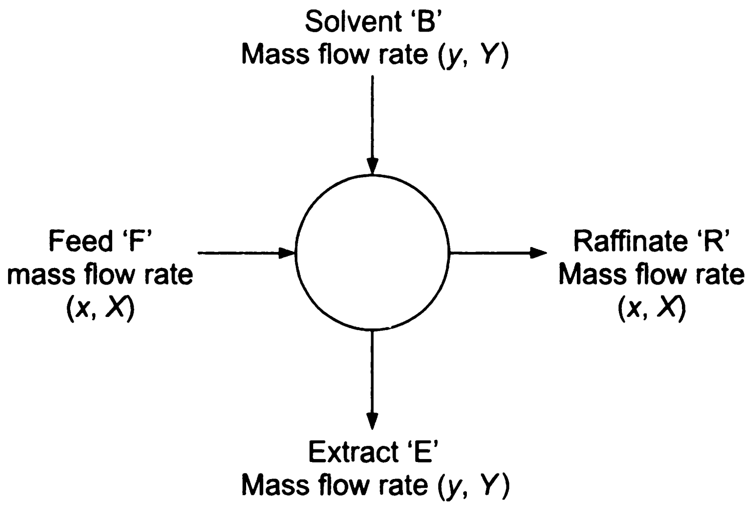
EXTRACTION

10.1 INTRODUCTION

Liquid extraction is the separation of the constituents of a liquid by contact with another insoluble liquid called *solvent*. The constituents get distributed between the two phases. The solvent rich phase is called *extract* and the residual liquid from which the solute has been removed is called *raffinate*. Some of the complicated systems may use two solvents to separate the components of a feed. A mixture of para or ortho–nitro benzoic acids can be separated by distributing them between the insoluble liquids chloroform and water. The chloroform dissolves the para isomer and water the ortho isomer. This is called *dual solvent* or *double solvent* or *fractional extraction*. Some of the components which are difficult to separate by other separation processes like distillation can effectively be separated by extraction or extraction followed by distillation, (e.g.) acetic acid – water separation. Similarly long chain fatty acids can be separated from vegetable oils economically by extraction rather than high vacuum distillation. The separation of fission products from nuclear energy process and separation of low cost metals can be effectively carried out by liquid extraction. Pharmaceutical products like penicillin are also separated by this technique. Mercaptans can be removed by using hydrocarbon oil as solvent. Phenol is extracted from coal tar using alkaline solution as solvent. Caprolactum is extracted with benzene as solvent.

10.2 EQUILIBRIA

In extraction operation generally ternary systems are involved. The solute distributes between solvent rich phase called *extract* and solvent lean phase called *raffinate*. The schematic diagram shown in Fig. 10.1 indicates the various streams involved in a typical liquid–liquid extraction operation. The equilibrium concentration of such systems can be represented in a triangular coordinate system.



x = mass fraction of solute in Feed and Raffinate stream
y = mass fraction of solute in Solvent and Extract stream
X = Mass of solute/mass of solute free components in Feed or Raffinate phase
Y = Mass of solute/mass of solute free components in Extract or Solvent phase

Fig. 10.1 Streams in extraction.

10.2.1 Equilateral-Triangular Coordinates

A mixture having a typical composition of 50% A, 30% B and 20% C is represented by point M as shown in Fig. 10.2. Now let us consider that P kg of a mixture at a point P is added to Q kg of mixture at Q, the resulting mixture is shown by point R on line PQ such that

$$\frac{P}{Q} = \frac{\text{Length of QR}}{\text{Length of PR}} = \frac{x_Q - x_R}{x_R - x_P} \tag{10.1}$$

The ternary systems usually follow any one of the two categories given below:

(i) one pair partially soluble and two pairs partially soluble
(ii) Insoluble systems.

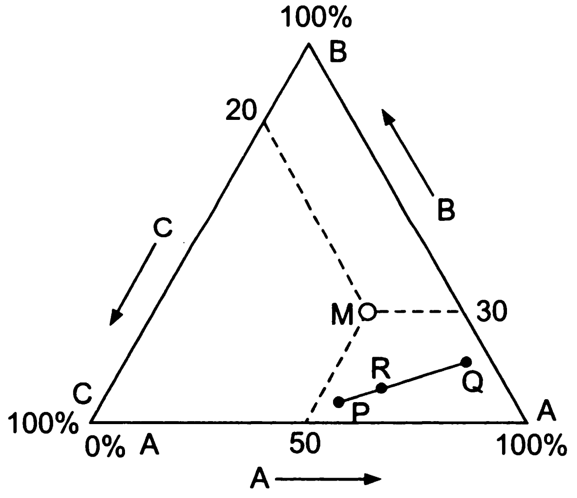


Fig. 10.2 Representation of ternary data in a triangular chart.

In all our subsequent discussions 'C' indicates the distributing solute, 'B' the solvent and 'A' the solute-free component in feed. Some of the common combinations of A, B and C are as follows:

A	*B*	*C*
Water	Chloroform	Acetone
Benzene	Water	Acetic acid

The equilibrium composition of mixtures can be represented in a triangular coordinate system. These diagrams drawn at constant temperatures are also called *isotherms*. A typical isotherm is shown in Fig. 10.3 in which 'C' is the solute which dissolves in A and B completely. A and B mutually dissolve to a limited extent. If the solubility of 'A' and 'B' is very minimal, then the points S and T will be very close to apexes A and B respectively. The curve SPQT is the *binodal solubility curve*. Any mixture outside the curve SPQT will be a homogeneous solution of the one liquid phase. Any point within the area bounded by the curve and the axis AB will form two insoluble saturated liquid phases, one rich in A phase and the other rich in B phase.

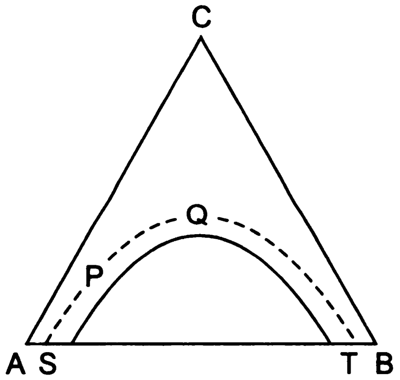


Fig. 10.3 Extraction isotherm.

10.3 SYSTEMS OF THREE LIQUIDS—ONE PAIR PARTIALLY SOLUBLE

Let us consider a ternary mixture whose effective composition is defined by point M as shown in Fig. 10.4. This mixture will form two insoluble but saturated phases. Many lines can be drawn through the point M. However, there can only be one *tie line* as indicated by the line RE passing through M. Tie line can be located by projecting the arbitrary lines passing through M to the distribution diagrams. Tie line is the one whose projections to the equilibrium distribution curve and $x = y$ (diagonal) line form a vertical line in the xy diagram as shown in Fig. 10.4. Whenever the distribution curve is above the diagonal line, as shown in Fig. 10.4, the extract stream will have a higher concentration of the solute than the raffinate stream. In such cases the tie line will have a positive slope as indicated by line RE. However, when the distribution curve is below the diagonal line, the raffinate will

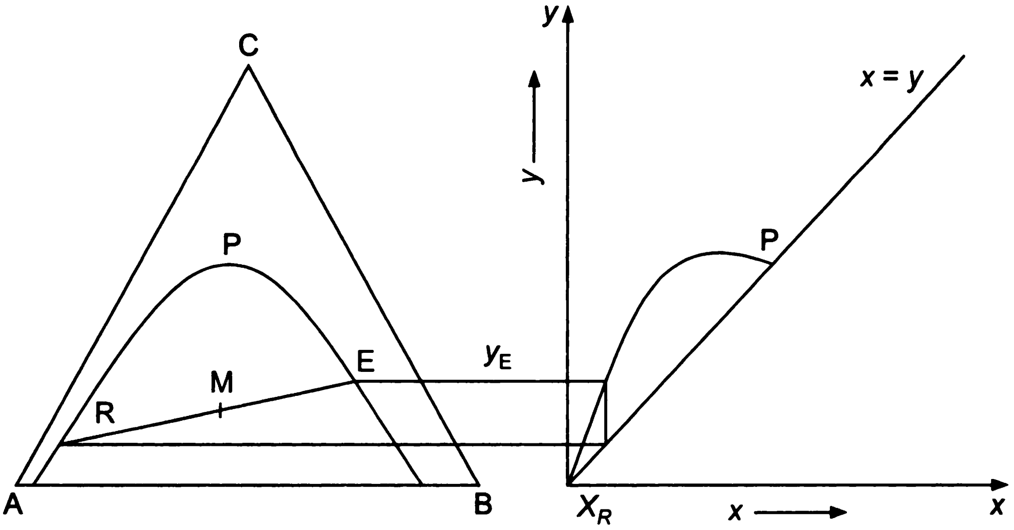


Fig. 10.4 Ternary system representation and Tie line.

have a higher concentration of solute compared to extract stream and the line RE instead of having a positive slope will have a negative slope. Occasionally, the tie lines change their slope from one direction to another and one such tie line will be horizontal. Such systems are called *solutropic systems.* When the tie line simply becomes a point 'P', it is called *Plait point* as shown in Fig. 10.4.

10.3.1 Effect of Temperature

The mutual solubility of A and B increases with increasing temperature and beyond some critical temperature, A and B are completely soluble. Thus, the heterogeneity decreases at higher temperatures. Also, the slope of tie lines and distribution curve vary with changes in temperature and it is shown in Fig. 10.5. Hence, it is preferable to operate below the critical temperature such that the heterogeneity is maintained.

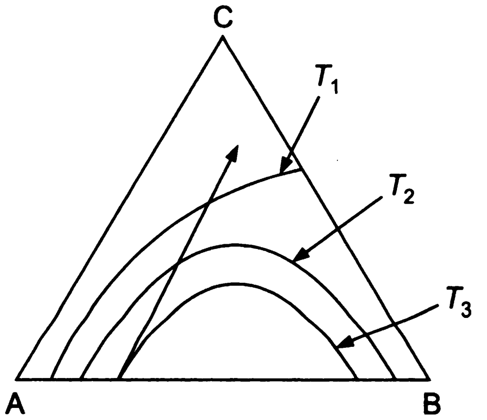


Fig. 10.5 Effect of temperature on Extraction Isotherm ($T_1 < T_2 < T_3$).

10.3.2 Effect of Pressure

Generally the effect of pressure is not very significant. It is preferable to operate above the vapour pressure of solutions.

10.4 SYSTEMS OF THREE LIQUIDS—TWO PAIRS PARTIALLY SOLUBLE

Let us assume that A and C are completely soluble, while the pairs A–B and B–C show limited solubility. A typical isotherm is shown below in Fig. 10.6. Points F and H indicate mutual solubilities of A and B and points G and J indicate those of B and C. Curves FKG is for A rich layer and HLJ is for B rich layer. The area bounded by FKGJLH indicates a heterogeneous mixture and outside this area the mixture is homogeneous. KL is a tie line which corresponds to the effective composition M. Increase in temperature usually increases the mutual solubilities and at the same time influences the slope of the tie lines.

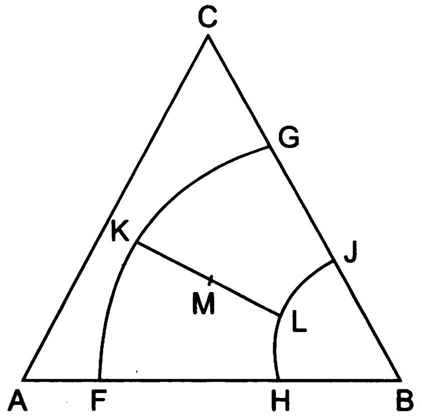


Fig. 10.6 Isotherm of system of three liquids—two pairs partially soluble.

10.5 TWO PARTIALLY SOLUBLE LIQUIDS AND ONE SOLID

When the solid does not form hydrates with the liquids, the characteristics of the isotherm will be as shown in Fig. 10.7. K and L indicate saturated solutions of C in A and B respectively. A and B are soluble only to the limited extent shown at H and J. Area bounded by HDGJ shows a heterogeneous mixture while the region KDHA and JGLB indicate homogeneous phase. RE indicates the tie line for a mixture whose effective composition is M. The region CDG consists of 3 phases,

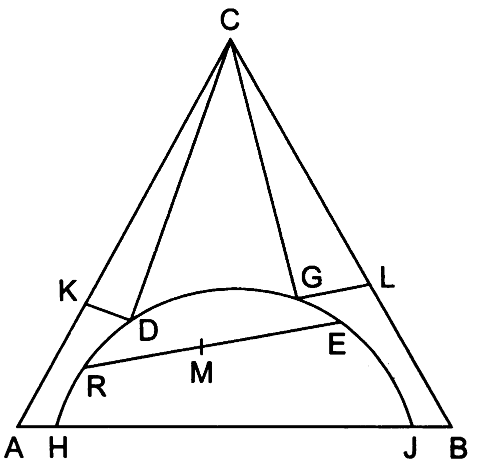


Fig. 10.7 Isotherm of system of two partially soluble liquids and one solid.

namely solid C and saturated liquid solutions at D and G. Liquid extraction is mainly confined to the heterogeneity area which is bounded by HDGJ. Temperature has a significant effect on the shape of the curve HDGJ.

10.6 OTHER COORDINATES

The equilibrium concentrations of ternary systems can also be expressed in rectangular coordinates. This is done by taking the concentration of B along x- axis and that of the concentrations of C in A rich phase, denoted conventionally as x and B rich phase, denoted conventionally as y, both on y-axis in rectangular coordinates. It will be more convenient to solve problems using graphical procedure with rectangular coordinate system. Rectangular coordinate system has been used in the worked examples presented in this chapter.

10.7 FACTORS INFLUENCING CHOICE OF SOLVENT

1. *Selectivity, β:* The effectiveness of solvent B for separating a solution of A and C into its components is measured by comparing the ratio of C to A in the B–rich phase to that in the A–rich phase at equilibrium and is called *selectivity* or *separation factor.* This is also analogous to relative volatility in distillation and it is defined as

$$\beta = \frac{[(\text{weight fraction of C})/(\text{weight fraction of A})]_{\text{Extract}}}{[(\text{weight fraction of C})/(\text{weight fraction of A})]_{\text{Raffinate}}}$$

$$= \left(\frac{y_E{}^*}{x_R}\right)\left(\frac{\text{weight fraction of A in raffinate}}{\text{weight fraction of A in extract}}\right) \tag{10.2}$$

   It is preferable to choose a solvent with selectivity higher than unity. Selectivity also varies with concentration and in some systems it will vary from high values through unity to fractional values. Such systems are analogous to azeotropes.

2. *Distribution coefficient:* It is defined as the concentration of solute in extract(y) to that in raffinate(x). It is preferable to have a higher ratio of y/x as it results in the use of lesser quantity of solvent.
3. *Recoverability of solvent:* The solvent has to be recovered from extract phase for reuse. This is normally done by distillation. Hence, one should ensure that the mixture does not form an azeotrope which has a higher relative volatility and its latent heat of vaporization shall be low so that lesser energy is spent during vaporization.
4. *Density:* A larger difference in densities is necessary both for stagewise and continuous contact operations as it will help in easier separation of phases. However, at plait point the density difference is zero.
5. *Interfacial tension:* If the interfacial tension of solvent is large, more readily the coalescence of droplets or emulsions will occur but

the dispersion of one liquid in the other will be difficult. Since coalescence is usually of greater importance in extraction operation, the interfacial tension should therefore be high. It is zero at plait point.

6. *Chemical reactivity:* Solvent should be thermally stable and chemically inert towards the other components of the system and also towards the material of construction.
7. *Other properties:* Viscosity, vapour pressure and freezing point should be low for ease in handling and storage. They should also be non-toxic, non-flammable and of low cost.

10.8 OPERATIONS

Extraction operations can be carried out either as a single stage or as a multistage operation. Again the multistage operation could be either a cross-current or a counter-current operation. The leaving streams, viz. the extract and raffinate from each stage is always in equilibrium. A combination of mixer-settler is said to constitute a stage and in a multistage operation they are arranged in cascades.

10.8.1 Single Stage Operation

A typical flow diagram of a single stage extraction operation is shown in Fig. 10.8.

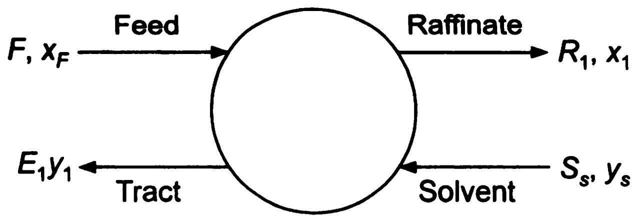


Fig. 10.8 Streams in a single stage operation.

F, R_1, E_1, and S are either the flow rates or quantities of different streams such as feed, raffinate, extract and solvent respectively and x_F, x_1, y_1, y_S are all weight fractions of solute in their respective streams.

The material balance gives

$$F + S = M_1 = E_1 + R_1 \tag{10.3}$$

where M_1 is the total weight of mixture (Feed + solvent or extract + raffinate)

A solute balance yields

$$Fx_F + Sy_S = M_1x_{M1} = E_1y_1 + R_1x_1 \tag{10.4}$$

where x_{M1} is the effective solute concentration in the extractor.

Eliminating M_1 from Eqs. (10.3) and (10.4), we get

$$\frac{S}{F} = \frac{x_F - x_{M_1}}{x_{M_1} - y_S} \tag{10.5}$$

The quantities of extract and raffinate can be computed from mixture rule given by Eq. (10.1) or by material balance given in Eq. (10.4)

$$E_1 y_1 + R_1 x_1 = M_1 x_{M_1} \tag{10.6}$$

$$E_1 y_1 + (M_1 - E_1)x_1 = M_1 x_{M_1} \tag{10.7}$$

$$E_1 = M_1 \left(\frac{x_{M_1} - x_1}{y_1 - x_1} \right) \tag{10.8}$$

Let us now try to use the phase diagram and distribution diagram to determine the product composition as shown in Fig. 10.9.

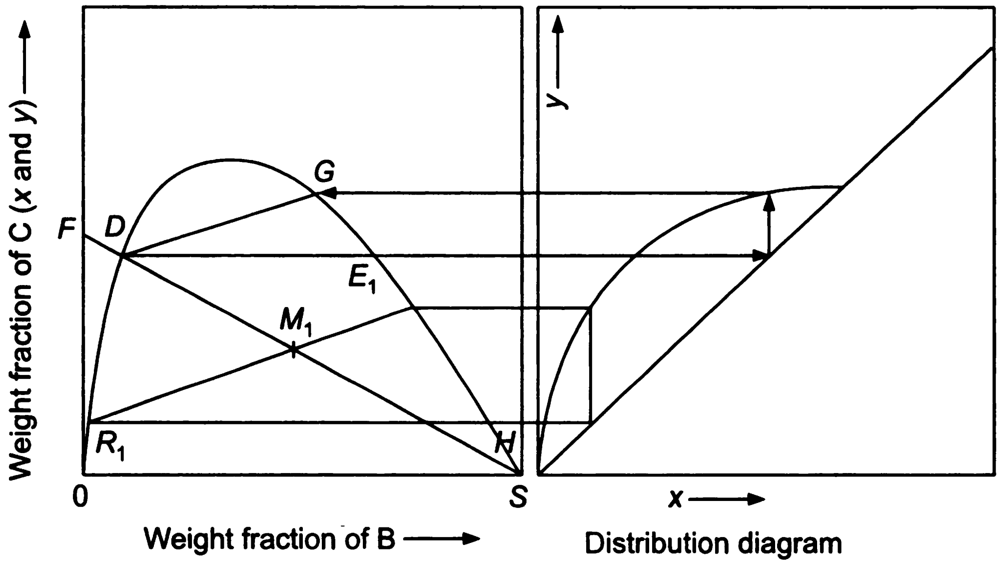


Fig. 10.9 Determination of minimum and maximum solvent.

The point F corresponds to feed mixture and S, the solvent. Once the feed and solvent are mixed, the mixture has an effective solute concentration of x_{M_1} and is located as M_1 which lies on the line joining F and S. Thus the point M_1 lies within the curve. However, on settling, the mixture forms the two phases E_1 and R_1 and the line joining the points E_1 and R_1 intersects the feed line FS which is M_1. Though many lines can be drawn through the point M_1, only one line could be the tie line which will correspond to the equilibrium composition of extract and raffinate phases. The tie line could be located by a trial and error procedure using the equilibrium curve as shown.

10.8.1.1 Minimum solvent requirement

If the point M_1 lies on the point of intersection of curve (of solvent lean phase side) with FS (the point D) as shown in Fig. 10.9, then the corresponding amount of solvent is the minimum solvent needed and it provides an infinitesimal amount of extract as indicated by G.

10.8.1.2 Maximum solvent requirement

If the point M_1 lies on H (solvent rich phase side), then the amount of solvent used becomes the maximum and the corresponding raffinate concentration K obtained by the tie line indicates the infinitesimal amount of raffinate.

10.8.1.3 Steps involved in the estimation of extract and raffinate quantities

1. Plot the ternary data and equilibrium curve.
2. Locate the feed point 'F' and solvent point 'S' on the ternary data plot.
3. Join FS and locate M_1 $\left[M_1 \text{ corresponds to } x_{M_1} = \dfrac{(Fx_F + Sy_s)}{(F+S)}\right]$.
4. Draw a suitable tie line through M_1 with the help of equilibrium curve.
5. Locate the points of intersection of this tie line on the ternary data curve as E_1 and R_1 on solvent rich layer and solvent lean layer respectively and find y_1 and x_1 values corresponding to these points.
6. The quantity of extract layer, $E_1 = M_1\left(\dfrac{x_{M_1} - x_1}{y_1 - x_1}\right)$ and that of raffinate layer, $R_1 = F + S - E_1$ can be determined.

10.8.2 Multistage Cross-current Operation

A typical flow diagram of a multistage cross-current operation is shown in Fig. 10.10

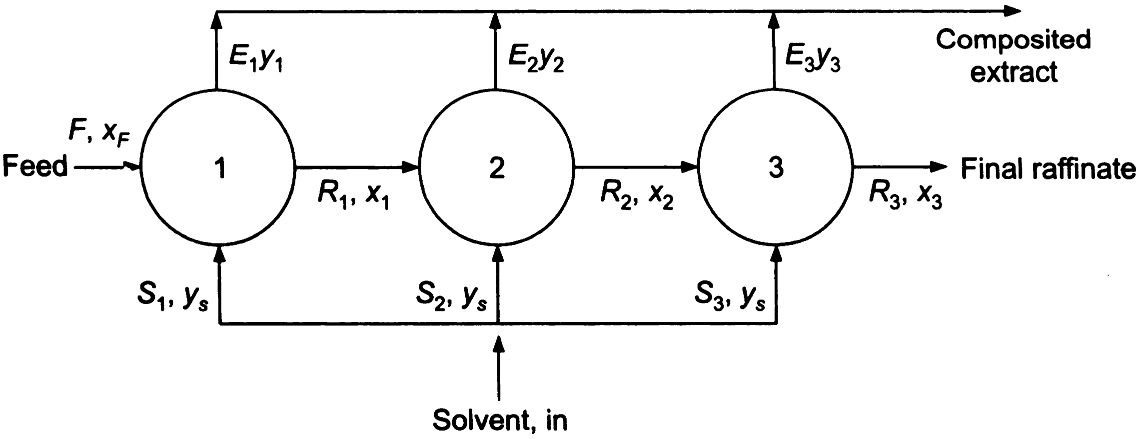


Fig. 10.10 A three stage cross-current extraction operation.

Consider a three-stage cross-current extraction process as shown in Fig. 10.10. The feed enters the first stage and the raffinate successively passes from stage (1) to (2) and (2) to (3) and finally leaves the system. Fresh or recovered solvent enters each stage. The solvent used could be of different concentrations but generally it will have the same value as it enters either fresh or after recovery from extract. The values of M_i, x_{Mi}, x_i and y_i, where i stands for the ith stage, can be computed as indicated in the single stage operation using material balances and tie lines. From these values the quantities of extract and raffinate from each stage can be computed.

Material balance across stage (1) gives

$$F + S_1 = R_1 + E_1 = M_1 \quad \text{(say)} \tag{10.9}$$

Component balance gives

$$Fx_F + S_1y_s = R_1x_1 + E_1y_1 = M_1x_{M1} \tag{10.10}$$

$$\therefore \qquad x_{M_1} = \frac{(Fx_F + S_1y_s)}{(F + S_1)} \tag{10.11}$$

Similarly for any stage i

$$x_{M_i} = \frac{(R_{i-1}x_{i-1} + S_iy_s)}{(R_{i-1} + S_i)} \tag{10.12}$$

10.8.2.1 Steps

1. Plot the ternary data and equilibrium curve.
2. Locate the feed point F and solvent point S_1 on the ternary data plot.
3. Join FS_1 and locate M_1. {M_1 corresponds to x_{M1} and is given by

$$x_{M_1} = \frac{(Fx_F + S_1y_s)}{(F + S_1)} \}$$

4. Draw a suitable tie line passing through M_1.
5. Locate the points of intersection of tie line on the ternary data as E_1 and y_1 on B – rich layer and R_1 on solvent lean layer respectively. Estimate y_1 and x_1 corresponding to these points.

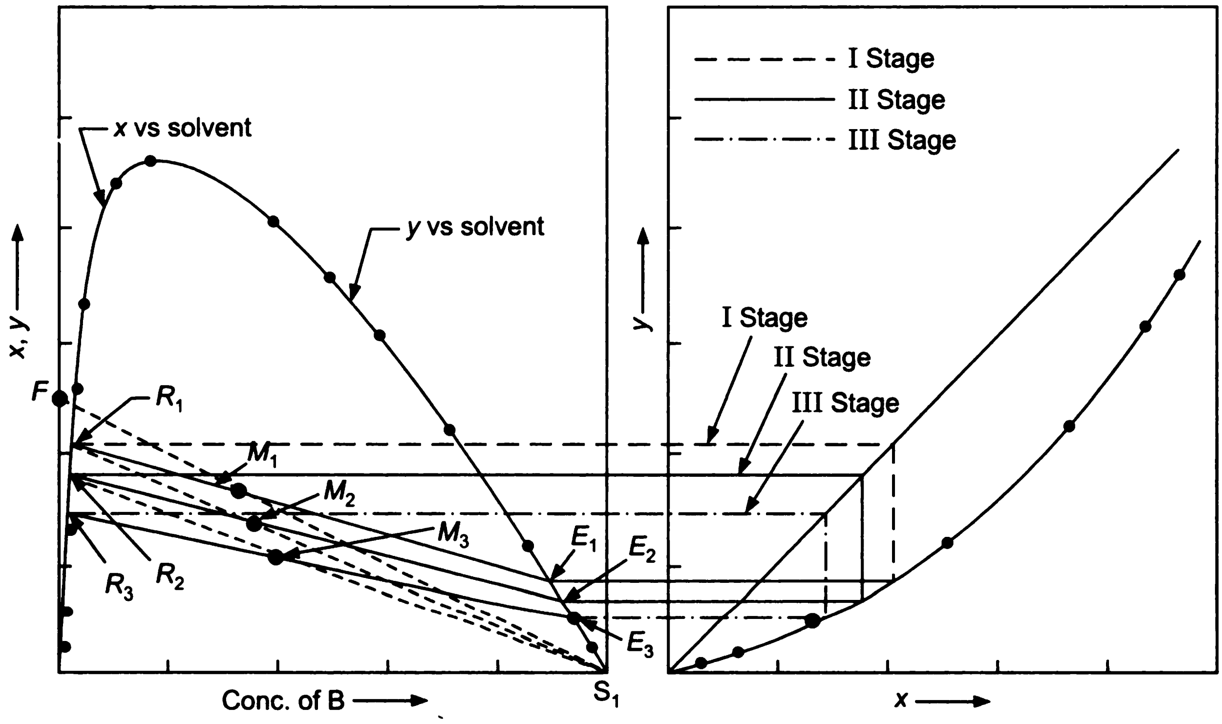


Fig. 10.11 Three stage cross-current operation.

6. The quantity of extract layer is given by $M_1\left(\dfrac{x_{M_1} - x_1}{y_1 - x_1}\right)$ and that of raffinate layer is given by $R_1 = F + S_1 - E_1$.

7. Join R_1S_2 and locate M_2. {M_2 corresponds to x_{M_2} and is given by

$$x_{M_2} = \frac{(R_1x_1 + S_2y_s)}{(R_1 + S_2)}\ \}$$

8. Draw a suitable tie line passing through M_2 to estimate y_2 and x_2 from graph.
9. The quantity of extract and raffinate E_2 and R_2 leading second stage are given by $E_2 = M_2\left(\frac{x_{M_2} - x_2}{y_2 - x_2}\right)$ and $R_2 = R_1 + S_2 - E_2$
10. Repeat the procedure for stage 3 as mentioned in steps (7) and (8) and obtain E_3, R_3, y_3 and x_3.

10.8.3 Multistage Countercurrent Extraction

A typical flow diagram of a multistage countercurrent operation is shown in Fig. 10.12.

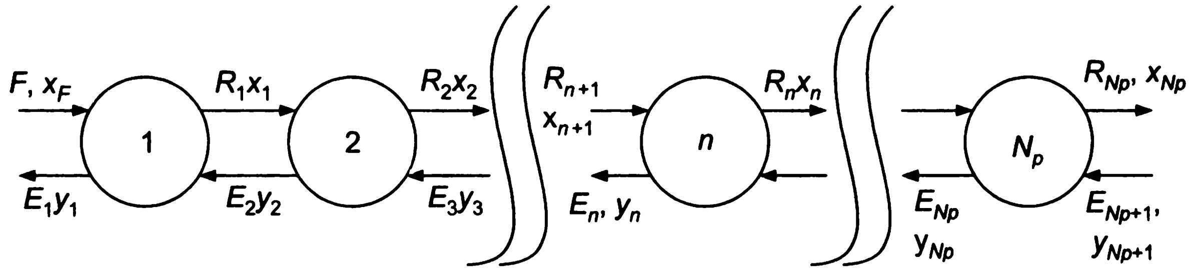


Fig. 10.12 Multistage countercurrent extraction operation.

Material balance for the system gives

$$F + E_{Np+1} = E_1 + R_{Np} \tag{10.13}$$

i.e.

$$F - E_1 = R_{Np} - E_{Np+1} \tag{10.14}$$

A component balance gives,

$$Fx_F + E_{Np+1}y_{Np+1} = E_1y_1 + R_{Np}\cdot x_{Np} \tag{10.15}$$

i.e.

$$Fx_F - E_1y_1 = R_{Np}\cdot x_{Np} - E_{Np+1}\cdot y_{Np+1} \tag{10.16}$$

A material balance from 1 to n stages gives

$$F + E_{n+1} = E_1 + R_n \tag{10.17}$$

$$F - E_1 = R_n - E_{n+1} \tag{10.18}$$

Hence, from Eqs. (10.14) and (10.18) , we get

$$F - E_1 = R_{Np} - E_{Np+1} = R_n - E_{n+1} \tag{10.19}$$

By substituting for n as 1, 2, 3, ... we can show that

$$F - E_1 = R_1 - E_2 = R_2 - E_3 = \Delta_R$$

Here Δ_R, which is defined as a difference point, is the net flow outward not only at the last stage but also between any two adjacent stages and it remains constant. In other words, any line joining FE_1, R_1E_2, R_2E_3, ... and extended must pass through the point Δ_R as shown in Fig. 10.13.

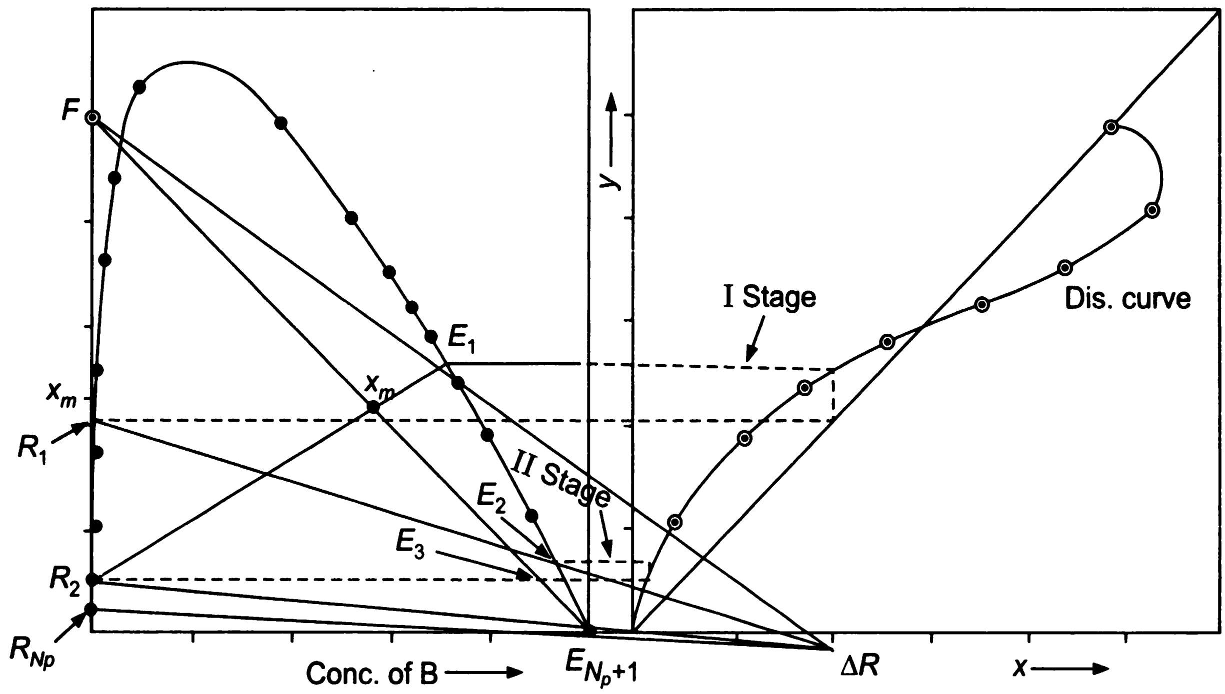


Fig. 10.13 Countercurrent operation—graphical representation of stages.

10.8.3.1 Steps involved in the determination of number of stages

1. Plot ternary data and draw the distribution curve adjacent to the ternary data in rectangular co-ordinates as shown in Fig. 10.13.
2. Locate the feed point (*F*), solvent point (E_{Np+1}) and the raffinate point (R_{Np}) leaving the systems based on their composition.
3. Join *FS* and locate x_m where, $x_m = \left[\dfrac{FX_F + (E_{N_p+1})(y_{N_p+1})}{F + E_{N_p+1}}\right]$.
4. Join R_{Np} and x_m and extend it to intersect the binodal curve which gives E_1.
5. Join *F* and E_1. Similarly join R_{Np} and E_{Np+1}.
6. Lines FE_1 and R_{Np} E_{Np+1} are extended to meet and the meeting point is Δ_R.
7. Through E_1 and with the help of distribution curve, locate R_1 on solvent lean layer.
8. Join R_1 with Δ_R and extend the line to obtain E_2 on the solvent rich layer part of the ternary data plot.
9. Through E_2 and with the distribution curve, obtain R_2.
10. Proceed similarly till R_{Np} is crossed, thus number of stages needed for a specific operation is obtained.

However, if the number of stages are specified, there are two possible questions that arise.

(a) *For a specified amount of solvent, what will be the raffinate concentration?*

(b) *For a specified raffinate concentration, what is the amount of solvent to be used?*

Both need trial and error technique.

For situation (a), assume R_{Np} and proceed as discussed earlier. As soon as the specified stages are completed, check whether the assumed R_{Np} value also matches with the theoretical value obtained. If not, make another assumption of R_{Np} and proceed as earlier till the assumed R_{Np} value and the number of stages coincides with the specified values.

For situation (b), assume the quantity of solvent, estimate x_m and proceed as earlier. Check whether the specified R_{Np} value is reached for the given number of stages. If not, assume a new value for the solvent quantity again and proceed as earlier till the R_{Np} value and the number of stages match.

10.8.3.2 Minimum solvent requirement

The minimum solvent needed is fixed by the tie line which passes through the point of intersection of line FE_{mm} and solvent lean layer curve (the corresponding point of intersection is F'). The procedure to determine the minimum amount of solvent is given below and shown in Fig. 10.14.

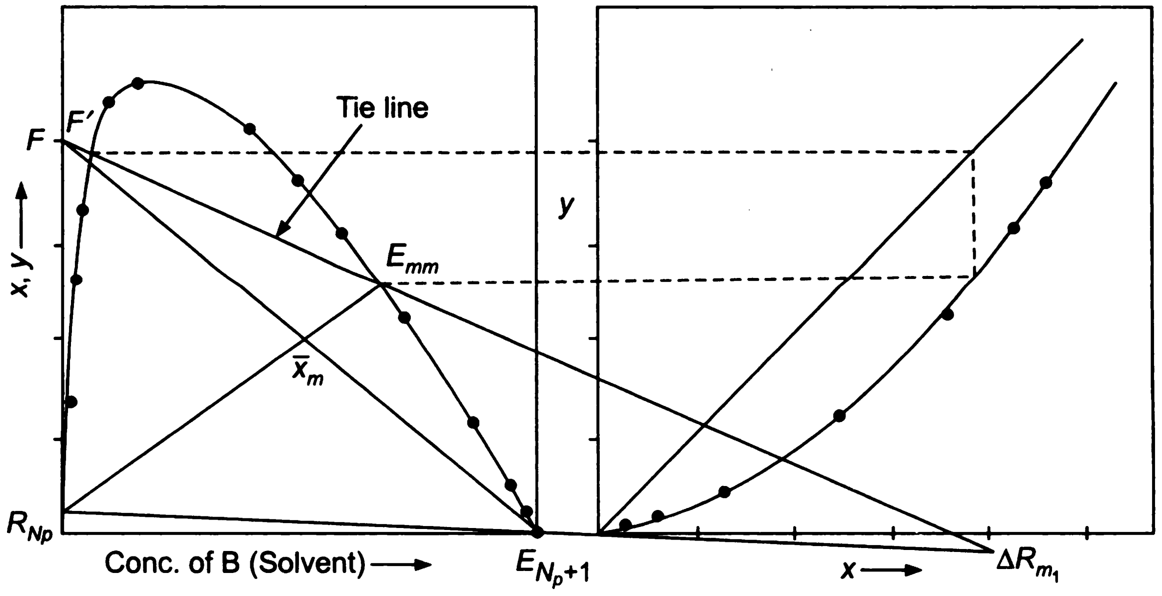


Fig. 10.14 Countercurrent operation—determination of minimum solvent.

Steps

1. Plot the ternary data and draw the distribution curve.
2. Locate F, E_{Np+1} and R_{Np}.
3. Arbitrarily draw the line R_{Np} E_{mm} and check with the help of x-y plot whether the points F' and E_{mm} correspond to a tie line. If not, by trial and error locate a suitable R_{Np} E_{mm} line which will ultimately correspond to tie line.
4. Join F E_{Np+1} and E_{mm} R_{Np} to find the intersection of these lines, $\overline{x_{mm}}$.
5. Since, $\overline{x_{mm}} = \dfrac{Fx_F + (E_{Np+1})(y_{Np+1})}{F + E_{Np+1}}$, the determined E_{Np+1} will be the minimum solvent required. (Since, all the other quantities are known.)

10.9 INSOLUBLE SYSTEMS (IMMISCIBLE SYSTEMS)

10.9.1 Cross-current Operation

In insoluble systems, the solvent (B) and the non-solute component in feed solution (A) are insoluble and remain so at all solute concentrations. Since A and B are insoluble, the amount of A and B both in their feed streams and the leaving streams remain constant. If X is the solute concentration in feed stream or raffinate stream expressed in mass ratio (kg of C/kg of A) and Y is the solute concentration in solvent or extract stream expressed in mass ratio (kg of C / kg of B), then a mass balance around stage n with reference to Fig. 10.15 yields

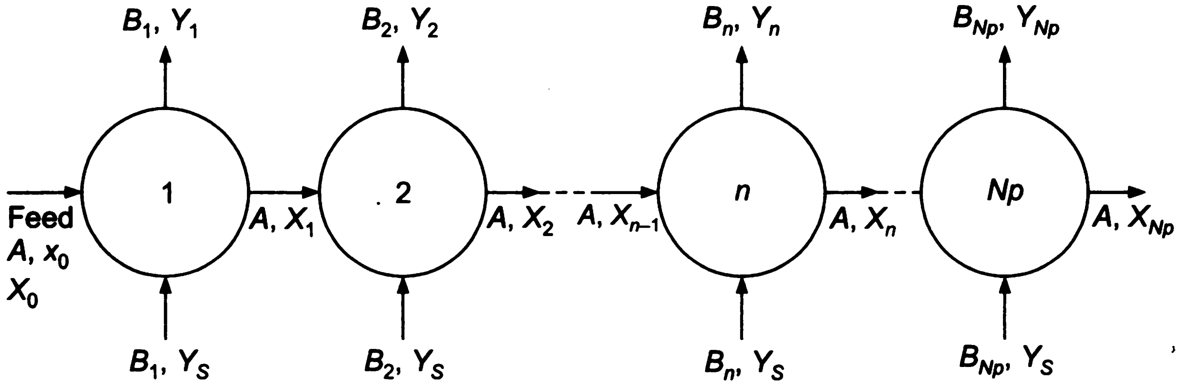


Fig. 10.15 Multistage cross-current operation for an insoluble system.

$$A \cdot X_{n-1} + B_n \cdot Y_S = B_n \cdot Y_n + A \cdot X_n \tag{10.20}$$

$$A\ [X_{n-1} - X_n] = B_n\ [Y_n - Y_S] \tag{10.21}$$

$$-\frac{A}{B_n} = \frac{(Y_n - Y_s)}{(X_n - X_{n-1})} \tag{10.22}$$

where A is the non-solute component in feed and B_n is the quantity of pure solvent used in nth stage, $-A/B_n$ is the slope of the operating line for stage n. For a typical three stage cross-current operation the construction of operating lines and the determination of final concentration of raffinate is shown in Fig. 10.16.

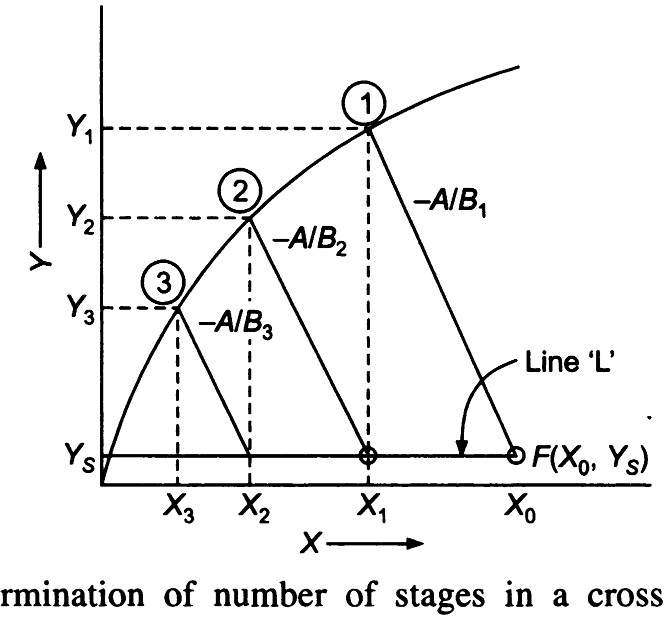


Fig. 10.16 Determination of number of stages in a cross-current operation.

10.9.1.1 Steps involved (Fig. 10.16)

1. Draw the equilibrium curve (X vs Y) on mass ratio basis.
2. Locate F (X_0, Y_s) and also draw a horizontal line L at $Y = Y_S$.
3. Draw a line with the slope $(-A/B_1)$ and allow it to intersect the curve at ①.
4. Draw a vertical line from ① to the horizontal line L and the point of intersection corresponds to (X_1, Y_S).
5. From (X_1, Y_S) draw a line with a slope of $(-A/B_2)$ to intersect curve at ②.
6. The vertical line drawn from ② to the horizontal line L gives the coordinates (X_2, Y_S).
7. Similarly proceed till X_{Np} is crossed and determine the number of stages needed or for the given number of stages, determine the X_{Np} value and hence the percentage extraction.

10.9.2 Countercurrent Operation

The flow of various streams in a countercurrent immiscible system with their compositions in a multistage operation is shown in Fig. 10.17.

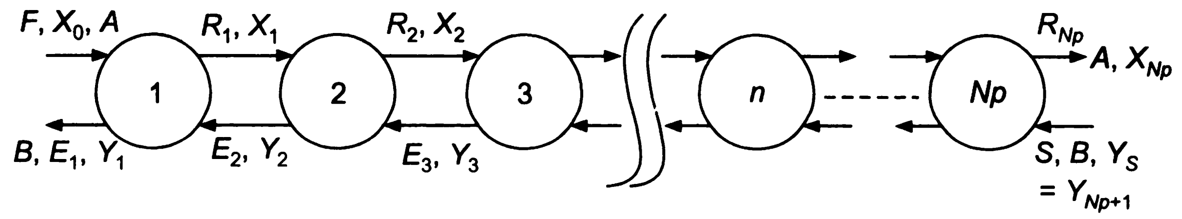


Fig. 10.17 Multistage countercurrent extraction operation for an insoluble system.

The material balance based on solute is given below:

$$A \cdot X_0 + B \cdot Y_{Np+1} = BY_1 + A \cdot X_{Np} \tag{10.23}$$

$$A\,[X_0 - X_{Np}] = B\,[Y_1 - Y_{Np+1}] \tag{10.24}$$

i.e.

$$\frac{A}{B} = \frac{(Y_1 - Y_{Np+1})}{(X_0 - X_{Np})} \tag{10.25}$$

i.e.

$$\frac{A}{B} = \frac{(Y_{\text{out}} - Y_{\text{in}})}{(X_{\text{in}} - X_{\text{out}})} \tag{10.26}$$

The operating line will have a slope of A/B and also pass through the points (X_0, Y_1) and (X_{Np}, Y_{Np+1}).

Once the operating line is constructed, the number of stages needed either for a specified percentage recovery or the exit concentration of raffinate stream can be found.

Sometimes the percentage recovery and the number of stages will be specified. The objective will be to fix the amount of solvent needed for the operation. This can be done by fixing the operating line by trial and error, which will exactly yield both the exit concentration of raffinate and the specified number of stages.

Minimum solvent requirement is estimated by drawing either a tangent to the equilibrium curve or based on the equilibrium solute concentration in the solvent rich layer for the exit concentration of raffinate. The slope of the tangent gives the slope of operating line under minimum solvent conditions. In the later case, it is estimated by the slope of the line joining the terminal conditions.

When the equilibrium curve is of constant slope, say m', then $m' = (Y^*/X)$. The number of stages N_p can be estimated by

$$\frac{(X_F - X_{Np})}{X_F - \dfrac{(Y_{Np+1})}{m'}} = \frac{\left(\dfrac{m'B}{A}\right)^{Np+1} - \left(\dfrac{m'B}{A}\right)}{\left(\dfrac{m'B}{A}\right)^{Np+1} - 1} \tag{10.27}$$

where, $\dfrac{m'B}{A}$ is called the *extraction factor.*

10.9.2.1 Steps involved (Fig. 10.18)

1. Draw the equilibrium curve.
2. Locate X_0, X_{Np} and Y_{Np+1}.
3. From the point (X_{Np}, Y_{Np+1}) draw a tangent to the equilibrium curve which will give slope of the operating line at minimum solvent condition, $(A/B)_{\min}$.
4. If B_{actual} in terms of $B_{\min}$ is known, then we can determine $(A/B)_{\text{actual}}$ and draw the actual operating line. Otherwise, if the quantity of B is given, draw the operating line directly.

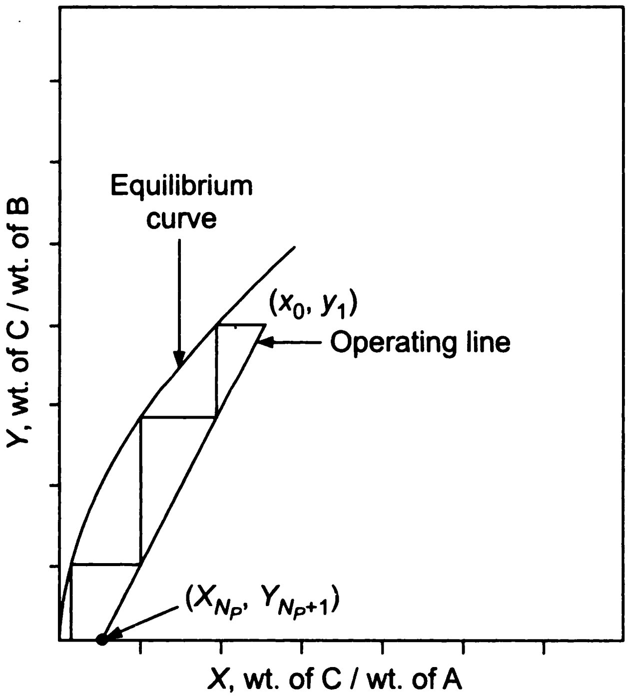


Fig. 10.18 Stages for countercurrent extraction.

5. At X_0 from the operating line draw a horizontal line to equilibrium curve which will give Y_1, the concentration of solute in final extract.
6. By stepwise construction from (X_0, Y_1), determine the number of stages needed to cross X_{Np}.
7. However, if the number of stages are prescribed, X_{Np} will have to be fixed by trial and error and checked for the prescribed number of stages.
8. In case the amount of solvent used is not given and X_{Np} along with the stages are known then the operating line has to be fixed by trial and error to ensure that both the prescribed X_{Np} and the number of stages are reached. From the slope of the operating line so fixed, we can estimate the solvent needed for the operation.

10.10 CONTINUOUS COUNTERCURRENT EXTRACTION WITH REFLUX

In a normal countercurrent extraction operation, the extract obtained will at the most be in equilibrium with the feed solution. However, the use of reflux at the extract end of the plant can provide a product even richer, as in the case of the rectifying section of a distillation column. Reflux is not used for the raffinate stream. A typical flow diagram of a countercurrent extraction with reflux is shown in Fig. 10.19.

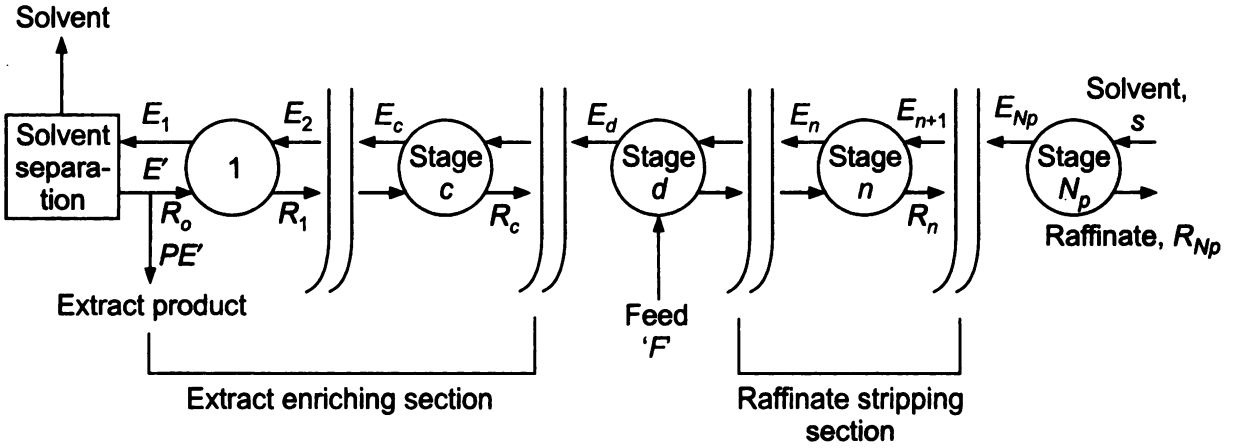


Fig. 10.19 Countercurrent extraction with reflux.

$$E_1' = E' = R_0 + P_E' \tag{10.28}$$

(The prime indicates the flow rate of solvent-free streams)

The procedure for determining the number of stages is quite similar to Ponchon–Savarit method discussed under distillation in Chapter 9.

Let us define 'N' as $\dfrac{B_{\text{out}}}{(A + C)_{\text{out}}}$ and X and Y as $\dfrac{C}{(A + C)}$ in raffinate and extract streams respectively.

Let Δ_E represent the net flow outwards from the enriching section.

i.e. $$\Delta_E' = P_E' \tag{10.29}$$

A component balance for solute indicates, $X_{\Delta E} = X_{PE}$
Balance for solvent B gives

$$B_E = \Delta_E' \cdot N_{\Delta E} \tag{10.30}$$

For all stages up to c, a balance for $A + C$ gives

$$E'_{c+1} = P_E' + R_c' = \Delta_E' + R_c' \tag{10.31}$$

i.e.

$$\Delta_E' = E'_{c+1} - R_c' \tag{10.32}$$

The component balance for A and C is

$$\Delta_E' X_{\Delta E} = E'_{c+1} Y_{c+1} - R_c' X_{Rc} \tag{10.33}$$

Similarly, a balance for B gives

$$\Delta_E' N_{\Delta E} = E'_{c+1} N'_{Ec+1} - R_c' N_{Rc} \tag{10.34}$$

Since c represents any stage, all lines radiating from point Δ_E represent extract and raffinate flowing between any two successive stages.

Solving Eq. (10.31) with Eqs. (10.33) and (10.34), we get the expression, for internal reflux ratio.

$$\frac{R_c'}{E'_{c+1}} = \frac{(N_{\Delta E} - N_{Ec+1})}{(N_{\Delta E} - N_{Rc})} = \frac{(X_{\Delta E} - Y_{c+1})}{(X_{\Delta E} - X_{Rc})} \tag{10.35}$$

$$= \frac{\text{line } \Delta_E E_{c+1}}{\text{line } \Delta_E R_c} \tag{10.36}$$

External reflux ratio

$$\frac{R_o'}{P_E'} = \frac{R_o}{P_E} = \frac{(N_{\Delta E} - N_{E_1})}{(N_{E_1})} \tag{10.37}$$

and this can be used to locate Δ_E point which will have coordinates as $(X_{\Delta E}, N_{\Delta E})$. Similarly, we can show that $R'_{NP} - S' = R'_{n-1} - E_n' = \Delta_R'$ (for a general stage n in stripping section) and hence all operating lines will pass through Δ_R' in stripping section. A material balance for the entire plant, on solvent-free basis, gives

$$F' + S' = P_E' + R'_{NP} \tag{10.38}$$

$$F' = P_E' + R'_{Np} - S' = \Delta_E' + \Delta_R' \tag{10.39}$$

Hence, the feed point F will lie on the line joining Δ_E' and Δ_R'.

The minimum reflux ratio occurs when the line radiating either from Δ'_E or Δ'_R coincides with a tie line and also pass through feed point F.

10.10.1 Steps

The procedure for determining the number of stages in continuous countercurrent with reflux is shown in Fig. 10.20.

1. Convert the data to solvent free basis and estimate N, X, Y.
2. Plot N vs X and Y.
3. Draw the X vs Y diagram and locate $X'_{P'_E}$ and $X'_{R'_{Np}}$.
4. Locate $X'_{P'_E}$ and $X'_{R'_{Np}}$ and draw vertical lines in N vs X, N vs Y plot.

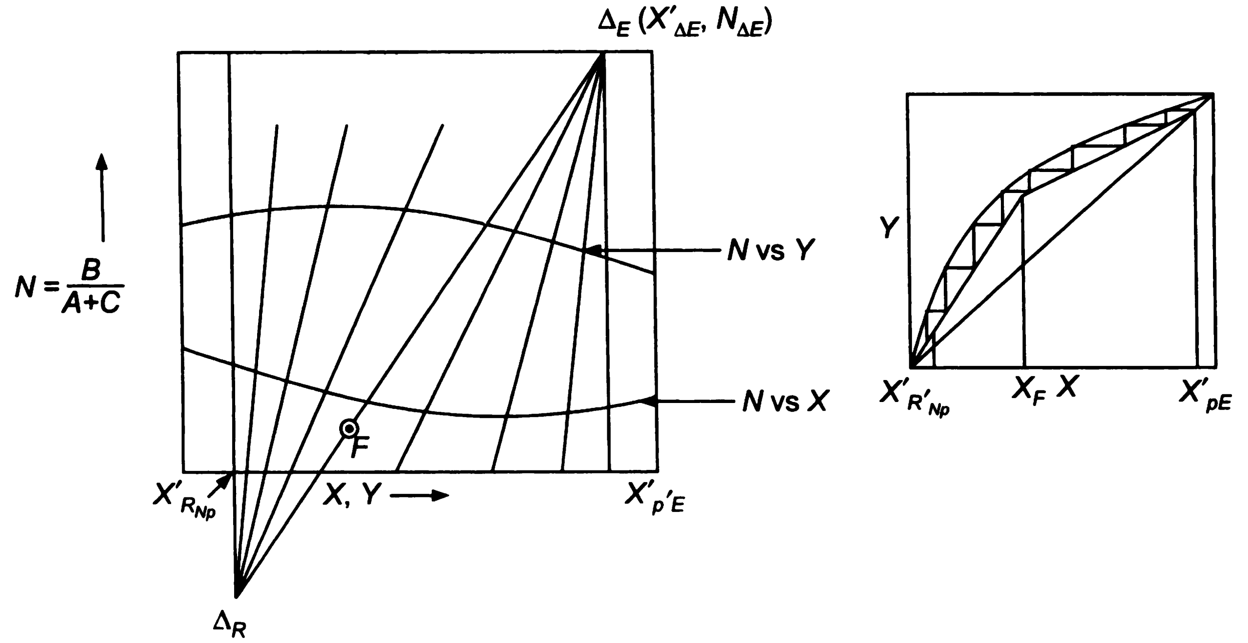


Fig. 10.20 Procedure to determine the number of stages in countercurrent extraction operation with reflux.

5. For the given reflux ratio estimate $N_{\Delta E}$ and plot $(X'_{\Delta E}, N_{\Delta E})$ point and call it Δ_E.
6. Locate feed point F (X_F, N_F).
7. Join Δ_E and F and produce it to cut the vertical line drawn at $X'_{R'_{Np}}$ to obtain Δ_R.
8. Draw arbitrary lines from Δ_E and Δ_R point to N vs X and N vs Y plot and obtain the coordinates of the operating line.
9. Plot the coordinates of operating line in X vs Y diagram.
10. By stepwise construction starting from $X'_{P'_E}$ determine the stages needed up to $X'_{R'_{Np}}$. The stage which crosses the feed point (corresponding to X_F), gives the location of feed point.

10.11 FRACTIONAL EXTRACTION

When a solution contains two solutes, both of which can be extracted by countercurrent extraction with a suitable solvent, then any great degree of separation of the solutes by this method is difficult, unless their distribution coefficients are very large. By using partially miscible solvents, separation can be achieved.

10.12 MULTICOMPONENT EXTRACTION

For systems containing more than four components, presentation of equilibrium data and the computation of stages are very difficult (as in the extraction of petroleum lubricating oils). In such cases the number of stages needed are determined experimentally in the laboratory.

10.13 CONTINUOUS CONTACT EXTRACTORS

In these extractors liquid flows countercurrently through a single piece of equipment and one extractor is equivalent to many theoretical stages. The flow is produced by virtue of the variation in densities of the liquids. Whenever the motivating force is gravity it has a vertical orientation and if the motivating force is centrifugal force, it is horizontal in nature. Flooding is one of the common problems encountered in the operation of these devices. They are also subjected to axial mixing which severely reduces the extraction rates. The tower design procedure is similar to the design of packed absorption tower. Raffinate stream corresponds to gas stream and extract stream corresponds to the liquid stream.

$$Z = H_{tR} \cdot N_{tR} \tag{10.40}$$

where

$$H_{tR} = \frac{R}{k_R a (1-x)_{im}} \tag{10.41}$$

$$N_{tR} = \int_{x_2}^{x_1} \frac{(1-x)_{im}\,dx}{(1-x)(1-x_i)} = \int_{x_2}^{x_1} \frac{dx}{(x-x_i)} + \frac{1}{2}\ln\frac{(1-x_2)}{(1-x_1)} \tag{10.42}$$

x_i = Interface concentration of solvents

k_R = mass transfer coefficient for raffinate phase

H_{tR} = height of raffinate transfer unit

N_{tR} = Number of raffinate transfer units

$(1 - x)_{im}$ = logarithmic mean of $(1 - x)$ and $(1 - x_i)$

The height of the tower can also be estimated using the overall mass transfer coefficients as in the case of absorption in which case,

$$Z = H_{toR} \cdot N_{toR} = H_{toE} \cdot N_{toE} \tag{10.43}$$

where,

$$H_{toR} = \frac{R}{K_R a (1-x)^*_m}; \quad H_{toE} = \frac{E}{K_E a (1-y)^*_m} \tag{10.44}$$

$$N_{toR} = \int_{x_2}^{x_1} \frac{(1-x)^*_M\,dx}{(1-x)(x-x^*)} = \int_{x_2}^{x_1} \frac{dx}{(x-x^*)} + \frac{1}{2}\ln\frac{(1-x_2)}{(1-x_1)} \tag{10.45}$$

$$N_{toE} = \int_{x_2}^{x_1} \frac{(1-y)^*_M\,dy}{(1-y)(y^*-y)} = \int_{x_2}^{x_1} \frac{dy}{(y^*-y)} + \frac{1}{2}\ln\frac{(1-y_1)}{(1-y_2)} \tag{10.46}$$

$$(1-x)^*_M = \frac{(1-x^*)-(1-x)}{\ln\left(\dfrac{(1-x^*)}{(1-x)}\right)} \tag{10.47}$$

$$(1-y)^*_M = \frac{(1-y)-(1-y^*)}{\ln\left(\dfrac{(1-y)}{(1-y^*)}\right)} \tag{10.48}$$

where x^* is the concentration in equilibrium with y and y^* is the concentration in equilibrium with x.

10.14 DILUTE SOLUTIONS

For dilute solutions and whenever the equilibrium curve and operating curve are linear in the operating range,

$$N_{toR} = \frac{(x_1 - x_2)}{(x - x^*)_m} \text{ and } N_{toE} = \frac{(y_1 - y_2)}{(y^* - y)_m} \tag{10.49}$$

If the equilibrium relationship is given by $m = y^*/x$, similar to Henry's law, then

$$N_{toR} = \frac{\ln\left[\left(\dfrac{x_1 - \left(\dfrac{y_2}{m}\right)}{x_2 - \left(\dfrac{y_2}{m}\right)}\right)\left(1 - \dfrac{R}{mE}\right) + \dfrac{R}{mE}\right]}{1 - \left(\dfrac{R}{mE}\right)} \tag{10.50}$$

$$N_{toE} = \frac{\ln\left[\left(\dfrac{y_2 - mx_1}{y_1 - mx_1}\right)\left(1 - \dfrac{mE}{R}\right) + \dfrac{mE}{R}\right]}{1 - \left(\dfrac{mE}{R}\right)} \tag{10.51}$$

Though the above expressions can be used in the design of continuous contactors, it is always advisable to go in for pilot plant studies at nearly the expected operating conditions to enable the design of extractors as lot of parameters influence extraction. These include physical properties of liquids, its flow rate, solubility of solute and the presence of surface active agents. The equipment also has its own impact on the extraction performance. The factors such as type of agitator and its size, the size of extractor, the presence of baffles and type of agitation have an influence on the performance of extraction.

10.15 EQUIPMENT

The equipment used for liquid-liquid extraction operations are classified as:

Single stage mixer settler
A multistage cascade of single stage mixer settler
Continuous contactors.

10.15.1 Mixer-settler

A single stage mixer-settler is a simple arrangement with two units. In the first unit, called 'mixer', mixing of two phases takes place which leads to transfer of mass and in the second unit, called 'settler', separation of phase takes place (Fig. 10.21). In a multistage operation, several such combinations are used.

The degree of dispersion depends on the type of contactor/mixer and liquid characteristics. The liquid phases can also be mixed by the use of different types of impellers such as marine impeller, flat blade turbine, etc. The normal ratio of impeller to tank diameter is 0.25 to 0.33. The dispersion can also be achieved by the dispersion of one liquid through another liquid in the form of fine droplets with the help of nozzles. In a multistage cascade arrangement, feed after entering the first mixer (subsequently raffinate) flows from the first settler to the next mixer-settler combination till it leaves from the last settler as final raffinate. The solvent enters the last mixer and from the last settler it passes on to the next mixer before it finally leaves as the concentrated extract from the first settler. The flow, thus, is countercurrent.

However, large towers are used when large volumes of liquid have to be handled and that too on continuous basis. In these towers, the liquids flow countercurrently. The heavy phase is introduced at the top and it flows downwards. The lighter phase is introduced at the bottom and this phase flows upwards. Some of the commonly used towers for this operation are briefly described here.

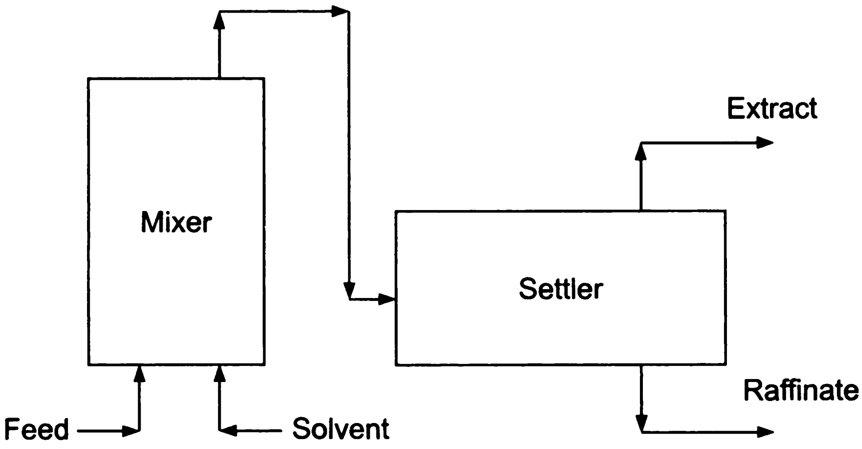


Fig. 10.21 A mixer-settler combination.

10.15.2 Mechanically Agitated Tower

These towers are provided with agitators which are mechanically agitated. The efficiency of separation increases due to agitation of the liquid streams. The agitators are of different configurations.

10.15.3 Oldshue-Rhuston Extractor

In this case the extractor is provided with flat blade disc turbine impeller for dispersing and mixing and horizontal compartmental plates which are provided to reduce axial mixing. This is a very old type of extractor.

10.15.4 Rotating Disc Contactor (RDC)

The schematic diagram of RDC is shown in Fig. 10.22. It comprises a tall vertical tower provided with inlets for both feed and solvent streams to enter and outlets

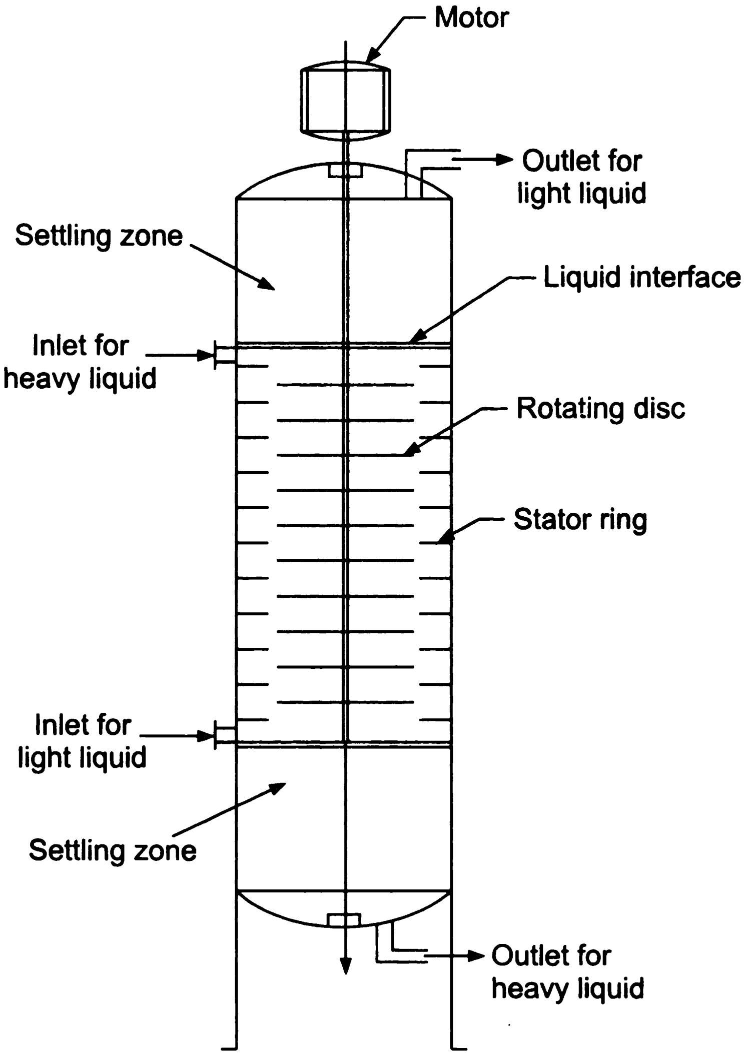


Fig. 10.22 Rotating disc contactor (RDC).

for both product (Raffinate and Extract) streams. It has a central shaft attached with rotor discs and is driven by a motor. Stators of centrally hollowed rings attached to the wall of the tower alternate position to the rotors. This can be operated at high speeds and it finds wide application in petroleum industries.

10.15.5 York-Scheibel Column

This column is provided with mixing and horizontal packed compartments arranged alternately as shown in Fig. 10.23. Mixing is done by a turbine impeller which is attached to a mechanically driven central shaft. The packed compartments are provided with wire mesh to reduce axial mixing.

10.15.6 Pulsed Column Extractor

In this extractor, there is no moving device. A reciprocating pulse input is hydraulically transmitted into the column due to which there is thorough contact between liquid streams. Column is provided with perforated plates attached as shown in Fig. 10.24. Due to the pulse input, the light and heavy liquids move upward and downward throughout the tower through the perforations. Since it has no moving parts, it finds extensive use in handling.

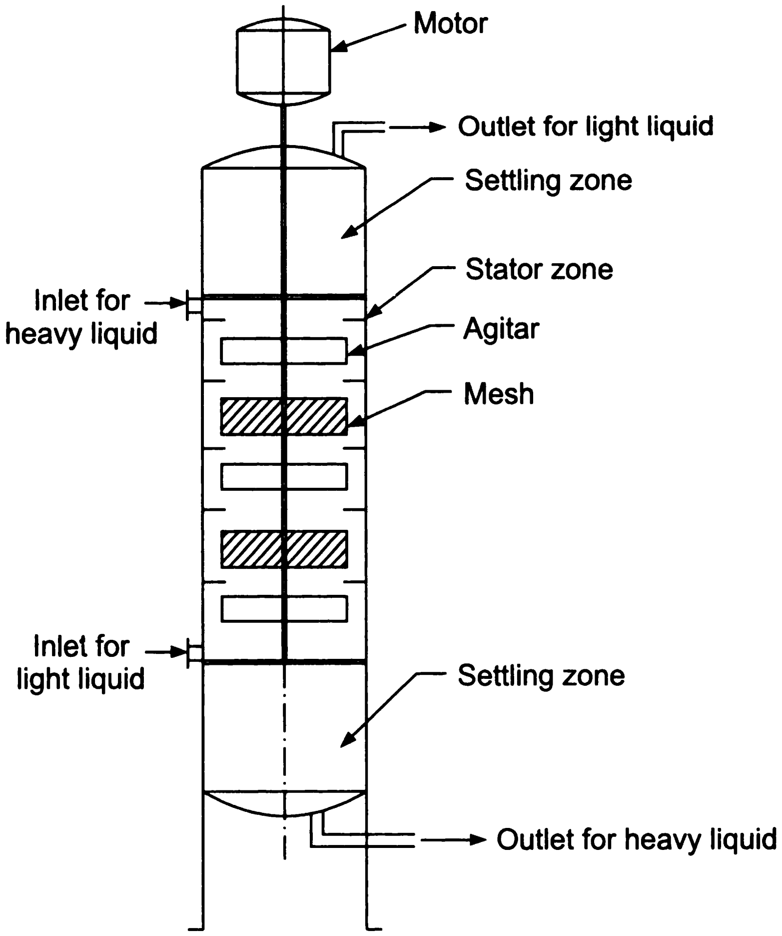


Fig. 10.23 York scheibel column.

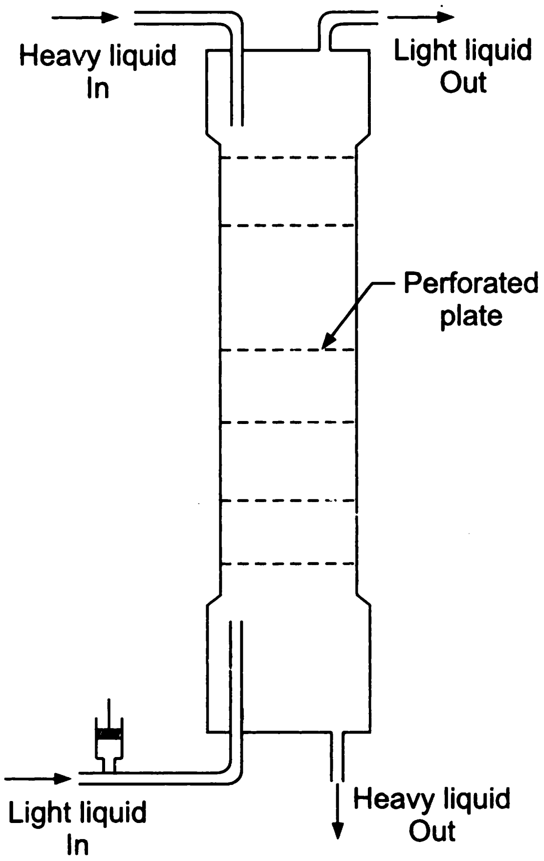


Fig. 10.24 Pulsed column extractor.

10.15.7 Other Extractors

Apart from these we have conventional packed towers, spray towers and for lesser density difference systems the centrifugal extractors.

WORKED EXAMPLES

1. A 5% (by weight) solution of acetaldehyde in toluene is extracted with water in a three stage cross-current unit. If 100 kg of water is used per stage for 500 kg of feed, calculate (using graphical method) the percentage extraction of acetaldehyde and the weights of final raffinate and mixed extract. The equilibrium relationship is given by the equation, $Y = 2.3\ X$ where Y = kg acetaldehyde/kg water and X = kg acetaldehyde/kg toluene. Assume that toluene and water are immiscible with each other.

Solution.

A : toluene, B : water, C : acetaldehyde,
$F = 500$ kg, $x_F = 0.05$, $Y = 2.3X$
$B = 100$ kg water/stage

Three stage cross-current operation
Assume solvent to be pure, i.e. $y_s = 0$

$$F = 500 \text{ kg},\ A = 475 \text{ kg, and } C = 25 \text{ kg}$$

$$\text{Slope} = (-\ A/B)$$

So $(-\ A/B)$ for each stage = $(-\ 475/100) = (-\ 4.75)$
Draw the operating line with a slope of $-\ 4.75$ for each stage

$$X_F = \frac{x_F}{(1-x_F)} = \frac{0.05}{1-0.95} = 0.0526$$

X (kg acetaldehyde/ kg toluene)	0	0.01	0.02	0.03	0.04	0.05	0.06
Y (kg acetaldehyde/ kg water)	0	0.023	0.046	0.069	0.092	0.115	0.138

Since system is immiscible, the whole of solvent goes in extract. The feed introduced in 1st stage just passes through all stages and comes out as final raffinate:

A plot between X and Y is drawn. The operating line is drawn with a slope of $-\ 4.75$ for each of the three stages.

Weight of A in final raffinate $= A = 475$ kg
Final raffinate contains $X_3 = 0.0161$ kg C/kg A (from graph)
Amount of C in raffinate $= 475 \times 0.016 = 7.6$ kg
Total weight of raffinate $= 475 + 7.6 = 482.6$ kg
Total C extracted $= (Y_1 + Y_2 + Y_3) \times 100$
$= 100 \times (0.082 + 0.055 + 0.037) = 17.4$ kg
In extract, the amount of B $= 100$ kg (in each stage)
$Y_3 = 0.037$ kg C/kg B (from graph)
Amount of C in final stage extract $= 0.037 \times 100 = 3.7$ kg
Total weight of extract $= 300 + 17.4 = 317.4$ kg
% Extraction $= (17.4/25) \times 100 = 69.6\%$

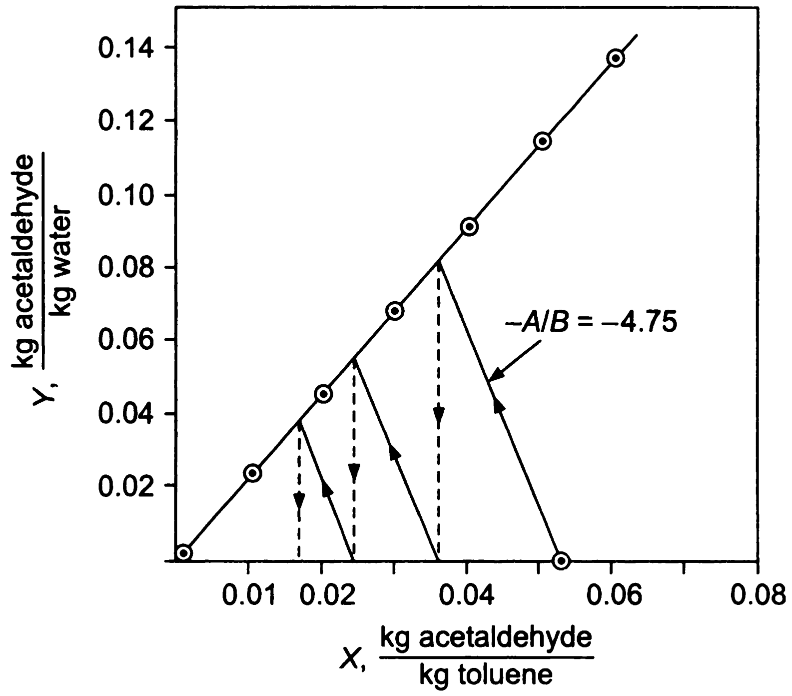


Fig. 10.25 Example 1.

2. 100 kg of a solution containing acetic acid and water containing 25% acid by weight is to be extracted with isopropyl ether at 20°C. The total solvent used for extraction is 100 kg. Determine the compositions and quantities of various streams if,

(i) The extraction is carried out in single stage

(ii) The extraction is carried out in two stages with 50 kg of solvent in each stage.

Equilibrium data:

Water layer (wt. %)		*Ether layer* (wt. %)	
Acid (*x*)	*Water* (*A*)	*Acid* (*y*)	*Water* (*A*)
0.69	98.1	0.18	0.5
1.41	97.1	0.37	0.7
2.9	95.5	0.79	0.8
6.42	91.7	1.93	1.0
13.3	84.4	4.82	1.9
25.5	71.1	11.4	3.9
36.7	58.9	21.6	6.9
44.3	45.1	31.1	10.8
46.4	37.1	36.2	15.1

Solution.

$A \rightarrow$ water, $B \rightarrow$ isopropyl ether, $C \rightarrow$ Acetic acid,

$F = 100$ kg, $A = 75$ kg, and $C = 25$ kg, $x_F = 0.25$

Total solvent used = 100 kg = B

B	0.0121	0.0149	0.016	0.0188	0.023	0.034	0.044	0.106	0.165
x	0.0069	0.0141	0.029	0.0642	0.133	0.255	0.367	0.443	0.464
B	0.9932	0.9893	0.9841	0.9707	0.9328	0.847	0.715	0.581	0.487
y	0.0018	0.0037	0.0079	0.0193	0.0482	0.114	0.216	0.311	0.362

(i) Single stage operation:

By total and component material balances,

$$F + S = M_1$$

$$100 + 100 = M_1 = 200 \text{ kg}$$

$$x_{M_1} = \frac{Fx_y + Sy_s}{F+S} = \frac{100 \times 0.25 + 100 \times 0}{100+100} = 0.125$$

Locate M_1 on the FS line corresponding to x_{M_1}. By trial and error, a tie line is drawn which passes through M_1.

The co-ordinates (x_1, y_1) obtained are (0.18, 0.075).

By material balance,

$$R_1x_1 + y_1E_1 = M_1x_{M_1}$$

$$R_1 + E_1 = M_1$$

$$R_1 \times 0.18 + 0.075E_1 = 200 \times 0.125$$

$$R_1 + E_1 = 200$$

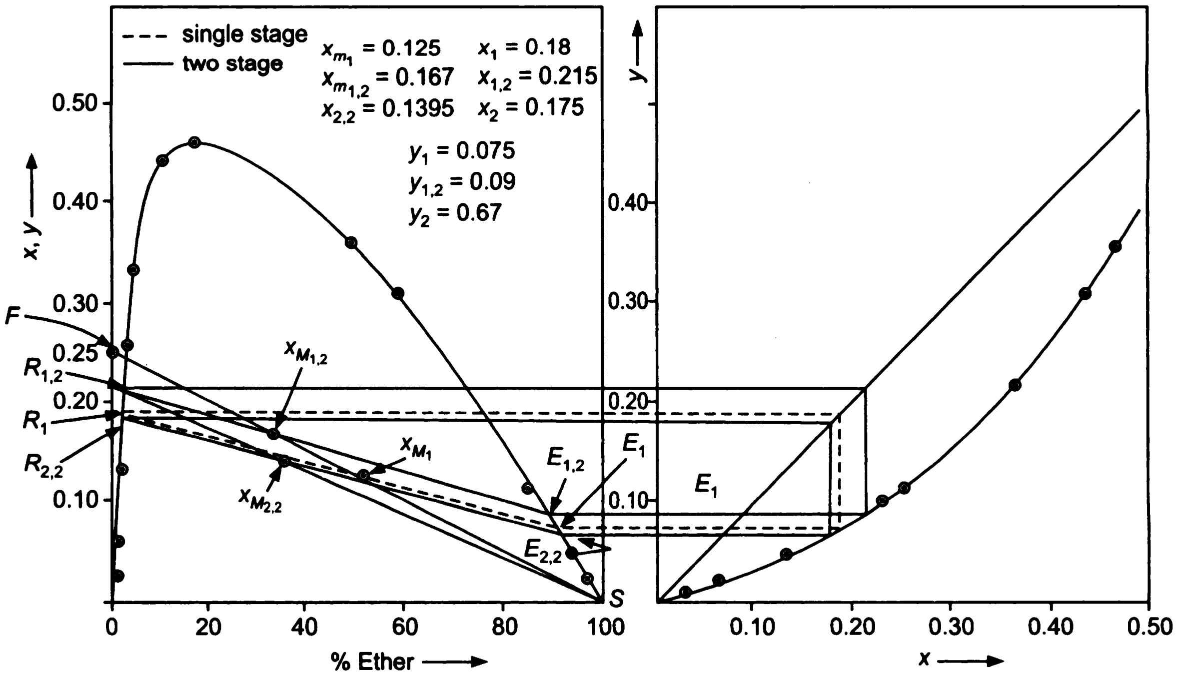


Fig. 10.26 Example 2.

Solving we get, $$E_1 = M_1\left(\frac{x_{M_1} - x_1}{y_1 - x_1}\right)$$

Quantities of product streams are

$$E_1 = 104.76 \text{ kg}$$

$$R_1 = 95.24 \text{ kg}$$

(ii) Two-stage operation:

$$F = 100 \text{ kg}, \quad S = 50 \text{ kg}$$

$$S + F = M_1$$

$$x_{M_{1,2}} = \frac{Fx_F + Sy_s}{F+S} = \frac{100 \times 0.25 + 50 \times 0}{100+50} = 0.167$$

$$M_1 = 50 + 100 = 150 \text{ kg}$$

Locate $M_{1,2}$ on the Fs line corresponding to $x_{M_{1,2}}$. By trial and error, a tie line is drawn which passes through M_{12}.

The co-ordinates (x_{12}, y_{22}) obtained are (0.215, 0.09)

By following the same procedure mentioned above and solving, we get

$$E_{12} = M_{12}\left(\frac{x_{M_{12}} - x_{12}}{y_{12} - x_{12}}\right) = 150\left(\frac{0.167 - 0.215}{0.09 - 0.215}\right) = 57.6 \text{ kg}$$

$$R_{12} = 150 - 57.6 = 92.4 \text{ kg}$$

Similarly for II stage, $x_{M22} = 0.1395$, $M_2 = 92.4 + 50 = 142.4$ kg

$$x_2 = 0.175 \text{ and } y_2 = 0.07 \text{ (from tie line)}$$

$$E_2 = 48.14 \text{ kg}$$

$$R_2 = 94.26 \text{ kg}$$

$$\text{Percentage recovery} = \frac{(25 - 94.26 \times 0.175)}{25} \times 100 = 34.02\%$$

3. 1000 kg/hr of an acetone-water mixture containing 20% by weight of acetone is to be counter-currently extracted with trichloroethane. The recovered solvent to be used is free from acetone. The water and trichloroethane are insoluble. If 90% recovery of acetone is desired estimate the number of stages required if 1.5 times the minimum solvent is used. The equilibrium relationship is given by $y = 1.65x$, where x and y are weight fractions of acetone in water and trichloroethane respectively.

Solution.

$$X_F = 0.2/(1 - 0.2) = 0.25$$

$$X_{N_P} = 0.25 \times 0.1 = 0.025$$

$$y_1 = 1.65 \times 0.2 = 0.33$$

$$Y_1 = 0.33/0.67 = 0.49$$

$$Y_s = 0 \text{ (Pure solvent)}$$

(the same value is got from plotting of the graph also)

X	0.05	0.1	0.175	0.25	0.325
$x = \frac{x}{1+x}$	0.0476	0.0909	0.149	0.20	0.245
$y = 1.65x$	0.0785	0.15	0.246	0.33	0.404
$Y = \frac{y}{1-y}$	0.085	0.176	0.326	0.493	0.678

$$\frac{A}{B_{\min}} = \frac{Y_1 - Y_s}{X_F - X_{Np}}$$

$$\frac{800}{B_{\min}} = \frac{0.49 - 0}{0.25 - 0.025}$$

$$B_{\min} = 367.35 \text{ kg}$$

$$B_{\text{act}} = 1.5 \times B_{\min} = 1.5 \times 367.35 = 551.025 \text{ kg}$$

$$\frac{A}{B_{\text{act}}} = \frac{Y_{1,\text{act}} - Y_s}{X_F - X_{Np}}$$

$$\frac{800}{551.025} = \frac{Y_{1,\text{act}} - 0}{0.25 - 0.025} = 1.452$$

$$Y_{1,\text{act}} = 0.327$$

An operating line with a slope of 1.452 is drawn and by stepwise construction the number of stages is determined as 5.

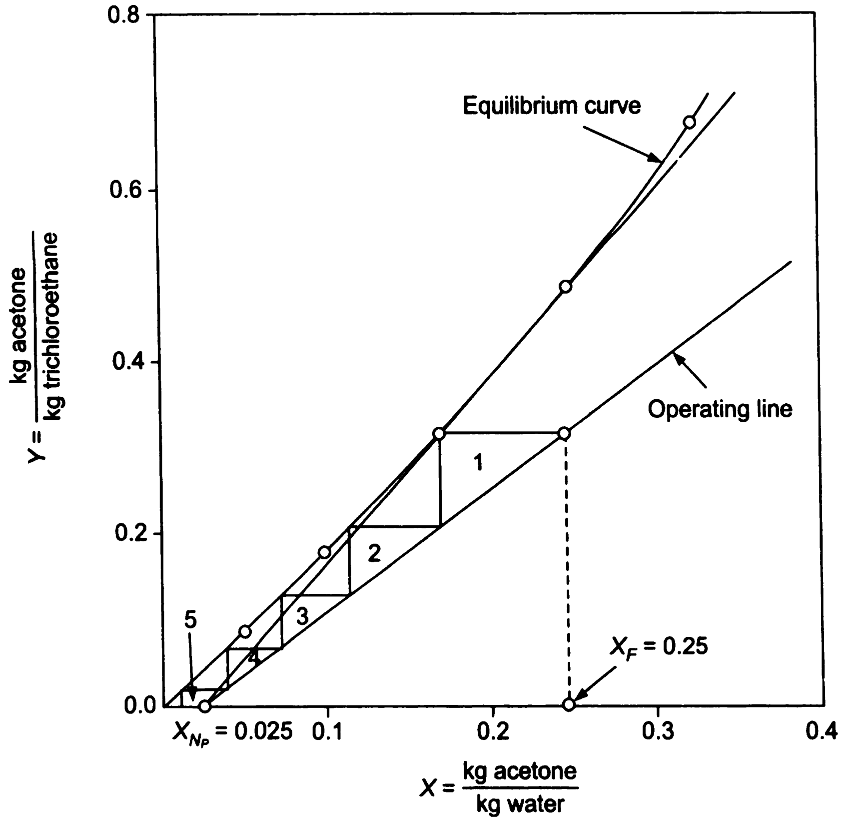


Fig. 10.27 Example 3.

4. Water–dioxane solution is to be separated by extraction process using benzene as solvent. At 25°C the equilibrium distribution of dioxane between water and benzene is as follows:

Weight % of dioxane in water	5.1	18.9	25.2
Weight % of dioxane in benzene	5.2	22.5	32.0

At these concentrations water and benzene are substantially insoluble. 1000 kg of a 25% dioxane water solution is to be extracted to remove 95% of dioxane. The benzene is dioxane free.

(i) Calculate the benzene requirement for a single batch operation.

(ii) Calculate the benzene requirement for a five-stage cross-current operation with 600 kg of solvent used in each stage.

Solution.

Solvent = amount of feed or raffinate in each stage

(B) = (F) or (R)

x	0.051	0.189	0.252
y	0.052	0.225	0.32
$X = x/(1-x)$	0.054	0.233	0.337
$Y = y/(1-y)$	0.05485	0.29	0.471

(i)

$$F = 1000 \text{ kg } (A = 750 \text{ kg}, C = 250 \text{ kg})$$

$$x_F = 0.25, \quad X_F = 0.25/0.75 = 0.333$$

$$X_{R_{Np}} = 0.05 \times 0.333 = 0.01665$$

$$Y_{\text{in}} = 0$$

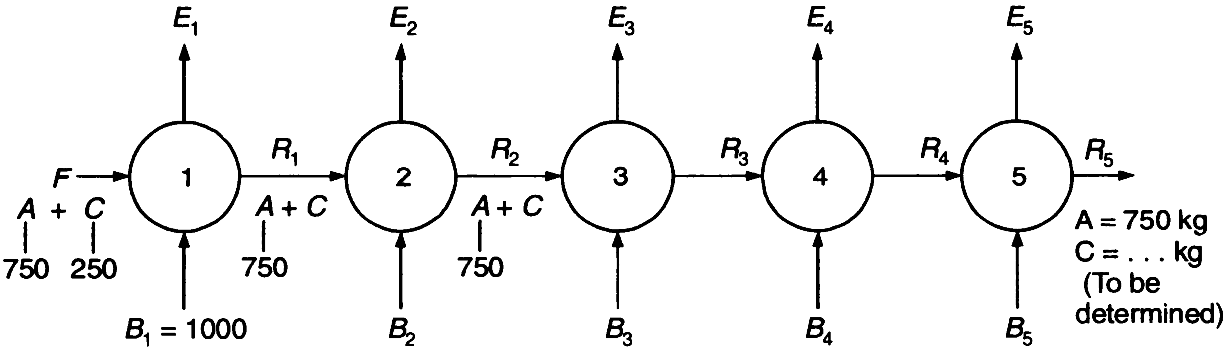
$$Y_1 = 0.0175 \text{ (From graph)}$$

$$\frac{A}{B} = \frac{Y_1 - Y_s}{X_F - X_{Np}}$$

$$\frac{750}{B} = \frac{0.0175 - 0}{0.333 - 0.01665}$$

$$B = 13557.86 \text{ kg}$$

(ii) Five-stage cross-current operation



Amount of solvent used is 600 kg

$$\frac{A}{B} = \frac{750}{600} = 1.25$$

Draw operating lines with a slope of –1.25 and determine the raffinate concentration.

$$X_{\text{final}} = 0.0175$$

$$\% \text{ recovery} = \frac{(0.333 - 0.0175) \times 100}{0.333} = 94.75\%$$

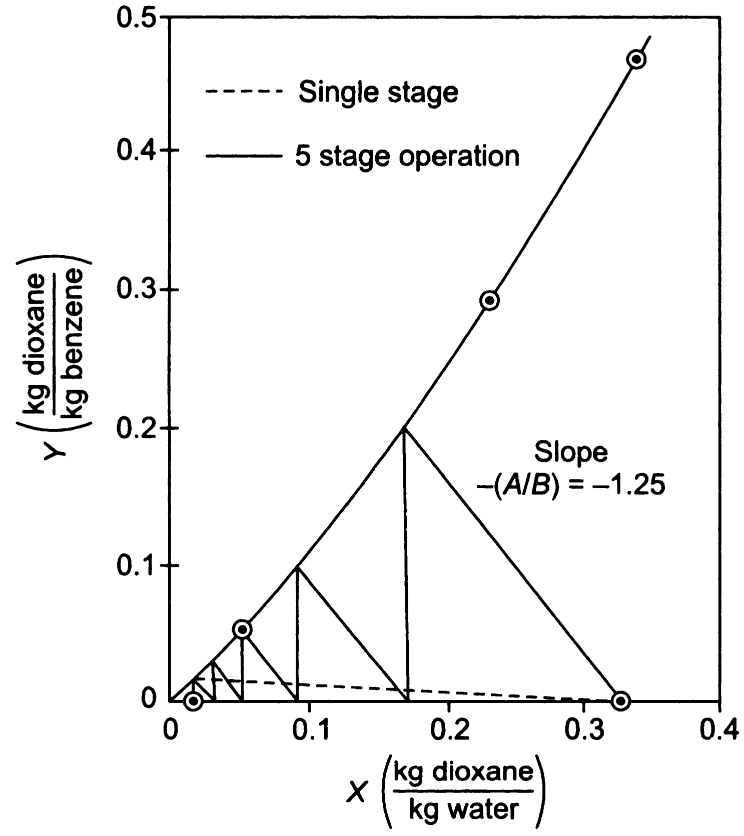


Fig. 10.28 Example 4.

5. 1000 kg per hour of a solution of *C* in *A* containing 20% *C* by weight is to be countercurrently extracted with 400 kg per hour of solvent *B*. The components *A* and *B* are insoluble. The equilibrium distribution of component *C* between *A* and *B* are as follows;

Wt. of *C*/Wt. of *A*	0.05	0.20	0.30	0.45	0.50	0.54
Wt. of *C*/Wt. of *B*	0.25	0.40	0.50	0.65	0.70	0.74

How many theoretical stages will be required to reduce the concentration of *C* to 5% in effluent?

Solution.

F = 1000 kg/h, (A = 800 kg/h, C = 200 kg/h)

$x_F = 0.2$, $x_{R_{Np}} = 0.05$

Assume solvent to be pure, then

countercurrent extraction $y_s = Y_s = 0$

solvent = B = 400 kg/h

A and *B* are insoluble

$X_F = 0.2/(1 - 0.2) = 0.25, \qquad X_{R_{Np}} = 0.05/(1 - 0.05) = 0.0526$

$$\frac{A}{B} = \frac{Y_1 - Y_s}{X_F - X_{Np}}$$

$$\text{Slope} = \frac{A}{B} = \frac{800}{400} = 2$$

$$\frac{A}{B} = \frac{Y_1 - 0}{0.25 - 0.0526}$$

$$Y_1 = 0.395$$

Plot *X* vs *Y* to obtain the equilibrium curve.
Draw an operating line between ($X_{R_{Np}}$, Y_s) and (X_F, Y_1) and determine the number of stages by stepwise construction.
Number of stages obtained = 3.

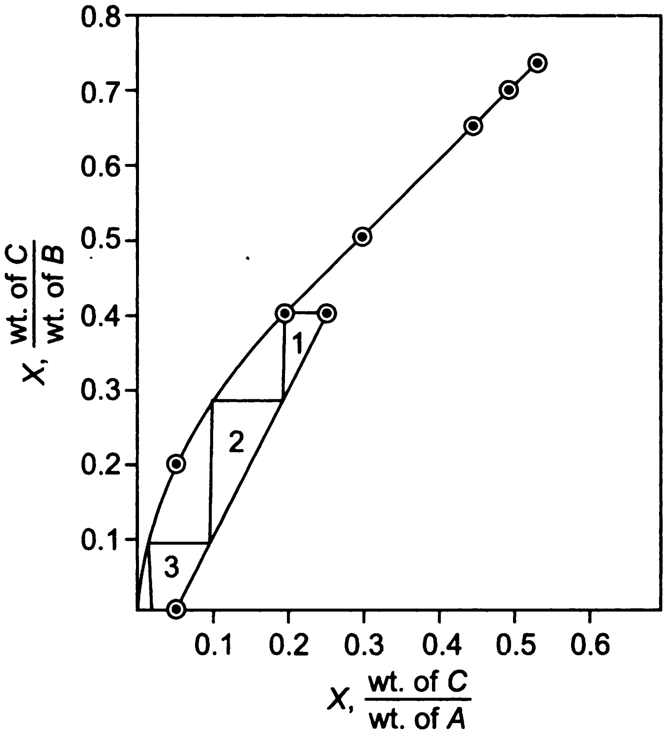


Fig. 10.29 Example 5.

6. Water–dioxane solution is to be separated by extraction process using benzene as solvent. At 25°C the equilibrium distribution of dioxane between water and benzene is as follows:

wt. % of dioxane in water	5.1	18.9	25.2
wt. % of dioxane in benzene	5.2	22.5	32.0

At these concentrations water and benzene are substantially insoluble. 1000 kg of a 25% dioxane water solution is to be extracted to remove 95% of dioxane. The benzene is dioxane free. Calculate minimum solvent required in kg/h if the extraction is done in countercurrent fashion. Estimate the number of stages needed if 1.5 times the minimum amount of solvent is used.

Solution.

Benzene: B Water: A Dioxane: C

$$F = 1000 \text{ kg } (A = 750 \text{ kg}, C = 250 \text{ kg})$$

x	0.051	0.189	0.252
y	0.052	0.225	0.32
$X = x/(1 - x)$	0.054	0.233	0.337
$Y = y/(1 - y)$	0.05485	0.29	0.471

$$x_F = 0.25,$$

$$X_F = 0.25/0.75 = 0.333$$

$$X_{R_{Np}} = 0.05 \times 0.333 = 0.01665$$

$$\frac{A}{B_{\min}} = \frac{Y_{Np+1} - Y_1}{X_{Np} - X_F}$$

$$\frac{A}{B_{\min}} = \frac{Y_{Np+1} - Y_1}{X_{Np} - X_F} = \frac{0 - 0.365}{0.01665 - 0.333} = 1.1154$$

$$B_{\min} = 650 \text{ kg}$$

$$B_{\text{act}} = 1.5 \times 650 = 975 \text{ kg}$$

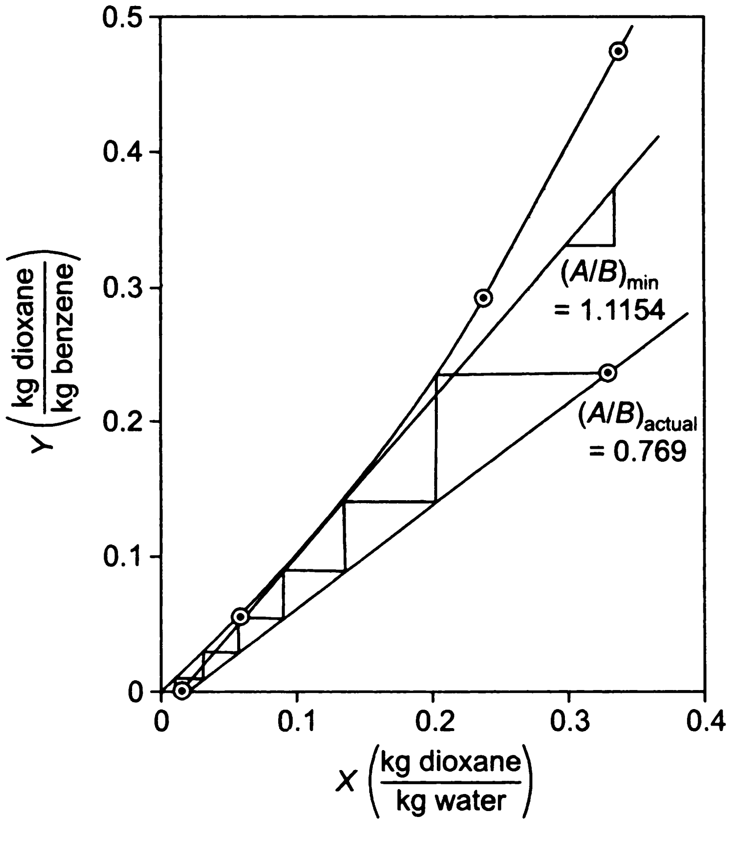


Fig. 10.30 Example 6.

$$\frac{A}{B_{\text{act}}} = \frac{Y_{Np+1} - Y_{1,\text{act}}}{X_{Np} - X_F}$$

$$\frac{750}{975} = \frac{0 - Y_{1,\text{act}}}{0.01665 - 0.333}$$

$$Y_{1,\text{act}} = 0.243$$

By stepwise construction, the number of stages can be determined as 6.

7. Nicotine in a water solution containing 1% nicotine is to be extracted once with kerosene at 20°C. Kerosene and water are insoluble.

Determine the percentage extraction if 1000 kg of feed solution is extracted once with 1500 kg solvent. What will be the extraction if three ideal stages are used with 500 kg solvent in each stage?

Equilibrium data:

X	0	0.00101	0.00246	0.00502	0.00751	0.00998	0.0204
Y	0	0.00081	0.001962	0.00456	0.00686	0.00913	0.0187

where X is kg Nicotine/kg water and Y is kg Nicotine/kg kerosene.

Solution.

Water: A, Kerosene: B, Nicotine: C

$$x_F = 0.01 \qquad X_F = X_0 = \frac{0.01}{(1-0.01)} = 0.0101$$

$F = 1000$ kg, ($C = 10$ kg, $A = 990$ kg), $B = 1500$ kg

$$-\frac{A}{B_n} = \frac{(Y_n - Y_s)}{(X_n - X_{n-1})} \quad \text{when } n = 1, \; -\frac{A}{B} = \frac{Y_1 - Y_s}{X_1 - X_0}$$

$$\frac{990}{1500} = \frac{Y_1 - 0}{0.0101 - X_1}$$

A line with a slope of -0.66 is drawn from (0.0101, 0) to obtain X_1 and Y_1.

$$Y_1 = 0.66\ [(0.0101) - X_1]$$

$$Y_1 = 0.0037 \text{ (From graph)}$$

$$X_1 = 0.0045$$

Amount of nicotine in extract = 0.0037 × 1500 = 5.55 kg

% extraction = (5.55/10) × 100 = 55.5%

For three stages

$$(-A/B) = \text{A } 990/500 = -1.98.$$

3 lines with a slope of -1.98 each are drawn starting from (0.0101,0)

$$X_3 = 0.0035, \qquad Y_3 = 0.003$$

Amount of nicotine in final extract = 0.003 × 500 = 1.5 kg

$$\text{Total } C \text{ extracted} = (Y_1 + Y_2 + Y_3) \times 500$$
$$= (0.0061 + 0.0037 + 0.003) \times 500 = 6.4 \text{ kg}$$
$$\% \text{ extraction} = (6.4/10) \times 100 = 64\%$$

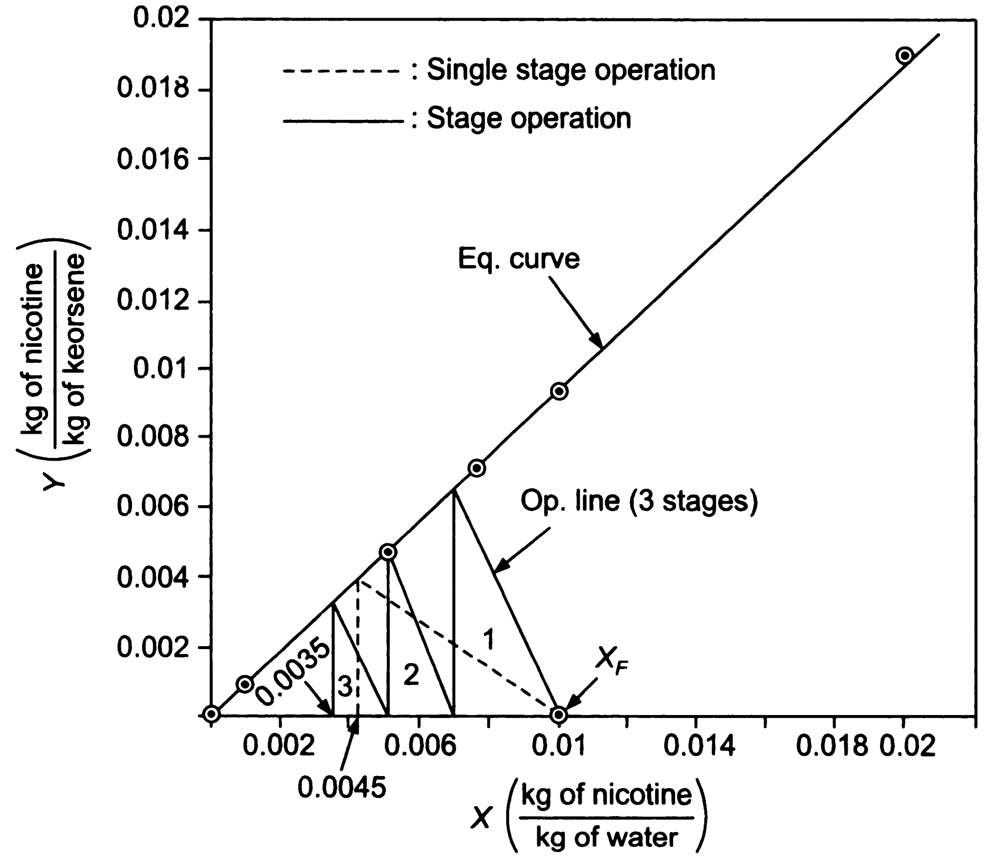


Fig. 10.31 Example 7.

8. 1000 kg/h of a water–dioxane solution containing 20% dioxane is to be continuously and counter-currently extracted with benzene at 25°C to recover 80% dioxane. Water and benzene are essentially insoluble and the equilibrium distribution of dioxane between them are as follows:

Dioxane in water wt. %	5.1	18.9	25.2
Dioxane in benzene wt. %	5.2	22.5	32.0

Determine the number of theoretical stages if the solvent rate is 1.5 times the minimum.

Solution.

Water: A Dioxane: C Benzene: B

x	0.051	0.189	0.252
y	0.052	0.225	0.32
$X = x/(1 - x)$	0.054	0.233	0.337
$Y = y/(1 - y)$	0.05485	0.29	0.471

$$F = 1000 \text{ kg/h}$$

$$x_F = 0.2, \qquad X_F = X_0 = 0.2/0.8 = 0.25$$

Countercurrent extraction

$$X_{Np} = 0.2 \times 0.25 = 0.05$$

$$\frac{A}{B_{\min}} = \frac{Y_{Np+1} - Y_1}{X_{Np} - X_F}$$

$$\frac{800}{B_{\min}} = \frac{0 - 0.3075}{0.05 - 0.25} \quad \text{(From Graph)}$$

$$B_{\min} = 520.33 \text{ kg}$$

$$B_{\text{act}} = 1.5B_{\min} = 1.5 \times 520.33 = 780.5 \text{ kg}$$

$$\frac{A}{B_{\text{act}}} = \frac{800}{780.5} = 1.025$$

Draw the operating line with a slope of 1.025 from (0.05,0) and by stepwise construction determine the number of stages.

No. of stages = 4

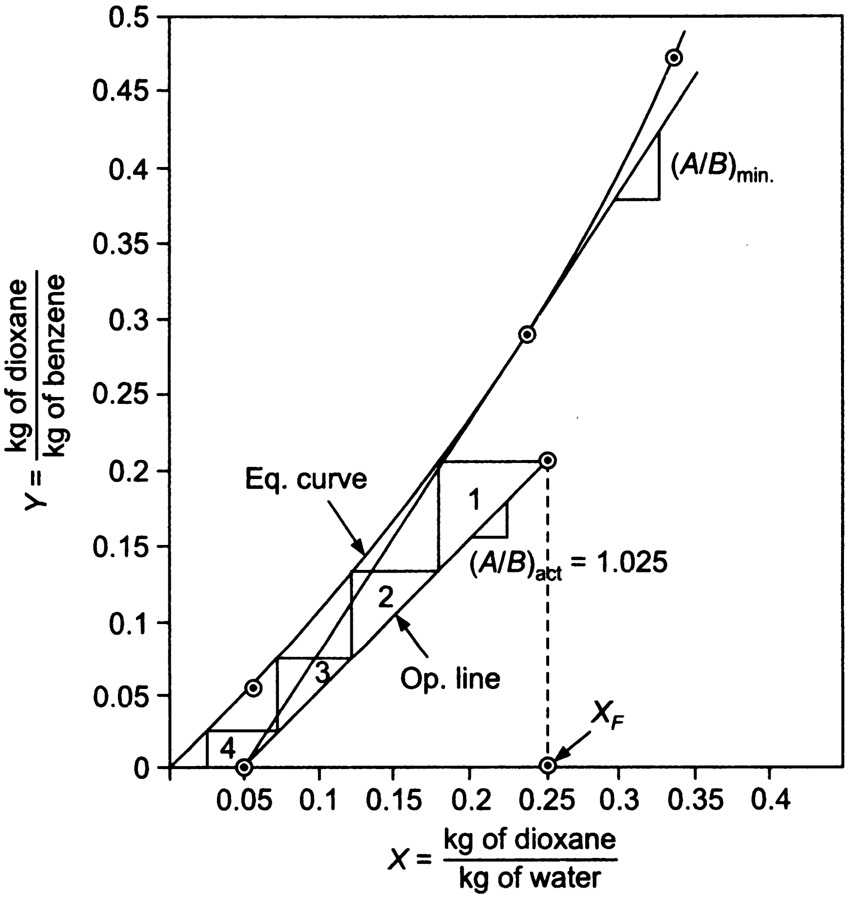


Fig. 10.32 Example 8.

EXERCISES

1. A 25% (weight) solution of dioxane in water is to be continuously extracted with 300 kg/hr of pure benzene in each stage in a cross-current extraction battery. The feed rate is 100 kg/h and if the extraction is carried out in 3 stages, estimate the % recovery.

   Equilibrium data:

Dioxane in water wt. %	5.1	18.9	25.2
Dioxane in benzene wt. %	5.2	22.5	32.0

2. Repeat the above problem for a counter current extraction process using 1.5 times the minimum solvent and determine the number of stages needed to recover 90% of dioxane for a feed rate of 100 kg/h.
3. 1000 kg/hr of an acetone-water mixture containing 10% by weight of acetone is to be countercurrently extracted with trichloroethane. The recovered solvent to be used is free from acetone. The water and trichloroethane are insoluble. If 95% recovery of acetone is desired, estimate the number of stages required if 1.5 times the minimum solvent is used. The equilibrium relationship is given by $y = 1.65x$, where x and y are weight fractions of acetone in water and trichloroethane respectively.
4. Repeat problem 3 for a 4-stage cross-current operation using 300 kg/h of solvent in each stage and determine the % of recovery.
5. A 10% (by weight) solution of acetaldehyde in toluene is extracted with water in a countercurrent unit. For a 500 kg of feed, calculate the number of stages needed for reducing the acetaldehyde to 0.5% using 1.5 times the minimum amount of solvent. The equilibrium relationship is given by the equation, $Y = 2.3X$ where Y = kg acetaldehyde/kg water and X = kg acetaldehyde/kg toluene. Assume that toluene and water are immiscible with each other.
6. 500 kg/h of an aqueous solution containing 8% acetone is to be countercurrently extracted using monochlorobenzene to reduce the acetone content to 4% of its initial value. Water and monochlorobenzene are immiscible with each other. (i) Determine the minimum solvent rate, and (ii) the number of theoretical stages required if 1.3 times the minimum solvent rate is used. The equilibrium data is as follows:

kg acetone/kg water	0.030	0.074	0.161	0.210
kg acetone/kg monochlorobenzene	0.029	0.071	0.158	0.204

7. 150 kg of a solution containing acetic acid and water containing 20% acid by weight is to be extracted with isopropyl ether at 20°C. The total solvent used for extraction is 200 kg. Determine the composition and quantities of various streams if,

(i) The extraction is carried out in single stage,

(ii) The extraction is carried out in two stages with 100 kg of solvent in each stage.

Equilibrium data:

Water layer (wt. %)		*Ether layer* (wt. %)	
Acid	*Water*	*Acid*	*Water*
0.69	98.1	0.18	0.5
1.41	97.1	0.37	0.7
2.9	95.5	0.79	0.8
6.42	91.7	1.93	1
13.3	84.4	4.82	1.9
25.5	71.1	11.4	3.9
36.7	58.9	21.6	6.9
44.3	45.1	31.1	10.8
46.4	37.1	36.2	15.1

8. Repeat the Problem 7 for a countercurrent operation using 1.5 times the minimum solvent. Determine the percentage recovery after two stages.

9. 1000 kg/h of a pyridine water solution containing 50% pyridine is to be reduced to 10% by using Chlorobenzene in a countercurrent extraction battery. (i) Determine the minimum solvent requirement. By using twice the minimum rate of solvent, estimate the number of stages needed.

Chlorobenzene layer		*Water layer*	
Pyridine	*Chlorobenzene*	*Pyridine*	*Chlorobenzene*
0	99.5	0	0.08
11.05	88.28	5.02	0.16
18.95	79.9	11.05	0.24
24.1	74.28	18.9	0.38
28.6	69.15	25.5	0.58
31.55	65.58	36.1	1.85
35.08	61	44.95	4.18
40.6	53	53.2	8.9
49	37.8	49	37.8

10. Repeat problem 9 for a cross-current operation using solvent equivalent to the amount of Raffinate/feed entering each stage and estimate the number of stages needed.

11. 1000 kg/h of a solution of *C* in *A* containing 10% *C* by weight is to be countercurrently extracted with 500 kg/hr of solvent *B*. The components *A* and *B* are insoluble. The equilibrium distribution of component *C* between *A* and *B* are as follows:

Wt. of *C*/Wt. of *A*	0.05	0.20	0.30	0.45	0.50	0.54
Wt. of *C*/Wt. of *B*	0.25	0.40	0.50	0.65	0.70	0.74

How many theoretical stages will be required to reduce the concentration of C in A to 2%?

12. Acetone is to be recovered from dilute aqueous solutions by liquid–liquid extraction using toluene as solvent. The acetone concentration in the feed solution is 0.05 kmol/m^3 and 90% of this acetone is to be extracted by countercurrent operation. The flow rate of aqueous phase is 1.5 m^3/min. The equilibrium distribution ratio of acetone in the solvent and in the aqueous phase could be described by the relation, $y = 1.5x$, where x and y are weight fraction units.

13. Nicotine in a water solution containing 1% nicotine is to be extracted with kerosene at 20°C. Kerosene and water are insoluble. Determine the number of stage needed if 100 kilogram of feed solution is extracted once with 1.6 times the minimum amount of solvent to recover 95% nicotine.

Equilibrium data:

X	0	0.00101	0.00246	0.00502	0.00751	0.00998	0.0204
Y	0	0.00081	0.001962	0.00456	0.00686	0.00913	0.0187

where X is kg nicotine/kg water and Y is kg nicotine/kg kerosene.

14. 100 kg/h of a water–dioxane solution containing 15% dioxane is to be continuously and countercurrently extracted with benzene at 25°C to recover 95% dioxane. Water and benzene are essentially insoluble and the equilibrium distribution of dioxane between them are as follows:

Dioxane in water wt. %	5.1	18.9	25.2
Dioxane in benzene wt. %	5.2	22.5	32.0

(i) Determine the number of theoretical stages if the solvent rate is 1.5 times the minimum. (ii) If the same operation is done in a three-stage cross-current battery with 60 kg of solvent in each stage, estimate the required number of stages.

11

LEACHING

11.1 INTRODUCTION

Leaching is one of the oldest operations in chemical industries which involves the use of a solvent to remove a solute from a solid mixture. Though originally it was referred to the percolation of liquid through a bed of solids, it is now used to refer the operations by other contacting means also. *Lixiviation* is used for the leaching of alkali from wood ashes. *Decoction* refers to the operation where the solvent at its boiling is used. Whenever the solute material is present largely on the surface of an insoluble solid and is merely washed off by the solvent, the operation is called *elutriation or elution.*

It is one of the most important operations in metallurgical industries for the extraction of metals from ores of Al, Ni, Co, Mn and Zn. It is also used for the extraction of sugar from sugar beets with hot water, extraction of oil from oil seeds using organic solvents, removal of tannin from various tree barks by leaching with water, preparation of tea and coffee and extraction of many pharmaceutical products from plant roots and leaves.

The success of this operation depends on the proper preparation of the given solid. Depending on the nature of solid, the solid is crushed and ground to desired size to accelerate the leaching action. For example, a certain copper takes about 6 hours if crushed to – 60 mesh size and about 5 days for a size of 6 mm. Gold is sparsely distributed in its ore. Hence it is crushed to – 100 mesh size to have an effective leaching. Sugar beets are cut into thin wedge shaped slices called cassettes before leaching to enable the solvent water to reach the individual plant cells. In the manufacture of pharmaceutical products from plants they are dried in order to rupture the cell walls so that solvent can reach the solute easily. Vegetable seeds when used for the extraction of oil are crushed to a size of 0.15 to 0.5 mm to enable easier extraction. However, when the solid is present on the surface, no grinding or crushing is necessary and the particles can be washed directly.
To summarize, the leaching action depends on:

- The nature of solid/cell structure.

- Diffusion of solute from the material to surface and then to the bulk of the solution.
- Particle size and its distribution.
- Solubility of solute in solvent and the temperature of operation.

11.2 UNSTEADY STATE OPERATION

These operations are carried out batchwise or semibatchwise.

11.2.1 In Place (in-situ) Leaching

This operation is also called *solution mining* which refers to the percolation leaching of minerals in place at a mine, by circulation of the solvent over and through the ore bed. This technique is adopted for the leaching of low-grade copper. In these operations, the solvent/reagent is injected continuously through one set of pipes drilled down to the ore and the resulting solution is pumped out through another set of pipes. Alternatively, the solvent/reagent can be pumped into the ore bed intermittently and withdrawn through the same well. In this technique crushing and grinding of ore are avoided. In place leaching also called in-situ leaching is shown in Fig. 11.1.

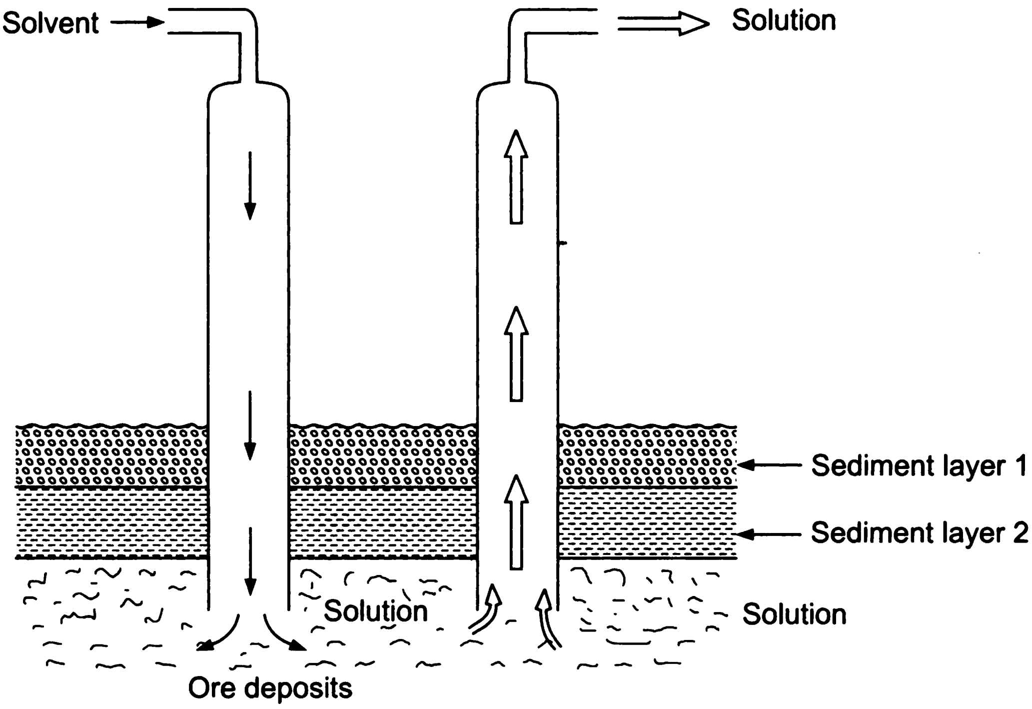


Fig. 11.1 In situ leaching.

11.2.2 Heap Leaching

Low-grade ores can be easily leached by this technique where the ore is gathered as a heap upon impervious ground. The leach liquor is pumped over the ore, which percolates through the heap and collected as it drains from the heap. This technique is used for the extraction of copper and uranium from their low grade ores. Heap leaching is shown in Fig. 11.2.

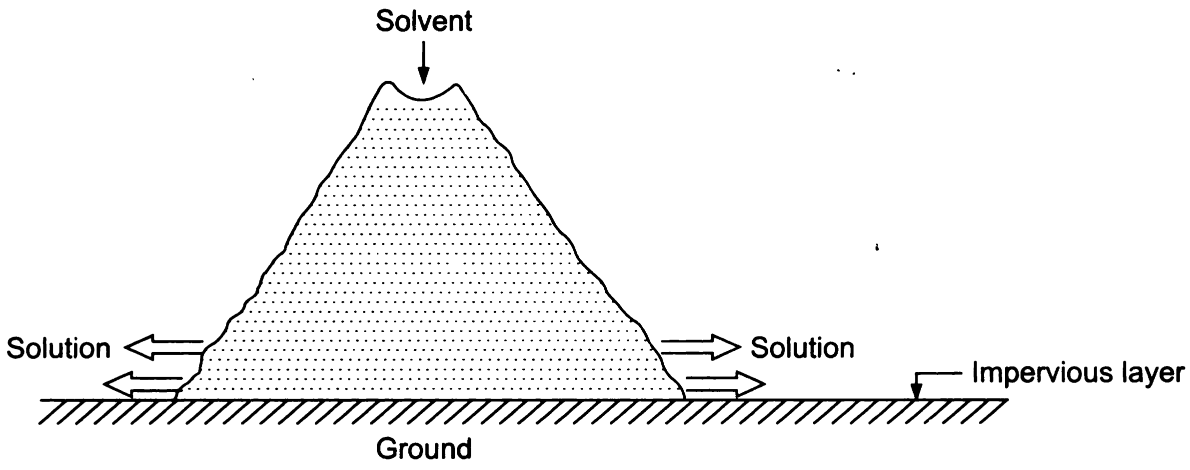


Fig. 11.2 Heap leaching.

11.2.3 Percolation Tank

Whenever small tanks are to be used, they can be made of metal or wood. The solid particles to be leached, rest on a false bottom which could be made of wood strips and may be covered by a coconut matting and a tightly stretched canvas filter cloth. The leach liquor flows to a collection pipe leading from the bottom of the tank. A very large percolation tanks are made of reinforced concrete and lined with lead or bituminous mastic. Small tanks may be provided with side doors near the bottom for removing the leached solid while the large tanks are emptied by excavating from the top. It is always preferable to fill the tanks with particles of uniform size so that voids will be more and the pressure drop required for flow of leaching liquid is least. This also leads to uniform leaching of individual particles.

For these operations the crushed solids may be filled in the tank initially and then the solvent is allowed to enter in. The solid and solvent may remain in contact with each other for a specified amount of time and then drained. During the process, if necessary, the liquid can also be circulated through the bed. The liquid can also be allowed to enter in continuously and also drained continuously. The liquid from the exit can also be recirculated, if necessary. The flow of liquid could either be downwards or upwards with proper distribution of liquid. Percolation tank is shown in Fig. 11.3.

11.2.4 Countercurrent Contact

At times, one is interested in getting a strong solution, which can be obtained by a countercurrent operation. This arrangement, also called *Shanks system*, contains number of tanks as shown in Fig. 11.4. The number of tanks generally vary from 6 to 16. In a typical system with 8 tanks at a particular time, tank 8 is empty and tanks 1 to 7 contain solids. Fresh solvent enters tank 1, where the solid has spent maximum amount of time and the material in tank 2, 3, 4, 5, 6 and 7 have progressively spent lesser time. The material in 7th tank has spent the least amount of time. The solution withdrawn from the 7th tank has the maximum solute concentration because the solution comes after contact with fresh solids. The solution withdrawn from tank 1 goes to tank 2, from tank 2 to tank 3, ..., tank 6

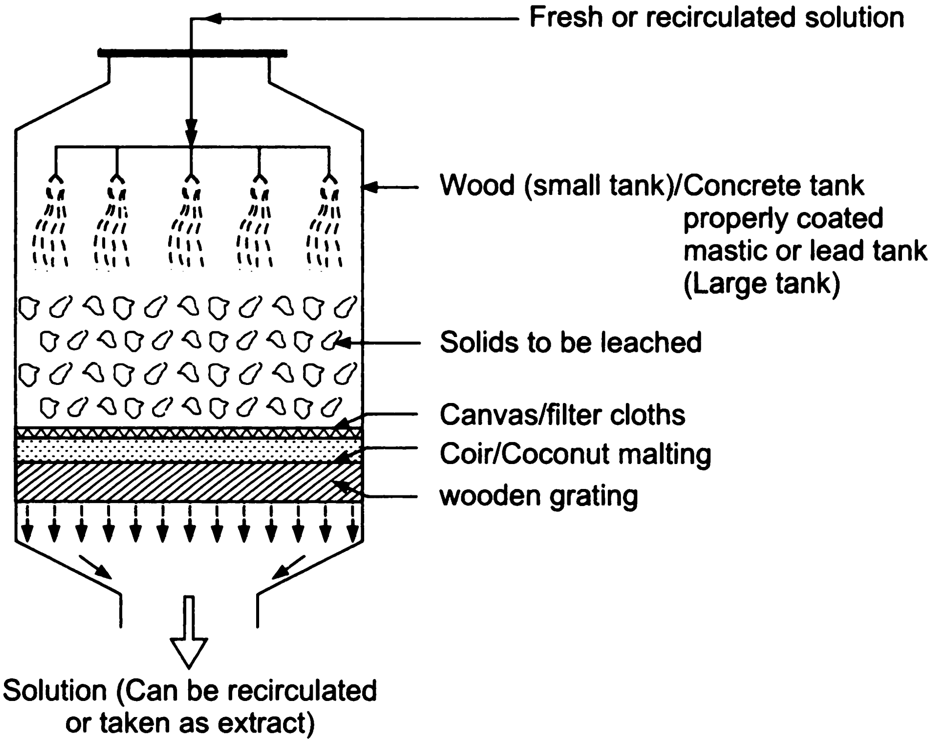


Fig. 11.3 Percolation tank.

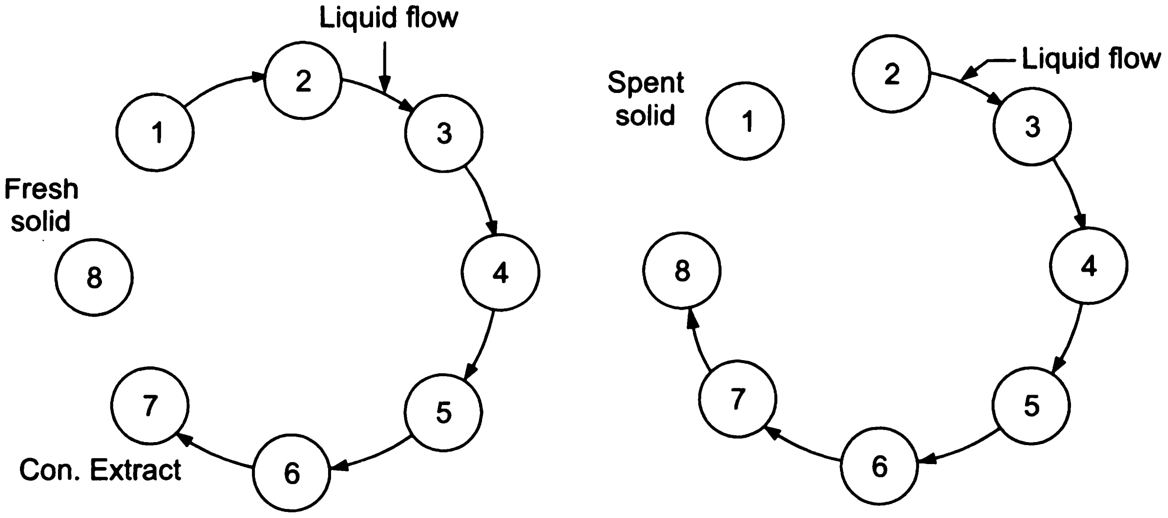


Fig. 11.4 Countercurrent system–shanks system.

to tank 7. The leached solid is discarded from tank 1 and fresh solid is now added in tank 8. The solution is transferred from tank 7 to 8, 6 to 7, 5 to 6, ..., 2 to 3. Here the fresh solvent is added in tank 2, and the solid from tank 2 is finally discarded. The solution now obtained from tank '8' will have maximum solute concentration. Tank 1 which is now empty will be loaded with a fresh batch of solids. This is nothing but advancing the tanks by one. The operation is continued in this manner by keeping successive tanks as the first tank in which the fresh solvent enters. The solids move counter currently to liquid flow.

11.2.5 Percolations in Closed Vessels

At times the pressure drop for flow of liquids by gravity is high or the solvent is highly volatile. Under such circumstances the liquid is pumped through the bed of solids in vessels called diffusers. The main advantage of these units is the prevention of evaporation losses of solvent, when they are operated above the boiling point of solvent (e.g. leaching of tannins using water at 120°C, 345 kN/m^2).

11.2.6 Filter–Press Leaching

When the solids are in finely divided form, percolation tanks are not suitable. Under such circumstances, solids can be filtered and leached in the filter press by pumping the solvent through the press cake. This is also a common feature while washing the filtered cakes.

11.2.7 Agitated Vessels

These are either vertical or horizontal closed cylindrical vessels with power-driven paddles or stirrers on vertical or horizontal shafts. They have a provision at the bottom for the withdrawal of leach solution at the end of the operation. In some of the designs, the horizontal drum is the extraction vessel, and the solid and liquid are tumbled about inside by rotation of the drum on rollers. They are operated on batch basis and each one is a single leaching stage. They can also be used in series for a multistage operation. For the leaching of finely divided solids, Pachuca tank is used. This finds extensive use in metallurgical industries. These tanks are constructed with wood, metal or concrete and lined with suitable material depending on the nature of leaching liquid. Agitation is accomplished by air lift. The bubbles rising through the central tube cause the upward flow of liquid and suspended solid in the tube and hence circulation of the mixture. Conventional mechanical agitators are also used for this purpose. Once the desired leaching is achieved, the agitation is stopped, the solids are allowed to settle and the clear supernatant liquid is decanted by siphoning over the top of the tank or by withdrawal through discharge pipes placed at appropriate level in the side of the tank. Whenever, the solids settled form a compressible sludge, the solution retained will be more and generally the last traces of solute in such cases are recovered in countercurrent manner.

11.2.8 Features of Percolation and Agitation Techniques

If a solid is in the form of big lumps, the question that arises is whether one should go in for percolation technique or agitation–settling technique. The problem is quite complicated due to the diverse leaching characteristics of the various solids and the value of solute. However, the following points are worth considering.

Though fine grinding is more costly and provides more rapid and possibly more thorough leaching, the quantity of liquid associated with the settled solid is very large. Hence, one may have to use large quantity of solvent to recover as much solute as possible. The composited extract thus obtained could be dilute. Coarsely ground particles, on the other hand, leach more slowly and possibly less thoroughly and may retain lesser quantity of solution. They may also require lesser washing and hence the extract could be a concentrated one due to the use of lesser quantity of solvent.

Practical results have shown that leaching in an agitated vessel is more effective than by percolation for a fibrous solid like sugar cane.

Hence, one may have to decide based on the economy and the case of operation.

11.3 STEADY STATE OPERATIONS

They are classified as stagewise or continuous contact operations. Stagewise equipment are sometimes assembled in multiple units to produce multistage effects, whereas, continuous contact equipment provide the equivalent of many stages in a single unit. Some of the solids may also require grinding in order to make the soluble portions accessible to the leaching solvents. In fact, wet grinding is an operation during which some leaching could be accomplished. For example, 50 to 75% of the soluble gold may be dissolved by grinding the ore in the presence of cyanide solution. Castor oil is also extracted suitably in an attrition mill with solvent.

11.3.1 Agitated Vessels

Finely ground solids which can be readily suspended in liquids by agitation can be handled in agitated vessels. These must be arranged for continuous flow of both liquid and solid in and out of the tank. Care must be taken to ensure that no accumulation of solid occurs. Due to thorough mixing, equilibrium is always there between the solid and liquid. The agitated vessels discussed earlier can also be used.

The average holding time can be estimated both for solids and liquids separately in an agitated vessel by dividing the vessel contents by the rate of flow of solids and liquids. The average holding time should be adequate to provide the required leaching action. Short circuiting is a disadvantage encountered which can be eliminated by passing the solid–liquid mixture through a series of smaller agitated vessels such that the cumulative holding time is the required leach time. The effluent from continuous agitators are sent to a filter for separating liquid from solid upon which the solid may be washed free of dissolved solids, or to a series of thickeners for countercurrent washing.

11.3.2 Thickeners

There are mechanical devices which are meant for increasing the ratio of solid to liquid in a suspension of finely-sized particles by settling and decanting, thus producing a thickened sludge and a clear supernatant liquid. They are generally installed before any filter to minimize the filtering costs. Since both effluents can be pumped and transported, thickeners are frequently used to wash leached solids and chemical precipitates free of adhering solution in a continuous multistage countercurrent arrangement and hence worth their use in leaching operations also.

The liquid content in the sludge varies from 15 to 75% and is greatly dependent on the nature of the solids and liquids and upon the time allowed for settling. This is shown in Fig. 11.5.

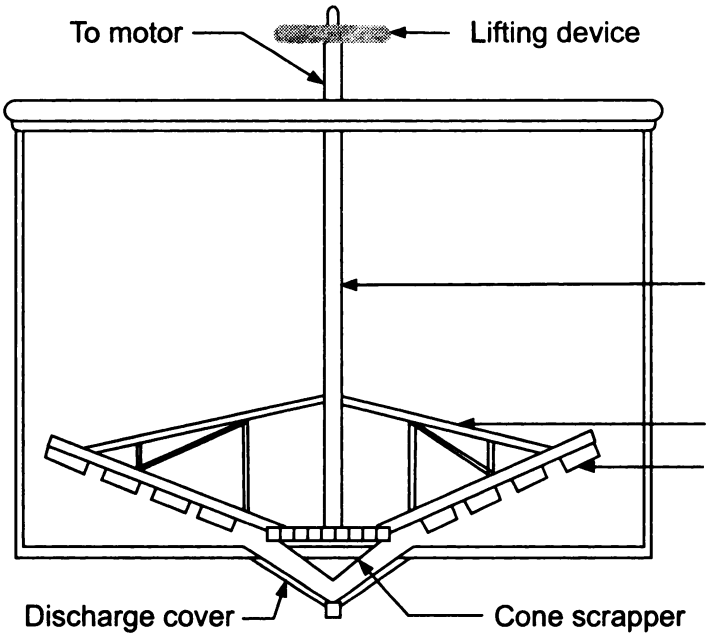


Fig. 11.5 Thickeners.

11.3.3 Continuous Countercurrent Decantation

It is an arrangement involving both the thickeners and agitators/grinders. The solids enter the first set of agitators/grinders and are mixed with overflow liquid from the 2nd thickener. Then the contents after through agitation/grinding enter the 1st thickener. The agitators along with thickener constitute the first stage. The sludge from the first thickener passes on to the 2nd thickener where it is mixed with overflow from the 3rd thickener and the sludge is then transferred to 3rd thickener where it is mixed with overflow liquid from 4th. Fresh solvent enters the last thickener. The overflow liquid taken out from the first thickener will have the maximum concentration of solute. If necessary the sludge from each stage can be thoroughly agitated with the solvent in order to effect better separation. This is shown in Fig. 11.6.

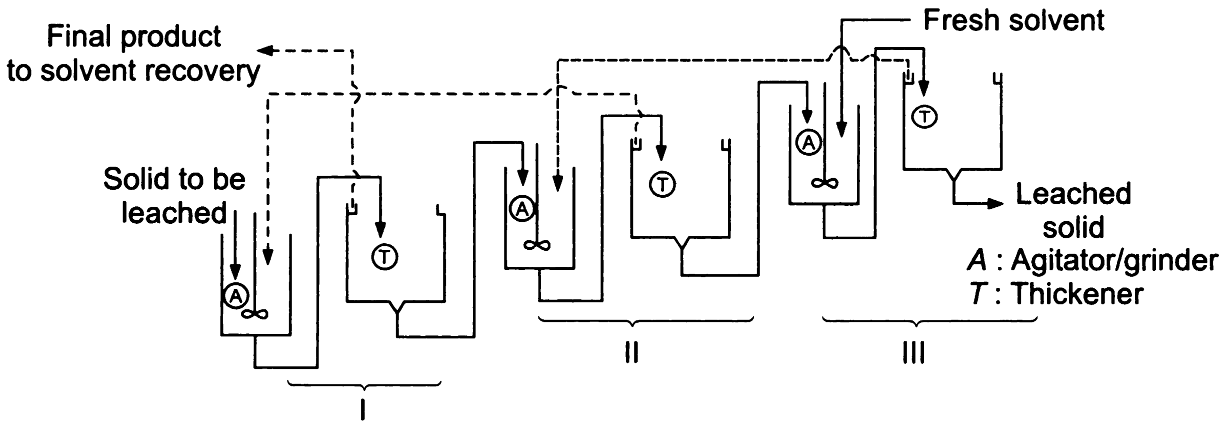


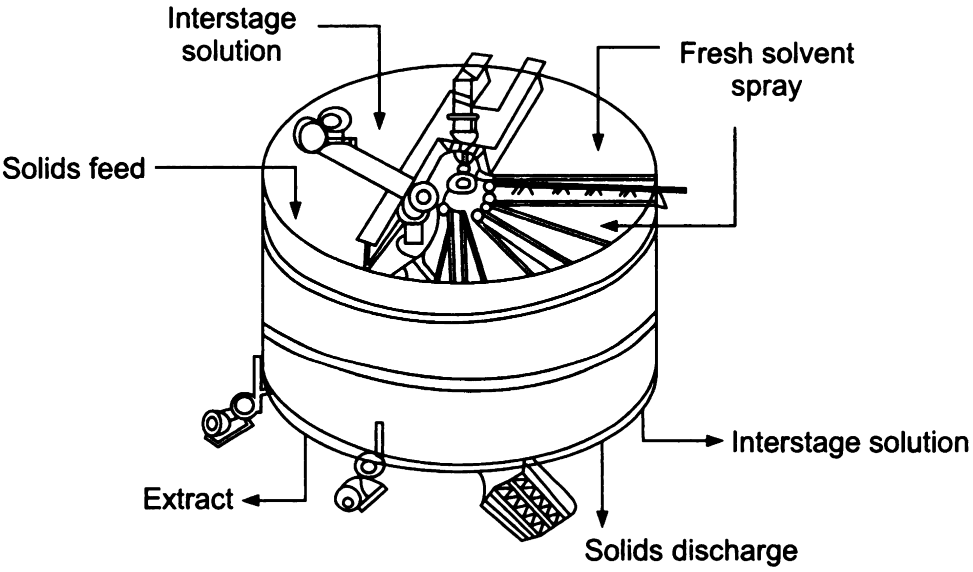
Fig. 11.6 Continuous countercurrent decantation.

11.3.4 Leaching of Vegetable Seeds

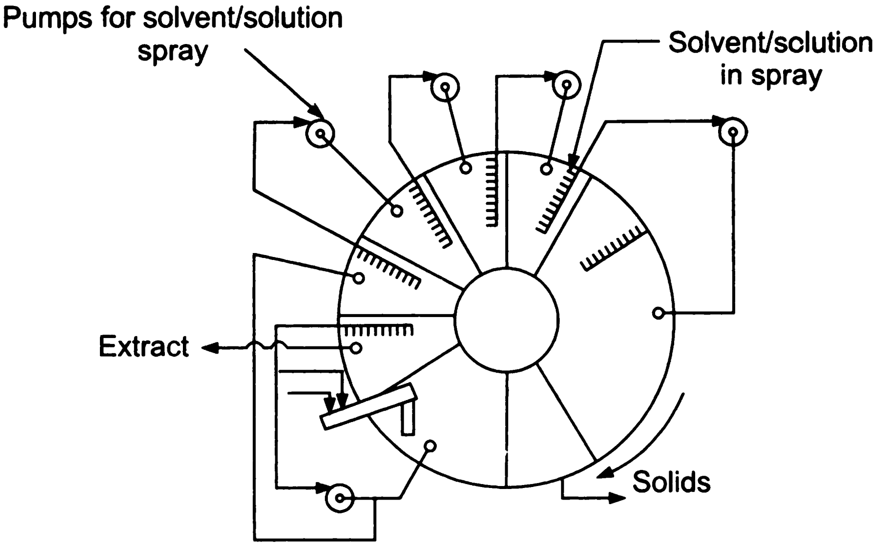
Soya beans, cotton seeds, rice bran and castor seeds are some of the products regularly leached with an organic solvent for removing the oil present in them. The process involves dehulling, precooking, adjustment of water content and flaking. In some cases solvent extraction of oil is preceded by mechanical expression of oil from oil seeds. Leaching solvents are generally petroleum fractions. Chlorinated hydrocarbons leave the residue meal a toxic one. The oil-solvent solution containing a small amount of finely divided suspended solids is called *miscella* and the leached solid is called *marc.*

11.3.4.1 Rotocel extractor

It is a modification of shanks system wherein the leaching tanks are continuously moved, permitting a continuous introduction and discharge of solids. It is shown in Fig. 11.7(a) and (b).



(a) Rotocel extractor (front view).



(b) Rotocel extractor (top view).

Fig. 11.7

It consists of a circular shell partitioned into several cells each fitted with a hinged screen bottom for supporting the solids. This shell slowly revolves above a stationary compartmented tank. As the rotor revolves, each cell passes in turn under the prepared solids feeder and then under a series of sprays by which the contents in each cell is periodically drenched with solvent for leaching. By the time one rotation is completed, when the leaching is expected to be completed, the leached solids of each cell are automatically dumped into one of the lower stationary compartments, from which they are continuously conveyed away. The solvent sprayed over each cell filled with solids, percolates downward through the solid and supporting screen into the appropriate compartment of the lower tank from which it is pumped to the next spray. The leaching is countercurrent, and the strongest solution comes from the cell which is filled with fresh solid. It is essential to maintain the equipment properly to ensure smooth operation. It is also enclosed in a vapour tight housing to prevent the escaping of solvent vapours.

11.3.4.2 Kennedy extractor

A schematic arrangement is shown in Fig. 11.8. It is a stagewise device, originally used for leaching tannins from tan bark. The solids are leached in a series of tubs and are pushed from one to next in the cascade by perforated paddles, while the solvent flows in countercurrent direction. Perforations in paddles permit drainage of liquid from solids between stages, and the solids are scrapped from each paddle as shown in Fig. 11.8. The number of tubs depends on the nature of solid, solvent and the level of extraction desired. Since it has a horizontal orientation, more floor space is required.

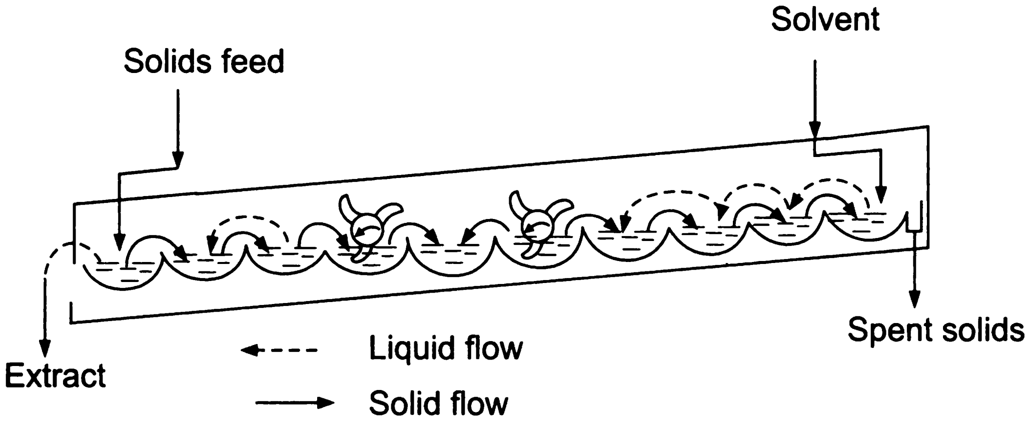


Fig. 11.8 Kennedy extractor.

11.3.4.3 Bollman extractor

It has a vertical orientation and has several perforated baskets attached to a chain conveyor for conveying solids. As the chain descends, the solids are leached in parallel flow by a dilute solvent – oil solution, called *half miscella*, pumped from the bottom of the vessel and sprayed over the baskets at the top. The liquid percolates through the solids from basket to basket and collects at the bottom as a final strong solution called *full miscella* and is withdrawn. On the ascent, the solids are leached countercurrently by a spray of fresh solvent and the product is called *half miscella.* A short drainage time is provided before leached solid in the baskets are dumped at the top. A schematic arrangement is shown in Fig. 11.9.

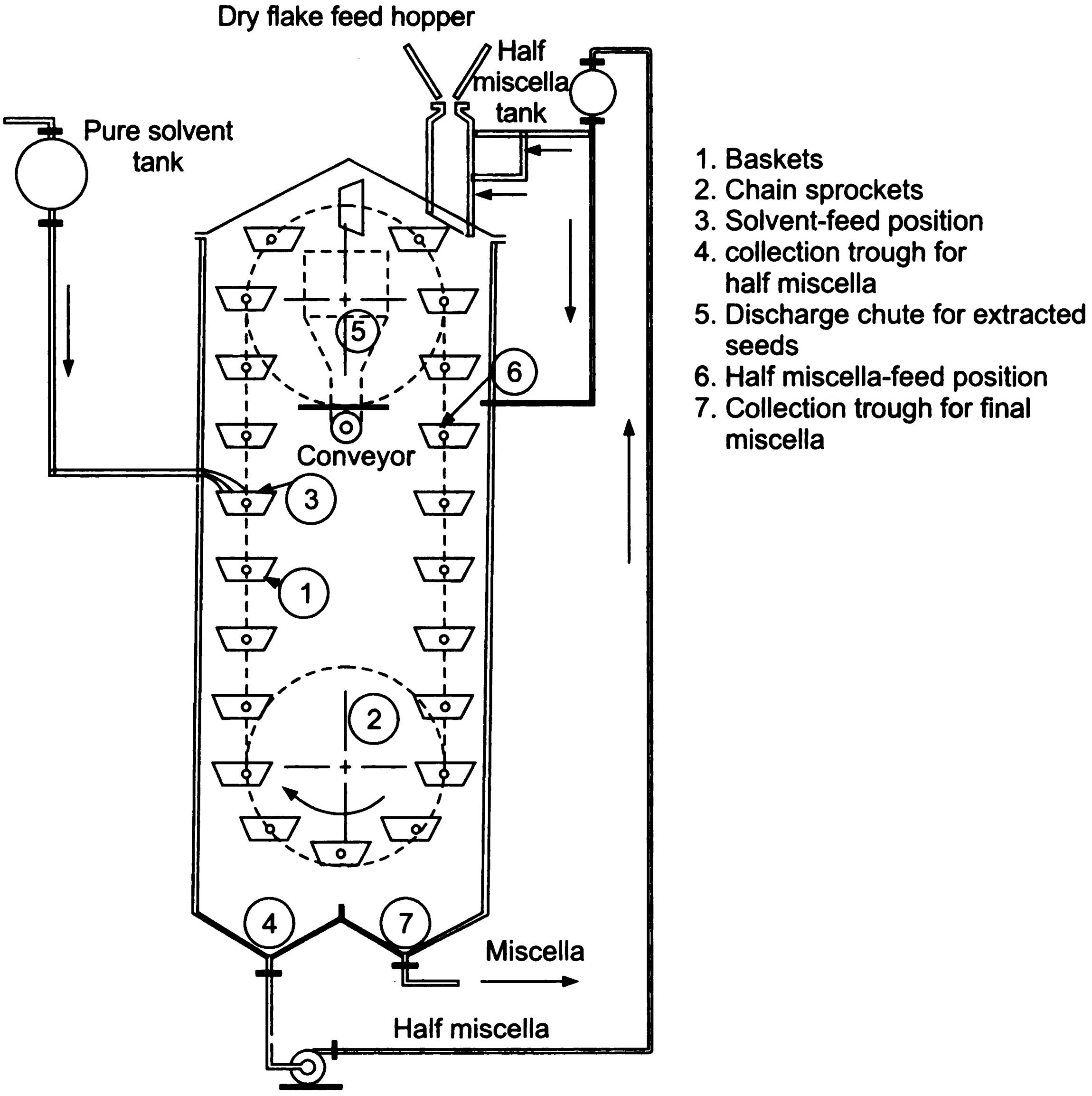


Fig. 11.9 Bollman extractor.

11.3.4.4 Continuous horizontal filter

A schematic arrangement of continuous horizontal filter is shown in Fig. 11.10. The filter in the form of a circular wheel is divided into a number of sectors and revolves in the horizontal plane. Here prepared seeds are slurried with solvent which has already been used for leaching, and the slurry is sent to the filter. The

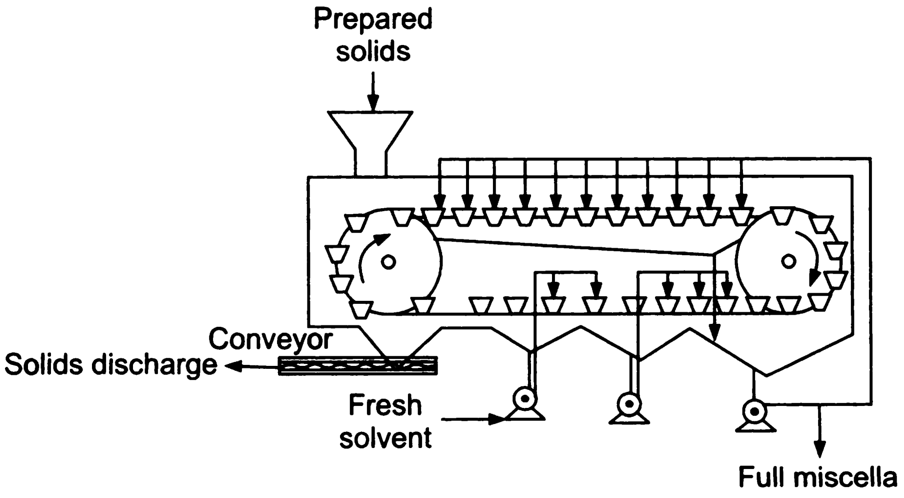


Fig. 11.10 Continuous horizontal filter.

first filtrate is passed again through the filter cake to remove finely divided solids (polishing) before being discharged as miscella. The principle behind the operation is quite similar to Rotocel extractor.

11.3.4.5 Recovery of oil

The recovery of solvent from both the miscella and leached solids is an essential feature in these operations. Recovery of oil in miscella is accomplished by evaporation of solvent and if necessary by further stripping in a tray column to remove the solvent–free oil. The oil in solid is removed by steaming and subsequent cooling. Vent gas from condensers can be sent to an absorber and scrubbed with petroleum white oil and the resulting mixture can be stripped to recover the solvent.

11.4 DEFINITIONS

Let, B = insoluble solid or inert solid (kg),
C = soluble solute (kg),
A = pure solvent (kg),

$x = \frac{C}{A+C}$; Weight fraction of solute in effluent solution (on B free basis)

$y = \frac{C}{A+C}$; Weight fraction of solute in the solid or slurry or sludge (on B free basis)

$N = \frac{B}{A+C}$; (in each phase)

The variation of N, x and y under different conditions are as follows:

(a) For a dry solid (free from solvent) $N = \frac{B}{C}$ $(\because\ A = 0)$
$y = 1.0$

(b) Solid free from solvent and solute $N = \infty$ $(\because\ A = 0;\ C = 0)$

(c) Pure solvent $x = 0,\ N = 0$ $(\because\ B = 0;\ C = 0)$

11.5 DIFFERENT TYPES OF EQUILIBRIUM DIAGRAMS

11.5.1 Type 1

A typical trend of N vs x, y and equilibrium relationship is shown in Fig. 11.11(a) characteristics of such systems are:

- Preferential adsorption of the solute occurs on solid.
- Solute is soluble in the solid B and distributes unequally between liquid and solid phases at equilibrium.
- Insufficient contact time between solute and solvent.
- EF is a tie line.

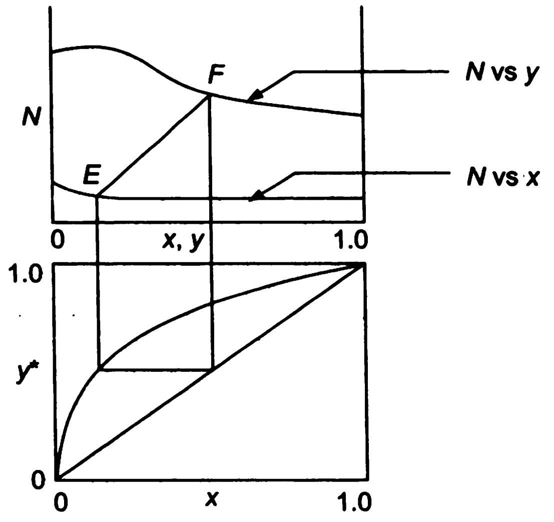


Fig. 11.11(a) Type I equilibrium.

11.5.2 Type II

A typical trend of N vs x, y and equilibrium relationship is shown in Fig. 11.11(b). The characteristics of such systems are:

- No adsorption of solute occurs.
- Solution withdrawn and the solution associated with the solid have the same composition.
- Tie lines are vertical.
- The distribution coefficient is unity.
- Solids are drained to the same extent at all solute concentrations and such a condition is known as *constant underflow condition.*
- No B is present in solution either dissolved or suspended.
-

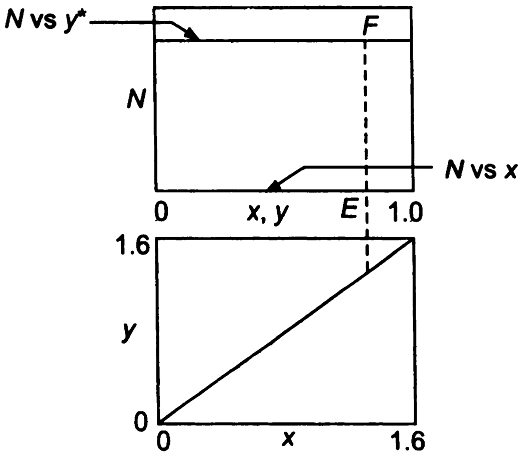


Fig. 11.11(b) Type II rquilibrium.

11.5.3 Type III

A typical trend of N vs x, y and equilibrium relationship is shown in Fig. 11.11(c). The characteristics of such systems are:

- Solute C has a limited solubility x_S in solvent A and one can never have a clear (leach) solution stronger than x_S.
- Tie lines joining slurry and saturated solution converge as shown.
- Till the concentration of x_S is reached, the solution retained in the solid and

the clear solution have some concentration and hence the distribution coefficient is unity, i.e. up to the tie line FE. No adsorption of solute occurs.

- The tie lines to the right of FE indicate the same solute concentration in clear solution but a different solute concentration in slurry as indicated by points G, H.

In practice we come across situations which will fall in any one of the above three types.

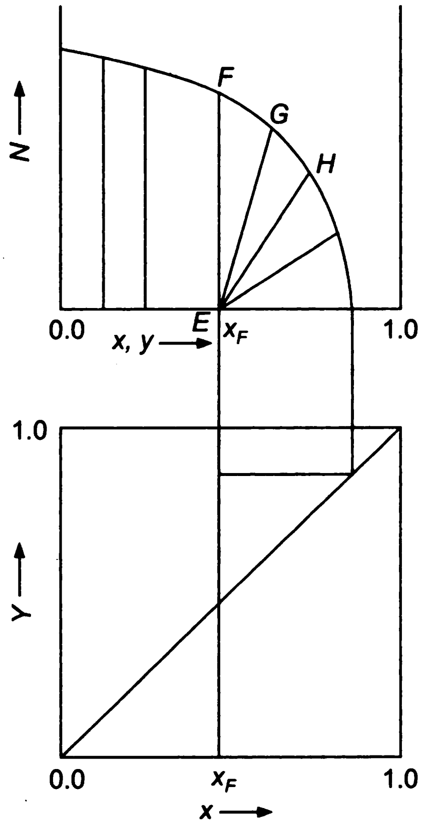


Fig. 11.11(c) Type III equilibrium.

11.6 SINGLE STAGE OPERATION

A typical single stage operation is shown in Fig. 11.2. The characteristics of various streams flowing into and out of the system are also shown. The flow rate of streams are on B free basis.

(All the streams are on absolute mass basis)

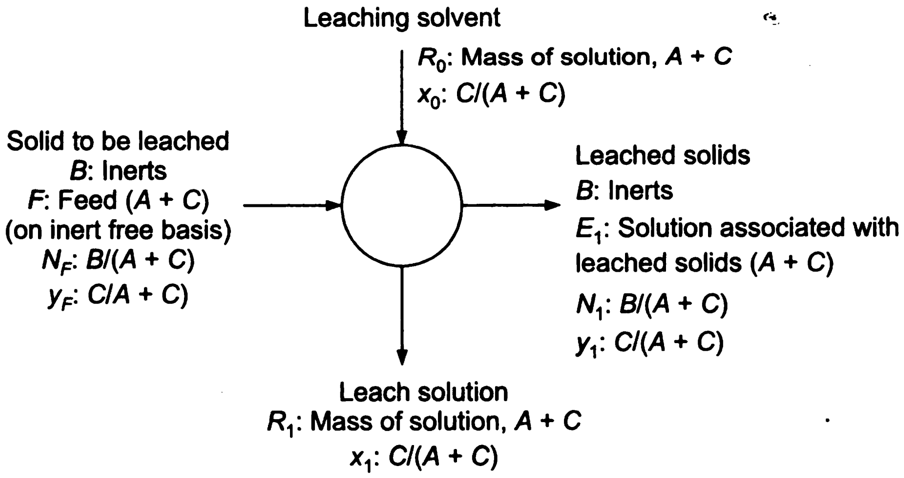


Fig. 11.12 Streams in a leaching operation.

$$N_F = \frac{B}{A+C} = \frac{B}{F}$$

$$N_1 = \frac{B}{A+C} = \frac{B}{E_1}$$

$$\therefore \qquad B = N_F \cdot F = E_1 N_1$$

Total material balance gives,

$$F + R_0 = E_1 + R_1 = M_1$$

Solute balance gives,

$$F y_F + R_0 x_0 = E_1 y_1 + R_1 x_1$$

Solvent balance gives

$$F\,(1 - y_F) + R_0\,(1 - x_0) = E_1\,(1 - y_1) + R_1\,(1 - x_1)$$

When the solids and the solvent are mixed together in a stage (say, stage 1), the effective value of 'N', called N_{M_1}, will be given by

$$N_{M_1} = \frac{B}{F + R_0} = \frac{B}{M_1}$$

Similarly the concentration of solute after thorough mixing in the stages is given by,

$$y_{M_1} = \frac{y_F F + R_0 X_0}{F + R_0}$$

Using the values of y_{M_1}, N_{M_1} and N vs. x, y diagram, one can determine the concentration and flow rates of leaving streams as indicated below.

(The co-ordinates (y_{M_1}, N_{M_1}) can be represented as shown in Fig. 11.13 in N vs x, y diagram).

Steps

(i) Draw the N vs x, y diagram.
(ii) Draw the distribution curve.
(iii) Locate F (y_F, N_F) and R_0 (x_0, N_0).
(iv) Join $R_0 F$.
(v) Locate M_1 (y_{M_1}, N_{M_1}) in R_0F line.
(vi) Draw the tie line R_1E_1 passing through M_1 with the help of distribution curve and read N_1 from N vs y curve.
(vii) $E_1 = B/N_1$ (weight of solution associated with sludge)

We know that,

$$F + R_0 = E_1 + R_1$$

Hence, R_1, the weight of clear solution can be estimated.

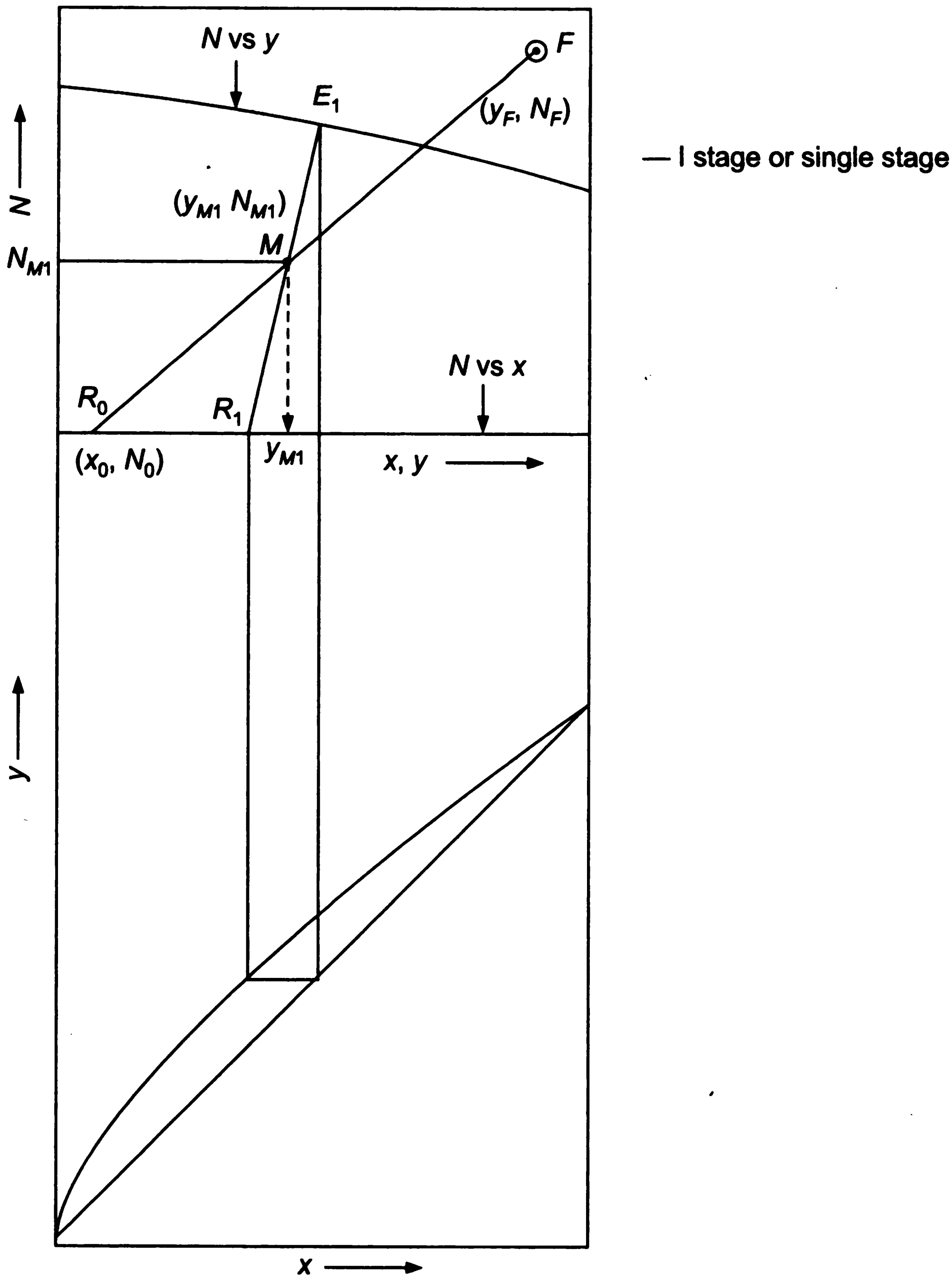


Fig. 11.13 Single stage operation.

11.7 MULTISTAGE CROSS-CURRENT LEACHING

In a multistage cross-current leaching E_1 stream from the I stage becomes the feed stream for the II stage and the E_2 stream from the II stage becomes the feed stream for the III stage. In each stage the mixture is contacted with a fresh stream of solvent.

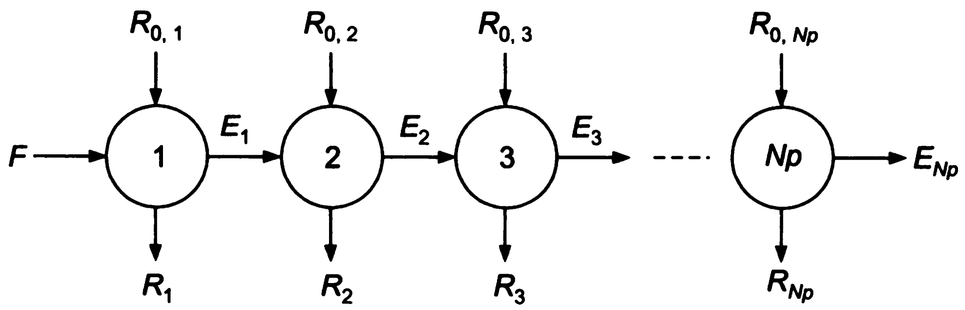


Fig. 11.14 A typical multistage cross-current operation.

Steps

(i) Proceed as per the procedure mentioned in steps (i) to (vii) of single stage operation of section 11.6.

(ii) Join E_1 with R_0 and locate M_2 (y_{M_2}, N_{M_2}). Generally R_{01}, R_{02}, R_{03}, ..., $R_{0,NP}$ are all same $R_{01} = R_{02} = R_{03} \ldots = R_{0,NP} = R_0$.

(iii) Draw the tie line E_2R_2 passing through M_2 and locate N_2.

(iv) $E_2 = \dfrac{B}{N_2}$

(v) We know from material balance, $E_1 + R_0 = E_2 + R_2$.

(vi) Hence, the unknown quantity R_2 (weight of clear solution) can be determined since the remaining quantities (E_1, R_0 and E_2) are all known.

(vii) Proceed in the same manner for other stages also.

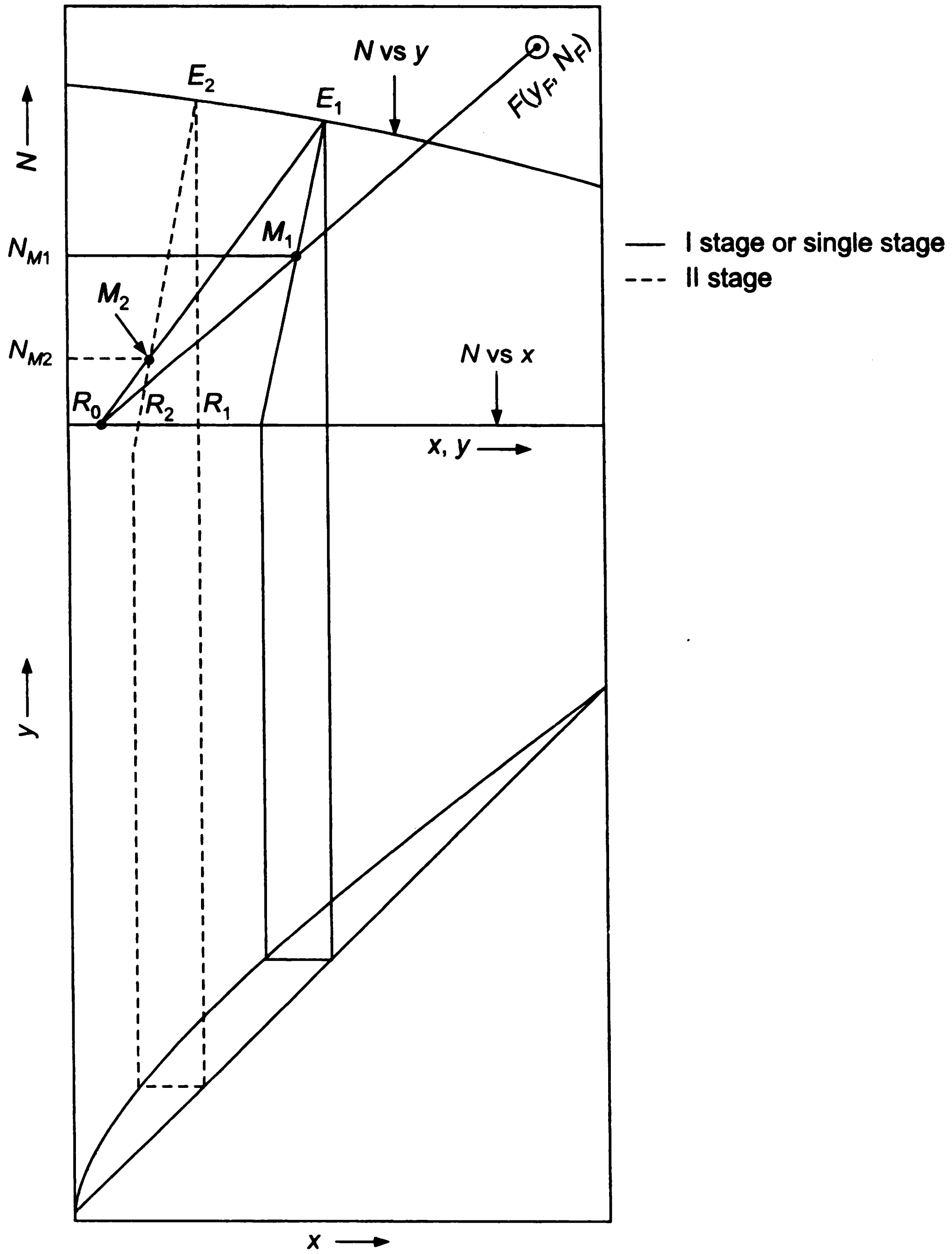


Fig. 11.15 Multistage cross-current operation.

11.8 MULTISTAGE COUNTERCURRENT OPERATION

Solution balance for the system as a whole gives,

$$F + R_{N_p+1} = R_1 + E_{N_p} = M$$

where M is the total mass of B (inert) free mixture.

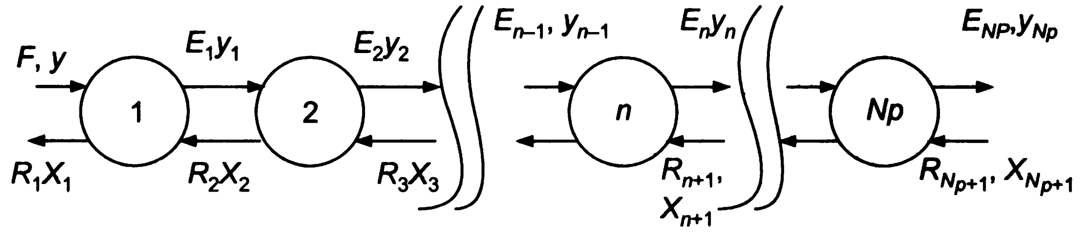


Fig. 11.16 A typical multistage countercurrent operation.

Solute balance gives,

$$F \cdot y_F + R_{N_p+1} \cdot X_{N_p+1} = R_1 x_1 + E_{N_p} \cdot y_{N_p} = M \cdot y_M$$

where,

$$N_M = \frac{B}{F + R_{N_p+1}}$$

$$y_M = \frac{F y_F + R_{N_p+1} X_{N_p+1}}{F + R_{N_p+1}}$$

$$F - R_1 = E_{N_p} - R_{N_p+1} = \Delta_R$$

A solution balance for the first two stages gives

$$F + R_2 = R_1 + E_1$$

i.e.

$$F - R_1 = E_1 - R_2 = \Delta_R.$$

Similarly a solution balance for the first two stages yields

$$F - R_1 = E_2 - R_3 = \Delta_R.$$

It clearly indicates that the difference in flow between streams at either ends in each stage remains constant.

In a typical operation, the number of stages (for a given recovery and a given amount of solvent) or concentration of solute in the leaving stream (for a given number of stages and solvent used) or the amount of solvent (for a given number of stages and percentage recovery) will be needed.

11.8.1 Analysis of Variable Underflow System

11.8.1.1 Case I

Determination of stages for a specified recovery or final concentration:

Steps

1. Draw N vs x and N vs y and the distribution curve.
2. Locate the points F, E_{N_p} and R_{N_p+1}.

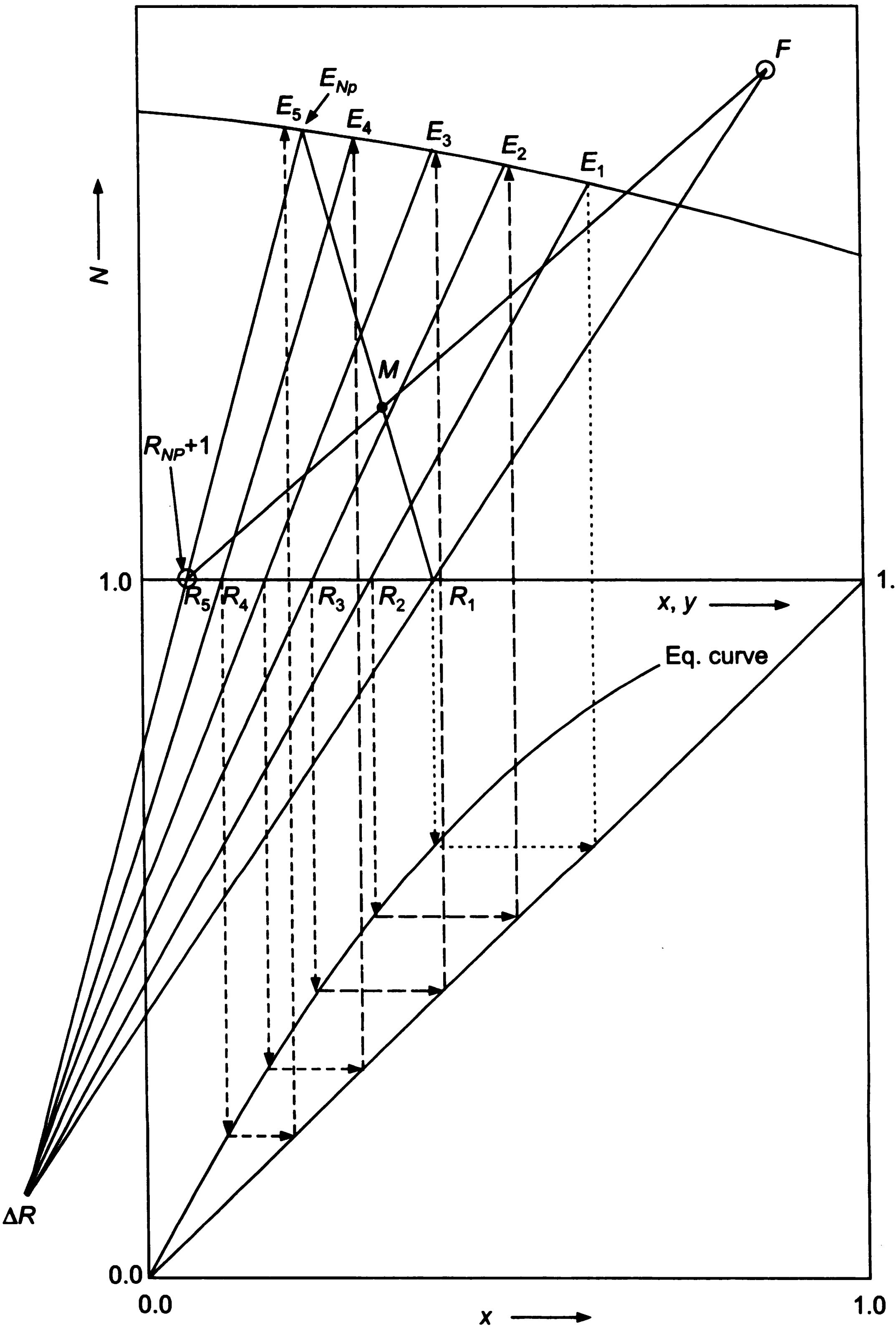


Fig. 11.17 Multistage countercurrent operation.

3. Estimate M (y_M, N_M) and locate it on FR_{N_p+1} line.
4. Join E_{N_p} with M and extend it to cut N vs x curve at R_1.
5. Join E_{N_p} with R_{N_p+1} and extend it.
6. Join F with R_1 and extend it to cut the $E_{N_p}R_{N_p+1}$ line and call the point of intersection as Δ_R.
7. Using R_1 and equilibrium curve, locate E_1. This corresponds to stage 1.
8. Join E_1 with Δ_R and this line cuts N vs x curve at R_2.

9. Using R_2 and equilibrium curve, locate E_2. This corresponds to stage 2.
10. Proceed in this manner till E_{N_p} is reached or crossed.
11. From this, the number of stages N_p can be determined.

11.8.1.2 Case II

If final concentration is needed or percentage recovery is needed for a given number of stages:

Assume some E_{N_p} value and proceed as mentioned above and verify whether the assumed E_{N_p} matches the given number of stages. If it does not match, assume a new value for E_{N_p} and proceed till the given number of stages and the assumed E_{N_p} value match.

11.8.1.3 Case III

If the solvent amount is needed:

Assume some solvent flow rate and check whether the E_{N_p} and stages match. If they do not match, assume a different value and proceed till the assumed E_{N_p} value and the given stages match.

11.8.1.4 Case IV

Minimum solvent requirement:

It is a specific solvent quantity at which the operating line becomes a tie line, i.e. FR_1 or E_1R_2 or E_2R_3, ..., becomes a tie line.

11.8.2 Number of Stages for a Constant Underflow System

The number of stages can be determined easily for constant underflow systems as the slope is constant ($m = y/x$) and operating line is straight, by using the Kremser, Brown and Souder's equation.

$$\frac{y_F - y_{N_p}}{y_1 - mx_{N_p+1}} = \frac{\left(\dfrac{R}{mE}\right)^{N_p+1} - \left(\dfrac{R}{mE}\right)}{\left(\dfrac{R}{mE}\right)^{N_p+1} - 1}$$

WORKED EXAMPLES

1. Oil is to be extracted from halibut liver in a countercurrent extraction battery. The entrainment of solution by the granulated liver mass is given below.

kg solution retained/ kg of exhausted liver	0.035	0.042	0.05	0.058	0.068	0.081	0.099	0.12
kg of oil/ kg of solution	0	0.1	0.2	0.3	0.4	0.5	0.6	0.68

In the extraction battery change is to be 100 kg based on completely exhausted liver. The unextracted liver contains 0.043 kg of oil/kg of exhausted material. 95% recovery is desired. The final extract is to contain 0.65 kg oil/kg of extract. The ether used as solvent is free from oil. How many kg of ether is needed per kg of liver? How many extractors are needed?

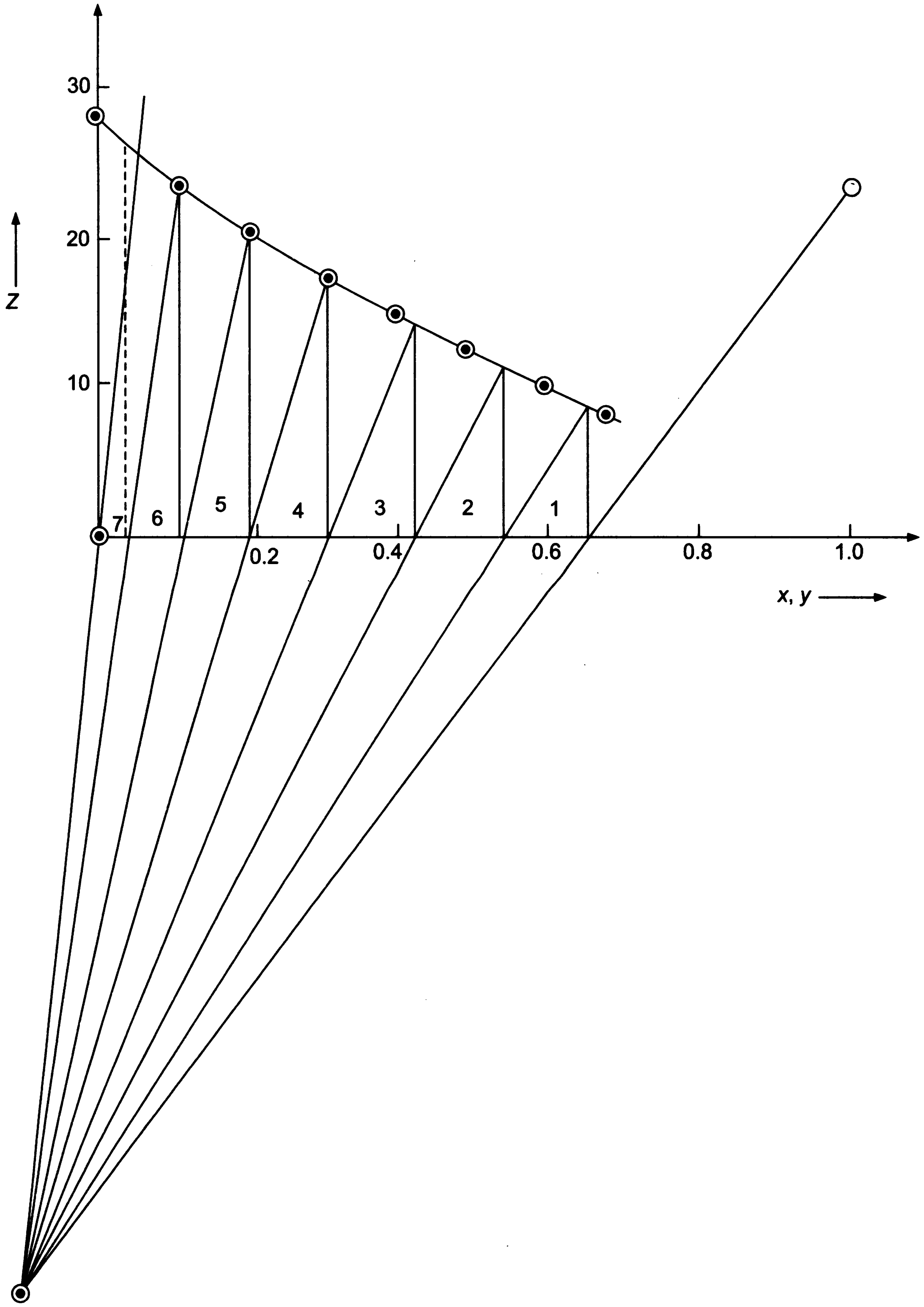


Fig. 11.18 Example 1.

Solution.

$\dfrac{\text{kg solution retained}}{\text{kg exhausted liver}}, 1/N$	0.035	0.042	0.05	0.058	0.068	0.081	0.099	0.12
$\dfrac{\text{kg oil}}{\text{kg solution}}, x, y$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.68
$N = \dfrac{\text{kg exhausted liver}}{\text{kg solution retained}}$	28.6	23.8	20.0	17.25	14.7	12.35	10.1	8.3

Basis: 100 kg of exhausted liver

i.e. $B = 100$ kg

$$C \text{ (oil)} = 100 \times 0.043 = 4.3 \text{ kg}$$

$$F = A + C$$

$$A = 0 \text{ (solvent is not present)}$$

$$N_F = \frac{B}{A+C} = \frac{100}{4.3} = 23.26$$

$$y_F = \frac{C}{A+C} = \frac{4.3}{0+4.3} = 1.0$$

∴ Feed point F is given by $(N_F, y_F) = (23.26, 1.0)$

The final extract contains 0.65 kg of oil/kg of extract

∴ R_1 is given by $(N_1, x_1) = (0, 0.65)$

R_{N_p+1} is given by $(N_{N_p+1}, x_{N_p+1}) = (0, 0)$

95% recovery of oil is to be achieved.

∴ 5% oil leaves with the liver.

i.e. oil leaving is 4.3 × 0.05 = 0.215 kg

$$\therefore \quad y_{N_p} = \frac{0.215}{A+0.215}$$

∴ E_{N_p} is given by (N_{Np}, y_{Np})

$$N_{Np} = \frac{B}{A+C} = \frac{100}{A+0.215}$$

$$\therefore \quad \text{Slope of operating line } \left(\frac{B}{A+C}\right) \Big/ \left(\frac{C}{A+C}\right) = \frac{100}{0.215} = 465$$

From the plot $E_{N_p} = (25.5, 0.055)$

Stages needed = 7.

$$N_{N_p} = 25.5 = \frac{B}{A+C}$$

$$\therefore \quad A + C = \frac{B}{25.5} = \frac{100}{25.5} = 3.92$$

$$y_{N_p} = 0.055 = \frac{C}{A+C}$$

$$A + C = 3.92$$

$$\therefore \quad A = 3.92 - C = 3.92 - 0.215 = 3.705 \text{ kg}$$

i.e. amount of solvent in liver = 3.705 kg

Quantity of ether used

Extract contains 0.65 kg oil/kg extract

i.e. Extract contains 0.35 kg ether/kg extract

$$R_1 = \frac{C}{A+C} = 0.65$$

But C, Oil in extract = Total oil fed – Oil in exhausted liver
= 4.3 – 0.215 = 4.085 kg

$$\therefore \quad R_1 = 0.65 = \frac{4.085}{A + 4.085}$$

$$\therefore \quad A = 2.2 \text{ kg}$$

∴ Total ether used = Amount in extract + Amount in exhausted liver
= 2.2 + 3.705 = 5.905 kg.

2. 10 tonnes/hour of day seashore sand containing 1% by weight of salt is to be washed with 10 tonnes/hour of fresh water running countercurrent to the sand through two classifiers in series. Assume perfect mixing of sand and water occurs in each classifier and that the sand discharged from each classifier contain one part of water for every two parts of sand by weight. If the washed sand is dried in kiln, what % of salt will it retain? What wash rate is required in a single classifier in order to wash the sand equally well?

Solution.

Let x be the fraction of salt in the underflow discharge from stage 1.

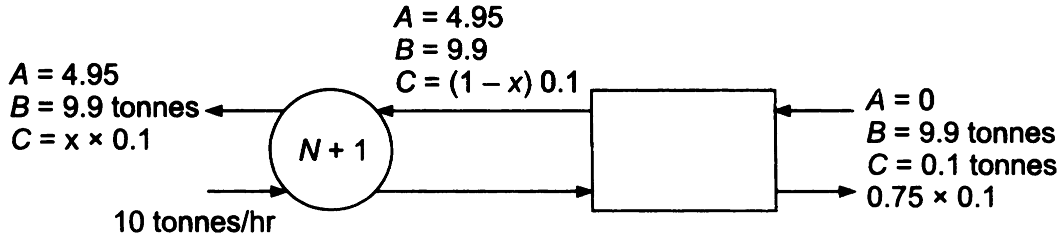


Fig. 11.19 Example 2.

Sand entering 9.9 tonnes/hour. Salt entering = 0.1 tonnes/hour. 1 part of sand discharged associated with 0.5 parts of water.

9.9 tonnes of sand leaving will be associated with 9.9/2 = 4.95 tonnes of water each stage.

By Coulson–Richardson method,

$$\frac{S_{n+1}}{S_1} = \frac{R-1}{R^{n+1}-1}$$

where S_1 = Quantity of solute in the sludge coming out from stage 1,
S_{n+1} = Quantity of solute in the sludge coming out from stage n + 1.

$$R = \frac{\text{Quantity of solution in overflow (solute or solvent)}}{\text{Quantity of solution in underflow (solute or solvent)}}$$

$$R = \frac{\text{weight of solution in overflow}}{\text{weight of soluton in underflow}} = \frac{10}{4.95} = 2.02$$

$$S_{n+1} = (x) \times (0.1)$$

$$S_1 = (1 - x) \times (0.1)$$

$$\therefore \quad = \frac{2.02 - 1}{(2.02)^2 - 1} = \frac{x}{(1 - x)} = \frac{1.02}{3.08}$$

$$\therefore \quad 3.02 = \frac{1 - x}{x}$$

$$\therefore \quad x = 0.249$$

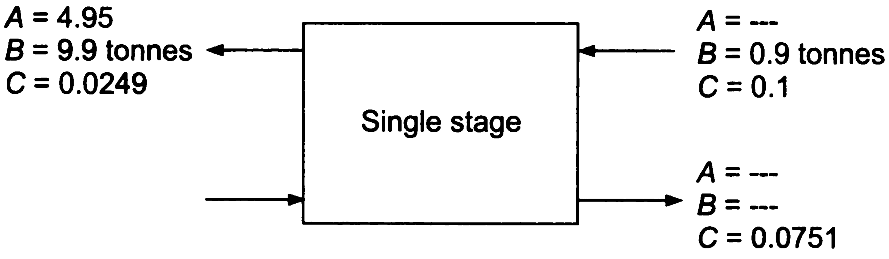


Fig. 11.20 Example 3.

Concentration in underflow

$$\therefore \quad x_1 = \frac{C}{A + C} = \frac{0.0249}{4.95 + 0.0249} = 0.5 \times 10^{-2}$$

x_1 in overflow (same as underflow) = $\dfrac{0.0751}{A + 0.0751} = 0.5 \times 10^{-2}$

∴ A = 14.93 (amount of water with extract)

Amount of water with sand = 4.95

∴ Total feed water = Water in extract + Water in sand
= 14.93 + 4.95 = 19.88

3. 100 tonnes of underflow feed containing 20 tonnes of solute. 2 tonnes of H_2O, 78 tonnes of inerts are to be leached with water to give an overflow of concentration, 15% solute. 95% recovery is desired. The underflow from each stage carries 0.5 kg of solution/kg of inert. Estimate the number of stages needed.

Solution.

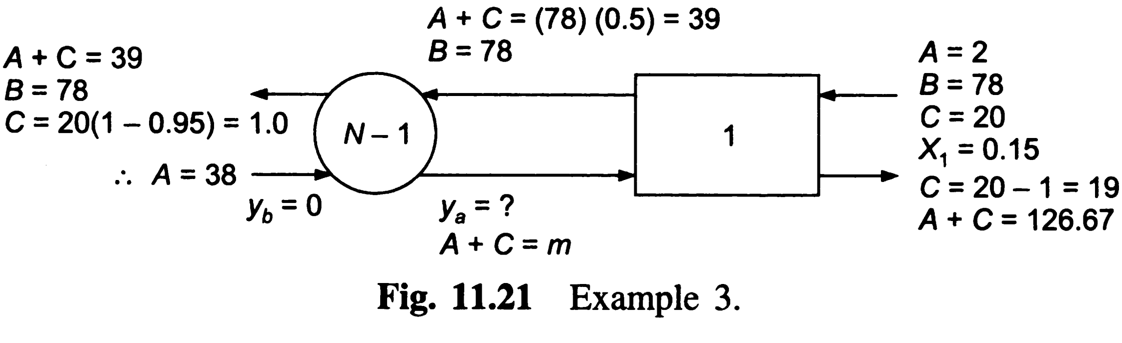


Fig. 11.21 Example 3.

$$y_b^* = \frac{C}{A+C} = \frac{1}{39} = 0.0256$$

x_1 (Desired outlet concentration of overflow) = 0.15

i.e.
$$\frac{C}{A+C} = 0.15 = \frac{19}{A+19}$$

$$\therefore \qquad A + C = 126.67 \text{ tonnes}$$

Let us make a mass balance around stage 1.
Entering liquid = Leaving liquid

$$22 + m = 126.67 + 39$$

$$\therefore \qquad m = 143.67 \text{ tonnes}$$

Similarly making a solute balance, we get

$$20 + 143.67\, y_a = 19 + 39 \times 0.15$$

$$\therefore \qquad y_a = 0.034$$

Solving by McCabe's method, we get

$$y_b = 0;\ y_b^* = 0.0256;\ y_a = 0.034;\ y_a^* = 0.15$$

($\because$ the leaving streams are in equilibrium)

$$(N-1) = \frac{\log\left[\dfrac{y_b - y_b^*}{y_a - y_a^*}\right]}{\log\left[\dfrac{y_b - y_a}{y_b^* - y_a^*}\right]} = \frac{-0.6562}{-0.5633} = 1.165$$

$$N = 2.165$$

Baker's method:

$$\frac{R^{n+1} - 1}{R - 1} = \frac{S_1}{S_{n+1}}$$

$$S_1 = 39 \times 0.15 = 5.85;\ S_{n+1} = 1.0$$

$$R = \frac{\text{solution/solute or solvent in overflow}}{\text{solution/solute or solvent in underflow}}\ \frac{143.7}{39} = 3.685$$

$$\frac{3.685^{n+1} - 1}{2.685} = \frac{5.85}{1};\ n + 1 = 2.159 \text{ stages}$$

4. A plant produces 100 tonnes/day of TiO_2 pigment which must be 99.9% pure when dried. The pigment produces by precipitation and the material as prepared is contaminated with 1 ton of salt solution containing 0.55 ton of salt/ton of pigment. The material is washed countercurrently with water in a number of thickeners arranged in series. How many thickeners will be required if water is added at the rate of 200 tonnes/day and the solid discharged from each thickener removed 0.5 ton of solvent/ton of pigment.

What will be the number of thickeners if the amount of solution removed in association with pigment varies in the following way with the concentration of the solution in the thickeners.

x	0	0.1	0.2	0.3	0.4	0.5
N	3.333	3.125	2.94	2.78	2.63	2.5

Solution.

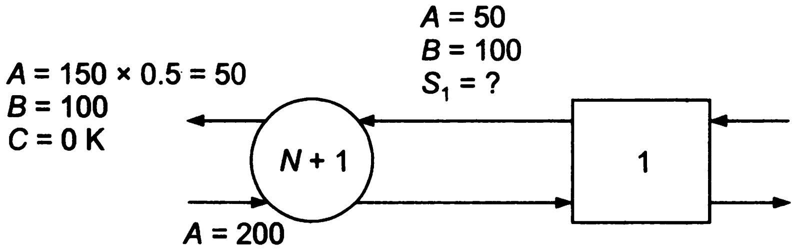


Fig. 11.22 Example 4.

Concentrated wash liquor is fed with the feed top concentrator = 1

$$A + C = 100;\ A = 45;\ B = 100$$

$$C = 0.55 \times 100 = 55$$

$$N_F = \frac{B}{A+C} = 1.0$$

$$y_F = \frac{C}{A+C} = 0.55$$

$$C = 55 - 0.1 = 54.9$$

$$A = 200 + 45 - 50 = 195$$

$$y = \frac{C}{A+C} = \frac{54.9}{249.9} = 0.22$$

$$x_1 = 0.22 = \frac{C}{A+C}$$

$$\frac{R^{n+1}-1}{R-1} = \frac{S_1}{S_{n+1}}$$

$$R = \frac{200}{50} = 4$$

$$S_1 = 14.1$$

$$S_{n+1} = 0.1$$

$$\frac{4^{n+1}-1}{4-1} = \frac{14.1}{0.1}$$

$$\therefore \quad n + 1 = 4.36$$

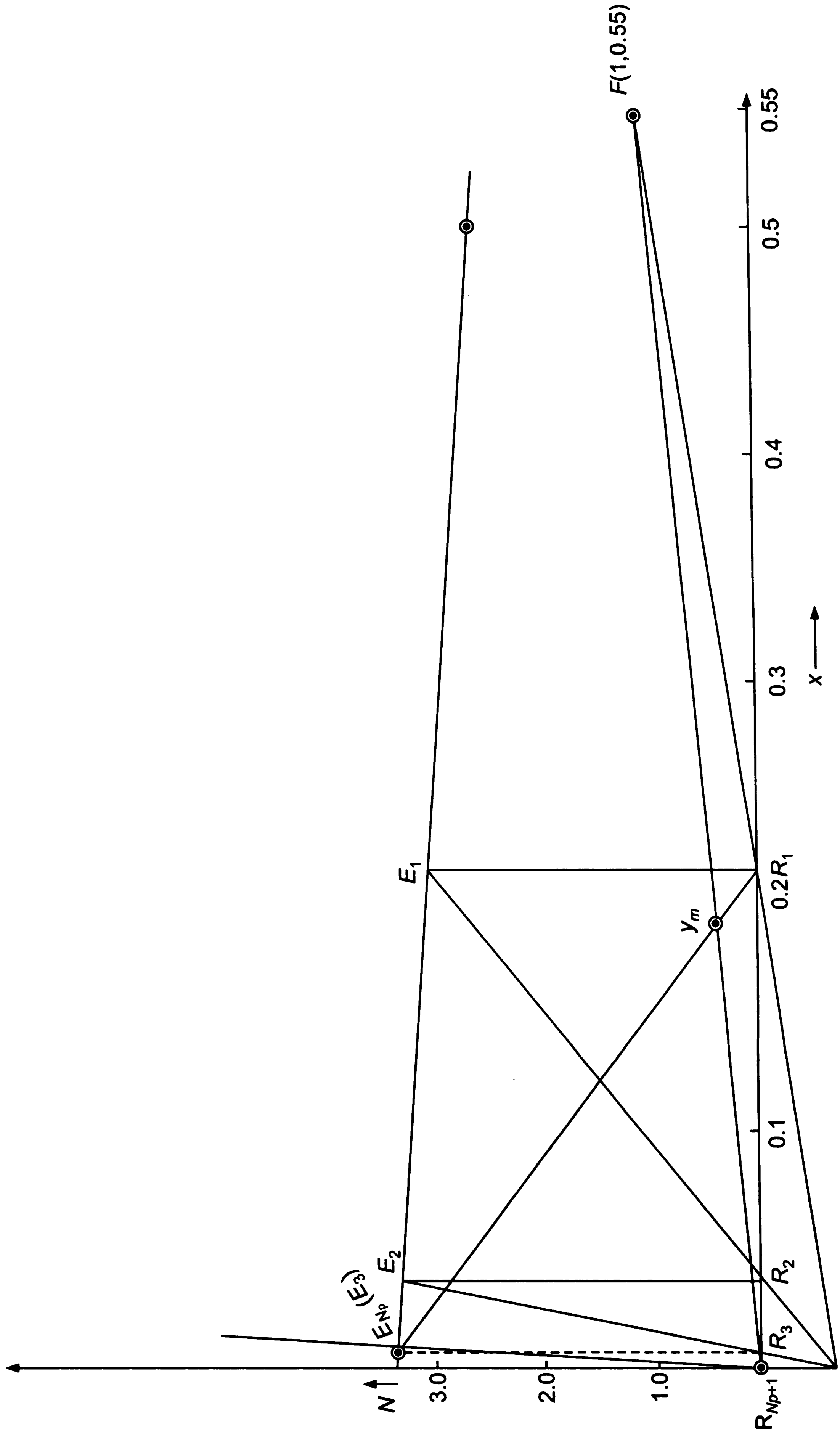


Fig. 11.23 Example 4.

(ii) Feed point F, $(N_F, y_F) = (1, 0.55)$

Leached solids leaving, E_{N_p} $(N_{N_p}, y_{N_p}) = (?, ?)$

Solvent entering, R_{N_p+1} $(N_{p+1}, x_{N_p+1}) = (0, 0)$

Solution leaving, R_1 $(N_1, x_1) = (0, ?)$

$$\bar{y} = \frac{F \cdot y_F + R_{N_p}\ x_{N_p+1}}{F + R_{N_p+1}} = \frac{(100)(0.55) + 0}{100 + 200} = 0.1833$$

$$\bar{N} = \frac{B}{A + C} = \frac{100}{300} = 0.333$$

Join F and R_{N_p+1} Locate $\bar{m}\,(\bar{N}, \bar{y})$.

By stagewise construction, the stages are estimated to be: 4

5. By extraction with kerosene two tonnes of waxed paper per day is to be dewaxed in a continuous countercurrent extraction system. The waxed paper contains 25% paraffin wax by weight and 75% paper pulp. The pulp which retains the unextracted wax must not contain over 0.2 kg of wax/100 kg of wax free pulp. The kerosene used for extraction contains 0.05 kg of wax/100 kg wax free kerosene, experiments show that pulp retains 2 kg of kerosene per kg of wax free pulp. The extract from battery contains 5 kg of wax/100 kg of wax free kerosene. How many stages are needed?

Solution.

Basis: 100 kg of wax and kerosene free pulp

Wax in the pulp = $100 \times \frac{25}{75} = 33.33$ kg

Wax in the solvent = 0.0005 kg of wax/kg of kerosene

Let s be the weight of solvent used.

∴ Total wax entering = wax from pulp + wax from kerosene = 33.33 + 0.0005s

Wax in the exiting pulp = 100 × 0.002 = 0.2 kg

Wax in the solution leaving

[Solvent entering – solvent carried away in leaving pulp] [Weight ratio of wax to solvent in leaving solution] .

$$= [s - (2)(100)]\,[0.05] = (0.05s - 10) \text{ kg}$$

∴ Total wax output = $(0.05s - 10) + (0.2) = (0.05s - 9.8)$

Wax input = wax output

i.e. $33.33 + 0.0005s = 0.05s - 9.8$

$$s = 871.3 \text{ kg}$$

Kerosene in the exhausted pulp = 2 × 100 = 200

Kerosene in the extract (overflow) solution = 871.3 – 200 = 671.3 kg

i.e. wax in the extract (overflow) solution = $671.3 \times \frac{0.5}{100} = 33.565$ kg

Concentration in underflow in II unit = Concentration in overflow from I stage

Wax in underflow leaving I solution = Weight of kerosene in underflow × wax concentration

$$= (200)\left(\frac{5}{100}\right) = 10 \text{ kg}$$

The wax in the overflow from II cell to I cell by wax balance

[Wax in underflow leaving I + wax in overflow solution leaving I – wax in pulp entering I]

$$10 + 33.565 - 33.33 = 10.235 \text{ kg}$$

Concentration of this solution is $\frac{10.235}{871.3} = 0.0117$

$$x_a = y_a^* = 0.05 \text{ and } y_a = 0.0117$$

$$x_b = y_b^* = \frac{0.2}{200} = 0.001,\ y_b = 0.0005$$

$$N - 1 = \frac{\log\left[\dfrac{0.0005 - 0.001}{0.0117 - 0.05}\right]}{\log\left[\dfrac{0.0005 - 0.0117}{0.001 - 0.05}\right]} = \frac{-1.88423}{-0.641} = 2.94$$

$\therefore$ $N = 3.94$ stage; $N \approx 4$ stage

6. A five-stage countercurrent extraction battery is to be used to extract the sludge from the reaction

$$Na_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2NaOH$$

The $CaCO_3$ leaving each carries with it 1.5 times its weight the solution, in flowing from one unit to other. It is desired to recover 98% of NaOH. The products from the reaction enter the first unit with no excess reactant but with 6.5 kg of water/kg of $CaCO_3$.

(i) How much wastewater must be used for 1 kg of $CaCO_3$?

(ii) What is the concentration of leaving solution assuming $CaCO_3$ is insoluble?

(iii) Using the same quantity of wastewater, how many units must be employed to recover 99.5% of NaOH.

Solution.

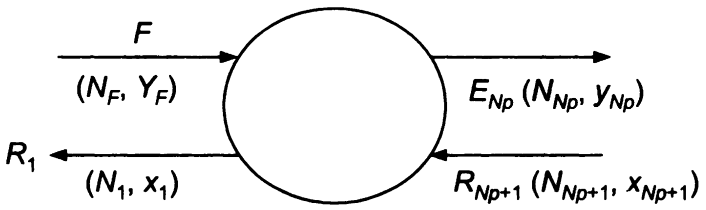


Fig. 11.24 Example 6.

Basis:

100 kg $CaCO_3$ formed
B (Inert) : 100 kg
A (Solvent) : 650 kg
C (Solute) : 80 kg (from stoichiometry)

$$\therefore \quad N_F = \frac{B}{A+C} = \frac{100}{650+80} = 0.137$$

$$y_F = \frac{C}{A+C} = \frac{80}{730} = 0.1096$$

$\therefore$ F (0.137, 0.1096)

$$N_{N_p} = \frac{1}{1.5} = 0.667$$

Recovery of NaOH is 987 = 78.4 kg
$\therefore$ NaOH in leaving stream = 1.6 kg

$$\therefore \quad y_{N_p} = \frac{C}{A+C} = \frac{C}{E_{N_p}}$$

$$E_{N_p} = \frac{B}{N_{N_p}} = \frac{100}{0.667} = 150$$

$$\therefore \quad y_{N_p} = \frac{1.6}{150} = 0.0107$$

Point E_{N_p} is (N_{N_p}, y_{N_p}) = (0.667, 0.0107)
Assume x_1 and hence locate R_1. $(0, x_1)$ locate E_{N_p} (0.667, 0.0107), F (0.137, 0.1096) and R_{N_p+1} (0, 0)
Join E_{N_p}, R_{N_p+1} and F, R_1 and produce them to cut at Δ_R.
By stepwise construction check whether both five stages and E_{N_p} (assumed) match.
If not, make a fresh assumption of x_1 and proceed till the stages and x_1 match.
By trial and error x_1 = 0.1
Total amount of wastewater

(i) Water in sludge $(A + C)$ = Weight of solution in sludge − weight of solute = 150 − 1.6 = 148.4 kg

(ii) Weight of water in overflow

Concentration in overflow = $x_1 = \dfrac{C}{A+C} = \dfrac{78.4}{A+C} = 0.1$

Weight of solution $A + C$ = 784 kg

$\therefore$ Weight of solvent (A) = 784 − 78.4 = 705.6 kg

$\therefore$ Total weight of water added = 148.4 + 705.6 − 650 = 204 kg

Concentration of leaving solution from each stage:

$x_1 = 0.1$; $x_2 = 0.068$; $x_3 = 0.044$; $x_4 = 0.026$; $x_5 = 0.0107$

(iii) For 99.5% recovery:

Concentration of NaOH leaving = 0.995 × 80 = 0.14.

$$\frac{F}{R}(N_F, y_F) = F(0.137, 0.1096)$$

$$R_1(N_1, x_1) = R_1(0, 0.1)$$

$$y_{N_p} = \frac{C}{A+C} = \frac{C}{E_{N_p}}$$

$$\therefore \qquad E_{N_p} = \frac{B}{N_{N_p}} = 150$$

$$\therefore \qquad y_{N_p} = \frac{0.4}{150} = 2.667 \times 10^{-3} = 0.002667$$

$$E_{N_p}(0.667, 2.667 \times 10^{-3})$$

$$R_{N_p+1}(0, 0)$$

By stagewise construction, we find the number of stages as 5.

In the previous problem worked out, it is found that the sludge retains the solution varying with the concentration as follows:

NaOH	0	5	10	15	20
$\frac{\text{kg of solution}}{\text{kg of CaCO}_3}, \frac{1}{N}$	1.5	1.75	2.2	2.7	3.6
N	0.667	0.571	0.455	0.370	0.278

It is desired to produce a 10% solution of NaOH. How many stages must be used to recover 99.5% of NaOH?

Recovered NaOH = 99.5%

i.e. 99.5 × 80 = 79.6 kg

Solute = 0.4 kg

$$x = \frac{C}{A+C} = \frac{79.6}{A+79.6} = 0.1$$

$$\therefore \qquad A = 716.4 \text{ kg}$$

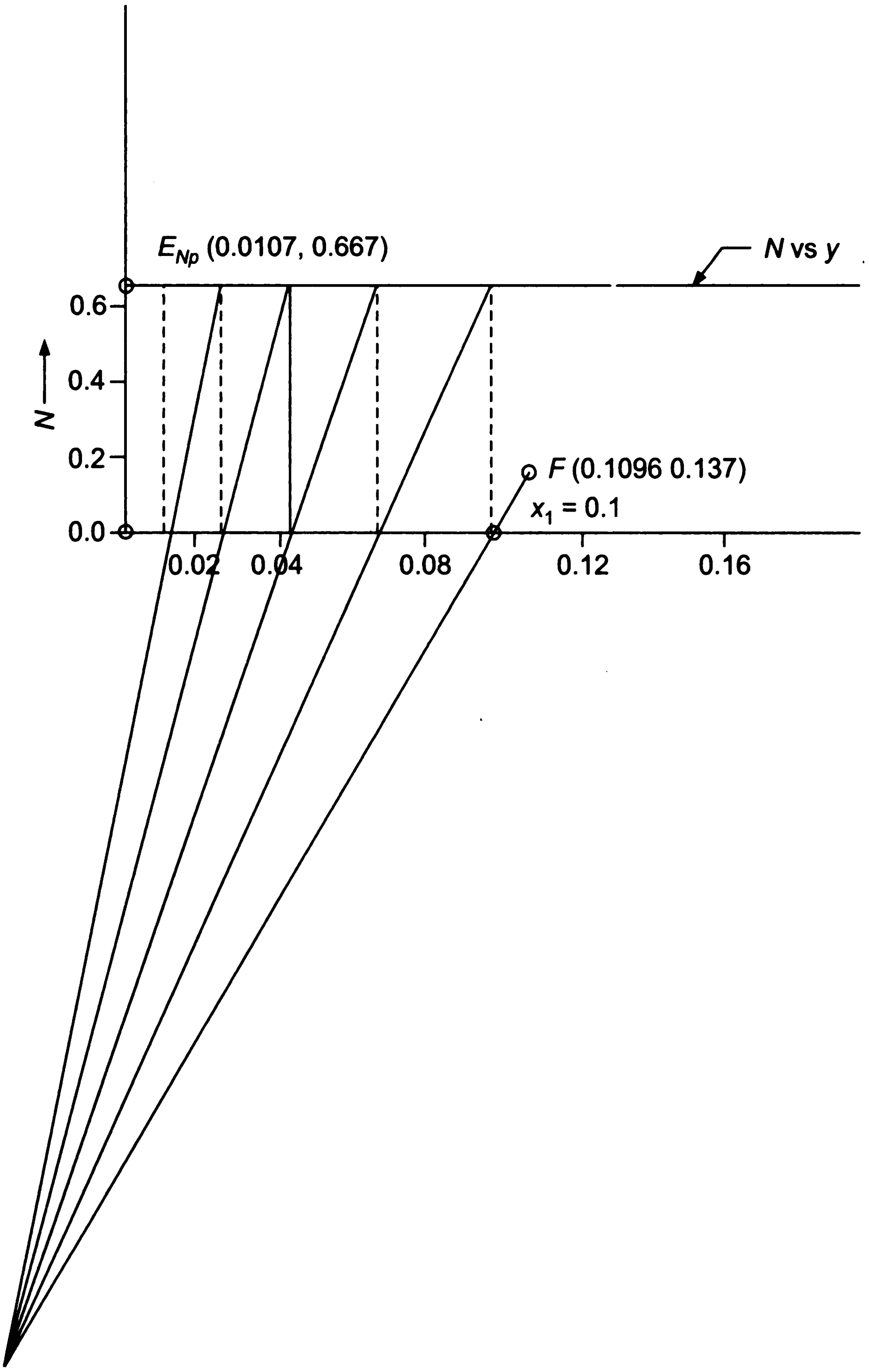


Fig. 11.25 Example 6.

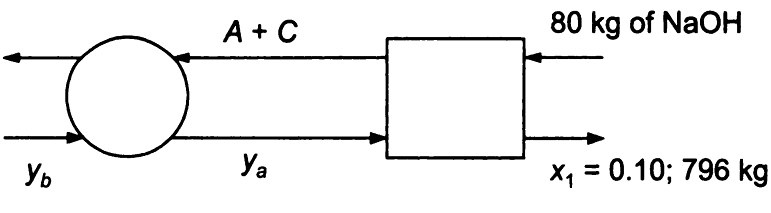


Fig. 11.26 Example 6.

EXERCISES

1. Seeds containing 25% oil by weight are to be extracted in a countercurrent plant and 95% of the oil is recovered in a solution containing 60% oil by weight. If the seeds are contacted with fresh solvent and 1 kg of solution is removed in the underflow in association with every 2 kg of insoluble matter, determine the theoretical stages required.
2. Crushed oil seeds containing 55% oil by weight are to be extracted at the rate of 5000 kg/hr using 8000 kg/hr of hexane containing 5% oil by weight as the solvent. A countercurrent two-stage extraction system is used. The oil seeds retain 1 kg of solution per kg of oil-free cake. Calculate the percent recovery of oil (based on original feed) obtained under the above conditions.
3. Seeds containing 20% oil by weight is extracted countercurrently with oil-free hexane as a solvent. Calculate the number of theoretical stages required is 90% of the oil is recovered in extract with 40% oil by weight and the amount of liquid (solvent + oil) in the underflow from each stage is 0.60 kg per kg of insoluble matter.

   Use triangular coordinates or rectangular coordinates.
4. In a lime-soda process a slurry containing 10 kg water, 1 kg sodium hydroxide (NaOH) and 1 kg calcium carbonate particles. The slurry is washed countercurrently with water in four stages. The solid discharged from each stage contains 3 kg water per kg calcium carbonate. Calculate the amount of wash water needed when the discharged calcium carbonate after drying contains a maximum of 0.01 kg sodium hydroxide per kg calcium carbonate.

12

ADSORPTION

12.1 INTRODUCTION

Adsorption operation involves contact of solids with either liquids or gases in which the mass transfer is towards solids. The reverse of this operation is called *Desorption.* Adsorption operations exploit the ability of certain solids to concentrate specific substances from fluid on to their surfaces. The adsorbed substance is called *adsorbate* and the solid substance is called *adsorbent.*

Typical applications of this solid–liquid operation are as follows:

- removal of moisture dissolved in gasoline
- de-colorization of petroleum products and sugar solutions
- removal of objectionable taste and odour from water.

The solid–gas operations include:

- dehumidification of air and gases
- removal of objectionable odours and impurities from gases
- recovery of valuable solvent vapours from dilute gas mixtures
- to fractionate mixtures of hydrocarbon gases such as methane, ethane and propane.

12.2 TYPES OF ADSORPTION

The two types of adsorption are *physical adsorption* or *physi-sorption* (van der Waals adsorption) and *chemi-sorption* (activated adsorption).

Physical adsorption is a readily reversible phenomenon, which results from the intermolecular forces of attraction between a solid and the substance adsorbed.

Chemi-sorption is the result of chemical interaction, generally stronger than physi-sorption between the solid and the adsorbed substance. This process is irreversible. It has importance in catalysis.

12.3 NATURE OF ADSORBENTS

Adsorbents are usually in granular form with their size ranging from 0.5 mm to 12 mm. They must neither offer high pressure drop nor get carried away by flowing stream. They must not loose their shape and size while handling. They must have larger surface area per unit mass and also lot of pores.

Some of the commonly used adsorbents, their sources and applications are given below:

Sl. No.	*Adsorbent*	*Source*	*Application*
1.	Fuller's earth	Naturally occurring clay is heated and dried to get a porous structure.	De-colorizing, drying of lubricating oils, kerosene and engine oils.
2.	Activated clay	Bentonite or other activated clay which are activated by treatment with sulfuric acid and further washing, drying and crushing.	Used for de-colorizing petroleum products.
3.	Bauxite	A naturally occurring hydrated alumina, activated by heating at 230–815°C.	Used for de-colorizing petroleum products and for drying gases.
4.	Alumina	A hard hydrated aluminium oxide, which is activated by heating to drive off the moisture and then crushed to desired size.	Used as desiccant.
5.	Bone-char	Obtained by destructive distillation of crushed bones at 600–900°C.	Used for refining sugar and can be reused after washing and burning.
6.	Activated carbon	(i) Vegetable matter is mixed with calcium chloride, carbonized and finally the inorganic compounds are leached away. (ii) Organic matter is mixed with porous pumice stones and then heated and carbonized to deposit the carbonaceous matter throughout the porous particle. (iii) Carbonizing substances like wood, sawdust, coconut shells, fruit pits, coal, lignite and subsequent activation with hot air steam. It is available in granular or pellated form.	De-colorizing of sugar solutions, chemicals, drugs, water purification, refining of vegetable and animal oils, recovery of gold and silver from cyanide ore-leach solution, recovery of solvent vapour from gas-mixtures, collection of gasoline hydro-carbons from natural gas, fractionation of hydrocarbon gases.

(*Contd.*)

(*Contd.*)

Sl. No.	*Adsorbent*	*Source*	*Application*
7.	Silica gel	A hard granular and porous product obtained from sodium silicate solution after treatment with acid. Normally has 4 to 7% water in the product.	Used for de-hydration of air and other gases, fractionation of hydrocarbons.
8.	Molecular sieves	These are porous synthetic zeolite crystals, metal alumino-silicates.	Dehydration of gases and liquids, and separation of gas–liquid hydrocarbon mixture.

12.4 ADSORPTION EQUILIBRIA

Different gases and vapours are adsorbed to different extent under comparable conditions as shown in Fig. 12.1.

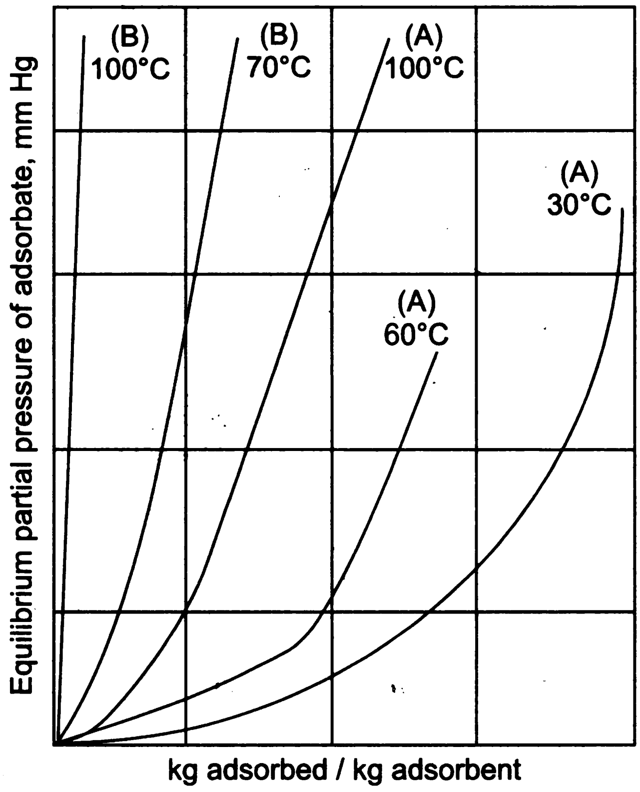


Fig. 12.1 Equilibrium adsorption on activated carbon.

As a general rule, vapours and gases with higher molecular weight and lower critical temperature are more readily adsorbed. To some extent, level of saturation also influences the degree of adsorption. The adsorption isotherms are generally concave to pressure axis. However, other shapes are also exhibited as shown in Fig. 12.2.

Repeated adsorption and desorption studies on a particular adsorbent will change the shape of isotherms due to gradual change in pore-structure. Further, adsorption is an exothermic process and hence the concentration of adsorbed gas

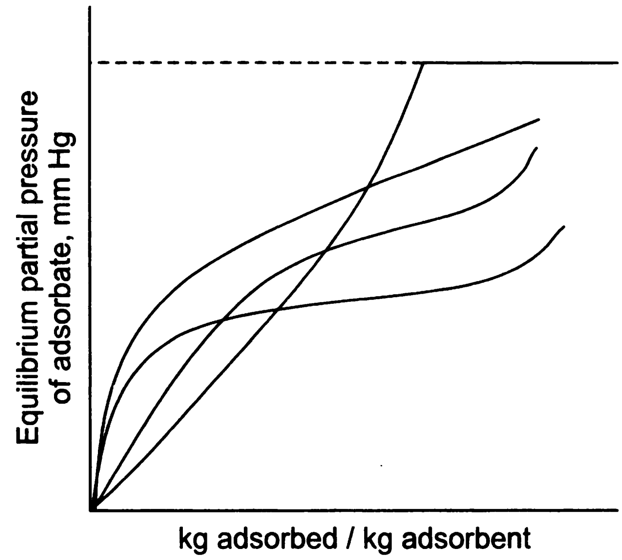


Fig. 12.2 Adsorption isotherms.

decreases with an increase in temperature at a constant pressure. Similarly an increase in pressure increases the concentration of adsorbed gas in the adsorbent at a constant temperature. There are three commonly used mathematical expressions to describe vapour adsorption equilibria, viz. Langmuir, Brunauer-Emmett-Teller (BET) and Freundlich isotherms. The first two are derived from theory whereas the last one is derived by a fit technique from the experimental data.

12.5 ADSORPTION HYSTERESIS

The adsorption and desorption operations exhibit different equilibrium phenomena as shown in Fig. 12.3 and is called adsorption hysteresis.

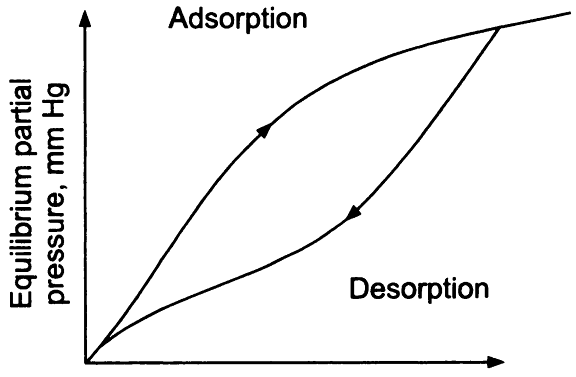


Fig. 12.3 Adsorption hysteresis.

This may be due to the shape of the openings to the capillaries and pores of the solid or due to the complex phenomena of wetting of the solid by the adsorbate. Whenever hysteresis is observed, the desorption curve is below the adsorption curve.

12.6 HEAT OF ADSORPTION

The differential heat of adsorption (–*H*) is defined as the heat liberated at constant temperature when unit quantity of vapour is adsorbed on a large quantity of solid already containing adsorbate. Solid so used is in such a large quantity that the adsorbate concentration remains unchanged.

The integral heat of adsorption, (ΔH) at any concentration X is defined as the enthalpy of the adsorbate–adsorbent combination minus the sum of the enthalpies of unit weight of pure solid adsorbent and sufficient pure adsorbed substance (before adsorption) to provide the required concentration X, at the same temperature.

The differential heat of adsorption and integral heat of adsorption are functions of temperature and adsorbate concentration.

12.7 EFFECT OF TEMPERATURE

Increase of temperature at constant pressure decreases the amount of solute adsorbed from a mixture. However, a generalization of the result is not easy. Figure 12.1 also indicates the effect of temperature.

12.8 EFFECT OF PRESSURE

Generally lowering of pressure reduces the amount of adsorbate adsorbed upon the adsorbent. However, the relative adsorption of paraffin hydrocarbon on carbon decreases at increased pressures.

12.9 LIQUIDS

The impurities are present both at low and high concentrations in liquids. These are normally removed by adsorption technique. The characteristics of adsorption of low and high concentration impurities are different. They are discussed below.

12.9.1 Adsorption of Solute from Dilute Solutions

Whenever a mixture of solute and solvent is adsorbed using an adsorbent, both the solvent and solute are adsorbed. Due to this, only relative or apparent adsorption of solute can alone be determined.

Hence, it is a normal practice to treat a known volume of solution of original concentration C_0, with a known weight of adsorbent. Let C^* be the final equilibrium concentration of solute in the solution.

If v is the volume of solution per unit mass of adsorbent (cc/g) and C_0 and C^* are the initial and equilibrium concentrations (g/cc) of the solute, then the apparent adsorption of solute per unit mass of adsorbent, neglecting any change in volume is $v(C_0 - C^*)$, (g/g). This expression is mainly applicable to dilute solutions. When the fraction of the original solvent which can be adsorbed is small, the C^* value depends on the temperature, nature and properties of adsorbent.

In the case of dilute solutions and over a small concentration range, *Freundich adsorption Isotherm* describes the adsorption phenomena,

$$C^* = K\,[v(C_0 - C^*)]^n \qquad (12.1)$$

Freundlich adsorption equation is also quite useful in cases where the actual identity of the solute is not known, e.g. removal of colouring substance from sugar solutions, oils etc. The colour content in the solution can easily be measured using spectrophotometer or colorimeter. The interpretation of this data is illustrated in worked example 2. If the value of *n* is high, say 2 to 10, adsorption is good. If it lies between 1 and 2, moderately difficult and less than 1 indicates poor adsorption characteristics. A typical adsorption isothermal for the adsorption of various adsorbates *A*, *B* and *C* in dilute solution at the same temperature for the same adsorbent is shown in Fig. 12.4.

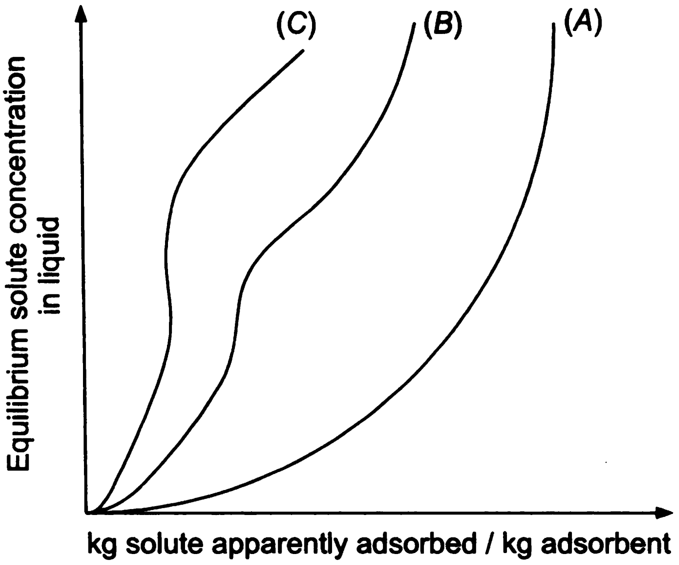


Fig. 12.4 Adsorption isotherms for various adsorbates.

12.9.2 Adsorption from Concentrated Solution

When the apparent adsorption of solute is determined over the entire range of concentrations from pure solvent (0% solute concentration) to pure solute (100% solute concentration), curves as shown in Fig. 12.5 will occur. Curve '1' occurs when the solute is more strongly adsorbed in comparison to solvent at all solute concentration. Whenever both solute and solvent are adsorbed to nearly the same extent, the 'S' shaped curve '2'occurs. In the range *PQ* solute is more strongly adsorbed than solvent. At point *Q* both are equally well adsorbed. In the range *QR* solvent is more strongly adsorbed.

12.9.3 Other Adsorption Isotherms

12.9.3.1 Langmuir adsorption isotherm

The theory proposed by *Langmuir* postulates that gases being adsorbed by a solid surface cannot form a layer more than a simple molecule in depth. His theory visualizes adsorption as a process consisting two opposite actions, a condensation of molecules from the gas phase on to the surface and an evaporation of molecules from the surface back into the body of the gas. When adsorption starts, every molecule colliding with the surface may condense on it. However, as adsorption

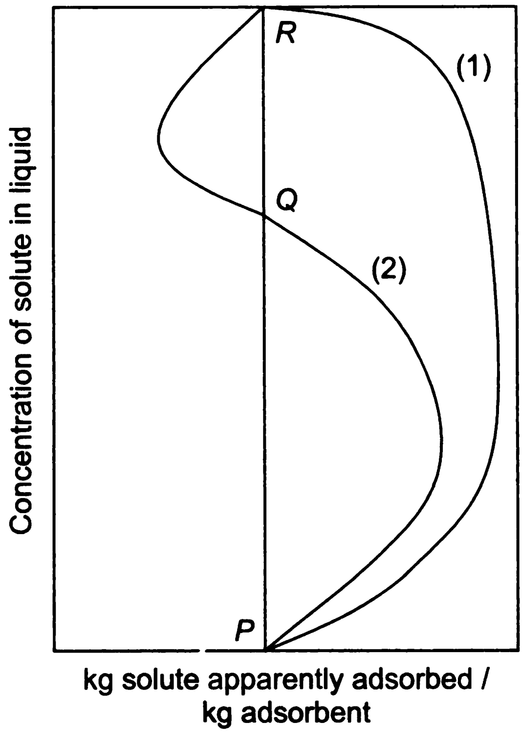


Fig. 12.5 Adsorption of solute in concentrated solutions.

proceeds, only those molecules which strike the uncovered area surface can be adsorbed. Due to this, the initial rate of condensation of molecules on the surface is very high and decreases as the time progresses. The molecules attached to the surface also get detached by factors like thermal agitation. The rate at which desorption occurs depends on the amount of surface covered by molecules and will increase as the surface becomes more fully saturated. When the rate of adsorption and desorption become equal, adsorption equilibrium is said to be reached. If 'θ' is the fraction of surface covered by adsorbed molecules at any instant, the fractional area available for adsorption is $(1 - \theta)$. The rate at which the molecules strike the unit area of surface is proportional to pressure.

Therefore the rate of condensation

$$= k_1(1 - \theta)P$$

where, k_1 is a constant.

Similarly, the rate of evaporation

$$\propto k_2\theta$$

where, k_2 is a constant.

Under adsorption equilibrium,

$$k_1(1 - \theta)P = k_2\theta$$

i.e.

$$\theta = \frac{k_1(1-\theta)P}{k_2 + k_1 P}$$

$$= \frac{bP}{1+bP} \quad \text{where, } b = \frac{k_1}{k_2} \qquad (12.2)$$

Now the gas adsorbed per unit area or unit mass of adsorbent, y, must obviously be proportional to the fraction of surface covered. Hence,

$$y = k\theta = k\left\{\frac{bP}{1+bP}\right\} = \frac{aP}{1+bP} \tag{12.3}$$

where, a and b are constants. This is Langmuir adsorption Isotherm

12.9.3.2 BET adsorption isotherm

This postulates that the adsorption phenomenon involves the formation of many multilayers on the surface rather than a single one. Based on this, Brunauer, Emmett and Teller derived the following adsorption isotherm popularly known as BET adsorption isotherm.

$$\frac{P}{[V(P^o - P)]} = \frac{1}{[V_m C]} + \left[\frac{(C-1)}{V_m C}\right]\left[\frac{P}{P^o}\right] \tag{12.4}$$

where, V is the volume, reduced to standard conditions of gas adsorbed at pressure P and temperature T, P° is the saturated vapour pressure of the adsorbate at temperature T, V_m is the volume of gas reduced to standard conditions, adsorbed when the surface is covered with a unimolecular layer, C is a constant at any given temperature given by exp $[(E_1 - E_2)/RT]$, where E_1 is the heat of adsorption for the first layer and E_2 is that for the second and higher layers.

12.10 TYPES OF OPERATION

Adsorption operations are carried out either on batch or continuous basis. Batch process is not very much used. However, a batch operation is quite useful in obtaining equilibrium data. Much widely used continuous operation can either be a single stage or a multistage operation. The multistage operation could once again either be a cross-current operation or a countercurrent operation.

12.10.1 Single Stage Operation

A schematic arrangement for a single stage operation is shown in Fig. 12.6.

The concentration of solute increases in the adsorbent from X_0 to X_1 (g/g) and the concentration of solute in the solution decreases from Y_0 to Y_1 (g/g).

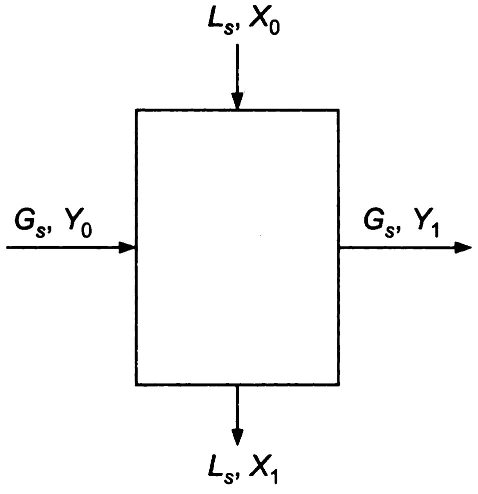


Fig. 12.6 Single stage operation.

The mass balance for solute gives

$$G_s\,[Y_0 - Y_1] = L_S\,[X_1 - X_0] \tag{12.5}$$

i.e.

$$-\frac{L_S}{G_S} = \frac{(Y_0 - Y_1)}{(X_0 - X_1)} \tag{12.6}$$

where (L_S/G_S) indicates the slope of the operating line passing through the points (X_0, Y_0) and (X_1, Y_1). If the leaving streams are in perfect equilibrium, then the point (X_1^*, Y_1^*) will lie on the equilibrium adsorption isotherm. If the equilibrium is not reached due to factors like poor contacting, then the point P represents the conditions of leaving streams as shown in Fig. 12.7.

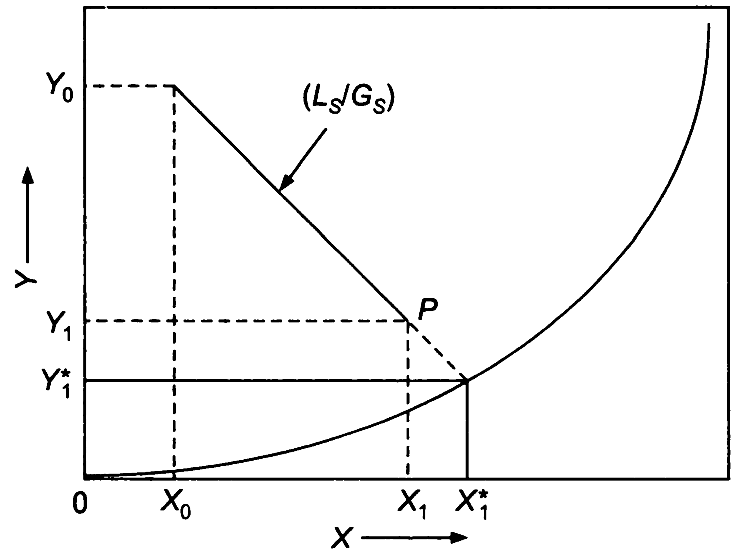


Fig. 12.7 Adsorption isotherm and operating line for a single stage operation.

Assuming the validity of Freundlich equation, especially when a low concentration of solute is involved, the equation can be written as

$$Y^* = mx^n \tag{12.7}$$

and at the final equilibrium conditions,

$$X_1 = \left(\frac{Y_1}{m}\right)^{1/n} \tag{12.8}$$

when the pure adsorbent is used, i.e. $X_0 = 0$.

Equation (12.8) yields

$$\frac{L_S}{G_S} = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} \tag{12.9}$$

12.10.2 Multistage Cross-current Operation

A schematic arrangement of multistage cross-current operation is shown in Fig. 12.8.

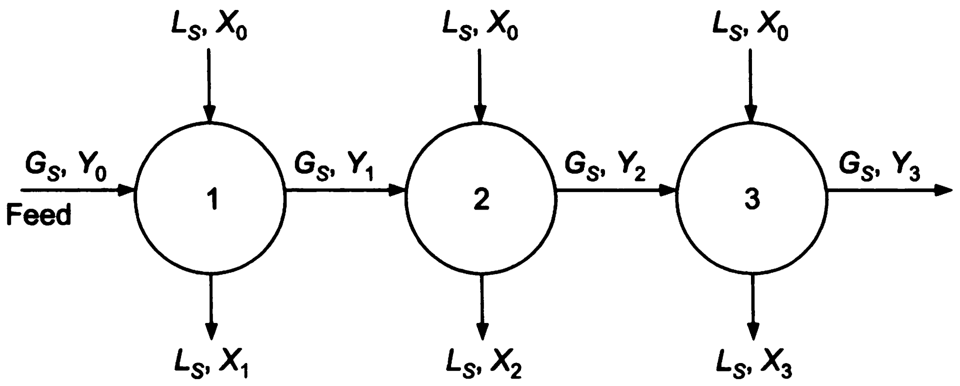


Fig. 12.8 Multistage cross-current operation.

Making a material balance of solute for stage 1 and use of Freundlich equation for the entry of pure adsorbent gives

$$G_S(Y_0 - Y_1) = L_{S1}(X_1 - X_0) \tag{12.10}$$

According to Eq. (12.9),

$$\frac{L_{S_1}}{G_S} = \frac{(Y_0 - Y_1)}{\left(\dfrac{Y_1}{m}\right)^{1/n}} \tag{12.11}$$

A material balance of solute for stage 2 yields,

$$G_S(Y_1 - Y_2) = L_{S_2}(X_2 - X_0) \tag{12.12}$$

Use of Freundlich equation for the entry of pure adsorbent gives

$$\frac{L_{S_2}}{G_S} = \frac{(Y_1 - Y_2)}{\left(\dfrac{Y_2}{m}\right)^{1/n}} \tag{12.13}$$

A similar material balance for stage p yields

$$G_S(Y_{p-1} - Y_p) = L_{Sp}(X_p - X_0) \tag{12.14}$$

Using Freundlich equation as before gives

$$\frac{L_{Sp}}{G_S} = \frac{(Y_{p-1} - Y_p)}{\left(\dfrac{Y_p}{m}\right)^{1/n}} \tag{12.15}$$

This operation is represented graphically as shown in Fig. 12.9.

12.10.2.1 Steps involved in the determination of number of stages needed for a cross-current adsorption process

1. Draw the equilibrium curve (X vs Y).
2. Locate the point (X_0, Y_0) and draw the operating line with a slope ($-L_{S1}/G_S$).
3. The intersection of operating line and equilibrium curve yields (X_1, Y_1) – the conditions of stream leaving from stage I.

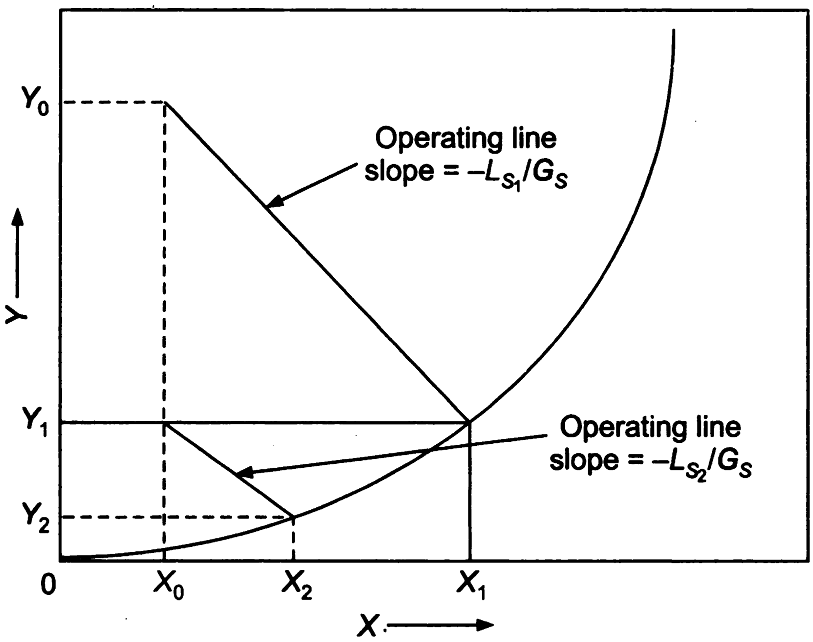


Fig. 12.9 Adsorption isotherm and operating line for a two-stage cross-current operation.

4. Locate (X_0, Y_1) and draw the operating line with a slope of ($-L_{S_2}/G_S$) (since X_0 remains constant for adsorbent for II stage).
5. Intersection of operating line and equilibrium curve yields (X_2, Y_2) — the conditions of leaving stream from stage II.
6. Proceed in the same way till the X_{Np} point is crossed and count the number of stages for the use of specified amount of adsorbent in each stage.

12.10.2.2 Optimisation of a two-stage cross-current operation

In a typical two-stage operation, the concentrations of solute both in the inlet solution stream and the outlet solution stream are fixed along with the feed rate of solution. The objective will be to use the minimum amount of adsorbent for this. If the quantity of the adsorbent is changed, the exit concentration of solution from each stage will also vary. However, the terminal conditions are always fixed and only the intermediate concentration is a variable. Hence, with one particular intermediate value, if the amounts of adsorbent used in both the stages are estimated, it will result in the minimum amount of adsorbent being used.

For the schematic arrangement shown in Fig. 12.10, the material balance equations for stages I and II are obtained from Eqs. (12.8) and (12.9) as

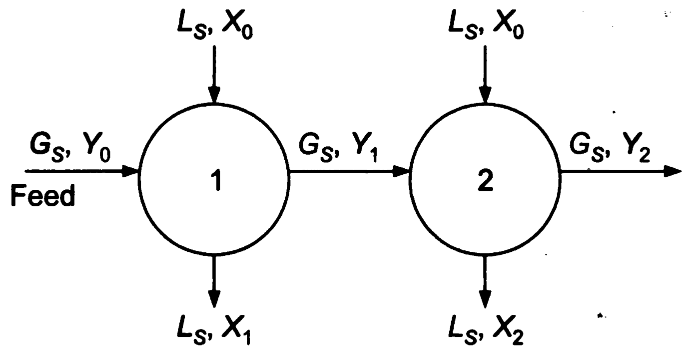


Fig. 12.10 Two-stage cross-current operation.

$$\frac{L_{S_1}}{G_S} = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}}$$

$$\frac{L_{S_2}}{G_S} = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}}$$

Adding Eqs. (12.11) and (12.12), we get

$$\left(\frac{L_{S_1} + L_{S_2}}{G_s}\right) = \frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} + \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}} \tag{12.16}$$

The total amount of adsorbent used can be optimised with respect to Y_1 (the intermediate concentration), the only variable on the R.H.S. of Eq. (12.16). The other parameters Y_0, Y_2, m and n are all fixed for a specified operation involving a specific adsorbent.

i.e.
$$\frac{d}{dY_1}\left[\frac{L_{S_1} + L_{S_2}}{G_S}\right] = \frac{d}{dY_1}\left[\frac{(Y_0 - Y_1)}{\left(\frac{Y_1}{m}\right)^{1/n}} + \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}}\right] \tag{12.17}$$

$$= m^{1/n} \frac{d}{dY_1}\left[\frac{Y_0 - Y_1}{(Y_1)^{1/n}} + \frac{(Y_1 - Y_2)}{(Y_2)^{1/n}}\right]$$

i.e.
$$= m^{1/n} \frac{d}{dY_1}\left[\frac{(Y_0 - Y_1)Y_2^{1/n} + (Y_1 - Y_2)Y_1^{1/n}}{[(Y_2)^{1/n}(Y_1)^{1/n}]}\right]$$

$$m^{1/n}(Y_2)^{-1/n} \frac{d}{dY_1}\left[\frac{[(Y_0Y_2^{1/n}) - (Y_1Y_2^{1/n})] + [Y_1^{(1+1/n)} - Y_2Y_1^{1/n}]}{Y_1^{1/n}}\right] \tag{12.18}$$

$$m^{1/n}(Y_2)^{-1/n} \frac{d}{dY_1}[Y_0Y_2^{1/n}Y_1^{-1/n} - Y_2^{1/n} \cdot Y_1^{(1-1/n)} + Y_1 - Y_2] \tag{12.19}$$

$$m^{1/n}(Y_2)^{-1/n}\,[Y_0 \cdot Y_2^{1/n}\,(-1/n)Y_1^{-1-1/n} - Y_2^{1/n}(1 - 1/n)Y_1^{-1/n} + 1 - 0] \tag{12.20}$$

For minimum adsorbent R.H.S. of (12.20) should be zero.

i.e.
$$Y_0Y_2^{1/n}(-1/n)Y_1^{-1-1/n} - (1 - 1/n)Y_2^{1/n}Y_1^{-1/n} + 1 - 0 = 0 \tag{12.21}$$

(since m, n and Y_2 have definite values)

Dividing by $\left(\frac{Y_2}{Y_1}\right)^{1/n}$, we get

$$\left(\frac{Y_0}{Y_1}\right)\left(\frac{-1}{n}\right) - \left(1 - \frac{1}{n}\right) + \left(\frac{Y_1}{Y_2}\right)^{1/n} = 0$$

i.e.

$$\left(\frac{Y_1}{Y_2}\right)^{1/n} - \left(\frac{1}{n}\right)\left(\frac{Y_0}{Y_1}\right) = 1 - \left(\frac{1}{n}\right) \tag{12.22}$$

Equation (12.22) can be solved by trial and error to get the intermediate concentration Y_1 which will optimise the total quantity of adsorbent to be used. However, also using the chart as shown in Fig. 12.11, we can get the intermediate concentration.

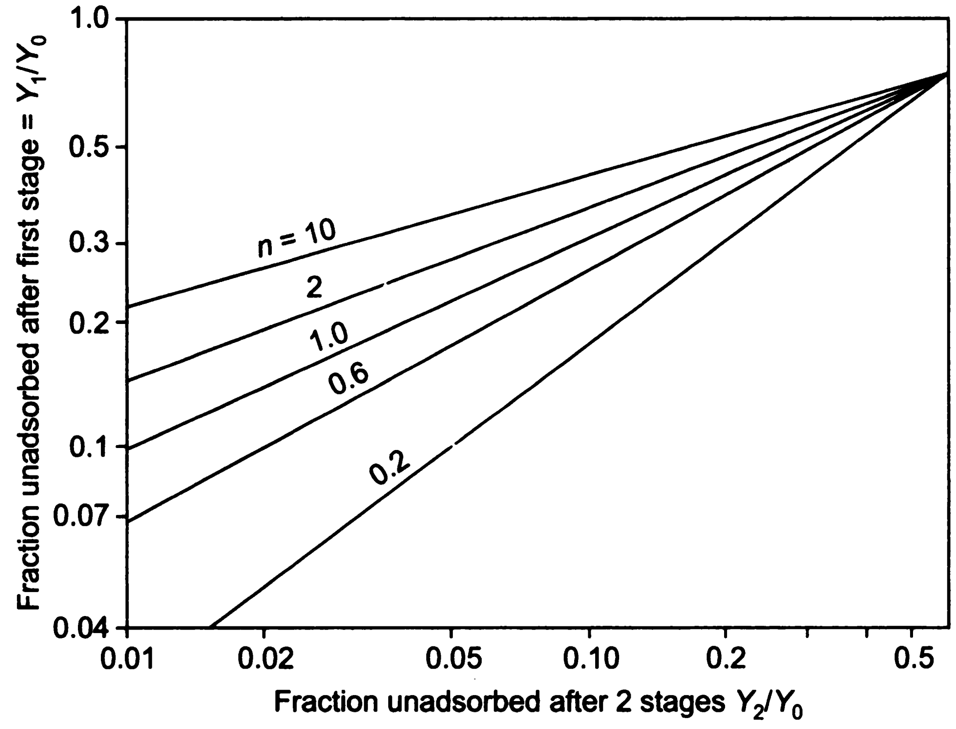


Fig. 12.11 Minimum total adsorbent two-stage cross-current Eq. (12.22).

12.10.3 Multistage Countercurrent Adsorption

The schematic arrangement as shown in Fig. 12.12 represents a multistage countercurrent operation.

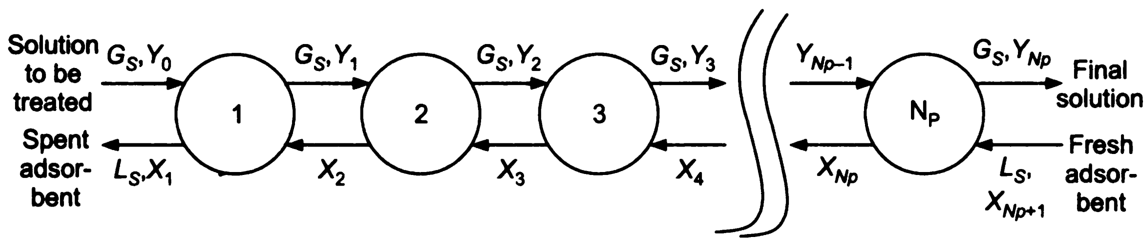


Fig. 12.12 Multistage countercurrent operation.

Solute balance for the system as a whole gives

$$G_S(Y_0 - Y_{Np}) = L_S(X_1 - X_{N_{p+1}}) \tag{12.23}$$

i.e.

$$\left(\frac{L_S}{G_S}\right) = \frac{(Y_0 - Y_{Np})}{(X_1 - X_{Np+1})} \tag{12.24}$$

Equation (12.24) gives the slope of the operating line passing through the terminal conditions (X_1, Y_0) and (X_{Np+1}, Y_{Np}). By conventional stepwise construction starting from the point (X_1, Y_0), the number of theoretical stages are estimated. This operation is represented graphically as shown in Fig. 12.13.

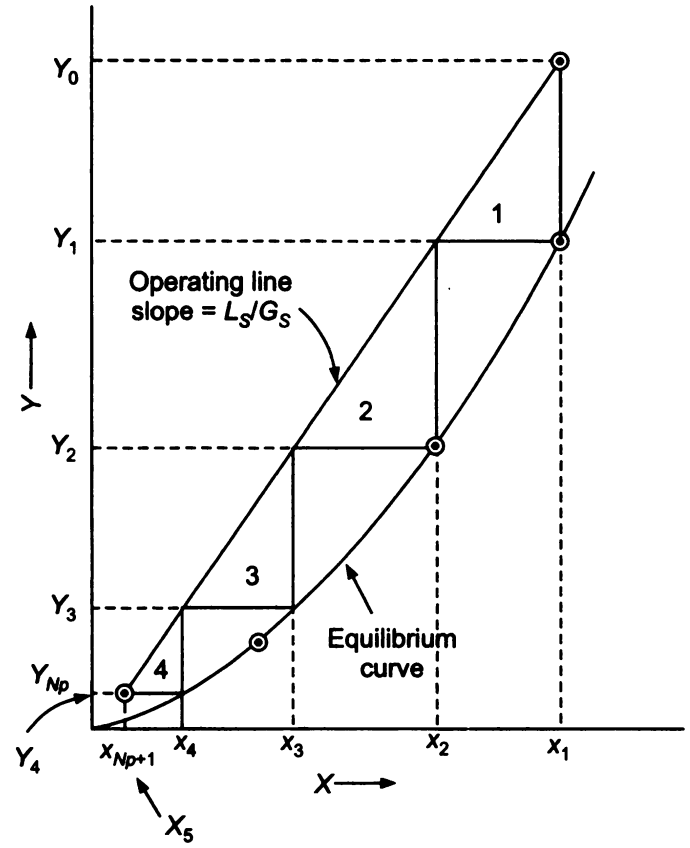
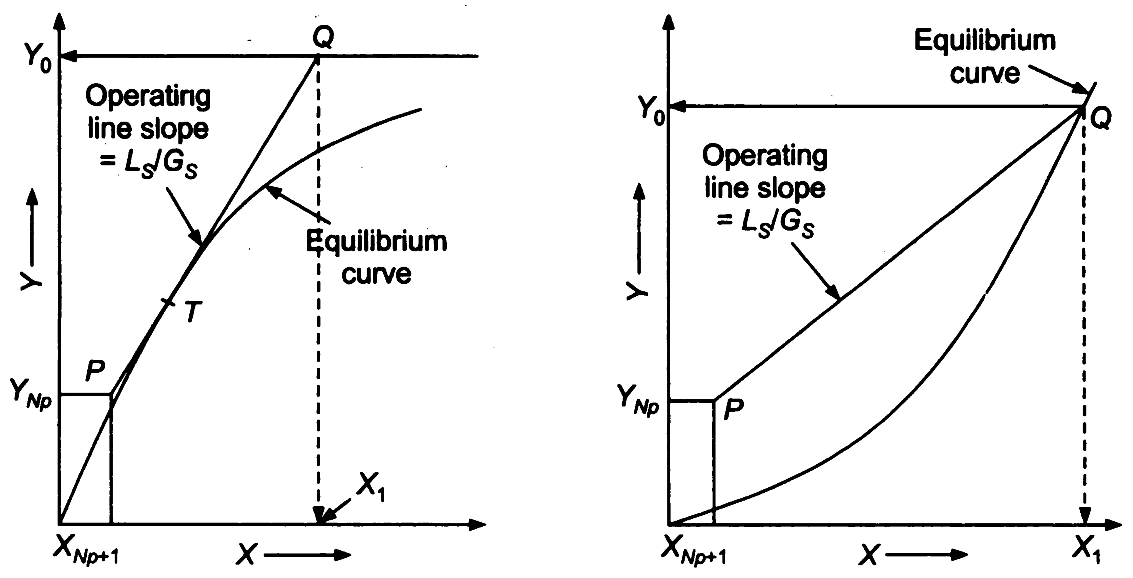


Fig. 12.13 Countercurrent multistage adsorption.

In order to determine the minimum amount of adsorbent for the process, draw a line from the point P (X_{Np+1}, Y_{Np}) which could be a tangent to the equilibrium curve. In such cases, the slope of the line gives the ratio of $(L_S/G_S)_{\min}$. However, in the case of equilibrium curve being a straight line or concave upwards, draw a horizontal line from Y_0 to intersect the equilibrium curve, (or line) at a point by Q and then join PQ which gives the slope of the operating line $(L_S/G_S)_{\min}$. The above two cases have been shown graphically in Figs. 12.14(a) and 12.14(b) respectively.



(a) (b)

Fig. 12.14 Operating line and minimum adsorbent/solvent ratio for infinite stages.

12.10.3.1 Steps involved in determining the number of stages in a multistage countercurrent operation

1. Draw the equilibrium curve.
2. Locate the point P (X_{Np+1}, Y_{Np}).
3. Draw a line with a slope of (L_S/G_S), where L_S is the mass flow rate of solute free adsorbent and G_S is the mass flow rate of solution on solute free basis.
4. Starting from (X_1, Y_0) by stepwise construction, estimate the number of stages till the point (X_{Np+1}, Y_{Np}) is crossed. The operation is graphically shown in Fig. 12.14.
5. If it is desired to determine the amount of adsorbent needed for a specified level of solute removal from a solution stream with a specified number of stages, draw the operating line of different slopes by trial and error and choose the one which gives exactly the same number of specified stages and the specified concentration in the liquid stream. From the slope of the operating line, thus chosen, determine the amount of adsorbent to be used and the solute concentration in the adsorbent.

12.10.3.2 Optimization of two-stage countercurrent adsorption

A typical two-stage countercurrent operation is shown schematically in Fig. 12.15.

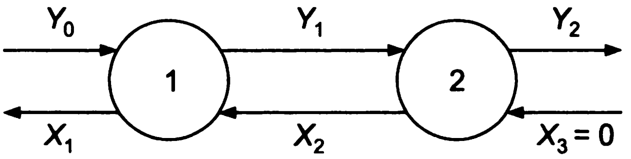


Fig. 12.15 Two-stage countercurrent adsorption.

Solute balance for the system as a whole with pure adsorbent yields

$$L_S(X_1 - 0) = G_S[Y_0 - Y_2] \tag{12.25}$$

Applying Eq. (12.8), we get

$$L_S\left(\frac{Y_1}{m}\right)^{1/n} = G_S(Y_0 - Y_2) \tag{12.26}$$

$$\frac{L_S}{G_S} = \frac{(Y_0 - Y_2)}{\left(\frac{Y_1}{m}\right)^{1/n}} \tag{12.27}$$

Applying a similar balance for stage 2, we get

$$G_S(Y_1 - Y_2) = L_S(X_2 - 0) = L_S\left(\frac{Y_2}{m}\right)^{1/n} \tag{12.28}$$

$$\left(\frac{L_S}{G_S}\right) = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}} \tag{12.29}$$

Equating Eqs. (12.27) and (12.29), we get

$$\frac{(Y_0 - Y_2)}{\left(\frac{Y_1}{m}\right)^{1/n}} = \frac{(Y_1 - Y_2)}{\left(\frac{Y_2}{m}\right)^{1/n}}$$

$$\frac{(Y_0 - Y_2)}{Y_2} = \frac{(Y_1 - Y_2)}{Y_2}\left[\left(\frac{Y_1}{m}\right)^{1/n} \times \left(\frac{Y_2}{m}\right)^{-1/n}\right]$$

$$\left(\frac{Y_0}{Y_2}\right) - 1 = \left(\frac{Y_1}{Y_2}\right)^{1/n}\left[\left(\frac{Y_1}{Y_2}\right) - 1\right] \tag{12.30}$$

Since Y_0, Y_2, n are all specific values for a specified level of adsorption and also a specific adsorbent, the only unknown Y_1, can be estimated by trial and error. Alternately, Y_1, can be estimated by the following chart as shown in Fig. 12.16.

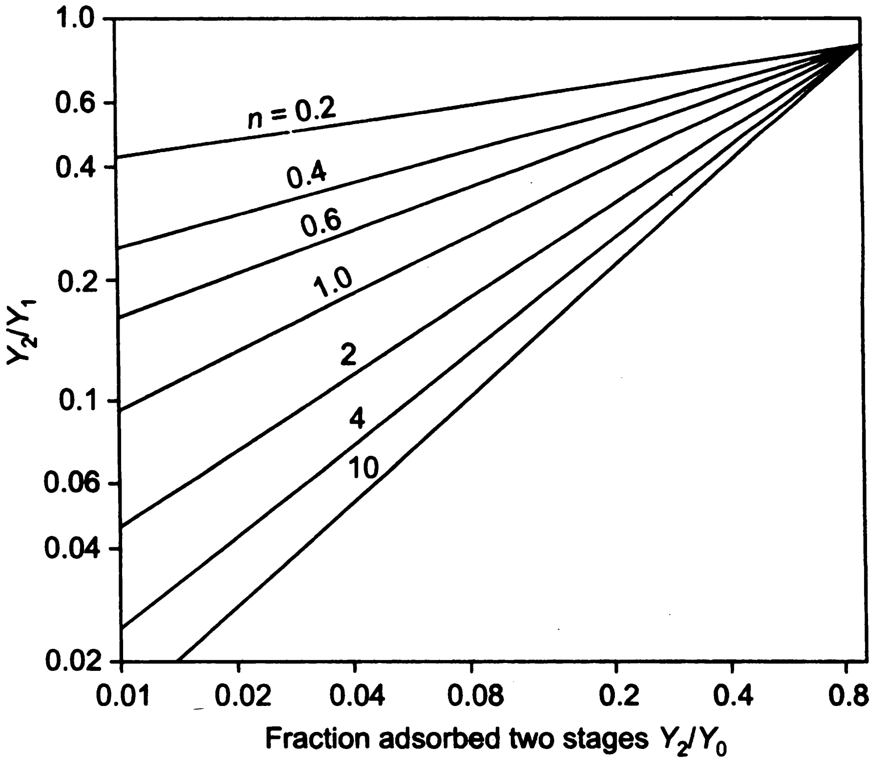


Fig. 12.16 Two-stage countercurrent adsorption Eq. (12.27).

12.11 CONTINUOUS ADSORPTION

In these adsorbers, the fluid and adsorbent are in continuous contact without any separation of the phases. This is quite analogous to gas absorption with the solid adsorbent replacing the liquid solvent. The operation can be carried out in strictly continuous, steady state fashion with both fluid and solid moving at constant rate and the composition remains constant at a particular point. It can also be operated on semi-continuous basis with solid particles remaining stationary and fluid in moving condition. Such operations constitute unsteady adsorption process.

12.11.1 Steady State Adsorption

Continuous differential contact tower is schematically represented in Fig. 12.17.

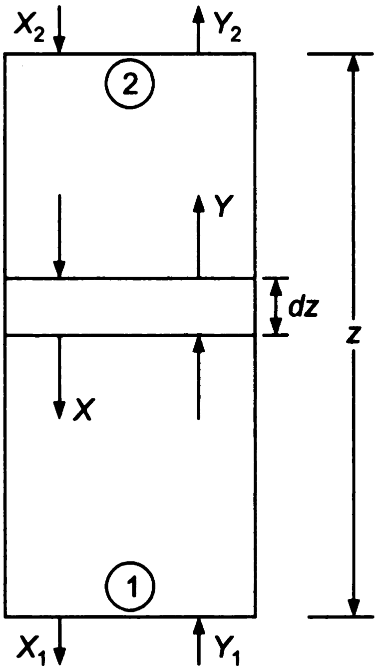


Fig. 12.17 Continuous differential contact tower.

Solute balance for the entire tower is

$$G_S(Y_1 - Y_2) = L_S(X_1 - X_2) \tag{12.31}$$

Solute balance for the upper part of the tower is

$$G_S(Y - Y_2) = L_S(X - X_2) \tag{12.32}$$

Using Eq. (12.31), one can draw the operating line and Eq. (12.32) gives us the concentration of the two phases at any point in the tower.

Making a solute balance across the element of thickness dZ,

$$L_S\,(dX) = G_S\,dY = K_ya\,(Y - Y^*)\,dZ \tag{12.33}$$

where K_y a is mass transfer coefficient based on the outside surface area a of particles, kg/m^3.s.(ΔY) and Y^* is the equilibrium concentration of the fluid corresponding to its concentration X.

Equation (12.33) on integration yields

$$N_{toG} = \int_{Y_2}^{Y_2} \frac{dY}{(Y - Y^*)} = \frac{K_ya}{G_S}\int_0^Z dZ = \frac{Z}{H_{toG}} \tag{12.34}$$

where $H_{toG} = G_S/K_ya$

N_{toG} can be determined graphically as usual.

12.11.2 Unsteady State Adsorbers

When a fluid mixture is passed through a stationary bed of adsorbent, the adsorbent adsorbs solute continuously and it results in an unsteady state operation. Ultimately, the bed may get saturated and no further adsorption results. The change in concentration of effluent stream is shown in Fig. 12.18. The system indicates an exit concentration varying from C, to a final concentration very close to inlet concentration. The point *A* indicates break point. The portion from *A* to *B* is termed the break through curve. Beyond this, very little adsorption takes place, indicating that the system has more or less reached equilibrium or saturation.

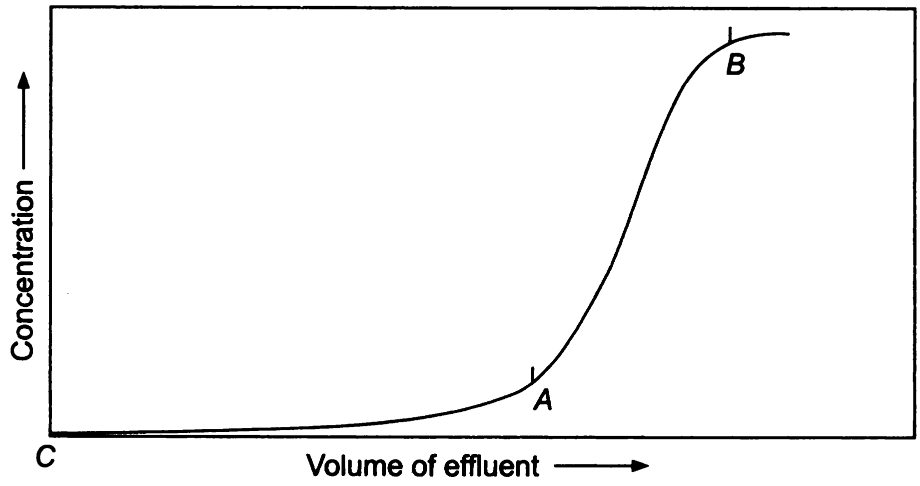


Fig. 12.18 The adsorption wave.

12.12 EQUIPMENT FOR ADSORPTION

Equipment are available for adsorption of a solute from a gaseous or a liquid stream. When the solute (which could be colouring matter, odorous substances, valuable solutes etc.) is strongly adsorbed from a liquid stream, one can use contact filtration equipment which can be operated as batch units, semi-continuous or as continuous ones. Continuous ones can be realized by fluidized bed techniques. These are similar to mixer-settler units used in extraction operations. Generally gases are treated with fluidized bed techniques.

12.12.1 Contact Filtration Equipment

The equipment consists of a mixing tank in which the liquid to be treated and the adsorbent are thoroughly mixed at the operating temperature and for a specified duration of time. In some cases like ion exchange sparging is done with air. Subsequently the slurry is filtered off to separate the solids from the solution. The filtration is done in a filter press or centrifuge or in a continuous rotary filter. Multi stage operations could easily be done by providing a number of tanks and filter combinations. The filter cake is usually washed to displace the solution. If the adsorbate is the desired product, then it can be desorbed by contact with a solvent other than the one which constituted the solution and the one in which the solute is more readily soluble. When the solute is more volatile, it can be removed by the passage of steam or warm air through the solid. Whenever the adsorbent is activated carbon, care must be taken so that the adsorbent does not burn away at high temperatures of desorption operation. Adsorbent can also be regenerated by burning away the adsorbate.

12.12.2 Fluidised Beds

When a mixtures of gases are to be treated on a continuous basis, it is preferable to use fluidized beds. This is done by passing the gases at high velocities through a bed of granular solids in which the adsorption occurs. The beds of solids remain in suspended condition throughout the operation. The bed can be regenerated by passing steam/air at high temperatures. To improve the effectiveness of operation, one can go in for the multistage counter operation with regeneration. In these operations one has to take care to minimize or prevent the carry over of solids.

12.12.3 Steady-state Moving Bed Adsorbers

In this category of adsorbers both the solids and fluid move continuously. The composition at any particular point is independent of time. They are operated with the solids moving downwards and the liquid in upward direction. The flow of solids is plug flow in nature and it is not in fluidized state.

The Higgins contactor developed for ion exchange is an excellent facility for adsorption. Figure 12.19 indicates the arrangement. This consists of two sections. In the top section to start with adsorption takes place. Simultaneously the bottom section of the bed undergoes regeneration. After some pre-calculated duration of operation, the flow of liquids is stopped and the positions of the valves are changed

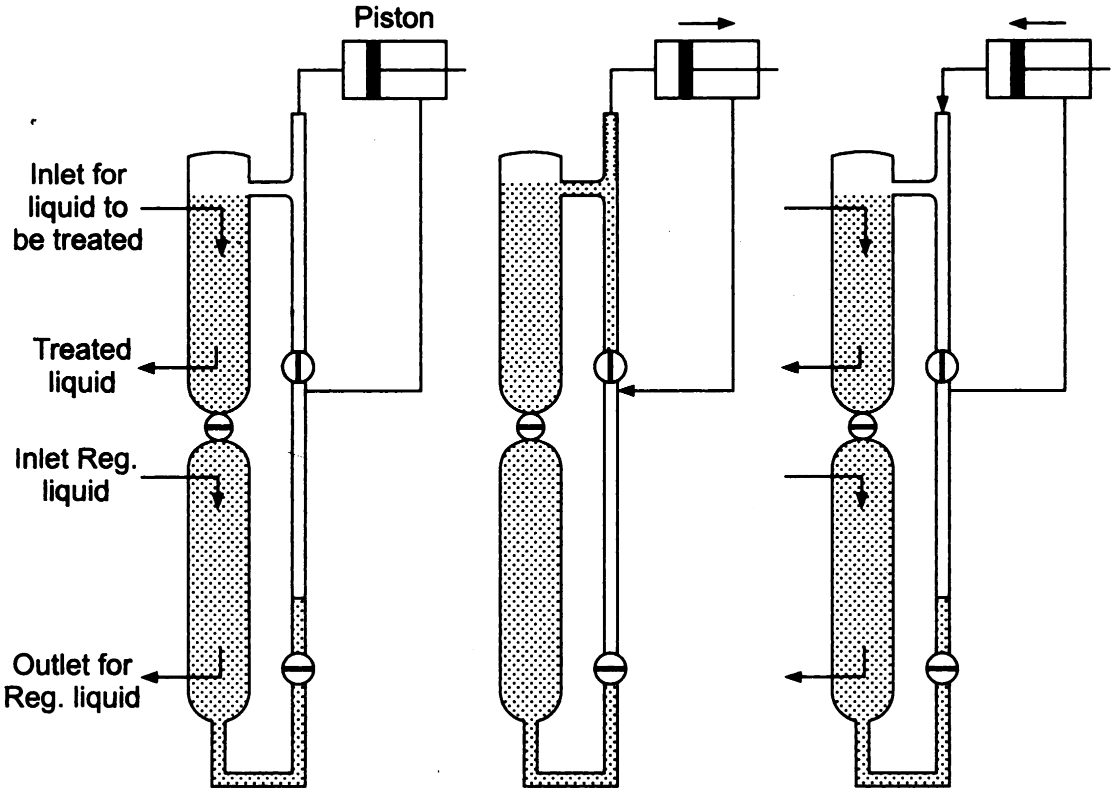


Fig. 12.19 Higgins contactor.

as indicated. The liquid-filled piston pump is moved and this leads to the clockwise movement of solids. Once again the valves are moved to their original position and the movement of solid also stops. The adsorption cycle once again starts in the top section of the unit and desorption at the bottom section.

WORKED EXAMPLES

1. One litre flask is containing air and acetone at 1 atm and 303 K with a relative humidity of 35% of acetone. 2 g of fresh activated carbon is introduced and the flask is scaled. Compute the final vapour composition and final pressure neglecting adsorption of air.

Equilibrium data:

g adsorbed/g carbon	0	0.1	0.2	0.3	0.35
Partial pressure of acetone, mm Hg	0	2	12	42	92

Vapour pressure of acetone at 30°C is 283 mm Hg.

Solution.

Let us convert the data from partial pressure to concentration in terms of g acetone/g of air.

i.e. $$\frac{2}{(760-2)} \times \frac{58}{28.84} = 5.28 \times 10^{-3} \text{ g acetone/g air}$$

Likewise the other values can also be converted to concentration in terms of mass ratios.

Hence,

X, g adsorbed/g carbon	0	0.1	0.2	0.3	0.35
Y, g acetone/g air	0	5.28×10^{-3}	32.1×10^{-3}	117×10^{-3}	276×10^{-3}

Originally the feed contains 35% RH acetone

i.e. Partial pressure/vapour pressure = 0.35

∴ Partial pressure of acetone = 283 × 0.35 = 99 mm Hg.

Partial pressure of air = 661 mm Hg.

$$\therefore \quad Y_0 = \frac{99}{(760-99)} \times \frac{58}{28.84} = 0.301 \text{ g of acetone/g of air}$$

$L_S = 2$ g

The feed point is $(X_0, Y_0) = (0.0, 0.301)$

Volume fraction of air in the original mixture = $\frac{(760-99)}{760} = 0.87$ liters.

i.e. volume of air = 0.87 l (At 1 atm and 303 K)

i.e. moles of air = $\frac{(0.87 \times 1)}{303} \times \frac{273}{1} \times \frac{1}{22.414} = 0.03496$ g moles

i.e. mass of air in the original mixture = 0.03496 × 28.84 = 1.008 g

$$\therefore \qquad \frac{L_S}{G_S} = \frac{2}{1.008} = 1.984$$

Y_1 (from graph) = 13×10^{-3} g acetone/g air

Grams of acetone left behind after adsorption, per gram of air = 0.013

i.e. $$\frac{\text{Partial pressure of acetone}}{\text{Partial pressure of air}} \times \frac{58}{28.84} = \text{g acetone/g air}$$

i.e. $$\frac{\text{Partial pressure of acetone}}{661} \times \frac{58}{28.84} = 0.013 \text{ g acetone/g air}$$

$\therefore$ Partial pressure of acetone in flask after adsorption = 4.27 mm Hg

$\therefore$ Total pressure = 661 + 4.27 = 665.27 mm Hg.

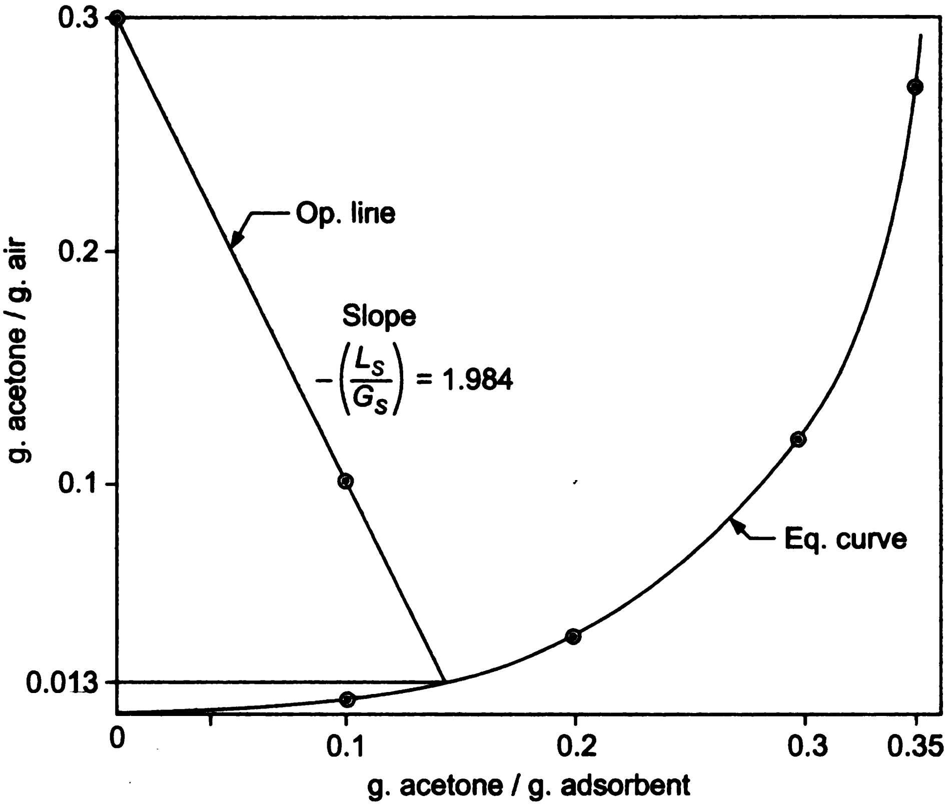


Fig. 12.20 Example 1.

2. A solid adsorbent is used to remove colour impurity from an aqueous solution. The original value of colour on an arbitrary scale is 48. It is required to reduce this to 10% of its original value. Using the following data, find the quantity of fresh adsorbent used for 1000 kg of solution for (a) a single stage and (b) a two-stage cross-current operation when the intermediate colour value is 24.

Equilibrium data:

kg adsorbent/kg of solution	0	0.001	0.004	0.008	0.02	0.04
Equilibrium colour (Y)	48	43	31.5	21.5	8.5	3.5

Solution.

(a) The given data will be converted to enable us to handle it more easily.

The initial values are X_o = units of colour/kg adsorbent = 0

Y_o = units of colour/kg solution = 48

When 0.001 kg of adsorbent is added tol kg of solution, the colour reduces from 48 units to 43 units. These 5 units of colour are thus transferred to 0.001 kg adsorbent.

$$\therefore \qquad X, \frac{\text{units of colour}}{\text{kg adsorbent}} = \frac{(48-43)}{0.001} = 5000$$

Similarly, by adding 0.004 kg adsorbent, colour drops by 16.5 units.

$$\text{i.e.} \qquad X = \frac{16.5}{0.004} = 4125$$

X, colour adsorbent/kg adsorbent	0	5000	4125	3312.5	1975	1112.5
Y, colour/kg solution	48	43	31.5	21.5	8.5	3.5

The final solution has 4.8 units of colour

(a) *Single stage operation:*

$$\text{Slope} = -\frac{L_S}{G_S} = -0.030 \text{ (from graph)}$$

G_S is 1000 kg of solution.

$\therefore$ Dosage of carbon = 0.03 × 1000 = 30 kg

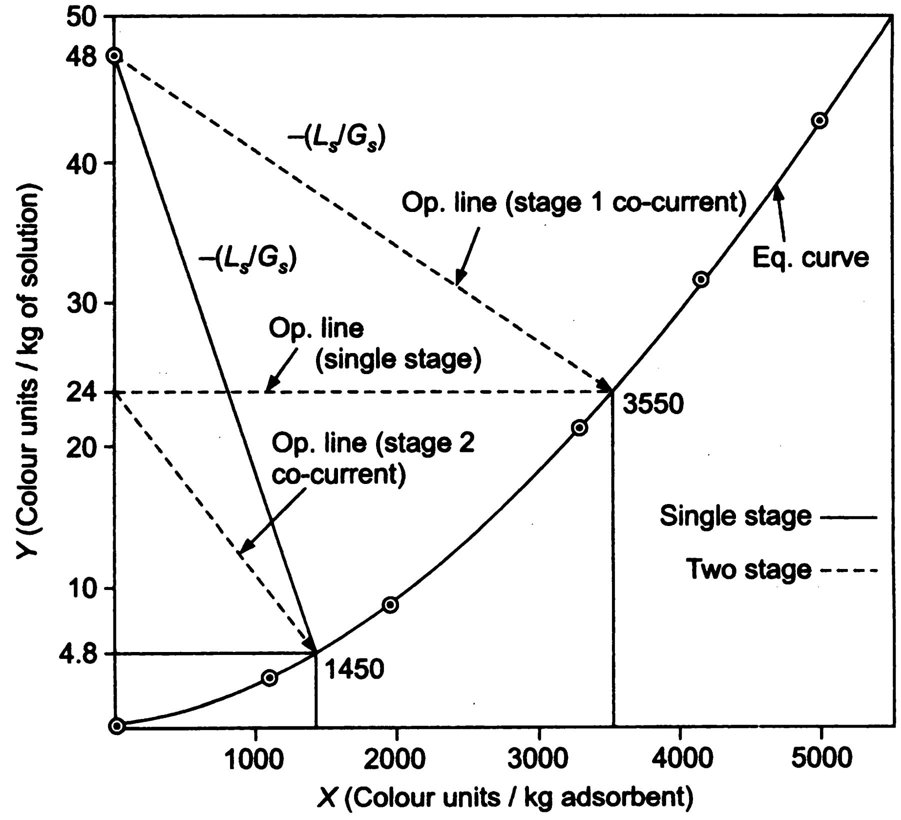


Fig. 12.21 Example 2.

(b) A two-stage cross-current operation

$$-\left(\frac{L_S}{G_S}\right)_1 = +\frac{(48-24)}{(0-3550)} = -\frac{24}{3550} = -6.76\times10^{-3}$$

$$-\left(\frac{L_S}{G_S}\right)_2 = +\frac{(24-4.8)}{(-1450+0)} = -0.01324$$

G_S is 1000 kg of solution

$$\therefore \qquad L_{S_1} + L_{S_2} = 6.76 + 13.24 = 20.00 \text{ kg}$$

3. The equilibrium decolourisation data for a certain system using activated carbon is given by the equation,

$$Y = 0.004X^2$$

where Y is g colouring impurity/kg impurity free solution and X is g colouring impurity/kg pure activated carbon.

Calculate the amount of activated carbon required per 1000 kg of impurity free solution to reduce the impurity concentration from 1.2 to 0.2 g/kg of impurity free solution using (i) a single stage operation and (ii) a two-stage cross-current operation with intermediate composition of 0.5 g. of colouring impurity per kg of impurity free solution.

$$Y = 0.004X^2$$

Solution.

Feed, G_S = 1000 kg of impurity free solution

(i) Y_0 = 1.2 g/kg of impurity free solution

Y_1 = 0.2 g/kg of impurity free solution

$X_0 = 0$

$$X_1 = \left(\frac{Y_1}{0.004}\right)^{0.5} = \left(\frac{0.2}{0.004}\right)^{0.5} = 7.07$$

$$-\frac{L_S}{G_S} = +\frac{(Y_0-Y_1)}{(X_0-X_1)} = +\frac{(1.2-0.2)}{(0-7.07)} = -\frac{1}{7.07} = -0.1414$$

$$\therefore \qquad L_S = 0.1414 \times 1000 = 141.4 \text{ kg of adsorbent}$$

(ii) Intermediate colour concentration is 0.5 g/kg of impurity free solution

$$\therefore \qquad X_1 = \left(\frac{0.5}{0.004}\right)^{0.5} = 11.18$$

$$\therefore \qquad -\left(\frac{L_S}{G_S}\right)_1 = \frac{(1.2-0.5)}{(0-11.18)} = -\frac{0.7}{11.18} = -0.06261$$

$$X_2 = X_{\text{final}} = 7.07$$

$$-\left(\frac{L_S}{G_S}\right)_2 = \frac{(0.5-0.2)}{(0-7.07)} = -0.04243$$

$$\therefore \qquad \left(\frac{L_S}{G_S}\right)_{\text{total}} = 0.06261 + 0.04243 = 0.10504$$

The adsorbent needed, L_S = 105.04 kg of adsorbent.

4. A solution of washed raw cane sugar of 48% sucrose by weight is coloured by the presence of small quantities of impurities. It is to be decolourised at 80°C by treatment with an adsorptive carbon in a contact filtration plant. The data for an equilibrium adsorption isotherm were obtained by adding various amounts of the carbon to separate batches of the original solution and observing the equilibrium colour reached in each case. The data with the quantity of carbon expressed on the basis of the sugar content of the solution are as follows:

$\frac{\text{kg carbon}}{\text{kg dry sugar}}$	0	0.005	0.01	0.015	0.02	0.03
% colour removed	0	47	70	83	90	95

The original solution has a colour concentration of 20 measured on an arbitrary scale and it is desired to reduce the colour to 2.5% of its original value.

(i) Convert the equilibrium data to Y and X.

(ii) Calculate the amount of carbon required for a single stage process for a feed of 1000 kg solution.

(iii) Estimate the amount of carbon needed for a feed of 1000 kg solution in a two-stage countercurrent process.

Solution.

Feed solution contains 48% sucrose.

$\frac{\text{kg carbon}}{\text{kg dry sugar}}$	0	0.005	0.01	0.015	0.02	0.03
% colour removed	0	47	70	83	90	95
$\frac{\text{kg carbon}}{\text{kg dry solution}}$	0	0.0024	0.0048	0.0072	0.0096	0.0144
$Y, \frac{\text{colour}}{\text{kg of solution}}$	20	0.53×20 = 10.6	0.30×20 = 6	0.17×20 = 3.4	0.10×20 = 2.0	0.05×20 = 1.0
$X, \frac{\text{colour}}{\text{kg carbon}}$	–	$\frac{(20-10.6)}{0.0024}$ = 3916.7	$\frac{(20-6)}{0.0048}$ = 2916.7	$\frac{(20-3.4)}{0.0072}$ = 2305.6	$\frac{(20-2)}{0.0096}$ = 1875	$\frac{(20-1)}{0.0144}$ = 1319.4

Feed is $(X_0, Y_0) = (0, 20)$

Final product is to have 2.5% original colour, i.e. 0.5 units = Y_1

$$\therefore \qquad -\left(\frac{L_S}{G_S}\right) = \frac{(20-0.5)}{(0-100)} = -\frac{19.5}{1000} = -0.0195$$

$$\therefore \qquad L_S = G_S \times 0.0195 = 19.5 \text{ kg}$$

(ii) The operating line is fixed by trial and error for exactly two stages.

$$\left(\frac{L_S}{G_S}\right) = \frac{19.5}{3175} = 6.142 \times 10^{-3}$$

$$\therefore \qquad L_S = 6.142 \text{ kg}$$

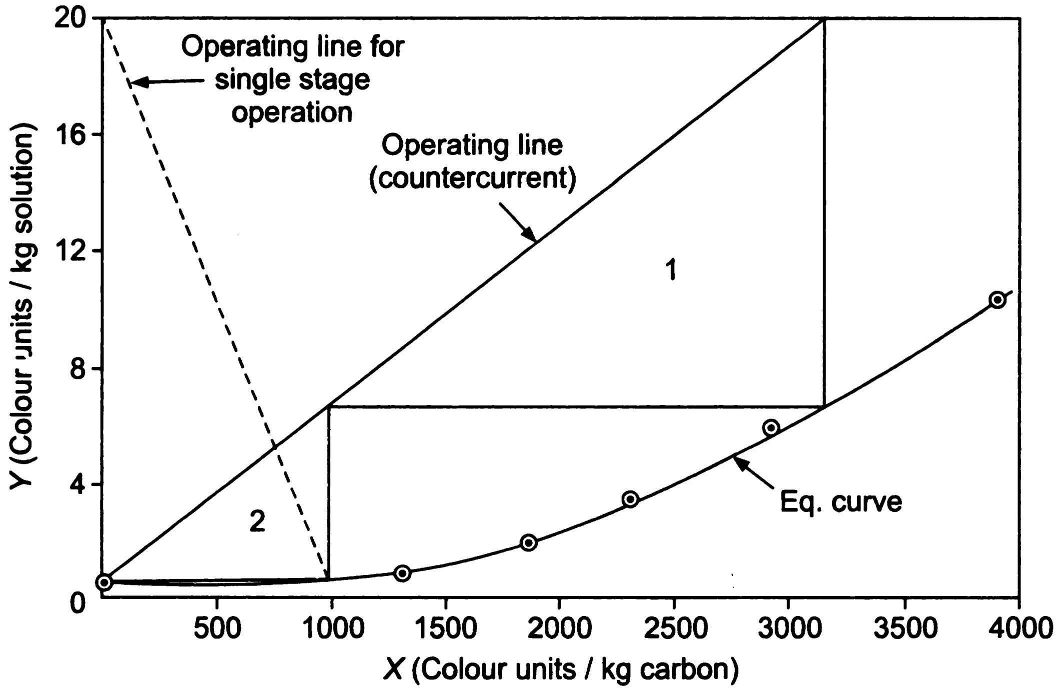


Fig. 12.22 Example 4.

5. NO_2 produced by a thermal process for fixation of nitrogen is to be removed from a dilute mixture with air by adsorption on silica gel in a continuous countercurrent adsorber. The gas entering at the rate of 0.126 kg/s contains 1.5% of NO_2 by volume and 90% of NO_2 is to be removed. Operation is isothermal at 25°C and 1 atm pressure. The entering gel will be free of NO_2.

Partial pressure of NO_2, mm Hg	0	2	4	6	8	10	12
kg NO_2/100 kg gel	0	0.4	0.9	1.65	2.6	3.65	4.85

(a) Calculate the minimum weight of gel required/h.

(b) For twice the minimum gel rate, calculate the number of stages required.

Solution.

Entering gas rate : 450 kg/hr = 0.126 kg/s

NO_2 present : 1.5 % by volume

Temperature : 25°C

Pressure : 1 std. atm.

Partial pressure of NO_2, mm Hg	0	2	4	6	8	10	12
kg NO_2/100 kg gel	0	0.4	0.9	1.65	2.6	3.65	4.85
Kg NO_2/kg gel, X	0	0.004	0.009	0.0165	0.026	0.0365	0.0485
(pp NO_2/pp air) × (46/28.84), Y, (kg/kg)	0	0.0042	0.00844	0.01269	0.01697	0.02127	0.0256

$$Y_{\text{in}} = 1.5\%$$

$$Y_{\text{in}} = (\text{kg/kg}) = \frac{1.5}{98.5} \times \frac{46}{28.84} = 0.0243$$

$$Y_{\text{in}}\ (\text{kg/kg of mixture})\ \frac{0.0243}{1.0243} = 0.0237$$

$$G_S = 450\ (1 - 0.0237) = 439.3\ \text{kg/h}$$

90% of NO_2 is to be recovered

$$Y_{\text{out}} = \frac{1.5 \times 0.1}{98.5} \times \frac{46}{28.84} = 0.00243$$

$$\left(\frac{L_S}{G_S}\right)_{\text{min}} = \frac{0.025}{0.0375} = 0.667$$

Weight of absorbent required, $L_S = 0.667 \times 439.3 = 291.1$ kg/h

Number of stages needed for twice the adsorbent rate

$$\therefore \qquad \left(\frac{L_S}{G_S}\right)_{\text{act}} = \frac{582.2}{439.3} = 1.334$$

No. of stages = 3

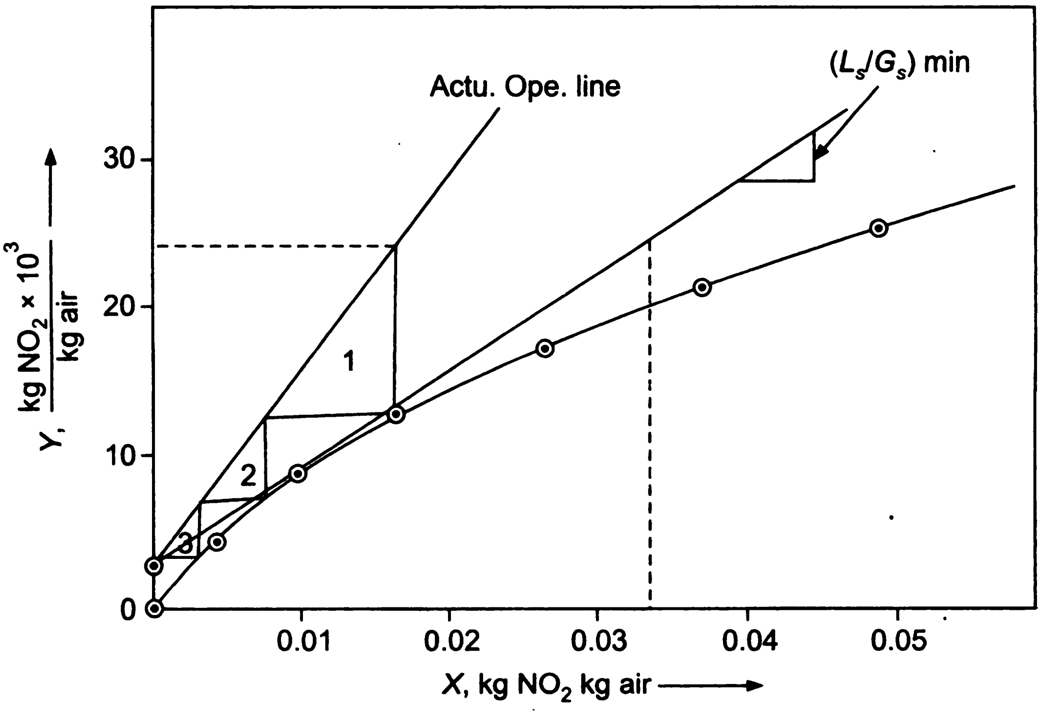


Fig. 12.23 Example 5.

6. 500 kg/min of dry air at 20°C and carrying 5 kg of water vapour/min. is to be dehumidified with silica gel to 0.001 kg of water vapour/kg of dry air. The operation has to be carried out isothermally and countercurrently with 25 kg/min. of dry silica gel. How many theoretical stages are required and what will be the water content in the silica gel leaving the last stage?

kg. of water vapour/ kg of dry silica gel, X	0	0.05	0.10	0.15	0.20
kg of water vapour/ kg of dry air, Y	0	0.0018	0.0036	0.0050	0.0062

Solution.

Quantity of dry air entering at 20°C, G_S = 500 kg/min

Quantity of water vapour entering = 5 kg/min

$$Y_1 = \frac{5}{500} = 0.01 \text{ kg water vapour/kg dry air}$$

Concentration of water vapour in leaving air, Y_2 = 0.001 kg water vapour/kg dry air

Quantity of silica gel entering, L_S = 25 kg/min

$$X_2 = 0$$

i.e.

$$\left(\frac{L_S}{G_S}\right) = \frac{25}{500} = 0.05$$

Making a material balance

$$L_S\,[X_1 - X_2] = G_S\,[Y_1 - Y_2]$$

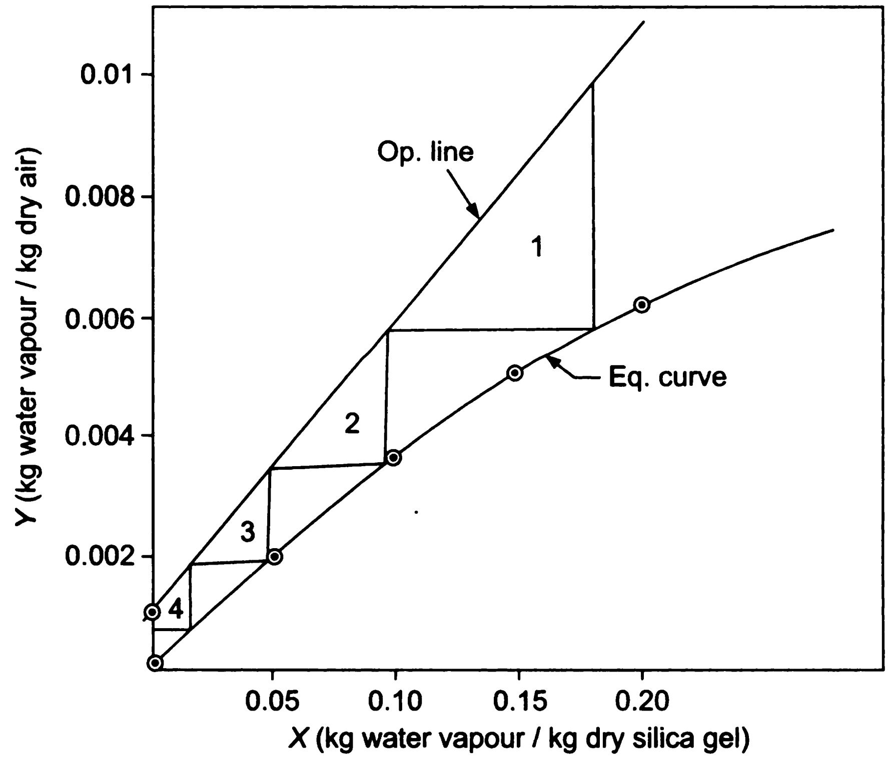


Fig. 12.24 Example 6.

$$\therefore \qquad X_1 = \frac{500 \times 0.009}{25} = 0.18$$

Total number of stages needed = 4

EXERCISES

1. The equilibrium relationship for the adsorption of colour from a carrier gas is given by $y = 0.57x^{0.5}$, where y is the gram of coloured substance removed per gram of adsorbent and x is the gram of colour/100 grams of colour free carrier. If 100 kg of the carrier containing 1 part of colour per 3 parts of total carrier is contacted with 25 kg of adsorbent, calculate the percent of colour removed by (i) single contact, (ii) two-stage cross-current contact dividing the adsorbent equally per contact.
2. Experiments on decolourisation of oil yielded the following relationship $y = 0.5x^{0.5}$, where y is the gram of colour removed per gram of adsorbent and x is the gram of colour/1000 grams of colour free oil. If 1000 kg of oil containing 1 part of colour per 3 parts of colour free oil is contacted with 250 kg of adsorbent, calculate the percent of colour removed by (i) single stage process, (ii) two-stage cross-current contact process using 125 kg adsorbent in each stage.
3. A solid adsorbent is used to remove colour impurity from an aqueous solution. The original value of colour on an arbitrary scale is 48. It is required to reduce this to 10% of its original value. Using the following data, find the number of stages needed for 1000 kg of a solution in a countercurrent operation if 1.5 times the minimum adsorbent needed is used.

   Equilibrium data:

kg adsorbent/kg of solution	0	0.001	0.004	0.008	0.02	0.04
Equilibrium colour (Y)	48	43	31.5	21.5	8.5	3.5

4. An aqueous solution containing valuable solute is coloured by the presence of small amounts of impurity. It is decolourised using activated carbon adsorbent. The equilibrium relationship is $Y = 0.00009X^{1.7}$, where X = colour units/kg carbon and Y = colour units/kg solution. If the original solution has 9.8 colour units/kg solution, calculate (i) the amount of colour removed by using 30 kg of adsorbent in a single stage operation and (ii) the amount of carbon needed for a two-stage countercurrent operation if the final colour in the solution is to be 10% of the original value and the solution leaving the first stage has 4 times the final colour of the solution.
5. The adsorption of moisture using silica gel varies with moisture content as follows: $Y = 0.035X^{1.05}$, where X = kg water adsorbed/kg dry gel and Y = humidity of air, kg moisture/kg dry air. 1 kg of silica gel containing 2% (dry basis) of moisture is placed in a vessel of volume 5 m^3 containing moist air. The partial pressure of water is 15 mm Hg. The total pressure and temperature are 1 atm. and 298 K respectively. What is the amount of water picked up by silica gel from the moist air in the vessel? Estimate the final partial pressure of moisture and final total pressure in the vessel.