

Figure 7.1 Schematic of a typical distillation column.

Distillation, which is one of the oldest mass transfer operations, is reported to have been invented in Alexandria (Egypt) in the first century AD. The early use was in the production of alcoholic beverages. The history of distillation has been described by Forbes (1948).

It will be useful to distinguish between distillation and evaporation since in the latter operation also, the components in solution are separated by volatilizing some of them. The major difference is that in evaporation a solution containing a volatile solvent and a non-volatile solute (or a solute having a very low volatility) is separated by vaporizing out a part or whole of the solvent. Examples are: evaporation of a sugar solution (sugar: a non-volatile solute; water: a volatile solvent), evaporation of a glycerol solution (glycerol: a solute having negligible volatility; water: a volatile solvent). But in distillation, the components (at least two of them) have reasonable volatility. Example: distillation of aqueous ethanol (both ethanol and water are volatile, but ethanol is more volatile).

Distillation is the most common mass transfer operation in the process industries, particularly the organic process industries. The function of distillation may be separation of products from a mixture (example: separation of aniline and nitrobenzene in the process of manufacture of aniline), recovery of a product (example: recovery of ethanol from its solution in water in the process of manufacture of alcohol), or increasing the purity of a product (example: drying of commercial benzene for the removal of traces of water present in it). Distillation is again the most important operation in a petroleum refinery. A petrochemical complex also uses a large number of distillation columns. Sometimes, distillation may be used in conjunction with a few other mass transfer operations (Stichlmair and Fair, 1998). For example, in an acrylonitrile plant, the product is separated from the reaction mixture by absorption in water. The aqueous solution of acrylonitrile leaving the absorption tower is separated in a distillation column to produce acrylonitrile of desired purity. Similarly, the extract and raffinate streams from an extraction column (discussed in Chapter 8) may be further separated in a distillation column depending upon the difference in volatility of the components (example: an aromatics extraction unit in a petroleum refinery). Because of its importance and wide use in separation of mixtures, distillation is called

‘the workhorse of chemical industries’. Despite the advent of newer and advanced separation processes, distillation still remains the most widely used separation technique of liquid mixtures and solutions (Fair, 1988; Kunesh et al., 1995). The estimated cost of annual worldwide throughput of distillation columns was 524 billion dollars about ten years ago as reported by Porter (1995). A few common examples of applications of fractional distillation are cited in Table 7.1. Here we shall briefly discuss the basic principles of distillation calculations and design. There are a few excellent books that deal with the topic elaborately (Billet, 1985, 1995; Kister, 1989, 1992; Stichlmair and Fair, 1998).

Table 7.1 A few examples of separation of liquid mixtures by distillation

Feed/Components	Industry/Plant	Product
Crude petroleum	Refinery	Various petroleum products
Ethylene oxide/Water	Petrochemical	Ethylene oxide
Acrylonitrile/Water	—do—	Acrylonitrile
Styrene/Ethylbenzene	—do—	Styrene
Benzene/Ethyl benzene/others	—do—	Ethylbenzene
Propylene/Propane	—do—	Propylene
Ethanol/Water	Fermentation/Distillery	Ethanol
Acetic acid/Acetic anhydride	Acetic anhydride plant	Acetic anhydride
Air	Air separation plant	Nitrogen, Oxygen, Argon
Aniline/Nitrobenzene	Aniline plant	Aniline

7.1 VAPOUR–LIQUID EQUILIBRIUM

Separation of a mixture by distillation is based on equilibrium distribution of the components between the liquid and the vapour phases. A knowledge of vapour–liquid equilibrium is therefore essential for understanding the principles of distillation. Consider an aqueous solution of ethanol taken in a closed vessel like the one shown in Figure 4.1. The solution is boiled for some time and the vapour along with air in the space above the liquid is expelled through a valve so that the vessel now contains molecules of ethanol and water only. The valve is now closed and the vessel is put in a constant temperature bath. What do we expect to happen? Given sufficient time, the system reaches equilibrium and the liquid and the vapour compositions as well as the total pressure in the vapour space (i.e. the total pressure exerted by the solution) attain unique values. Now the vessel is taken out of the bath, some amount of ethanol (or water) is pushed into it and the vessel is again maintained at the same temperature in the bath. The system will attain a new equilibrium state, i.e. it will have a different set of liquid and vapour concentrations and a new total pressure in the vapour space. Under a *given set of conditions*, the equilibrium vapour composition is related to the liquid composition. This is what is called the *vapour–liquid equilibrium* (VLE).

But what is meant by ‘a given set of conditions’? The answer is given by Gibb’s phase rule (discussed before in Chapter 4) expressed as

$$\bar{F} = \bar{C} - \bar{P} + 2 \quad (7.1)$$

In the above example of equilibrium in the ethanol–water system, the number of components, $\bar{C} = 2$; the number of phases, $\bar{P} = 2$ (the vapour and the liquid phase). So $\bar{F} = 2$ and the system

has two degrees of freedom. The total number of parameters and variables is four—temperature, total pressure, liquid composition and vapour composition. Since the number of degrees of freedom (\bar{F}) is 2, two of these four quantities need to be fixed to define the system in equilibrium. Thus if temperature and pressure are fixed, the liquid and the vapour compositions will be automatically fixed (i.e. there can be only one set of liquid and vapour compositions for which the total pressure exerted in the vapour space is equal to the given pressure at the given temperature). Similarly, if the temperature and the liquid composition are fixed, the total pressure and the vapour compositions will be automatically fixed if the system is in equilibrium. Extension to a multicomponent system is not difficult.

Vapour–liquid equilibria constitute the physical basis of separation of a mixture by distillation. The higher concentration of the more volatile component(s) in the vapour phase compared to the liquid phase makes separation by distillation possible (see the x – y data for the methanol–water system given in Example 7.15). Accurate VLE data are essential for reliable design of a distillation column. If the experimental data are not available (this happens frequently for multicomponent systems), a suitable predictive method (e.g. UNIFAC method) can be adopted for computation of equilibrium data. Now we shall describe a simple experimental setup for the determination of vapour–liquid equilibrium in the laboratory. This will be followed by a description of common types of equilibrium relationships exhibited by various liquid mixtures.

7.1.1 Experimental Determination of Vapour–Liquid Equilibrium (VLE)

Different types of experimental setup have been devised for the measurement of composition and temperature/pressure of liquid and vapour phases in equilibrium. The basic functions of an equilibrium still are to continuously vaporize a liquid mixture, condense all the vapour in a condenser (using a suitable coolant) and recycle the condensate to the still or the boiling flask. This kind of apparatus is called a ‘liquid-recirculation still’. After equilibrium is reached, a sample of the liquid is drawn from the still and analyzed to determine the liquid composition (x , mole fraction). A sample of the condensate (which has the same composition as that of the vapour) is analyzed to get the composition of the vapour at equilibrium[†] (y^* , mole fraction). Experiments are repeated with liquid mixtures of different compositions to generate the vapour–liquid equilibrium data (x – y^* data) covering the entire range of composition of the binary ($0 \leq x \leq 1$).

An early version of the device used for this purpose is the ‘Othmer still’ devised by D.F. Othmer as early as in 1928. Various modifications of this apparatus have been suggested from time to time—for example, Colburn still, Gillespie still, Scheeline and Gilliland still, etc. Two common sources of error in the experiments are: (i) superheating of the liquid (the thermocouple/thermometer indicates a wrong boiling temperature of the liquid mixture as a result); (ii) heat loss from the still or the boiling flask causing partial condensation of the vapour before it leaves the boiling flask. A modified version of the Gillespie still (Yuan and Lu, 1963) which is free from these problems is described in Figure 7.2.

A liquid mixture is taken in the boiling flask (B) which is provided with an internal electric heating coil (H) within a glass sheath (G). The liquid–vapour mixture flows through the vertical tube P (sometimes called ‘Cottrell pump’) and enters the equilibration chamber (E) in which the vapour and the liquid phases get separated and reach equilibrium. The liquid flows to the liquid

[†] A star (*) is often used to indicate the equilibrium value; x and y refer to the more volatile in a binary.

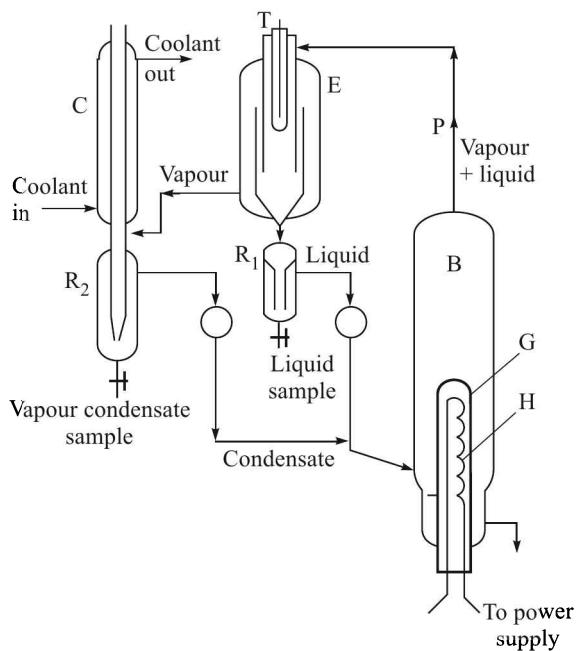


Figure 7.2 Schematic of a modified Gillespie still. B: boiling flask or 'still'; H: internal electric heater; G: glass sheath of the heater; P: Cottrell pump; E: equilibration chamber; R₁: liquid receiver; C: total condenser of a vapour; R₂: condensate receiver; T: thermometer or thermocouple.

receiver (R₁) and the vapour flows to the condenser (C). The condensate is collected in another receiver (R₂). Since all the vapour flowing into the condenser is condensed (it is a 'total condenser'), the composition of the vapour and that of the condensate are equal. The boiling flask (B), the equilibrium chamber (E) and the liquid receiver (R₁) are well-insulated. (If the insulation is not good, condensation of a little vapour may occur in E and R₁ causing 'rectification' of the vapour. As a result, the vapour will be more enriched in the more volatiles than it should be at 'equilibrium'). The liquid from R₁ and the condensate from R₂ continuously overflow and get recycled back to the boiling flask through the connecting tubes as shown in Figure 7.2. The still is operated for a sufficiently long time to reach equilibrium. Samples of the liquid and of the vapour (condensed in the receiver R₂) are collected by opening the stop cocks and then analyzed to find out the equilibrium compositions of the phases. The temperature in the equilibrium chamber is measured by inserting a thermocouple or a thermometer in the thermowell, T. The temperature indicated at equilibrium is equal to the bubble point of the liquid and also equal to the dew point of the equilibrium vapour. (It is to be noted that if the boiling temperature is measured by inserting a thermometer in a thermowell in the boiling flask, there may be an error because of the superheat of the liquid.) A suitable arrangement for maintaining the pressure in the still is made if it is operated at a pressure different from the ambient pressure.

The apparatus described above is useful to measure the 'constant pressure' equilibrium data. With some modifications, it can be used to measure 'constant temperature' equilibrium—when the total pressure, in addition to the equilibrium liquid and vapour concentrations, is measured at a given constant temperature.

7.1.2 Constant Temperature or Constant Pressure Binary Equilibria

By repeating the above experiment with liquid mixtures of various compositions, we can collect the $T-x-y^*$ data for a system. If the boiling temperature is plotted versus the liquid composition x , we get the ‘bubble point curve’. A plot of the temperature versus y^* , the equilibrium vapour composition, gives the ‘dew point’ curve. The bubble and dew point curves for binary mixtures of cyclo-pentane(A) and benzene(B) at 1 atm total pressure are shown in Figure 7.3(a). Both the liquid and vapour phase concentrations (x and y^*) of cyclo-pentane (the more volatile) are plotted along the horizontal axis and the temperature is plotted along the vertical axis. The equilibrium diagram ($x-y^*$ diagram) is shown below the $T-x-y^*$ diagram in which x is plotted along the horizontal axis and y^* along the vertical axis [Figure 7.3(b)]. A two-dimensional representation

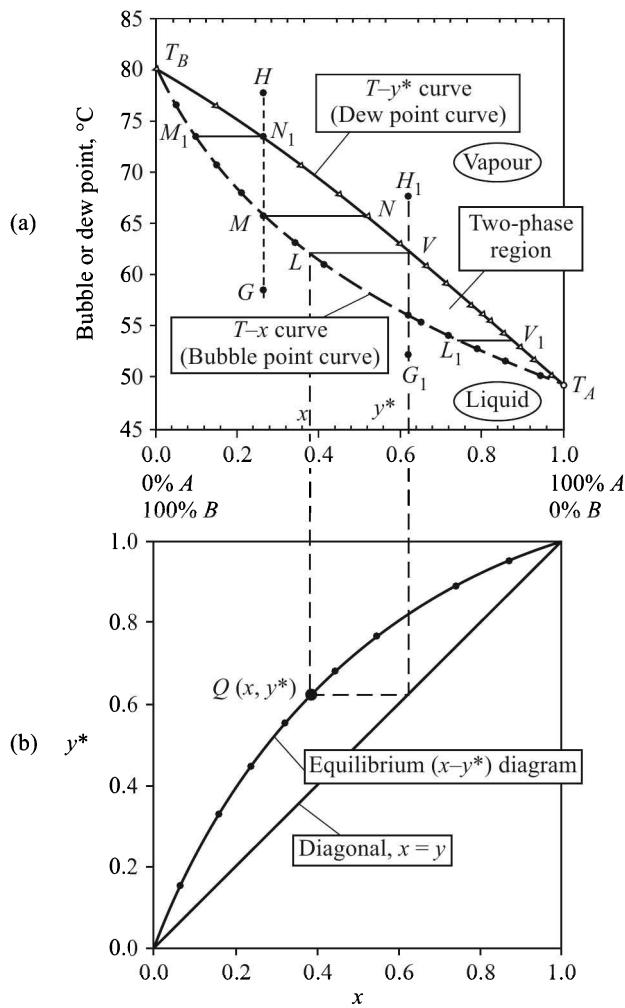


Figure 7.3 (a) Bubble and dew point curves, and (b) equilibrium diagram of cyclo-pentane (1)–benzene (2) system at 1 atm. [Myers, *Ind. Eng. Chem.*, 48(1956) 1104.]

of $T-x-y$ or $x-y$ data is possible only for binary mixtures. For a three-component system, such data may be represented by surfaces in a three-dimensional space or in the tabular form.

On a horizontal line segment, say LV in Figure 7.3(a), the abscissa of the point L gives the concentration of A in the saturated[†] liquid phase (x), and that of the point V gives its equilibrium vapour-phase concentration (y^*); LV is called a ‘tie line’. The lines LV , MN , M_1N_1 , and L_1V_1 in the figure are also tie lines.

Let us imagine that a small amount of a liquid mixture having a mole fraction x (a subscript is not generally used to denote the concentration of the more volatile in a binary mixture) of cyclopentane and the rest benzene is taken at a constant pressure of 1 atm in a vessel fitted with a ‘frictionless piston’ and heated gradually. The temperature and composition of the liquid are given by the point G in Figure 7.3(a). When its temperature reaches the point M , it starts boiling and the composition of the initial vapour is given by the abscissa of the point N , which is the other end of the tie line through M . It is seen that $y^* > x$; i.e. the vapour is richer in A , the more volatile species in the mixture. As heating proceeds, more and more vapour is generated (we assume that all the vapour generated remains in the vapour space above the liquid at a constant pressure). The mole fraction of the more volatile component A in the residual liquid decreases and the boiling point of the liquid continues to increase along the $T-x$ curve. The last droplet of liquid to vaporize has a composition and boiling point given by the point M_1 . When all the liquid is vaporized, the accumulated vapour must have a composition equal to that of the initial liquid. No further heating is done and the final state of the vapour (as given by its temperature and composition) is given by the point N_1 on the vertical line through G . However, if further heating of this vapour (which is now saturated) is done, its temperature will only rise along the vertical line GH (this is superheating of the vapour). The line $T_B-M_1-L-L_1-T_A$ is the bubble point curve; $T_B-N_1-N-V_1-T_A$ is the dew point curve. The bubble and the dew point curves meet at the points T_B (the boiling point of pure B at the given pressure) and at T_A (the boiling point of pure A).

Similarly, if some amount of superheated vapour, whose state is represented by the point H_1 is taken in a vessel fitted with a frictionless piston and is gradually cooled while maintaining a constant pressure of 1 atm, condensation starts when the vapour temperature drops to the point V . The composition of the first droplet of liquid formed is given by the point L (the other end of the tie line through V). As condensation proceeds, the vapour composition changes along VV_1 and the composition of the condensate follows LL_1 . When the entire vapour is condensed and the liquid is cooled, we reach a point G_1 vertically below H_1 in the subcooled liquid domain. The boiling point of pure B lies vertically above the point $x = 0$ ($x = 0$ means pure B). Similarly, T_A occurs vertically above $x = 1$.

The region below the bubble point curve $T_B-M_1-M-L-L_1-T_A$ represents a single liquid phase; the region above $T_B-N_1-N-V_1-T_A$ represents a single vapour phase. A point in the region enclosed by these curves represents a mixture of liquid and vapour. Any such mixture (given by the point F in Figure 7.5(a), for example) splits into a liquid and a vapour phase in equilibrium given by the ends of the tie line LV through the point F .

Let the amount of the two-phase mixture taken be also denoted by F kmol^{††} at a concentration z_F . It splits into a liquid phase of amount L kmol (concentration = x) and an

[†] A liquid at its bubble point is called a ‘saturated liquid’; a vapour at its dew point is a ‘saturated vapour’.

^{††}This practice of representing a stream and its flow rate or amount by the same notation is pretty common in the study of mass transfer operations.

equilibrium vapour phase of amount V kmol (concentration = y^*). Now we may write the following mass balance equations [refer to Figure 7.5(a)].

$$\text{Overall mass balance: } F = L + V \quad (7.2)$$

$$\text{Component A balance: } Fz_F = Lx + Vy^* \quad (7.3)$$

Eliminating F from Eqs. (7.2) and (7.3), we get

$$(L + V)z_F = Lx + Vy^* \\ \Rightarrow \frac{L}{V} = \frac{y^* - z_F}{z_F - x} = \frac{\text{length of the section } FV}{\text{length of the section } LF} \quad (7.4)$$

Thus, the amounts of liquid and vapour produced after phase separation of the mixture F can be calculated using Eq. (7.4). This equation is sometimes called the *Lever-arm Rule*. It is useful in the calculation of flash vaporization, calculations involving liquid–liquid and solid–liquid extraction, etc.

Figure 7.3(b) shows the equilibrium diagram on the x - y plane. It can be obtained directly by plotting the experimental x - y^* data (note that both x and y^* vary from 0 to 1). It can also be drawn from the bubble point and dew point curves, following the procedure indicated in the figure. The point Q on the x - y^* curve corresponds to the tie line LV on the T - x - y diagram. Because $y^* > x$, the equilibrium line lies above the diagonal (at any point on the diagonal, $x = y$). The kind of data given in Figure 7.3 represent the equilibrium data collected at *constant pressure*.

Equilibrium data can also be collected at constant temperature. If so, the total vapour pressure P exerted by the solution at equilibrium depends upon its composition. At a lower concentration of A (i.e. at a higher concentration of the less volatile species B), the mixture will exert a lower total vapour pressure. Typical plots of such data, x - P and y^* - P , are shown in Figure 7.4(a). A horizontal line such as LV is a *tie line*. The terminals (the points L and V) indicate the liquid and vapour phase concentrations of A under equilibrium. The liquid, the vapour and the two-phase regions are demarcated in the

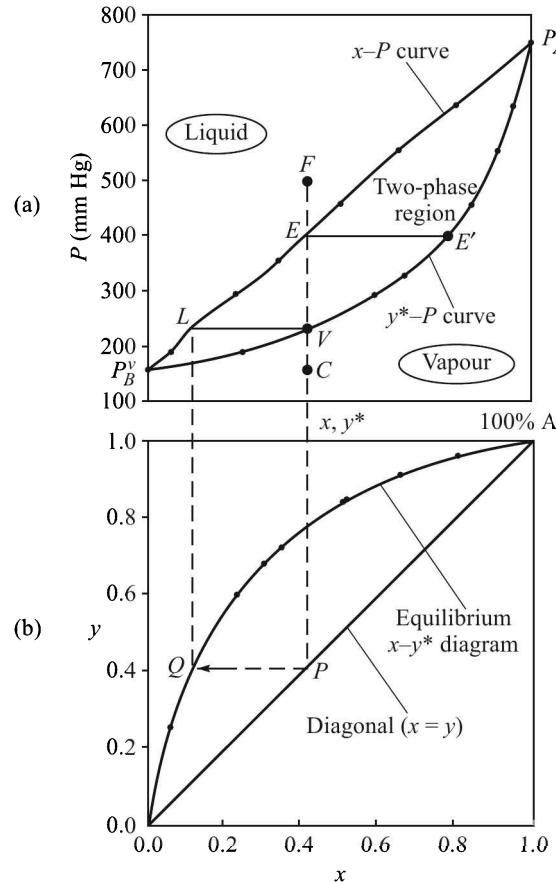


Figure 7.4 (a) Bubble point pressure (x - P and y^* - P), and (b) equilibrium (x - y^*) diagrams for dichloromethane-1, 2-dichloroethane system at 40°C. [Davies et al. *J. Soc. Chem. Ind. (Lond)*, 68(1949) 26.]

figure. The region below the curve $P_B^v - V - E' - P_A^v$ represents the ‘superheated’ vapour; the region above $P_B^v - L - E - P_A^v$ represents the ‘subcooled’ liquid (P_A^v and P_B^v are the vapour pressures of the pure liquids at the given temperature). If an amount of superheated vapour at the state given by the point C is compressed isothermally, it starts condensing as it reaches the point V and the first droplet of liquid formed has a composition given by the point L . On further compression, more vapour condenses and the composition of the accumulated condensate liquid changes along LE and the composition of the vapour changes along VE' . At a pressure corresponding to the point E , the vapour condenses completely. Now the liquid composition is the same as the composition of the original vapour. If the pressure is raised further, the liquid may be considered ‘subcooled’. The equilibrium compositions corresponding to the tie line LV is represented by the point QP on the x - y diagram in Figure 7.4(b). The two-phase region on a T - x - y or P - x - y plot narrows down with increasing temperature and pressure and eventually disappears at the critical point. The details of these phenomena are available in standard texts on thermodynamics.

7.1.3 The Raoult’s Law

Raoult’s law which describes the vapour–liquid equilibria of *ideal solutions*, has been discussed in Section 4.3.1. Equation (4.1), which is the expression for Raoult’s law, is written below [Eq. (7.5)] for both the components A and B to give the equilibrium partial pressures of the components in a binary liquid mixture. If x is the mole fraction of A in the binary solution, that of B is $(1 - x)$.

$$p_A^* = xP_A^v \quad \text{and} \quad p_B^* = (1 - x)P_B^v \quad (7.5)$$

$$\text{The total pressure: } P = p_A^* + p_B^* = xP_A^v + (1 - x)P_B^v \quad (7.6)$$

Here p_A^* and p_B^* are the equilibrium partial pressures of A and B in the vapour; P_A^v and P_B^v are the vapour pressures of A and B at the given temperature. The mole fraction of A in the vapour is given by

$$y_A^* = p_A^*/P = (xP_A^v)/P \quad (7.7)$$

Equation (7.7) can be used to calculate the vapour–liquid equilibrium data (x - y^*) for an ideal binary mixture. The procedure to calculate the equilibrium concentrations as well as the bubble point and the dew point at a constant total pressure P , is described below.

- Find the vapour pressures (P_A^v and P_B^v) of A and B at a temperature T ($T_A < T < T_B$).
- The total pressure P being known, calculate x from Eq. (7.6).
- Calculate y^* from Eq. (7.7).

The procedure is illustrated in Example 7.1. The constants of the Antoine equation for vapour pressure of some selected liquids are given in Table 7.2.

Table 7.2 Constants of the vapour pressure relation (Antoine equation)

Compound	BP (°C)	A'	B'	C'
Acetaldehyde	20.5	16.6006	2532.41	234
Acetic acid	118	18.47233	4457.83	258.46

(Contd.)

Table 7.2 Constants of the vapour pressure relation (Antoine equation) (*Contd.*)

Compound	BP (°C)	A'	B'	C'
Acetone	56.2	16.39112	2787.5	229.67
Acetonitrile	81.5	16.90395	3413.1	250.48
Acrylonitrile	77.5	15.92847	2782.21	222
Ammonia	-33.4	17.51202	2363.24	250.54
Aniline	184.5	16.67784	3858.22	200
Benzaldehyde	179	6.73163	1369.460	177.081
Benzene	80	15.9037	2789.01	220.79
<i>n</i> -Butane	-0.5	15.68151	2154.9	238.74
<i>n</i> -Butanol	117.6	17.62995	3367.12	188.7
<i>iso</i> -Butane	-11.7	15.77506	2133.24	245
<i>iso</i> -Butanol	108	18.02933	3413.34	199.97
Butyl acetate	126	16.4145	3293.66	210.75
Carbon disulphide	46	15.77889	2585.12	236.46
Carbon tetrachloride	76.5	15.8434	2790.78	226.46
Chlorobenzene	131.5	16.4	3485.35	224.87
Chloroform	61.2	16.017	2696.25	226.24
Cyclohexane	80.5	15.7794	2778	223.14
Cyclohexanol	161	19.23534	5200.53	251.7
Cyclohexanone	155.5	16.40517	3677.63	212.7
Cyclopentane	49.2	15.8602	2589.2	231.36
1,4-Dioxane	101.5	17.1151	3579.78	240.35
Dichloromethane	40	17.0635	3053.08	252.6
Diethyl ether	34.5	16.5414	2847.72	253
Diethylamine	55.5	15.73382	2434.73	212
Ethanol	78.3	18.68233	3667.70	226.1
Ethyl acetate	77	16.35578	2866.6	217.9
Ethyl benzene	136	16.04305	3291.66	213.8
Ethylamine	16.5	7.3862	1137.300	235.85
Formic acid	100.5	15.9938	2982.45	218
Furfural	162	15.14517	2760.09	162.8
<i>n</i> -Hexane	69	15.9155	2738.42	226.2
<i>n</i> -Heptane	98.5	15.877	2911.32	226.65
Methanol	64.5	18.61042	3392.57	230
Methyl acetate	57	16.58646	2839.21	228
Nitrobenzene	131.5	16.42172	3485.35	224.84
Nitrogen	-195.8	15.3673	648.59	270.02
<i>n</i> -Octane	126	15.9635	3128.75	209.85
Oxygen	-183	15.06244	674.59	263.07
1-Octanol	195	7.18653	1515.427	156.767
<i>n</i> -Pentane	36	15.8365	2477.07	233.21
Phenol	180	15.9614	3183.67	159.5

(Contd.)

Table 7.2 Constants of the vapour pressure relation (Antoine equation) (Contd.)

Compound	BP (°C)	A'	B'	C'
n-Propanol	97.2	17.8349	3310.4	198.5
iso-Propanol	82.2	20.4463	4628.95	252.64
Propane	-42	15.7277	1872.82	250
Pyridine	115	16.1520	3124.45	212.66
Styrene	135	15.94618	3270.26	206
Tetrahydrofuran	66	16.11023	2768.37	226.3
Toluene	110.6	16.00531	3090.78	219.14
Trichloroethylene	87	15.01158	2345.48	192.73
Triethylamine	89	15.7212	2674.7	205
o-Xylene	134.5	7.00154	1476.393	213.872
p-Xylene	129.2	6.99052	1453.430	215.307
Water	100	18.5882	3984.92	233.43

$$\text{Antoine equation: } \ln P_A^v = A' - \frac{B'}{C' + \theta}; \quad P_A^v \text{ in mm Hg, } \theta \text{ in } ^\circ\text{C}$$

EXAMPLE 7.1 (*Calculation of bubble point, dew point and equilibrium data for an ideal binary mixture*) Cyclo-pentane(A) and benzene(B) form nearly ideal solutions.

- Using the vapour pressure equation given in Table 7.2 (and assuming ideal behaviour), prepare the bubble point, the dew point and the vapour–liquid equilibrium curves for this binary at 1 atm total pressure.
- If one kilomole of a two-phase mixture having 42 mole% A at 68°C is allowed and 1 atm total pressure is allowed to separate into a liquid and a vapour phase at 1 atm total pressure, calculate the amounts and compositions of the two phases.
- Consider an equimolar mixture of A and B at 600 mm total pressure. (i) What is the bubble point of the mixture and the composition of the initial vapour? (ii) If a small quantity of the mixture is slowly vaporized in a closed vessel and *the vapour remains in contact and in equilibrium with the liquid*, calculate the composition of the last drop of the liquid.
- If an equimolar mixture of the compounds has a bubble point of 100°C, calculate the total pressure exerted at that temperature at equilibrium.

Solution

- (a) The bubble and dew points of mixtures of different compositions remain within 49.2°C (boiling point of pure cyclo-pentane at 1 atm) and 80°C (boiling point of pure benzene at 1 atm). The total pressure remains constant at 1 atm (= 760 mm Hg). The vapour pressure of a component is *explicitly* given as a function of temperature. In order to compute the T–x–y data, it is convenient to begin with a temperature and to calculate the corresponding liquid and vapour compositions at equilibrium. A sample calculation is shown below.

$$\text{Take } T = 70^\circ\text{C. } \ln P_A^v = 15.8602 - 2589.2/(231.36 + 70) \Rightarrow P_A^v = 1434 \text{ mm Hg}$$

$$\ln P_B^v = 15.9037 - 2789.01/(220.79 + 70) \Rightarrow P_B^v = 551 \text{ mm Hg}$$

Using Eq. (7.6), total pressure, $P = 760 \text{ mm Hg} = x(1434) + (1 - x)(551) \Rightarrow x = 0.237$

Therefore, at $T = 70^\circ\text{C}$ and $P = 760 \text{ mm Hg}$, the mole fraction of A in liquid at equilibrium is $x = 0.237$.

Mole fraction of A in the equilibrium vapour, $y^* = x(P_A^v/P) = (0.237)(1434)/760 = 0.447$

So the bubble point of a solution having 0.237 mole fraction of A at 1 atm total pressure is 70°C . This is also the dew point of a vapour having 0.447 mole fraction of A .

The bubble and dew points of liquids and vapours of other compositions are similarly calculated and plotted in Figure 7.5(a). The calculated $x-y^*$ data are plotted in Figure 7.5(b). The experimental $x-y^*$ data are also shown on the same figure. It is seen that the deviation from ideal behaviour is small. The system is nearly ideal.

(b) The state of the feed (68°C ; 1 atm; $z_F = 0.42$) is represented by the point F that lies in the two-phase region in Figure 7.5(a). Now the mixture is allowed to separate into a liquid and a vapour phase at equilibrium. Draw a horizontal line through F that meets the bubble point curve at L and the dew point curve at V . The abscissa of the point $L(x)$ gives the composition of the liquid; that of the point $V(y^*)$ gives the composition of the equilibrium vapour. From Figure 7.5(a), we get $x = 0.294$, $y^* = 0.521$.

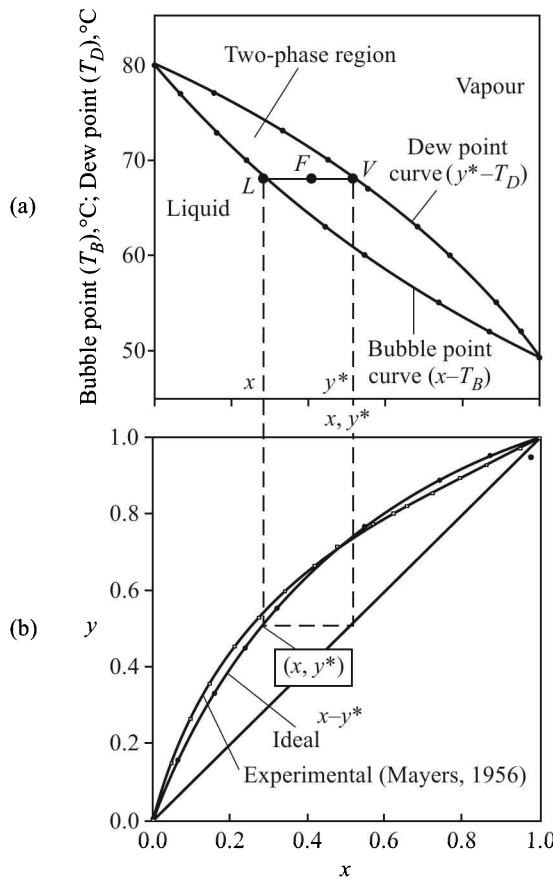


Figure 7.5 (a) The calculated $T-x-y^*$ data (Raoult's law) for cyclo-pentane-benzene mixtures, and (b) the experimental $x-y^*$ data from Mayers, *Ind. Eng. Chem.* 48(1956) 1104.

To calculate the amounts of the liquid and vapour phases produced on phase separation, use the following material balance equations. Total amount of the mixture is $F = 1$ kilomole.

$$F = L + V \Rightarrow 1 = L + V \text{ and } Fz_F = Lx + Vy^* \Rightarrow (1)(0.42) = L(0.294) + V(0.521)$$

Solving the preceding material balance equations,

$$\text{Moles of liquid, } L = [0.555 \text{ kmol}] \text{ and moles of vapour, } V = [0.445]$$

(c) Consider an equimolar mixture of the components (i.e. $x = 0.5$) at 600 mm Hg total pressure.

(i) If the bubble point is θ , using Eq. (7.6) and the given vapour pressure equations, we can write

$$P = x_A P_A^v + (1 - x_A) P_B^v \Rightarrow 600 = (0.5)10^{\left(\frac{15.8602 - \frac{2589.2}{231.36+\theta}}{231.36+\theta}\right)} + (1 - 0.5)10^{\left(\frac{15.9037 - \frac{2789.01}{220.79+\theta}}{220.79+\theta}\right)}$$

Solving this equation, the bubble point of the equimolar mixture at 600 mm Hg pressure is

$$\theta = [54^\circ\text{C}]$$

At 54°C, the vapour pressures of the individual compounds are:

$$P_A^v = 885.7 \text{ mm Hg}; \quad P_B^v = 315.3 \text{ mm Hg}$$

From Eq. (7.7), the composition of the *initial vapour*,

$$y^* = P_A^v x/P = (885.7)(0.5)/600 = [0.738 \text{ mole fraction}]$$

(ii) *Composition of the last drop of liquid remaining:* When all the liquid is vaporized except a tiny drop of it, the vapour composition is virtually the same as that of the initial liquid, i.e. $y_A = 0.5$, $y_B = 0.5$. In other words, the equimolar vapour containing A and B is at its dew point. Let us first calculate this dew-point temperature.

If x is the mole fraction of A in the last drop of the liquid (which is in equilibrium with the vapour of $y = 0.5$), then

$$\text{Partial pressure of } A \text{ in the vapour} = Py_A = P_A^v x_A \Rightarrow (600)(0.5) = 300 = P_A^v x_A$$

$$\text{Similarly, the partial pressure of } B \text{ in the vapour, } 300 = P_B^v x_B = P_B^v (1 - x_A)$$

Eliminating x_A from the above two equations, $(300/P_A^v) + (300/P_B^v) = 1$. Putting the expressions for P_A^v and P_B^v (the vapour pressure equations) and solving for θ , we have $\theta = 61.4^\circ\text{C}$.

$$\text{At } \theta = 61.4^\circ\text{C}, P_A^v = 1114 \text{ mm Hg and } P_B^v = 411.3 \text{ mm Hg.}$$

$$\text{Then the liquid composition, } x_A = Py_A/P_A^v = (600)(0.5)/(1114) = 0.27$$

The last drop of liquid contains [27 mole% of cyclo-pentane(A)].

(d) Vapour pressures of the components at 100°C are:

$$P_A^v = 3120.2 \text{ mm Hg}; \quad P_B^v = 1350.5 \text{ mm Hg}$$

The equilibrium total pressure exerted above an equimolar mixture at 100°C is given by

$$P = P_A^v x_A + P_B^v (1 - x_B) = (0.5)(3120.2) + (1350.5)(1 - 0.5) = [2235.3 \text{ mm Hg}]$$

[Note: The problem can also be solved using the K -values of the components; see Section 7.1.6]

7.1.4 Deviation from Ideality and Formation of Azeotropes

Qualitative criteria of ideal behaviour of a solution have been listed in Section 4.3.1. As a matter of fact, most solutions *do not* exhibit ideal behaviour. In other words, they show deviations from

ideality. Deviations may be of two types—*positive deviation* and *negative deviation*. A liquid mixture exerting an equilibrium total vapour pressure more than that calculated by Eq. (7.6) is said to exhibit a ‘positive deviation from ideality’. If the total vapour pressure is less than that calculated from Eq. (7.6), the deviation is called a ‘negative deviation’.

Two extreme cases of deviation from ideal behaviour lead to what are called *azeotropes*. If there is a large positive deviation from ideality and the vapour pressures of the components A and B are not much different, the total pressure curve may pass through a maximum at a certain liquid concentration. A liquid mixture of such character and composition is a ‘constant boiling mixture’[†] and is called a minimum boiling azeotrope. The x - P and y^* - P curves touch at the azeotropic composition (at the azeotropic point $x = y^*$); the x - T and y^* - T curves pass through a common minimum. This is why such an azeotrope is called *minimum boiling*. The equilibrium curve (x - y^*) crosses the diagonal line at the azeotropic composition. The equilibrium in a minimum boiling binary azeotropic system is shown in Figure 7.6.

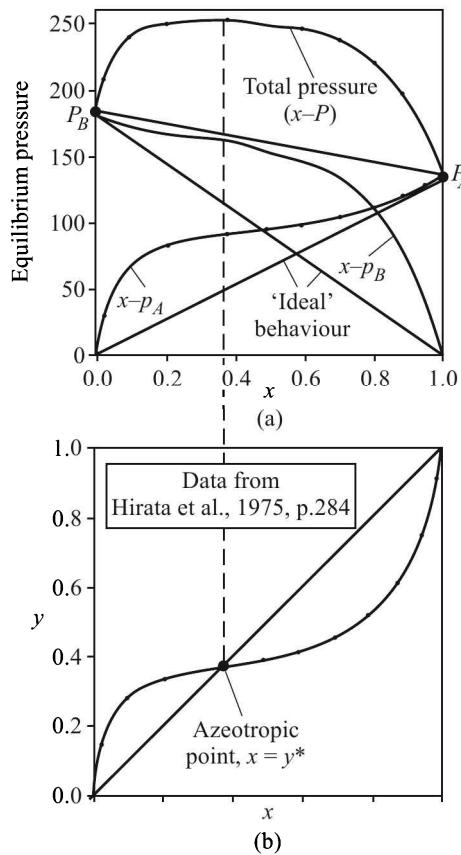


Figure 7.6 Isothermal vapour–liquid equilibrium diagram of a minimum-boiling azeotrope (ethanol–benzene, 40°C): (a) bubble point pressure, and (b) equilibrium diagrams.

[†] A ‘constant boiling mixture’ generates vapour of a composition equal to that of the liquid. So the liquid composition and the boiling temperature remain the same even if a part of the liquid is boiled out. Such a mixture cannot be separated by ordinary distillation.

Similarly, if the deviation from the ideal behaviour is negative and large, the partial pressures of the individual coefficients are less than the ideal values. The plots of the total pressure against the liquid and the vapour compositions at a constant temperature pass through a common minimum at the azeotropic point [Figure 7.7(a)]. The corresponding $x-y^*$ diagram is shown in Figure 7.7(b). An azeotrope exhibiting such behaviour is called *maximum boiling* because the boiling temperature at the azeotropic point is maximum if the total pressure is held constant.

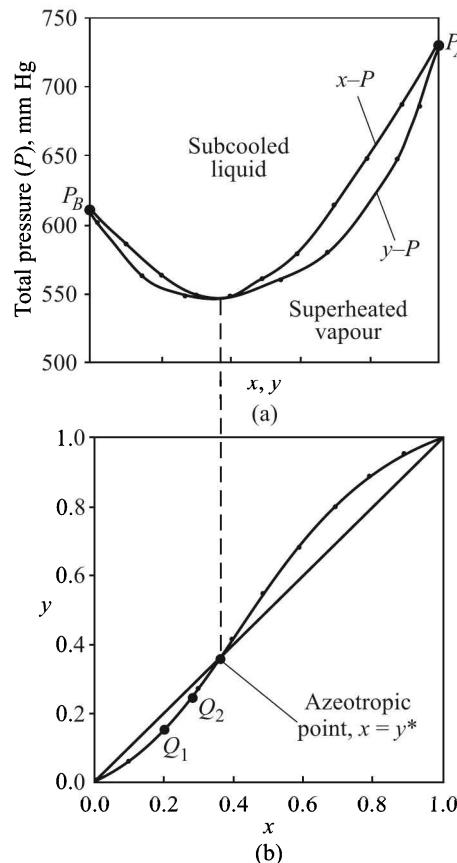


Figure 7.7 Isothermal vapour-liquid equilibrium diagram of a maximum-boiling azeotrope, acetone (A)–chloroform (B) at 55°C.

7.1.5 Relative Volatility

Relative volatility of a component A in a mixture indicates the ease of its separation from another component B . It is defined as the concentration ratio of A to B in the vapour divided by the same ratio in the liquid phase. It is usually denoted by α . For a binary mixture,

$$\alpha \text{ (or } \alpha_{AB}) = \frac{y^*/(1 - y^*)}{x/(1 - x)} = \frac{(1 - x)y^*}{(1 - y^*)x} \quad (7.8a)$$

$$\Rightarrow y^* = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (7.8b)$$

If A is the more volatile component in the mixture, α is larger than 1 (this is *not true* over the entire range of concentration if the system is azeotropic). Using Eqs. (7.5) and (7.7), the relative volatility α ($= \alpha_{AB}$) in an ideal binary solution can be expressed in terms of the vapour pressures of the components, i.e.

$$\begin{aligned}\alpha &= \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{(p_A^*/P)/(p_B^*/P)}{(p_A^*/P_A^v)/(p_B^*/P_B^v)} \\ &= \frac{P_A^v}{P_B^v} \quad (= \text{ratio of vapour pressures of } A \text{ and } B)\end{aligned}\quad (7.9)$$

In a multicomponent mixture, the relative volatility of component i with respect to component j is given by

$$\alpha_{ij} = \frac{y_i^*/y_j^*}{x_i/x_j} \quad (7.10)$$

The quantity α_{ij} gives a measure of the degree of enrichment of component i in the vapour compared to component j when a liquid mixture is partially vaporized. Its definition has been extended to other equilibrium separation processes as well. In mass transfer operations like extraction, membrane separation, etc. a quantity similar to α is called the *separation factor*.

7.1.6 Equilibrium in a Multicomponent System

Separation of multicomponent mixtures rather than binaries is much more common in the chemical process industries. Experimental VLE data for most multicomponent mixtures are not available and have to be computed by using the available equations or correlations. The job becomes pretty simple if we have an *ideal multicomponent system* so that Raoult's law is applicable. Hydrocarbons of a homologous series form nearly ideal solutions. For the i th component in an ideal solution, we can write

$$y_j^* P = p_j^* = x_j P_j^v \quad \text{and} \quad P = \sum_{i=1}^n p_i^* \quad (7.11)$$

$$\Rightarrow y_j^* = \frac{p_j^*}{P} = \frac{x_j P_j^v}{\sum_{i=1}^n x_i P_i^v} \quad (7.12)$$

where, P_j^v = vapour pressure of component j at the given temperature

At a given temperature, the vapour pressures of the components, P_i^v 's are known. Therefore, for a particular liquid composition (i.e. given for given values of x_1, x_2, \dots, x_n), the vapour compositions ($y_1^*, y_2^*, \dots, y_n^*$) can be calculated. Noting that $\alpha_{ij} = P_i^v/P_j^v$, Eq. (7.12) can be rewritten as

$$y_j^* = \frac{x_j}{(1/P_j^v) \sum_{i=1}^n x_i P_i^v} = \frac{x_j}{\sum_{i=1}^n \alpha_{ij} x_i} = \frac{\alpha_{ji} x_j}{\sum_{k=1}^n \alpha_{ki} x_k} \quad (7.13)$$

Once the equilibrium vapour phase mole fractions are known, the partial pressures and the total pressure can be calculated from Eq. (7.11).

For hydrocarbon mixtures, a quantity called *equilibrium vaporization ratio* (denoted by K_i for the i th component) is extensively used for VLE computation. It is defined as

$$K_i = \frac{y_i}{x_i} = \frac{P_i^v}{P} \quad (7.14a)$$

Distillation calculations, including the bubble and dew point calculations, can be done using the K -values, if available. The DePriester chart [Figures 7.8(a) and (b)] may be conveniently used to obtain K -values for lower hydrocarbons at different temperatures and pressures.

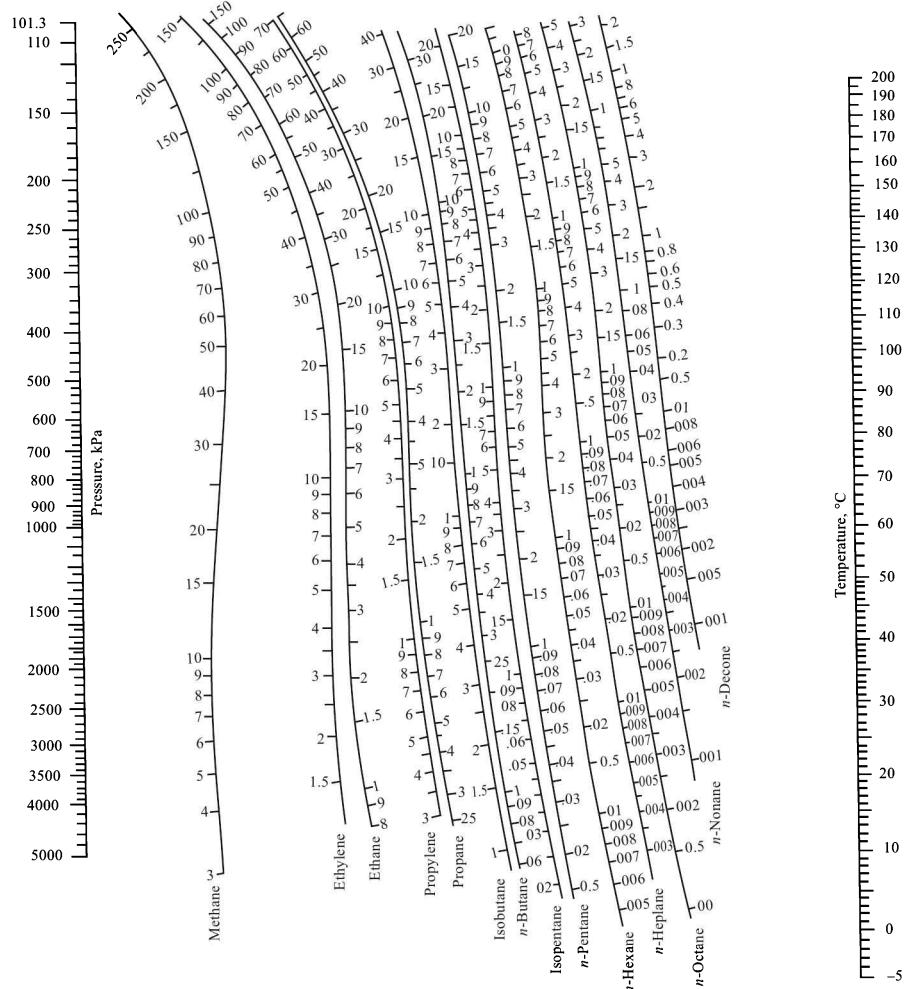


Figure 7.8(a) DePriester chart—high temperature range.

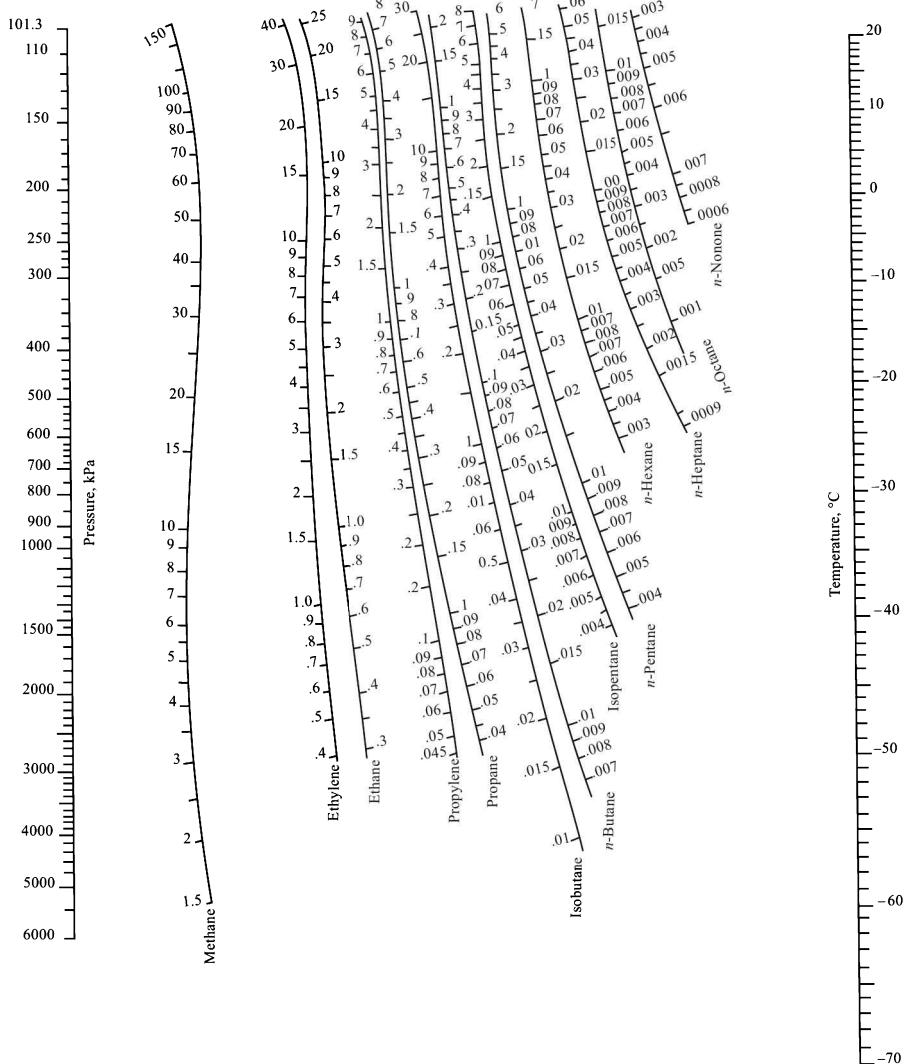


Figure 7.8(b) DePriester chart—low temperature range.

The computation of the bubble point, the dew point and equilibrium in a multicomponent mixture involves an *iterative approach*. We describe here a technique using the equilibrium vaporization ratio, K (more about this quantity for real solutions is given in the Appendix).

Bubble point calculation: In an n -component mixture, let us select the r th component as the ‘reference component’. The relative volatility of the i th component with respect to the r th is given as

$$\alpha_{ir} = \frac{y_i / y_r}{x_i / x_r} = \frac{y_i / x_i}{y_r / x_r} = \frac{K_i}{K_r}$$

Therefore, $K_i = K_r \alpha_{ir} \Rightarrow y_i = K_i x_i = K_r \alpha_{ir} x_i \Rightarrow \sum_{i=1}^n y_i = K_r \sum_{i=1}^n \alpha_{ir} x_i$ (7.14b)

In a bubble point calculation problem, the liquid composition is known and the total pressure is given. We start with an assumed temperature and calculate the vapour pressures or K -values of all the components. Then we can calculate the values of $y_i = K_i x_i$ ($= x_i P_i^v / P$ if the solution is ideal). At the bubble point, the sum of the y_i 's should be unity, i.e.

$$\sum_{i=1}^n y_i = \sum_{i=1}^n K_i x_i = 1 \quad (7.15a)$$

The boiling point of the reference substance may be taken as the *initial guess*. The values of K_i ($i = 1, 2, \dots, r, \dots, n$) and α_{ir} are calculated at this temperature and put in Eq. [7.14(b)] to get a revised value of K_r . We use this revised value of K_r to determine the *second approximation* to the bubble point. Computation is repeated till Eq. [7.14(b)] is satisfied to the desired degree of accuracy. The computational procedure is illustrated in Example 7.2.

EXAMPLE 7.2 (*Calculation of the bubble point of an ideal multicomponent mixture*) Calculate the bubble point of an *ideal solution* containing 20 mole% *n*-pentane(1) and 40 mole% each of *n*-hexane(2) and *n*-heptane(3) at 1.5 bar total pressure. Use the vapour pressure equation given in Table 7.2.

Solution

Step 1: Calculate the average molecular weight of the mixture.

Since $M_1 = 72$, $M_2 = 86$, and $M_3 = 100$, $M_{av} = (0.2)(72) + (0.4)(86) + (0.4)(100) = 88.8$.

This is close to the molecular weight of *n*-hexane. We select *n*-hexane as the *reference component*.

Step 2: Calculate the boiling point of the reference component (i.e. *n*-hexane) at the given pressure (1.5 bar = 1125 mm Hg). From the Antoine equation,

$$\ln(1125) = 15.9155 - 2738.42/(\theta + 226.2) \Rightarrow \theta = 82^\circ\text{C} \Rightarrow T = 355 \text{ K}$$

Take this temperature as the *first approximation* of the bubble point of the mixture. Calculate the relative volatility of the other components — *n*-pentane (1) and *n*-heptane (3) — with respect to the reference component, i.e. *n*-hexane(2).

At 355 K, vapour pressure of *n*-pentane,

$$\ln P_1^v = 15.8365 - 2477.07/(82 + 233.21) \Rightarrow P_1^v = 3.8604 \text{ bar}$$

Vapour pressure of *n*-heptane,

$$\ln P_3^v = 15.877 - 2911.32/(82 + 226.65) \Rightarrow P_3^v = 0.6066 \text{ bar}$$

Since the solution is *ideal*, $\alpha_{12} = P_1^v/P_2^v = 3.8604/1.5 = 2.5736$; $\alpha_{32} = 0.6066/1.5 = 0.4044$

Now use Eq. [7.14(b)].

$$K_r \sum_{i=1}^3 \alpha_{i2} x_i = 1 \Rightarrow K_r [2.5736(0.2) + (1)(0.4) + (0.4044)(0.4)] = 1 \Rightarrow K_r = 0.9289$$

Step 3: We have to recalculate the whole thing taking the above ‘revised value’ of K_r .

$$\begin{aligned} K_r &= P_2^v/P; P = 1.5 \text{ bar}; \text{i.e. } 0.9289 = P_2^v/P = P_2^v/1.5 \\ \Rightarrow P_2^v &= (0.9289)(1.5) = 1.3934 \text{ bar} = 1045.4 \text{ mm Hg} \end{aligned}$$

Recalculate the boiling point of the reference component, *n*-hexane (2), at 1.3934 bar pressure

$$\ln(1045.4) = 15.9155 - 2738.42/(\theta + 226.2) \Rightarrow \theta = 79.5^\circ\text{C} \Rightarrow T = 352.5 \text{ K}$$

Vapour pressures of the other two components at this temperature (352.5 K) are:

$$\text{*n*-pentane: } P_1^v = 3.625 \text{ bar; } \text{*n*-heptane: } P_3^v = 0.5586 \text{ bar}$$

$$K\text{-values are: } K_1 = 3.625/1.5 = 2.4167; \quad K_2 = K_r = 0.9289; \quad K_3 = 0.5586/1.5 = 0.3724$$

Step 4: Check if the recalculated K -values satisfy Eq. [7.15(a)].

$$\sum_{i=1}^3 K_i x_i = (2.4167)(0.2) + (0.9289)(0.4) + (0.3724)(0.4) = 1.004 \approx 1$$

This is good enough. Another cycle of calculation may be done if still better accuracy is desired.

Dew point calculation: For the calculation of the dew point of a vapour of known composition, i.e. known y_i ’s, we may start with an assumed value of the dew point, and obtain the vapour pressures (or K -values) of all the components at this temperature. Since the total pressure is given, we can calculate the mole fractions of the components in the liquid phase, $x_i = y_i/K_i$. ($= y_i P/P_i^v$ if the solution is ideal). If the assumed temperature is the correct dew point, the sum of x_i ’s must be unity. The following equations may be used for an efficient iterative computation.

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{y_i}{K_i} = \sum \frac{y_i}{K_r \alpha_{ir}} = \frac{1}{K_r} \sum \frac{y_i}{\alpha_{ir}} = 1 \quad (7.15b)$$

One of the components is selected as the *reference component* and the boiling point of the reference component is taken as the *initial guess* of the dew point of the vapour mixture. The vapour pressures and the values of α_{ir} of all the components are calculated at this assumed temperature and substituted in Eq. [7.15(b)]. A revised value of K_r and the corresponding temperature are then obtained. This is the *second approximation* to the dew point. The computation is repeated till the desired accuracy is achieved. The procedure is illustrated in Example 7.3.

EXAMPLE 7.3 (*Calculation of the dew point of an ideal vapour mixture*) Calculate the dew point of a vapour containing 15 mol% *n*-butane(1), 15 mol% *n*-pentane(2), 20 mol% cyclohexane(3), 20 mol% *n*-hexane(4) and 30 mol% *n*-heptane(5) at 1.5 bar total pressure. Raoult’s law applies. Use Table 7.2 to calculate vapour pressures of the components.

Solution

Step 1: Calculate the average molecular weight of the vapour mixture. The molecular weights of the individual components are: $M_1 = 58$, $M_2 = 72$, $M_3 = 84$, $M_4 = 86$, and $M_5 = 100$.

Average molecular weight,

$$M_{av} = (0.15)(58) + (0.15)(72) + (0.20)(84) + (0.20)(86) + (0.30)(100) = 83.6$$

This is close to the molecular weight of *cyclo*-hexane(3). Take this as the reference component.

Calculate the boiling point of *cyclo*-hexane(3) at 1.5 bar pressure (= 1125 mm Hg = given total pressure) using the vapour pressure equation,

$$\ln(1125) = 15.7794 + 2778/(\theta + 223.14) \Rightarrow T = 367.5 \text{ K}$$

Take 367.5 K (94.3°C) as the first approximation of the dew point of the mixture.

Step 2: Calculate the vapour pressures of the other components at the *assumed* bubble point, 367.5 K.

n-Butane: $\ln P^v(1) = 15.68151 - 2154.9/(94.3 + 238.74) \Rightarrow P^v(1) = 9985.8 \text{ mm Hg} = 13.31 \text{ bar}$

Similarly, $P^v(2) = 5.211 \text{ bar}; P^v(4) = 2.122 \text{ bar}; P^v(5) = 0.8978 \text{ bar}$

The relative volatilities (with respect to the reference component, *cyclo*-hexane) are:

$$\alpha_{13} = P^v(1)/P^v(3) = 13.31/1.5 = 8.873; \alpha_{23} = P^v(2)/P^v(3) = 5.211/1.5 = 3.474;$$

$$\alpha_{43} = P^v(4)/P^v(3) = 2.122/1.5 = 1.415; \alpha_{53} = P^v(5)/P^v(3) = 0.8978/1.5 = 0.5985$$

$$\text{From Eq. (7.17), } \frac{1}{K_3} \sum_{i=1}^5 \frac{y_i}{\alpha_{i3}} = 1$$

$$\Rightarrow \frac{1}{K_3} \left(\frac{0.15}{8.873} + \frac{0.15}{3.474} + \frac{0.20}{1.0} + \frac{0.20}{1.415} + \frac{0.30}{0.5985} \right) = 1 \Rightarrow K_3 = 0.9027$$

$$\text{Now } K_3 = P^v(3)/P \Rightarrow 0.9027 = P^v(3)/1.5$$

$$\Rightarrow P^v(3) = (0.9027)(1.5) = 1.354 \text{ bar} (= 1016 \text{ mm Hg})$$

From Antoine Eq. for *cyclo*-hexane (3),

$$\ln(1016) = 15.7794 - 2778/(\theta + 223.14) \Rightarrow T = 363.8 \text{ K}$$

Step 3: Take $T = 363.8 \text{ K}$ ($= 90.6^\circ\text{C}$) as the second approximation to the dew point of vapour mixture. Calculate the vapour pressures of the other components at this temperature.

n-butane: $\ln P^v(1) = 15.68151 - 2154.9/(90.6 + 238.74) \Rightarrow P^v(1) = 12.3772 \text{ bar}$

Similarly, at $T = 363.8 \text{ K}$, $P^v(2) = 4.7802 \text{ bar}; P^v(4) = 1.417 \text{ bar}; P^v(5) = 0.5924 \text{ bar}$.

Now calculate the K -values of all the components at $T = 363.8 \text{ K}$.

$$K_1 = P^v(1)/P = 12.3772/1.5 = 8.2514$$

$$K_2 = P^v(2)/P = 4.7802/1.5 = 3.187$$

$$K_3 = P^v(3)/P = 1.354/1.5 = 0.9027$$

$$K_4 = P^v(4)/P = 1.417/1.5 = 1.279$$

$$K_5 = P^v(5)/P = 0.5924/1.5 = 0.5347$$

Step 4: Use these K -values to check if Eq. 7.15(b) is satisfied.

$$\sum_{i=1}^5 \frac{y_i}{K_i} = \frac{0.15}{8.2514} + \frac{0.15}{3.187} + \frac{0.20}{0.9027} + \frac{0.20}{1.279} + \frac{0.30}{0.5347} = 1.004$$

So Eq. 7.15(b) is satisfied. The bubble point is 363.8 K . Another iteration may be done if further accuracy is desired.

7.1.7 Equilibrium in a Nonideal System

Equilibrium in a real system cannot generally be represented by Raoult's law or the Henry's law[#]. At equilibrium, the fugacities of the component i in the vapour and in the liquid phase are equal, i.e.

$$f_i^v = f_i^l \quad (7.16a)$$

The two fugacities are given by

$$f_i^v = \varphi_i^v y_i P \quad (7.16b)$$

$$f_i^l = x_i \varphi_i^l P = x_i \gamma_i f_i^0 \quad (7.16c)$$

where

φ_i^v = the fugacity coefficient

γ_i = the activity coefficient of component i in solution

f_i^0 = fugacity of component i at standard state.

For low-to-moderate pressures, the fugacity at standard state can be approximately taken as the vapour pressure of a component at the prevailing temperature, i.e.

$$f_i^l = x_i \gamma_i P_i^v \quad (7.16d)$$

Thus at equilibrium

$$\varphi_i^v y_i P = x_i \gamma_i P_i^v \quad (7.17)$$

Here P_i^v is the vapour pressure of component i at the given temperature. For a known liquid composition (i.e. known x_i), the activity coefficient γ_i can be calculated using a suitable equation (for example, the Wilson equation) or technique (e.g. UNIFAC). If the pressure is 'low', the vapour phase may be considered 'ideal' ($\varphi_i^v = 1$) and the corresponding vapour phase composition can be calculated directly from Eq. (7.17). If the pressure is above moderate, non-ideality of the vapour-phase has to be taken into account and the fugacity coefficient φ_i^v of the component has to be calculated using a suitable equation of state. Since φ_i^v depends upon the vapour composition (i.e. y_i) an iterative approach is necessary. This is illustrated in the Appendix.

In the following discussion we shall explain and illustrate the principles of distillation either assuming a solution to be *ideal* or using experimental vapour–liquid equilibrium data. This will be done in order to make the presentation simple and easily understandable. However, for problems involving non-ideal solutions, either experimental equilibrium data or that calculated using fugacity and activity coefficients of the components should be used. For obvious reasons, experimental multicomponent equilibrium data available in the literature are scanty and calculated equilibrium data are almost invariably used in process design.

7.2 ENTHALPY–CONCENTRATION DIAGRAM

A change in the composition of a phase during distillation is accompanied by a change in its enthalpy. Enthalpy–concentration diagrams of liquid and vapour phases in equilibrium are useful in distillation calculation. For a given temperature T and concentration x of a liquid, the molar enthalpy H_L can be calculated using the following equation[†].

$$H_L = c_{ps} M_{av} (T - T_0) + \Delta H_s \quad (7.18)$$

[#] Henry's law describes a real system only at low concentrations. In a sense, this law is also a kind of idealization.

[†] We take the following steps to get a solution of specified composition. The components are mixed at the reference temperature. The enthalpies of the pure components are zero at the reference temperature. The only heat effect occurs due to the release of the heat of solution. The mixture is then heated to the required temperature.

where

H_L = molar enthalpy of the solution at temperature T , in kJ/kmol

c_{ps} = specific heat of the solution, in kJ/kg·K

M_{av} = average molecular weight of the solution

T_0 = reference temperature

ΔH_s = heat of solution at the reference temperature T_0 , in kJ/kmol.

Since the heat of mixing of the vapour is negligible, we can use the following equation^{††} to calculate the molar enthalpy of the saturated vapour H_V at a given temperature T and concentration y^* .

$$H_V = y^* M_A [c_{pA}(T - T_0) + \lambda_A] + (1 - y^*) M_B [c_{pB}(T - T_0) + \lambda_B] \quad (7.19)$$

where

c_{pA} , c_{pB} = specific heats of the pure liquids A and B , in kJ/kg·K

λ_A , λ_B = heats of vaporization of A and B at temperature T , in kJ/kg.

The calculation of enthalpies of solutions and vapours is illustrated in Example 7.4.

EXAMPLE 7.4 (*Calculation of enthalpy-concentration data*) Enthalpy-concentration data have to be calculated for acetone(A)-water(B) system at 1 atm total pressure. The integral heat of solution (at 15°C) at different concentrations, the specific heats of solutions and the x - y^* data are given below (x , y^* = mole fractions of acetone in solution and in the equilibrium vapour respectively).

Temperature, θ (°C)	x	y^*	ΔH_s (kcal/kmol)	c_{ps} (kcal/kg·K)
56.5	1.0	1.0	0	0.54
57	0.95	0.963	0	0.56
57.5	0.90	0.935	-10.55	0.56
58.2	0.80	0.898	-23.88	0.61
58.9	0.70	0.874	-41.11	0.66
59.5	0.60	0.859	-60.3	0.70
60	0.50	0.849	-83.56	0.75
60.4	0.40	0.839	-121.5	0.80
61	0.30	0.83	-171.7	0.85
62.2	0.20	0.815	-187.7	0.91
66.6	0.1	0.755	-159.7	0.96
75.7	0.05	0.624	-106.8	0.98
91.7	0.01	0.253	-22.2	1.0
100	0.0	0.0	0	1.0

The other relevant data: average specific heat of liquid acetone, $c_{pA} = 0.57$ kcal/kg·K; average specific heat of water, $c_{pB} = 1.0$ kcal/kg·K; heat of vaporization of acetone, $\lambda_A = 125.8 - 0.252(\theta - 50)$ kcal/kg; θ = temperature in °C; average heat of vaporization of water, $\lambda_B = 550$ kcal/kg.

Solution

The enthalpy-concentration data can be calculated by using Eq. (7.18) for a solution and Eq. (7.19) for a vapour. We select a reference temperature, $T_0 = 15^\circ\text{C}$ (at which the integral heats of solution are given). Sample calculations for a solution and for the equilibrium vapour are shown.

^{††} It is assumed that the individual components are heated to the temperature T from the reference temperature T_0 , followed by vaporization and mixing of the vapours.

Consider a solution having 20 mole% acetone ($T = 62.2^\circ\text{C}$), i.e. $x_A = 0.20$. Molecular weights: acetone–58; water–18. Average molecular weight of the solution, $M_{av} = (0.20)(58) + (0.80)(18) = 26$. From Eq. (7.18),

$$H_L = c_{ps}M_{av}(T - T_0) + \Delta H_s = (0.91)(26)(62.2 - 15) - 187.2 = \boxed{929 \text{ kcal/kmol solution}}.$$

Calculate H_V from Eq. (7.19) at 62.2°C (composition of the equilibrium vapour: $y_A^* = 0.815$, given)

$$\begin{aligned} H_V &= y_A^* M_A [c_{pA}(T - T_0) + \lambda_A] + (1 - y_A^*) M_B [c_{pB}(T - T_0) + \lambda_B] \\ &= (0.815)(58)[(0.57)(62.2 - 15) + \{125.8 - (0.252)(62.2 - 50)\}] \\ &\quad + (1 - 0.815)(18)[(1)(62.2 - 15) + 550] \\ &= \boxed{9056 \text{ kcal/kmol vapour}}. \end{aligned}$$

The enthalpy values at other concentrations have been calculated. Some of the values are given below. The enthalpy values have been plotted in Figure 7.9(a)

x	1.0	0.90	0.80	0.60	0.20	0.10	0.05	0.01	0.0
y^*	1.0	0.935	0.898	0.859	0.815	0.755	0.625	0.253	0.0
H_L (kcal/kmol)	1300	1297	1294	1248	929	930	1083	1390	1530
H_V (kcal/kmol)	8500	8722	8812	8916	9056	9259	9659	10,754	11,250

The typical $x-H_L$ and y^*-H_V curves (system: methanol–water) are also shown in Figure 7.9. A point in the region below the $x-H_L$ curve represents a liquid (a point on the $x-H_L$ curve represents a saturated liquid, i.e. a liquid at its bubble point). A point in the region above the y^*-H_V curve represents a vapour (a saturated vapour if the point is on the y^*-H_V curve). A point, say F , in the region between the two curves represents a two-phase vapour–liquid mixture. The mixture tends to separate into a liquid and a vapour phase at equilibrium represented by the points W and D on the ‘tie line’ through the point F [comparable to the tie line LV in Figure 7.3(a)]. The amounts of the liquid and vapour phases can be determined by the Lever-arm Rule, Eq. (7.4). The line IJ is another tie line. The point R on the $(x-y^*)$ diagram [Figure 7.9(b)] drawn below the $H-x-y^*$ diagram corresponds to the tie line WD ; the point Q on the equilibrium diagram corresponds to the tie line IJ on the enthalpy diagram.

Similarly, let us take two solutions whose *states* (given by the enthalpies and compositions) and amounts are both represented by M and N . The solutions are mixed to produce another solution having its state and composition represented by the point P [Figure 7.9(a); here the point P represents a stream by composition as well as by flow rate and should not be confused with total pressure]. Following the nomenclature used before, we may write the material and enthalpy balance equations as given below.

$$\text{Total material balance: } M + N = P \tag{7.20}$$

$$\text{Component } A \text{ balance: } Mz_M + Nz_N = Pz_P \tag{7.21}$$

$$\text{Enthalpy balance: } MH_M + NH_N = PH_P \tag{7.22}$$

Here z stands for the concentration of the species A in a phase and H is its molar enthalpy (the notation z , instead of x , has been used because the phases represented by the points M and N may be two-phase mixtures in the general case).

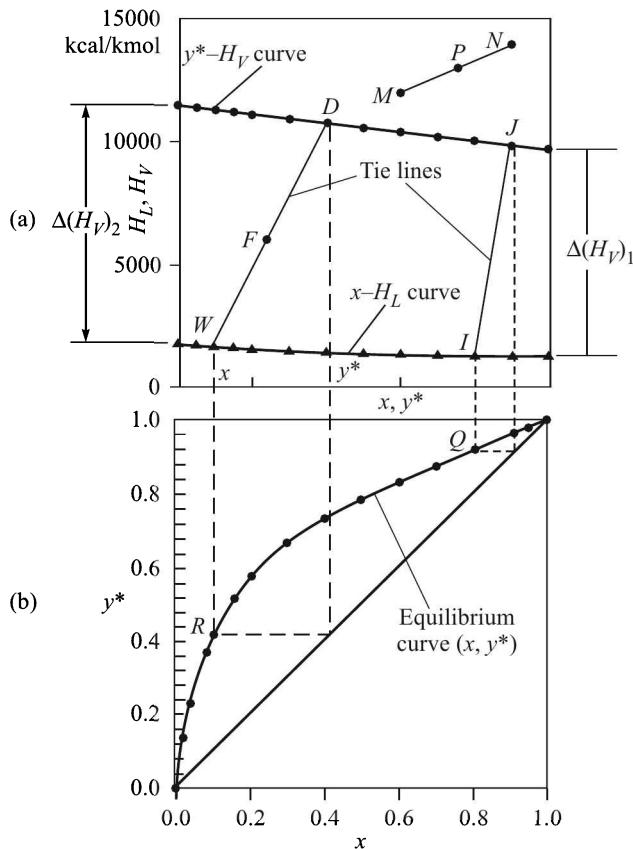


Figure 7.9 (a) Enthalpy-concentration ($x-y^*-H$), and (b) equilibrium diagrams for the methanol (1)-water (2) system [Henley and Seader, 1982]. —▲— enthalpy of liquid; —●— enthalpy of vapour.

Eliminating P from Eqs. (7.20) and (7.21),

$$\frac{M}{N} = \frac{z_N - z_P}{z_P - z_M} \quad (7.23)$$

Similarly, eliminating P from Eqs. (7.20) and (7.22),

$$\frac{M}{N} = \frac{H_N - H_P}{H_P - H_M} \quad (7.24)$$

$$\Rightarrow \frac{H_N - H_P}{z_N - z_P} = \frac{H_P - H_M}{z_P - z_M} \quad (7.25)$$

The left-side of Eq. (7.25) gives the slope of the section NP and its right-side gives that of MP [Figure 7.9(a)]. So the points M , N and P are collinear. The relation among the points M , N and P may be viewed in another way as well. If we have a mixture represented by the point P (in respect of both state and amount), and we remove a part of it represented by the point M (again in respect of both state and quantity), the part of P left behind should have enthalpy and composition represented by the point N .

After this brief introduction to the relevant physico-chemical principles, we shall now discuss the principles of the more important distillation operations.

7.3 FLASH VAPORIZATION (ALSO CALLED FLASH DISTILLATION)

If a sufficiently hot liquid mixture is throttled into a vessel, a part of it will vaporize. The vapour produced will be richer in the more volatile component(s) and thus partial separation of the desired component(s) will be achieved. This is called *flash vaporization* or *equilibrium vaporization*. A schematic sketch of a flash vaporization unit is shown in Figure 7.10. The feed is first heated in a heat exchanger under pressure and then led to a flash drum by throttling where partial vaporization of the feed occurs under reduced pressure. The vapour leaves the drum at the top and is condensed to get the top product. The fraction having a higher concentration of the less volatiles leaves the drum as a liquid bottom product. Liquid droplets are formed when a part of the liquid flashes into a vapour vigorously. The flash drum should have internals like baffle plates in order to reduce ‘entrainment’ of liquid droplets in the outgoing vapour stream. Pressure in the drum is suitably adjusted. It is often assumed that the liquid and vapour streams leaving the flash drum are in equilibrium (the process is also called *equilibrium vaporization*). But the phases may not reach equilibrium in reality. Flash vaporization is a single-stage distillation operation. However, the bottom product (or even the condensed top product) from the flash drum may be heated and flashed again in a second unit to get a purer product.

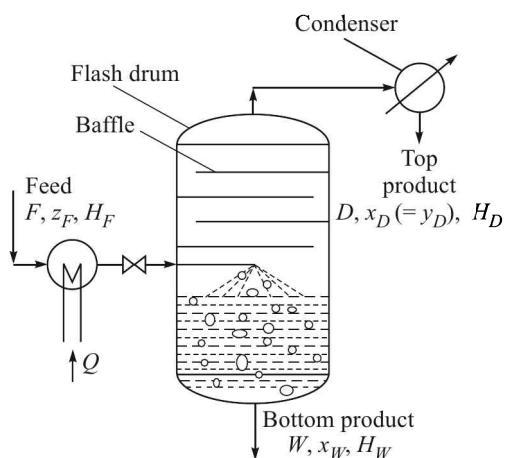


Figure 7.10 Schematic of a flash distillation unit.

7.3.1 Flash Vaporization of a Binary Mixture

We start with a binary mixture of the components *A* and *B*. If the flow rate, the composition, and enthalpy of the feed, the condensed top product (or *distillate*) and the bottom liquid product are denoted as (F, z_F, H_F) , (D, x_D, H_D) , and (W, x_W, H_W) , respectively, and Q is the rate of supply of heat to the heat exchanger, we may write the following material and energy balance equations for a steady-state equilibrium vaporization unit.

$$\text{Total material balance:} \quad F = D + W \quad (7.26)$$

$$\text{Component } A \text{ balance:} \quad Fz_F = Dx_D + Wx_W \quad (7.27)$$

$$\Rightarrow (D + W)z_F = Dx_D + Wx_W \quad (7.28)$$

$$\text{Enthalpy balance:} \quad FH_F + Q = DH_D + WH_W \quad (7.29)$$

Eliminating F from Eqs. (7.26) and (7.29) and using Eq. (7.28), we have

$$-\frac{W}{D} = \frac{x_D - z_F}{x_W - z_F} = \frac{H_D - (H_F + Q/F)}{H_W - (H_F + Q/F)} \quad (7.30)$$

[†] The vapour leaving the flash chamber is condensed into a liquid. So its composition is denoted by x_D . The subscript ‘*D*’ stands for the distillate.

Binary flash vaporization problems can be solved by graphical construction and the above equation is extremely useful for this purpose. Vapour–liquid equilibrium data and also the enthalpy–concentration data are required for the graphical construction and calculations. The *cold feed* (if the feed is below its bubble point under the given pressure, it is called *cold feed*) is represented by the point F_1 on Figure 7.11(a) under Example 7.6. The feed passes through the heat exchanger and receives an amount of heat energy Q . The state of the hot feed is represented by the point F that lies in the two-phase region of the H – x – y diagram. It flashes into a vapour and a liquid phase upon throttling into the flash drum. The enthalpy and the composition (in terms of mole fraction of A) of the vapour and the liquid streams, denoted by the points D and W , are obtained by drawing the tie line through F . The point $F'(z_F, z_F)$ is located on the diagonal on the x – y plot [see Figure 7.11(b) under Example 7.6], and the point P is located on the equilibrium curve such that the slope of the line $F'P$ is $-W/D$ by virtue of Eq. (7.30). The line $F'P$ is, in fact, the ‘operating line’ for the single-stage flash vaporization process.

By using the enthalpy and equilibrium curves, the amounts and the compositions of the two products can be calculated for a given feed for the given rate of heat supply, Q . Alternatively, if the fraction of feed to be vaporized is specified, the required rate of heat supply Q can be calculated. In the above analysis, we have tacitly assumed that the flash vaporization represents an ideal stage. The analysis can be easily extended to the case of a real stage of given stage efficiency. The stage efficiency typically ranges between 0.8 and 1.0.

Single-stage flash calculations are illustrated in Examples 7.5 and 7.6.

EXAMPLE 7.5 (Binary flash distillation) A mixture of 40 mol% benzene and 60 mol% toluene is being flash-distilled at a rate of 10 kmol/h at 1 atm total pressure. The liquid product should not contain more than 30 mol% benzene. Calculate the amounts and the compositions of the top and the bottom products. The relative volatility of benzene in the mixture is 2.5. Solve analytically as well as graphically.

Solution

Refer to Figure 7.10.

Algebraic solution

$$\text{Total material balance: } F = D + W; \quad \text{given: } F = 10, z_F = 0.4 \Rightarrow 10 = D + W \quad (\text{i})$$

$$\text{Benzene balance: } F z_F = D x_D + W x_W$$

Given: x_W = mole fraction of benzene in the bottom product = 0.3

$$\Rightarrow (10)(0.4) = D x_D + W(0.3) \quad \text{i.e.} \quad 4 = D x_D + (0.3)W \quad (\text{ii})$$

In equilibrium flash distillation, the distillate (vapour) and the bottom products (liquid) are in equilibrium, i.e. x_D and x_W are in equilibrium, and are related through the relative volatility as follows:

$$\frac{x_D/(1-x_D)}{x_W/(1-x_W)} = 2.5 \quad (\text{iii})$$

Equations (i), (ii) and (iii) can be solved for the three unknowns to get:

$$D = \boxed{4.61}; \quad W = \boxed{5.39 \text{ mol/h}}; \quad x_D = \boxed{0.517}.$$

Graphical solution

The equilibrium line is plotted using the given value of the relative volatility [see Eq. 7.8(b)].

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad \text{i.e.} \quad y = \frac{2.5x}{1 + 1.5x}$$

The point $F(z_F, z_F)$, i.e. (0.4, 0.4) is located on the diagonal, and the vertical line through $x_W = 0.3$ meets the equilibrium line at $P(0.3, 0.52)$. The slope of the line FP equals $(-W/D)$. Calculations are left as a small exercise problem.

EXAMPLE 7.6 (Calculation of the energy requirement in binary flash vaporization) Fifty kmol of 35 mole% aqueous solution of acetone at 25°C is heated and flashed in a drum at 1 atm pressure when 35% of the liquid is vaporized. Using the enthalpy-concentration data of Example 7.4, calculate (a) the amounts and the concentrations of the vapour and liquid products, and (b) the heat supplied to the feed.

Solution

(a) Let F (= 50 kmoles; $z_F = 0.35$) be the moles of feed, and W and D be the moles of liquid and vapour products. Fraction of liquid vaporized = 0.35. Therefore,

$$D/F = D/(W + D) = 0.35 \Rightarrow W/D = 1.86$$

(i) Locate the point $F'(z_F, z_F)$ on the x - y diagram drawn below the enthalpy-concentration diagram in Figure 7.11(b) and draw a line $F'P$ of slope $-W/D = -1.86$ through the point F' which meets the equilibrium curve at P .

Concentration of acetone in the liquid product, $x_W = \boxed{0.105}$; that in the (condensed) vapour product, $x_D = \boxed{0.765}$.

We have $W + D = 50$ and $W(0.105) + D(0.765) = (50)(0.35)$

$$\Rightarrow W = \boxed{31.44 \text{ kmol}} \quad D = \boxed{18.56 \text{ kmol}}$$

(b) Draw the tie line WD on the enthalpy-concentration diagram corresponding to the point P . A vertical line through F' meets WD at the point F [see Figure 7.11(b)]. The coordinates of the point F are $(z_F, H_F + Q/F)$.

From Figure 7.11(b), $H_F + Q/F = 4000 \text{ kcal/kmol}$

Average molecular weight of the feed is 32. The integral heat of solution is taken as $\Delta H_s = -145 \text{ kcal/kmol}$ and $c_{ps} = 0.825 \text{ kcal/kg}\cdot\text{K}$ (*interpolated* from the data of Example 7.4). Taking a reference temperature of 15°C, the enthalpy of the feed ($x_A = 0.35$; temp., $T = 25^\circ\text{C}$) is

$$H_F = (0.825)(32)(25 - 15) - 145 = 119 \text{ kcal/kmol}$$

$$\Rightarrow 119 + Q/50 = 4000 \Rightarrow Q = \boxed{1.94 \times 10^5 \text{ kcal} = \text{required heat input}}.$$

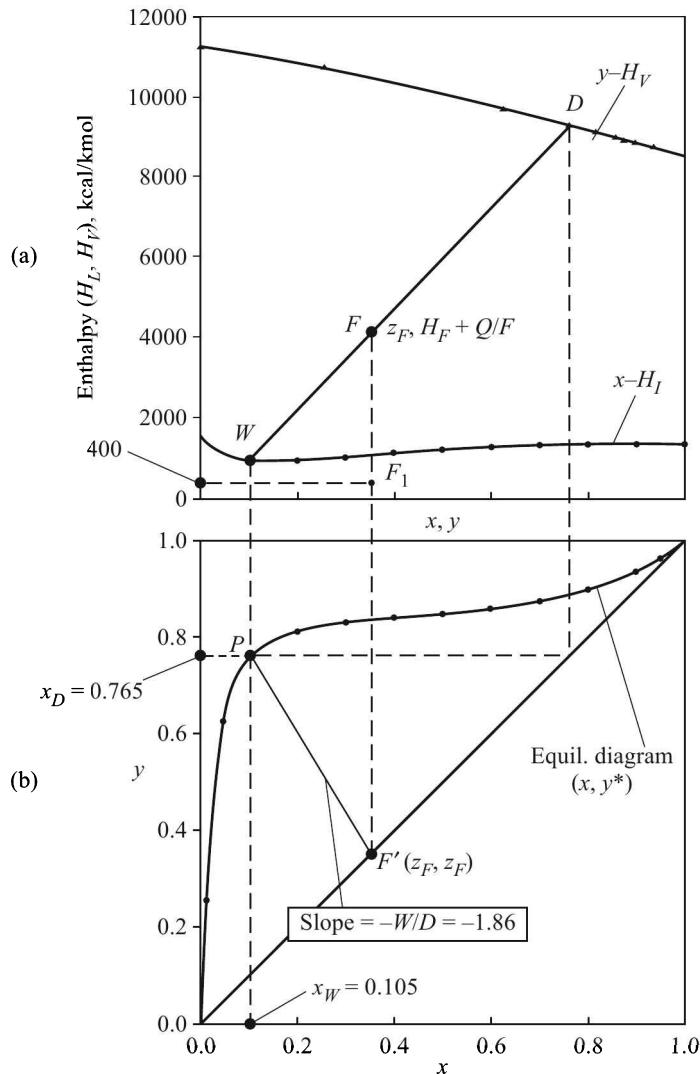


Figure 7.11 (a) Enthalpy–concentration, and (b) equilibrium diagram of acetone–water system at 1 atm pressure.

7.3.2 Multicomponent Flash Distillation

We shall now analyze flash vaporization of an n -component mixture. For simplicity, we assume that vapour–liquid equilibrium of the multicomponent mixture can be quantitatively described by K -values (see Section 7.1.6). The material balance equations for the component i are given below (the notations are the same as in the previous section; an additional subscript i is used to denote the i th component).

$$\text{Total material balance: } F = D + W \quad (7.31)$$

$$\text{Component } i \text{ balance: } Fz_{Fi} = Dx_{Di} + Wx_{Wi} \quad (7.32)$$

Eliminating F from Eqs. (7.31) and (7.32),

$$\frac{W}{D} = \frac{x_{Di} - z_{Fi}}{z_{Fi} - x_{Wi}} = \frac{y_{Di} - z_{Fi}}{z_{Fi} - x_{Wi}} \quad (7.33)^{\#}$$

Putting $x_{Wi} = y_{Di}/K_i$ [see Eq. (7.14a)] and simplifying,

$$\Rightarrow y_{Di} = \frac{z_{Fi}(1 + W/D)}{(1 + W/K_i D)} \quad \text{and} \quad \sum_{i=1}^n y_{Di} = 1 \quad (7.34)$$

The above equation can also be written for x_{Wi} by putting $y_{Di} = K_i x_{Wi}$.

$$x_{Wi} = \frac{z_{Fi}(1 + W/D)}{(K_i + W/D)}; \quad \sum_{i=1}^n x_{Wi} = 1 \quad (7.35)$$

If we define a *vaporization ratio* (it is the ratio of the moles of liquid to the moles of vapour produced on phase separation) as $f = W/D$, we may write

$$1 = \sum_{i=1}^n y_{Di} = \sum_{i=1}^n \frac{z_{Fi}(1 + f)}{1 + f/K_i} = (1 + f) \sum_{i=1}^n \frac{K_i z_{Fi}}{K_i + f} \Rightarrow (1 + f) \sum_{i=1}^n \frac{K_i z_{Fi}}{K_i + f} = 1 \quad (7.36)$$

If the temperatures of the flash drum and the feed composition are known, K_i 's can be calculated from the vapour pressure equations (or the De Priester chart, Figure 7.8), and Eq. (7.36) can be solved by using any suitable numerical technique to calculate f , i.e. the fraction of liquid vaporized on flashing (see Example 7.7).

It is rather simple to determine if a mixture would at all flash into two phases. We may specify the following conditions in this regard.

$$\sum_{i=1}^n K_i z_{Fi} > 1 \quad (7.37)$$

$$\sum_{i=1}^n \frac{z_{Fi}}{K_i} > 1 \quad (7.38)$$

If the above two inequalities are satisfied, the mixture would separate into two phases under the given conditions.

EXAMPLE 7.7 (Multicomponent flash distillation) We have a mixture of 25 mol% *n*-hexane(1), 40 mol% *n*-heptane(2) and 35 mol% *n*-octane(3) at 400 K and 2 bar total pressure. Will the mixture separate into two phases? If so, calculate the amounts and the compositions of the liquid and the vapour products. Assume the solution to be ideal. See Table 7.2 for the Antoine constants.

Solution

Vapour pressure of *n*-hexane(1) at 400 K (= 127°C):

$$\ln P^v(1) = 15.9155 - 2738.42/(127 + 226.2) = 3490 \text{ mm Hg} = 4.652 \text{ bar}$$

[#] Since the vapour generated on flashing is completely condensed, the composition of the condensate is the same as that of the vapour ($x_{Di} = y_{Di}$).

Vapour pressures of the other two components are: $P^v(2) = 2.177$ bar and $P^v(3) = 1.05$ bar.

If we assume ideal behaviour, the vaporization equilibrium constants are:

$$K_1 = P^v(1)/P = 4.652/2.0 = 2.326$$

$K_2 = 1.0885$; $K_3 = 0.525$ [The K -values can also be obtained from Figure 7.8.]

Composition of the mixture: $z_1 = 0.25$; $z_2 = 0.4$; $z_3 = 0.35$.

Now,

$$\sum_{i=1}^3 z_{F_i} K_i = (0.25)(2.326) + (0.40)(1.0885) + (0.35)(0.525) = 1.2006 > 1$$

$$\sum_{i=1}^3 \frac{z_{F_i}}{K_i} = \frac{0.25}{2.326} + \frac{0.40}{1.0885} + \frac{0.35}{0.525} = 1.1416 > 1$$

Since the conditions of existence of two phases [Eqs. (7.37) and (7.38)] are satisfied, the mixture will split into two phases. The fraction of vapour is to be calculated by solving Eq. (7.36), i.e.

$$\begin{aligned} \frac{K_1 z_{F1}}{K_1 + f} + \frac{K_2 z_{F2}}{K_2 + f} + \frac{K_3 z_{F3}}{K_3 + f} &= \frac{1}{1+f} \\ \Rightarrow \quad \frac{(2.326)(0.25)}{2.326 + f} + \frac{(1.0885)(0.40)}{1.0885 + f} + \frac{(0.525)(0.35)}{0.525 + f} &= \frac{1}{1+f} \end{aligned}$$

The solution of the above equation gives the vaporization ratio, $f = 0.812$.

Taking $F = 1$ kmol = $D + W$ and $f = W/D = 0.812$, W and D can be easily calculated. The compositions of the liquid and vapour products can be obtained from Eqs. (7.34) and (7.35).

A simpler technique of flash calculations was suggested by Eubank et al. (2000). If ζ is the fraction of the feed vaporized in the flash chamber,

$$\zeta = \frac{D}{W+D} = \frac{1}{1+W/D} = \frac{1}{1+f} \quad (7.39)$$

From Eqs. (7.35), (7.36) and (7.39),

$$\begin{aligned} 1 &= \sum_{i=1}^n x_{Wi} = \sum_{i=1}^n y_{Di} \Rightarrow \sum_{i=1}^n \frac{z_{Fi}}{1+\zeta(K_i-1)} = \sum_{i=1}^n \frac{K_i z_{Fi}}{1+\zeta(K_i-1)} \\ \Rightarrow \quad \sum_1^n \frac{K_i z_{Fi}}{1+\zeta(K_i-1)} - \sum_1^n \frac{z_{Fi}}{1+\zeta(K_i-1)} &= 0 \\ \Rightarrow \quad \psi(z_{Fi}, \zeta) = \sum \frac{z_{Fi}(K_i-1)}{1+\zeta(K_i-1)} &= 0 \end{aligned} \quad (7.40)$$

It is easy to establish that $\partial\psi/\partial\zeta < 0$ for positive values of ζ (in fact, ζ lies between 0 and 1). So Eq. (7.40) has a unique solution within $0 < \zeta < 1$. The root of Eq. (7.40) can be obtained by a numerical technique like the Newton–Raphson[#] method. It is interesting to note that for a

[#] See the Appendix for more about the solution of Eq. (7.40).

ternary mixture, Eq. (7.40) reduces to a quadratic algebraic equation. If we put the data of Example 7.7 in Eq. (7.40), we get

$$\frac{(0.25)(2.326 - 1)}{1 + (2.326 - 1)\zeta} + \frac{(0.4)(1.0885 - 1)}{1 + (1.0885 - 1)\zeta} + \frac{(0.35)(0.525 - 1)}{1 + (0.525 - 1)\zeta} = 0 \Rightarrow \zeta = 0.552$$

The vaporization ratio, $f = (1 - \zeta)/\zeta = (1 - 0.552)/0.552 = 0.812$.

7.4 STEAM DISTILLATION

When a solution boils, the mole fraction of a component A in the vapour (y^*) depends upon its mole fraction in the liquid (x). If the solution is an ideal binary, the vapour phase mole fraction of A is given by Eq. (7.7). However, if the components A and B are not miscible, their mixture exerts a total vapour pressure which is equal to the sum of the vapour pressures of the individual liquids at the given temperature. So the bubble temperature of such a mixture is lower than the boiling point of either A or B . This property of an immiscible liquid mixture forms the basis of steam distillation.

Steam distillation is a separation process in which live steam is blown through a liquid containing a component A (usually having a low volatility and low solubility in water) when A vaporizes slowly (depending upon its vapour pressure at the operating temperature) and leaves with the steam. The compound A is the target compound which we want to recover in a reasonably pure state. The mixture to be separated may contain traces of a non-volatile impurity or it may be a mixture of A and another compound C which is essentially non-volatile. In some cases steam distillation is similar to steam stripping. The schematic of a steam distillation unit is shown in Figure 7.12. The feed is taken in the distillation vessel or still through which live steam is sparged at the bottom. The vapour containing the vaporized product A as well as steam is led to a condenser. If A has only little miscibility with water, the condensate forms two layers (a layer of the target material A and another of water) and can be easily separated to recover the product. Some loss of heat occurs from the distillation unit. Energy is also required for heating the feed to its bubble point and for vaporization of A . A steam coil may be provided in the still to make up such energy requirements and to avoid condensation of the live steam. Steam distillation may be conveniently used in the following cases:

- Separation of a high boiling material from a solution. Examples: decolourization/deodorization of vegetable oils, recovery and purification of essential oils
- Separation and purification of hazardous and inflammable substances like turpentine
- Separation of a thermally unstable substance from a mixture

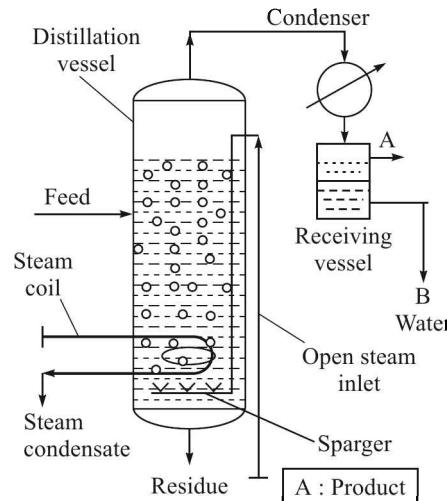


Figure 7.12 Schematic of a steam distillation unit.

- Separation of volatile impurities from waste water. Examples: removal of ammonia, volatile organic compounds (VOCs) like halogenated hydrocarbons from waste water.

We consider the following two important cases of calculation of steam requirement for a steam distillation process. Case 2 is discussed after Example 7.8.

Case 1: *The substance A is immiscible with water. The feed contains A and traces of non-volatile impurities.*

Let P_A^v be the vapour pressure of A at the operating temperature, P_B^v be the vapour pressure of water ($B = \text{water}$), and P be the total pressure. Since A (the target compound) and B (water) are essentially immiscible, the total pressure is the sum of the individual vapour pressures (here the partial pressure of a substance is the same as its vapour pressure).

$$P = P_A^v + P_B^v \quad \Rightarrow \quad P_B^v = P - P_A^v$$

If m_A moles of the substance is volatilized out by putting in m_B moles of steam, and if the system operates at equilibrium, we may write

$$\frac{m_A}{m_B} = \frac{P_A^v}{P_B^v} = \frac{P_A^v}{P - P_A^v} \quad \Rightarrow \quad m_A = m_B \frac{P_A^v}{P - P_A^v} \quad (7.41)$$

However, if the system does not operate at equilibrium, the partial pressure of A will be less than its vapour pressure. To take into account such a deviation, we define a factor called *vaporizing efficiency* E of the product such that the partial pressure of A in the steam phase is $p_A = EP_A^v$. Equation (7.41) then becomes

$$m_A = m_B \frac{EP_A^v}{P - EP_A^v} \quad (7.42)$$

The vaporization efficiency usually ranges between 0.6 and 0.9. Equation (7.42) can be used to calculate the steam requirement for a desired separation.

EXAMPLE 7.8 (Simple steam distillation) Geraniol ($C_{10}H_{18}O$) is an essential oil of commercial value. It is conventionally purified by steam distillation. A pilot scale unit is charged with 0.5 kg of crude geraniol containing a small amount of non-volatile impurities. Live saturated steam at 105°C is passed through the still at a rate of 20 kg/h. Calculate the distillation time assuming that geraniol is immiscible with water. Neglect condensation of steam. The vaporization efficiency is 0.8. Vapour pressure of water at 105°C is 1.211 bar and that of geraniol(A) is given by

$$\ln P_A^v = 21.1 - 7217/T; \quad P_A^v \text{ is in mm Hg and } T \text{ in K.}$$

Solution

From the given equation, vapour pressure of geraniol at 105°C , $P_A^v = 7.48 \text{ mm Hg}$.

Vapour pressure of water at 105°C (given),

$$P_B^v = 1.211 \text{ bar} = (1.211/1.013)(760) = 908.7 \text{ mm Hg}$$

Molecular weight of geraniol, $M_A = 154.1$; moles of geraniol in the feed, $m_A = 0.5/154.1 = 3.244 \times 10^{-3} \text{ kmol}$.

Use Eq. (7.42) to calculate the moles of steam required,

$$\begin{aligned} m_B &= m_A \frac{P_B^v}{EP_A^v} = (3.244 \times 10^{-3}) \frac{908.7}{(0.8)(7.48)} \\ &= 0.493 \text{ kmol} = (0.493)(18) = 8.874 \text{ kg steam} \end{aligned}$$

$$\text{Steam rate} = 20 \text{ kg/h. Time required} = 8.874/20 \text{ h} = \boxed{26.6 \text{ min}}$$

Case 2: The feed is a mixture of A and C; C is an essentially non-volatile substance. A and C form an ideal solution and are immiscible with water.

Let us start with a feed containing m_{Ai} moles of A [here the subscript *i* means initial, and *f* means final] and m_C moles of C. At the operating temperature, the vapour pressure of A is P_A^v and that of steam is P_B^v . Since C is non-volatile, m_C remains constant. We need to calculate the amount of steam required to reduce the number of moles of A from m_{Ai} to m_{Af} . The vaporization efficiency is E .

If the moles of A in the still at any time t is m_A , its mole fraction in C is

$$x_A = \frac{m_A}{m_A + m_C} \quad (7.43)$$

Partial pressure of A in the vapour is: $p_A = Ex_A P_A^v$

$$\text{Moles of A per mole of steam} = \frac{p_A}{P_B^v} = \frac{Ex_A P_A^v}{P - Ex_A P_A^v}$$

If \dot{m}_B is the rate of supply of steam, the rate of volatilization of A may be written as

$$-\frac{dm_A}{dt} = \dot{m}_B \frac{p_A}{P_B^v} = \dot{m}_B \frac{Ex_A P_A^v}{P - Ex_A P_A^v} \quad (7.44)$$

Substituting for x_A from Eq. (7.43) in Eq. (7.44), rearranging and integrating from $t = 0$, $m_A = m_{Ai}$ to $t = t$, $m_A = m_{Af}$,

$$\begin{aligned} - \int_{m_{Ai}}^{m_{Af}} \left[P \left(1 + \frac{m_C}{m_A} \right) - EP_A^v \right] dm_A &= E \dot{m}_B P_A^v \int_{t=0}^t dt \\ \Rightarrow \left(\frac{P}{EP_A^v} - 1 \right) (m_{Ai} - m_{Af}) + \frac{P m_C}{EP_A^v} \ln \frac{m_{Ai}}{m_{Af}} &= \dot{m}_B t = \text{total steam required} \quad (7.45) \end{aligned}$$

Example 7.9 illustrates the theoretical principles discussed above.

EXAMPLE 7.9 (Steam distillation of a substance from a mixture) Thirty kilograms of crude citronellol ($C_{10}H_{20}O$), an essential oil, is to be purified by steam distillation. The material contains 20 mass% of the essential oil and the rest constitute non-volatile impurities of average molecular weight 260. Assuming Raoult's law to apply, calculate the rate of steam supply for the recovery of 90% of the oil if the batch time is 2 hours. It is estimated that 2% of the inlet steam condenses to make up the heat losses from the still and also to supply sensible and latent heat to the oil. The operating temperature is 105°C and the vaporization efficiency is 75%. Vapour pressure of citronellol(A) can be calculated from the equation: $\ln P_A^v(\text{mm Hg}) = 21.33 - 7241/T$.

Solution

Use Eq. (7.45). Vapour pressure of citral at 105°C (calculated from the above equation), $P_A^\gamma = 8.8 \text{ mm Hg}$. Total mass of the crude product = 30 kg with 20% of the oil. Mol. wt. of the oil = 156.1.

$$\text{Mass of oil} = (30)(0.20) = 6 \text{ kg} = 6/156.1 \text{ kmol} = 0.03842 \text{ kmol} = m_{Ai}$$

$$\text{Mass of non-volatile impurities} = 24 \text{ kg} = 24/260 \text{ kmol} = 0.0923 \text{ kmol} = m_C$$

90% of the oil is to be recovered.

$$\text{Moles of the oil left, } m_{Af} = (0.03842)(0.10) = 0.003842 \text{ kmol}$$

$$\text{Vapour pressure of water}(B), P_B^\gamma = 908.7 \text{ mm Hg}$$

$$\text{Vaporization efficiency, } E = 0.75$$

$$\text{Total pressure, } P = 908.7 + 8.8 = 917.5 \text{ mm Hg}$$

Putting the values of different quantities in Eq. (7.45),

$$\dot{m}_B t = \left[\frac{917.5}{(0.75)(8.8)} - 1 \right] (0.03842 - 0.003842) + \frac{(917.5)(0.0923)}{(0.75)(8.8)} \ln \frac{0.03842}{0.003842} = 34.32 \text{ kmol}$$

Heat loss = 2% \Rightarrow Actual steam requirement = $34.32/0.98 = 35 \text{ kmol} = 630 \text{ kg}$

The batch time, $t = 2 \text{ h}$. Steam rate, $\dot{m}_B = 35/2 = 17.5 \text{ kmol/h} = \boxed{315 \text{ kg/h}}$

7.5 BATCH DISTILLATION (ALSO CALLED DIFFERENTIAL DISTILLATION OR RAYLEIGH DISTILLATION)

In batch distillation, the feed is charged to the stillpot to which heat is supplied continuously through a steam jacket or a steam coil. As the mixture boils, it generates a vapour richer in the more volatiles. But as boiling continues, concentrations of more volatiles in the liquid decrease. It is generally assumed that equilibrium vaporization occurs in the still. The vapour is led to a condenser and the condensate or top product is collected in a receiver. At the beginning, the condensate will be pretty rich in the more volatiles, but the concentrations of the more volatiles in it will decrease as the condensate keeps on accumulating in the receiver. The condensate is usually withdrawn intermittently having products or *cuts* of different concentrations. Batch distillation is used when the feed rate is not large enough to justify installation of a continuous distillation unit. It may also be used when the constituents greatly differ in volatility. Two cases of batch distillation are discussed below. Batch

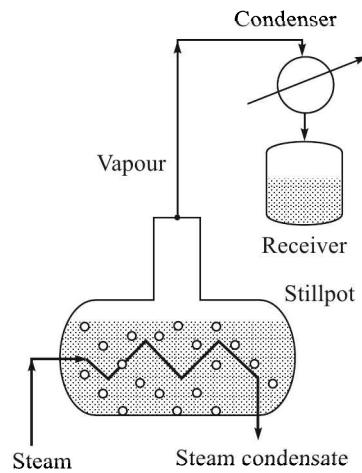


Figure 7.13 A batch distillation setup.

distillation with reflux will be dealt with in Section 7.7. The schematic of a batch distillation setup is shown in Figure 7.13.

7.5.1 Batch Distillation of a Binary Mixture

Theoretical analysis of batch distillation is based on a ‘differential mass balance’ because the liquid and the vapour phase concentrations of the components change continuously as distillation proceeds. Let, at any moment, the number of moles of liquid in the still be L having a mole fraction x of the more volatile component (i.e. A) and let the moles of *accumulated* condensate be D . Concentration of the equilibrium vapour is y^* . Over a small time, the change in the amount of liquid in the still is dL and the amount of vapour withdrawn is dD . The following differential mass balance equations may be written:

$$\text{Total material balance:} \quad -dL = dD \quad (7.46)$$

$$\text{Component A balance:} \quad -d(Lx) = y^*dD \quad (7.47)$$

$$\Rightarrow -Ldx = y^*dD + xdL = y^*dD - xdd = (y^* - x)dD \quad (7.48)$$

Equation (7.46) means that the total amount of vapour generated must be equal to the decrease in the total amount of liquid (note that dL is inherently negative and a negative sign is used in this equation so that it is consistent with respect to sign). Similarly, Eq. (7.47) means that loss in the number of moles of A from the still because of vaporization is the same as the amount of A in the small amount of vapour generated.

Putting $dD = -dL$ in Eq. (7.48) and rearranging,

$$\frac{dL}{L} = \frac{dx}{y^* - x} \quad (7.49)$$

If distillation starts with F moles of feed of concentration x_F and continues till the amount of liquid reduces to W moles (composition = x_W), the above equation can be integrated to give

$$\int_F^W \frac{dL}{L} = \int_{x_F}^{x_W} \frac{dx}{y^* - x} \quad \Rightarrow \quad \ln \frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{y^* - x} \quad (7.50)$$

Equation (7.50) is the basic equation of batch data distillation and is called the ‘Rayleigh equation’. If the vapour–liquid equilibrium data (x – y^*) are available in a tabular form, the right side of Eq. (7.50) can be evaluated graphically. If an algebraic relation between x and y^* is available, analytical integration may be possible. For example, if the relative volatility α of A in the binary mixture is constant (as it happens in the case of an ideal solution), the relation between x and y^* may be obtained from Eq. [7.8(b)]. Substituting for y^* from Eq. [7.8(b)] in the right-side of Eq. (7.50), the integration can be performed to have

$$\ln \frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{\frac{\alpha x}{1 + (\alpha - 1)x} - x} = \frac{1}{(\alpha - 1)} \ln \frac{x_F(1 - x_W)}{x_W(1 - x_F)} + \ln \frac{1 - x_W}{1 - x_F} \quad (7.51a)$$

The integral can be expressed in an alternative, and sometimes more convenient form

$$\ln \frac{Fx_F}{Wx_W} = \alpha \ln \frac{F(1-x_F)}{W(1-x_W)} \quad (7.51b)$$

Equation (7.51) involves four quantities— F , W , x_F , and x_W . If any three of these are known, the remaining one can be calculated. The average composition ($y_{D,\text{av}}$) of the accumulated distillate (D) can be obtained by a simple material balance.

$$Fx_F = Dy_{D,\text{av}} + Wx_W \quad \text{and} \quad F = D + W \quad (7.52)$$

EXAMPLE 7.10 (Simple batch distillation) A charge of 50 kmol of a mixture of benzene and chlorobenzene having 55 mol% of the less volatile is to be batch-distilled. (a) If 25 moles of the solution is vaporized and condensed as the distillate, calculate the concentration of the accumulated distillate. (b) If the concentration of the accumulated product is found to be 72 mol% benzene, calculate its amount. The relative volatility of benzene in the mixture is 4.15.

Solution

Use Eq. [7.51(b)]. Given: moles of feed, $F = 50$ kmol; feed concentration, $x_F = 1 - 0.55 = 0.45$.

(a) Distillate, $D = 25$ kmol, and $W = 25$ kmol; $y_{D,\text{av}} (= x_D) = ?$ Putting the values in Eq. [7.51(b)],

$$\ln \left[\left(\frac{50}{25} \right) \left(\frac{0.45}{x_W} \right) \right] = (4.15) \ln \left[\left(\frac{50}{25} \right) \left(\frac{1-0.45}{1-x_W} \right) \right]; \quad \text{solving, we get } x_W = 0.218$$

Material balance: $Fx_F = Wx_W + Dy_{D,\text{av}} \Rightarrow (50)(0.45) = (25)(0.218) + (25)y_{D,\text{av}}$

$$\Rightarrow y_{D,\text{av}} = 0.682$$

Composition of the distillate collected, $x_D = y_{D,\text{av}} = \boxed{0.682}$

(b) Given: $y_{D,\text{av}} = x_D = 0.72$; $D = ?$

Total material balance, $50 = D + W$; benzene balance, $(50)(0.45) = Wx_W + D(0.72)$

$$\text{From the above two equations, } W = \frac{13.5}{0.72 - x_W}$$

Substituting in Eq. [7.51(b)],

$$\ln \left[\left(\frac{50}{13.5/(0.72 - x_W)} \right) \left(\frac{0.45}{x_W} \right) \right] = (4.15) \ln \left[\left(\frac{50}{13.5/(0.72 - x_W)} \right) \left(\frac{1-0.45}{1-x_W} \right) \right]$$

$$\text{Solving, } x_W = 0.309; \quad W = (13.5)/(0.72 - 0.309) = 32.85$$

$$\text{Amount of distillate, } D = F - W = 50 - 32.85 = \boxed{17.15 \text{ kmol}}$$

EXAMPLE 7.11 (Batch distillation with gradual addition of the feed) Sixty kilomoles of a mixture of benzene and toluene containing 60 mol% benzene is to be separated by batch distillation. A still that can hold 20 kmol of the mixture is available. It is planned to start distillation with a charge of 20 kmol and to add the rest (i.e. 40 kmol) to the still continuously over a period

of one hour. It is possible to maintain a constant rate of heat supply to the still by steam coils so that the rate of vaporization becomes the same as the rate of addition of the feed mixture to the still. Calculate the amount and concentration of the composited distillate that would be obtained at the end of an hour. Relative volatility of benzene in the mixture is 2.51.

Hints: Let F = kmol feed initially charged with a benzene concentration, x_F ; F' = the hourly rate of addition of the mixture to the still; x = mole fraction of benzene in the liquid in the still and y^* = mole fraction of benzene in the vapour generated at any time t . Since the rates of addition and vaporization are the same, moles of liquid in the still remain constant at F . An instantaneous material balance gives

$$\frac{d}{dt}(Fx) = F'x_F - F'y^* = F \frac{dx}{dt}$$

The above equation means that the rate of accumulation of benzene in the still is the difference between the rate of its addition with the incoming feed and the rate of removal with the vapour.

Rearranging and integrating the above equation,

$$\frac{F'}{F} \int_0^t dt = - \int_{x_F}^x \frac{dx}{y^* - x_F} = \int_x^{x_F} \frac{\alpha x}{1 + (\alpha - 1)x} dx = \int_x^{x_F} \frac{[1 + (\alpha - 1)x]dx}{x[\alpha - (\alpha - 1)x_F] - x_F}$$

The integral is of the form:

$$I = \int \frac{(1 + ax)dx}{bx - c} = \frac{a}{b} \int \frac{(bx - c) + (c + b/a)}{bx - c} dx = \frac{a}{b} x + \left(\frac{a}{b}\right)\left(c + \frac{b}{a}\right)\left(\frac{1}{b}\right) \ln(bx - c)$$

Putting the values of the different quantities in the integrated equation, we have

$$2t = -0.4254 - 0.9414x - 0.9756 \ln(1.604x - 0.6); t = 1 \text{ hour} \Rightarrow x = 0.49$$

The concentration of the composited distillate can be found by material balance, $x_D = 0.695$

We may consider a situation that a large quantity of feed is available and the distillation can be continued for a long time, i.e.

$$\text{At } t = \infty, \ln(1.604x - 0.6) \rightarrow -\infty \Rightarrow 1.604x - 0.6 = 0 \Rightarrow x = 0.374$$

This is the concentration of the liquid in the still at a large time. The corresponding vapour phase concentration of benzene is 0.6. This indicates that at large time steady state is attained and the vapour leaves at the rate and concentration as that of the feed entering the still.

7.5.2 Batch Distillation of a Multicomponent Mixture

Consider L moles of a solution containing components 1, 2, ..., n at mole fractions x_1, x_2, \dots, x_n . So the number of moles of the individual components in the solution are:

$$L_1 = Lx_1; \quad L_2 = Lx_2; \quad \dots \quad L_n = Lx_n \quad (7.53)$$

For simplicity we assume the solution to be ideal. The relative volatility α_{ij} of the component i with respect to another component j is taken as a constant. Further, we shall take component j as the base or ‘reference component’ with respect to which the relative volatility of any other component in the mixture is defined. The differential mass balance equations for components i and j become

$$\text{For the component } i: \quad -dL_i = -y_{Di}^* dL \quad (7.54)$$

$$\text{For the component } j: \quad -dL_j = -y_{Dj}^* dL \quad (7.55)$$

$$\Rightarrow \frac{dL_i}{dL_j} = \frac{y_{Di}^*}{y_{Dj}^*} = \alpha_{ij} \frac{x_i}{x_j} = \alpha_{ij} \frac{L_i}{L_j} \quad [\text{from Eqs. (7.53) to (7.55)}]$$

Integrating from the initial to the final state,

$$\ln \frac{(L_i)_{\text{initial}}}{(L_i)_{\text{final}}} = \alpha_{ij} \ln \frac{(L_j)_{\text{initial}}}{(L_j)_{\text{final}}} \quad (7.56)$$

This equation can be written for all possible pairs with the component j as common to get

$$\left[\frac{(L_i)_{\text{initial}}}{(L_i)_{\text{final}}} \right]^{\alpha_{ji}} = \left[\frac{(L_j)_{\text{initial}}}{(L_j)_{\text{final}}} \right] = \dots = \left[\frac{(L_n)_{\text{initial}}}{(L_n)_{\text{final}}} \right]^{\alpha_{jn}} \quad [\text{Since } \alpha_{ij} = 1/\alpha_{ji}] \quad (7.57)$$

Equation (7.57) together with the condition $x_1 + x_2 + x_3 + \dots + x_n = 1$, can be used to solve a multicomponent batch distillation problem.

EXAMPLE 7.12 (Multicomponent batch distillation) A mixture of 0.3 kmol *n*-pentane (1), 0.3 kmol *n*-hexane (2) and 0.4 kmol *n*-octane (3) is batch distilled at 1 atm pressure to remove 90% of *n*-pentane. Calculate the amount and composition of the distillate. Take the *K*-values from the DePriester chart, Figure 7.8(b).

Solution

The initial number of moles of the components are: $(L_1)_{\text{in}} = 0.3$, $(L_2)_{\text{in}} = 0.3$, and $(L_3)_{\text{in}} = 0.4$. These are also the mole fractions of the components at the beginning. (‘in’ = initial; ‘fi’ = final). Initial bubble point temperature of the mixture is 64°C (the calculations are not shown here; this may be obtained by following the procedure of Example 7.2 and using the *K*-values given in Figure 7.8).

Amount of *n*-pentane removed = 90% of 0.3 kmol = 0.27 kmol. Pentane remaining = 0.03 kmol = $(L_1)_{\text{fi}}$. Taking *n*-hexane as the reference component, the working equation [Eq. (7.57)] can be written as

$$\frac{(L_2)_{\text{in}}}{(L_2)_{\text{fi}}} = \left[\frac{(L_1)_{\text{in}}}{(L_1)_{\text{fi}}} \right]^{\alpha_{21}} = \left[\frac{(L_3)_{\text{in}}}{(L_3)_{\text{fi}}} \right]^{\alpha_{23}} \Rightarrow \frac{0.3}{(L_2)_{\text{fi}}} = \left[\frac{0.3}{(0.03)_{\text{fi}}} \right]^{\alpha_{21}} = \left[\frac{0.4}{(L_3)_{\text{fi}}} \right]^{\alpha_{23}} \quad (\text{i})$$

If α_{21} and α_{23} are known, the final amounts of components 2 and 3 in the mixture can be easily calculated. The values of α at the beginning can be obtained at 101.3 kPa and 64°C (the initial bubble point) using the *K*-values from Figure 7.8(b). However, as boiling continues, the more volatile components are preferentially removed and the bubble point of the liquid gradually increases. The *K*-values and relative volatilities also change as a result.

An approximate method of calculation uses the average values of α over the boiling point range. For this purpose, the final boiling temperature is *guessed* and the relative volatilities (α_{21} and α_{23}) at this temperature are found out. The steps are given below.

- (i) The initial bubble point temperature, the K -values and the α -values are determined.
- (ii) The final temperature is guessed. The K -values and α -values are determined at this temperature.
- (iii) The arithmetic mean values of α are determined. The final number of moles of the components are calculated from Eq. (7.57) or Eq. (i).
- (iv) The final bubble point is now calculated. The values of α at this temperature are determined. The mean α -values and the number of moles (L_i 's) are recalculated from Eq. (i). The procedure can be repeated for better accuracy, if necessary.

At 101.3 kPa (1 atm) and 64°C, $K_1 = 2.3$, $K_2 = 0.87$, $K_3 = 0.144$ [from Figure 7.8(b)]

$$\alpha_{21} = K_2/K_1 = 0.87/2.3 = 0.378; \alpha_{23} = K_2/K_3 = 0.87/0.144 = 6.04$$

Assume a final boiling temperature (when 90% of *n*-pentane is removed) of 95°C. At this temperature,

$$K_1 = 4.65, K_2 = 2.03 \text{ and } K_3 = 0.45 \Rightarrow \alpha_{21} = 2.03/4.65 = 0.437 \text{ and } \alpha_{23} = 4.51$$

Average values of α :

$$\alpha_{21} = (0.378 + 0.437)/2 = 0.407 \quad \text{and} \quad \alpha_{23} = (6.04 + 4.51)/2 = 5.27$$

Putting these values of α in Eq. (i),

$$(L_2)_{fi} = (L_2)_{in}/(10)^{(1/0.407)} = \boxed{0.1175 \text{ kmol}}; \quad (L_3)_{fi} = \boxed{0.335 \text{ kmol}}.$$

Check for the assumed final temperature of 95°C:

$$\text{Total number of moles at the end} = 0.03 + 0.1175 + 0.335 = 0.482$$

Liquid composition:

$$x_1 = 0.03/0.482 = 0.0623; \quad x_2 = 0.1175/0.482 = 0.245; \quad x_3 = 0.3337/0.482 = 0.6927$$

$$\sum_{i=1}^3 K_i x_i = (4.65)(0.0623) + (2.03)(0.245) + (0.45)(0.6927) = 1.0987 > 1$$

So the assumed final temperature of 95°C is *a bit too high*. Because the component 2 (*n*-hexane) is the reference component, its revised K -value is taken as

$$K_2 = (K_{2,95^\circ\text{C}})/1.0987 = 2.03/1.0987 = 1.85$$

The corresponding temperature [from Figure 7.8(b)] is 91°C. The K -values for components 1 and 3 at this temperature are:

$$K_1 = 4.4, K_3 = 0.39; \quad \alpha_{21} = 1.85/4.4 = 0.42, \alpha_{23} = 1.85/0.39 = 4.74$$

Average α -values are:

$$\alpha_{21} = (0.378 + 0.42)/2 = 0.4; \quad \alpha_{23} = (6.04 + 4.74)/2 = 5.4$$

The values of $(L_i)_{fi}$ are recalculated.

$$(L_2)_{fi} = (L_2)_{in}/(10)^{0.4} = 0.1194 \text{ kmol}; \quad (L_3)_{fi} = 0.3373 \text{ kmol}$$

These values are pretty close to the previous estimates. The total moles of the final liquid are:

$$0.03 + 0.1194 + 0.3373 = 0.4867$$

Mole fractions:

$$x_1 = 0.03/0.4867 = 0.0616$$

$$x_2 = 0.12/0.4867 = 0.2466$$

$$x_3 = 0.692$$

$$\sum_{i=1}^3 K_i x_i = (4.4)(0.0616) + (1.85)(0.2466) + (0.39)(0.692) = 0.9971 \approx 1.0$$

So the estimate of the final temperature (91°C) is good enough.

$$\text{Number of moles of distillate} = 1.0 - 0.4867 = \boxed{0.5133 \text{ kmol}}$$

Composition:

$$(x_1)_D = (0.3 - 0.03)/0.5133 = \boxed{0.526}$$

$$(x_2)_D = (0.3 - 0.12)/0.5133 = \boxed{0.351}$$

$$(x_3)_D = \boxed{0.123}$$

7.6 CONTINUOUS MULTISTAGE FRACTIONATION OF BINARY MIXTURES

Separation of a volatile liquid mixture to relatively pure products is very often done in a continuous fractionating column. A packed or a tray tower can be used, the choice depending upon several factors. Understandably, a continuous column is much more effective than multistage flash distillation or batch distillation. In this section we shall discuss the basic design principles of a continuous tray tower for the distillation of a binary mixture.

A tray column and the flow rates and the concentrations of the vapour and the liquid phases at different trays are schematically shown in Figure 7.14(a). For the sake of simplicity, we discuss here the basic principles of fractionation of a binary liquid mixture. The feed (it may be a liquid, a vapour or a two-phase mixture containing components *A* and *B*; *A* is the more volatile component) enters the column at a suitable location. The liquid stream flows down the column from one tray to the next lower tray; the vapour stream flows up bubbling through the liquid on the trays. The vapour from the top tray is condensed and the condensate is collected in a *reflux drum*. A part of this liquid is drawn as the *top product* and the other part is fed back to the top tray (the top tray is marked tray no. 1) as *reflux*. The top product contains the more volatile component *A* and a little of the less volatile *B*. The liquid from the bottom tray goes to a *reboiler* where it is partly vaporized, the vapour is fed back to the tower and the liquid part is continuously withdrawn as the *bottom product*. The bottom product is rich in the less volatile component *B* and has only a small amount of *A* in it. An intimate contact between the liquid and the vapour phases occurs on a tray, facilitating rapid exchange of mass between them. Transport of the more

volatile component *A* occurs from the liquid to the vapour phase, while transport of the less volatile *B* occurs from the vapour to the liquid phase. Thus, a distillation column involves counter-diffusion of the components (*not necessarily equimolar*). As the vapour flows up, it becomes progressively richer in *A*. Similarly, the liquid becomes richer in the less volatile *B* as it flows down the column.

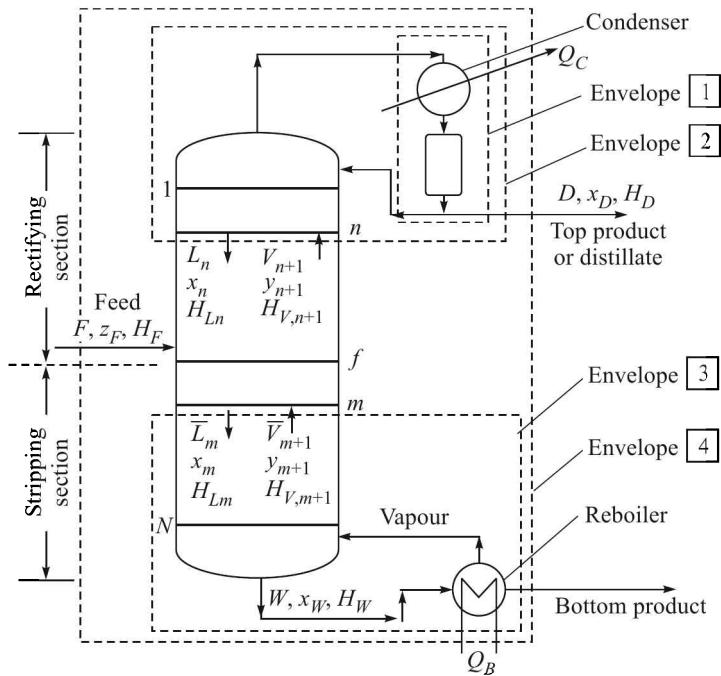


Figure 7.14(a) Material and energy balance envelopes in continuous distillation.

In the section of the column above the feed point, the concentration of the more volatile is larger than that in the feed. This means that the vapour is enriched or ‘purified’ by discarding the less volatile component *B* into the downflowing liquid. So the section of the column above the feed tray is called the *rectifying* or *enriching section*. In the section of the column below the feed tray, the more volatile component is removed or *stripped* out of the liquid (by the process of counterdiffusion, of course) to get a relatively pure *B* at the bottom. So this section is called the *stripping section*.

Now we shall deal with the basic principles of design of a trayed distillation tower. We shall first describe the more important variables, parameters and factors involved in the design.

- *The flow rate, composition and state of the feed.* The state of the feed may be described by its temperature, pressure, phase, etc. The feed may be a liquid, a vapour, or a mixture of liquid and vapour (i.e. a two-phase mixture).
- *The required degree of separation.* The degree of separation is mainly determined by the requirement of quality or purity of the products drawn from the column. Example: Oxygen (bottom product) and nitrogen (top product) are the product streams from a

liquid air distillation column. Nitrogen must be of very high purity (~99.99%) if it is to be used for creating an inert atmosphere (*blanketing*), for example, for a special welding job. A high purity oxygen is required for steel making (> 99%) or for the partial oxidation of naphtha (> 98%) in a fertilizer plant. But oxygen of lesser purity (about 90%) is good enough for medical purposes. The higher the required degree of separation, the more is the number of trays and the more expensive will be the tower.

- *The reflux ratio and the condition of the reflux.* The ratio of the reflux fed back to the top tray and the top product withdrawn is called the *reflux ratio* (L_0/D). This is an important design parameter. A specified degree of separation can be achieved with a lesser number of trays if the reflux ratio is increased. The condition of reflux means whether the reflux is a saturated liquid or a subcooled liquid.
- *The operating pressure and the allowable pressure drop across the column.* The operating pressure also determines the temperature of the column. The pressure drop for the vapour flow depends upon the type, the number and the hydraulic design of the trays. Pressure drop becomes a more important factor if a column is run at a low pressure.
- *Tray type and column internals.* The efficiency of separation (given by the *tray efficiency*) is largely determined by these factors.

In a column design problem for continuous multistage distillation, the rate, the composition and the state of the feed are given. The design engineer has to select the operating conditions (these may be sometimes specified in the problem also), the reflux ratio, the tray type and the column internals, and has to determine the number of trays. He has also to design the column, the tray, the column internals (see Chapter 5) and the auxiliaries like the reboiler and the condenser. It must be kept in mind that the design variables and parameters are interrelated. If a few of them are given or selected, the rest can be determined. Sometimes the number of trays may be known and the engineer has to check if it is suitable for achieving a desired degree of separation of a mixture. For example, we may have a problem of determining if an existing column containing a fixed number of trays of a particular design can be used for the separation of a given feed at a given rate. In this case the reflux ratio and the operating conditions are the important quantities to be calculated in order to ascertain if the existing column is at all suitable for the purpose.

Counter-transport of the components *A* and *B* takes place on each tray of a fractionating column. The molecules of the more volatile component leaving the liquid phase absorb latent heat of vaporization. Also, transport of the less volatile component from the vapour to the liquid phase causes its condensation accompanied by release of latent heat. So the mass transfer of the components between the vapour and the liquid has associated thermal effects (this has been indicated before in a simple problem on non-equimolar counterdiffusion, Example 2.5). The solution of a distillation problem involves the solution of mass and energy balance equations over the trays and over the column. We develop here the relevant equations over three sections of a column and also over the whole device.

Pictures of a few distillation columns in one of the major petrochemical complexes in India are shown in Figure 7.14(b).



Figure 7.14 (b) A few distillation columns in Haldia Petrochemicals Limited (India).

7.6.1 Material and Energy Balance Equations

The determination of the number of trays is based on steady-state material and energy balance equations over the envelopes shown in Figure 7.14(a). A subscript is used with the flow rate, enthalpy and concentration terms to indicate the tray from which it originates. The notations L and V denote the liquid and the vapour flow rates above the feed tray; \bar{L} and \bar{V} denote the same quantities below the feed tray. Thus V_n is the molar flow rate of vapour leaving the n th tray; $H_{L,n}$ is the molar enthalpy of the liquid leaving the n th tray. The rate of reflux to the top tray is L_0 ; the suffix ‘0’ signifies that the stream is as if coming from the ‘hypothetical’ 0th plate above the top tray (the top tray is tray no. 1). The rate at which heat is removed from the overhead condenser (*the condenser heat load*) is Q_C . The rate of heat supply to the reboiler (*the reboiler heat load*) for vaporizing a part of the liquid leaving the bottom tray is Q_B . The feed rate to the column is F having a mole fraction z_F of the more volatile. The distillate (x_D = mole fraction of A , the more volatile, in the distillate) is removed from the reflux drum at a rate of D mole/h;

the bottom product leaves the reboiler at a rate W and the mole fraction of A in it is x_W . We define a reflux ratio (also called the *external reflux ratio*) as

$$\frac{L_0}{D} = R = \text{reflux ratio} (\Rightarrow L_0 = RD) \quad (7.58)$$

Consider envelope **1** (enclosing the *condenser* and the *reflux drum*) in Figure 7.14(a).

Total material balance: $V_1 = L_0 + D = RD + D = D(R + 1)$ (7.59)
 total input total output

Component A balance: $\frac{V_1 y_1}{\text{input of } A} = \frac{L_0 x_0}{\text{output of } A} + D x_D$ (7.60)

Energy balance: $\frac{V_1 H_{V1}}{\text{input}} = \frac{L_0 H_{L0}}{\text{output}} + D H_D + Q_C$ (7.61)

From Eqs. (7.59) and (7.61),

$$\begin{aligned} D(R + 1)H_{V1} &= L_0 H_{L0} + D H_D + Q_C \\ \Rightarrow Q_C &= D[(R + 1)H_{V1} - R H_{L0} - H_D] \end{aligned} \quad (7.62)$$

The condenser heat load Q_C can be calculated from the above equation.

Now we consider envelope **2** (enclosing a part of the *rectifying section* and the *condenser* in Figure 7.14(a)).

Total material balance: $V_{n+1} = L_n + D$ (7.63)

Component A balance: $V_{n+1} y_{n+1} = L_n x_n + D x_D$ (7.64)

Energy balance: $V_{n+1} H_{V,n+1} = L_n H_{L,n} + D H_D + Q_C$ (7.65)

Considering envelope **3** (enclosing a part of the *stripping section* and the *reboiler*),

Total material balance: $\bar{L}_m = \bar{V}_{m+1} + W$ (7.66)

Component A balance: $\bar{L}_m x_m = \bar{V}_{m+1} y_{m+1} + W x_W$ (7.67)

Energy balance: $\bar{L}_m H_{L,m} + Q_B = \bar{V}_{m+1} H_{V,m+1} + W H_W$ (7.68)

Envelope **4** (enclosing the *entire column*, the *condenser* and the *reboiler*) gives

Total material balance: $F = D + W$ (7.69)

Component A balance: $F z_F = D x_D + W x_W$ (7.70)

Energy balance: $F H_F + Q_B = D H_D + W H_W + Q_C$ (7.71)

A material balance and an energy balance equation are also to be written over the feed tray. All the above equations together with the vapour–liquid equilibrium relationship can be solved *algebraically* to determine the number of ideal trays required to achieve a specified degree of separation of the feed. The oldest method of calculation that uses a tray-by-tray approach is called the Sorel method (Sorel, 1893). Many computational methods and strategies have been devised over the years for multicomponent distillation problems. However, a graphical procedure

can be conveniently used to determine the number of trays required for the separation of a *binary* mixture.

7.6.2 Determination of the Number of Trays—the McCabe–Thiele Method

The McCabe–Thiele method developed in 1925 involves a graphical solution of the material balance equations described in Section 7.61 together with the equilibrium relation or the equilibrium data.

Assumptions

The most important assumption underlying the McCabe–Thiele method is that the molar rate of overflow of the liquid from one tray to another is constant over any section of the column. Thus, $L_0 = L_1 = L_2 = \dots = L_n = L = \text{constant}$ in the ‘rectifying section’, and $\bar{L}_m = \bar{L}_{m+1} = \dots = \bar{L}_N = \bar{L} = \text{constant}$ in the ‘stripping section’. The constant flow rates of the liquid (or vapour) in the two sections differ by the rate of input of liquid (or vapour) feed to the column at the feed tray. By virtue of the material and energy balance Eqs. (7.63) and (7.66), the molar vapour rates in the respective sections also remain invariant. This assumption is called the *constant molar overflow* (CMO). The assumption is obviously true when the molar heat of vaporization of the mixture does not depend upon the composition or the temperature in the column (example: a mixture of hydrocarbons not differing much in the molecular weight); for many liquid mixtures the assumption is a good approximation. Lewis (1922) showed that the use of the constant molar overflow assumption greatly simplifies the tray-by-tray calculation by the Sorel method. If constant molar overflow occurs, the mass exchange between the phases occurs in the *equimolar counterdiffusion* mode. Tray-by-tray calculation for a ternary mixture is illustrated in Example 15.3.

Another assumption made in the following analysis is that heat loss from the column is negligible. Let L and \bar{L} represent the constant liquid flow rates, and V and \bar{V} the constant vapour flow rates in the rectifying and the stripping sections. Since the flow rates are constant, the suffixes indicating the trays from which they come out have been dropped. It is to be noted that if there is heat loss or gain, there will be accompanying condensation or vaporization within the column, and the flow rates will vary along the column as a result. The major steps of the graphical construction in the McCabe–Thiele method are to draw: (i) the equilibrium curve using the available data, (ii) the operating lines for the rectifying and the stripping sections, and (iii) the steps between the equilibrium and the operating lines to find out the number of ideal trays.

The rectifying section

Equation (7.63) that represents the material balance of component A over envelope [2] is rewritten below. The reflux is assumed to be at its bubble point.

$$V y_{n+1} = L x_n + D x_D \quad (7.72)$$

From Eq. (7.58), $R = L_0/D = L/D$; from Eq. (7.59), $R + 1 = V/D$

$$\Rightarrow y_{n+1} = \frac{L}{V} x_n + \frac{D}{V} x_D = \frac{L/D}{V/D} x_n + \frac{x_D}{V/D} \Rightarrow y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \quad (7.73)$$

This is the equation of a straight line on the x - y plane with a slope $R/(R + 1)$ and an intercept $x_D/(R + 1)$ on the y -axis. Also the equation is satisfied by the point $x_n = x_D$, $y_{n+1} = x_D$. So the straight line passes through the point (x_D, x_D) which is a point (say D) on the diagonal (see Figure 7.15). Equation (7.68) is called the equation of the operating line of the rectifying section. It is called an *operating line* because it relates the concentrations of the liquid and the vapour phases leaving or entering a section. Usually the reflux ratio R and the distillate composition x_D are the known quantities (if the reflux ratio is not given, the designer has to select a suitable value), and the operating line can be drawn. It is, however, easier to draw this line through (x_D, x_D) with an intercept of $x_D/(R + 1)$ on the y -axis [rather than using the slope, $R/(R + 1)$]. This is illustrated in Example 7.13 and Figure 7.15. A vertical length segment between the operating line and the equilibrium line effectively stands for the overall vapour phase driving force at the particular location in a column.

The stripping section

With the constant molar overflow assumption, the material balance for component A over envelope 3 given by Eq. (7.67) can be rewritten as

$$\bar{L}x_m = \bar{V}y_{m+1} + Wx_W \quad (7.74)$$

Putting $\bar{V} = \bar{L} - W$ [from Eq. (7.66)],

$$y_{m+1} = \frac{\bar{L}}{\bar{V}}x_m - \frac{W}{\bar{V}}x_W = \frac{\bar{L}}{\bar{L} - W}x_m - \frac{W}{\bar{L} - W}x_W \quad (7.75)$$

This is the equation of the operating line for the stripping section. It has a slope of $\bar{L}/(\bar{L} - W)$ and passes through the point (x_W, x_W) which lies on the diagonal. This line is also shown in Figure 7.15.

Similar to the reflux ratio defined for the rectified section, we may define a quantity called the *boil-up ratio*, R_v , for the stripping section.

$$R_v = \frac{\bar{V}}{W} = \frac{\text{moles of vapour leaving the reboiler per hour}}{\text{moles of liquid drawn as the bottom product per hour}} \quad (7.76)$$

EXAMPLE 7.13 (Drawing the operating lines) A mixture of benzene and toluene containing 40 mole% benzene is to be separated continuously in a tray tower at a rate of 200 kmol/h. The top product should have 95 mole% of benzene and the bottom must not contain more than 4 mole% of it. The reflux is a saturated liquid and a reflux ratio of 2.0 is maintained. The feed is a saturated liquid (i.e. it is at its bubble point). Obtain and plot the operating lines for the rectifying and the stripping sections on the x - y plane. What is the boil-up ratio? The vapour–liquid equilibrium data at the operating pressure of 101.3 kPa are given below.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
y	0	0.21	0.38	0.511	0.627	0.719	0.79	0.853	0.91	0.961	1.0

Solution

Assume ‘constant molar overflow’. Given: feed rate, $F = 200 \text{ kmol/h}$; feed composition, $z_F = 0.4$ mole fraction; top product composition, $x_D = 0.95$; bottom product composition, $x_W = 0.04$; reflux ratio, $R = 2.0$.

Total material balance [Eq. (7.69)]:

$$F = D + W \Rightarrow 200 = D + W$$

Total benzene balance [Eq. (7.70)]:

$$Fz_F = Dx_D + Wx_W \Rightarrow (200)(0.4) = D(0.95) + W(0.04)$$

Solving the above equations, we get $D = 79.1 \text{ kmol/h}$ and $W = 120.9 \text{ kmol/h}$

$$R = L_0/D \Rightarrow 2.0 = L_0/79.1$$

$$\Rightarrow L_0 = 158.2; V_1 = D(R + 1) = (79.1)(2 + 1) = 237.3, \text{ from Eq. (7.59).}$$

Since the feed is a liquid, the vapour rate remains constant at $V = V_1 = 237.3 \text{ kmol/h}$ in the rectifying section.

Flow rates in the stripping section: Since the feed is a saturated liquid, the liquid rate increases by 200 kmol/h below the feed plate. However, the vapour rate remains constant all through.

Liquid flow rate, $\bar{L} = L + 200 = 158.2 + 200 = 358.2$; vapour rate, $\bar{V} = V = 237.3$

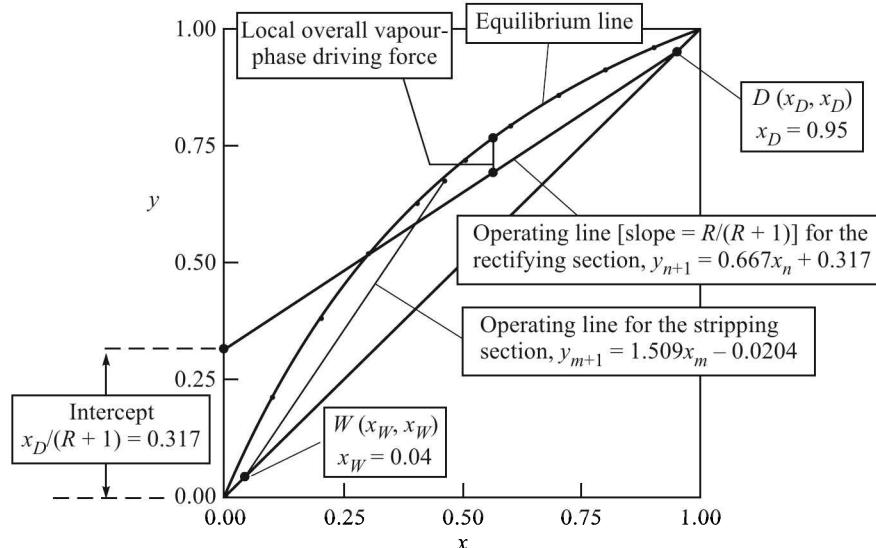


Figure 7.15 The operating lines on the x - y plane.

Operating lines: rectifying section, Eq. (7.73): $y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$

$$\Rightarrow y_{n+1} = \frac{2}{2+1}x_n + \frac{0.95}{2+1}$$

$$\Rightarrow y_{n+1} = 0.667x_n + 0.317 \quad (\text{i})$$

Stripping section, Eq. (7.75), $y_{m+1} = \frac{\bar{L}}{\bar{L}-W}x_m - \frac{W}{\bar{L}-W}x_w$

$$\Rightarrow y_{m+1} = \frac{358.2}{358.2-120.9}x_m - \frac{(120.9)(0.04)}{358.2-120.9}$$

$$\Rightarrow y_{m+1} = 1.509x_m - 0.0204 \quad (\text{ii})$$

Equations (i) and (ii) are the rectifying and stripping section operating lines respectively.

The equilibrium line is plotted on the x - y plane (Figure 7.15). The operating line (i) for the rectifying section passes through the point $D(x_D, x_D)$, i.e. (0.95, 0.95) and has an intercept of 0.317. The line is shown in Figure 7.15. The stripping section operating line (ii) passes through the point $W(x_w, x_w)$, i.e. (0.04, 0.04) and has a slope of 1.509. This line is also shown in the figure.

The boil-up ratio, $R_v = \frac{\bar{V}}{W} = \frac{237.3}{120.9} = [1.963]$

The feed line

As the feed enters the column, the liquid and vapour flow rates undergo step changes depending upon the state of the feed (i.e. upon how much liquid and vapour it has). We shall now write the material and energy balance equations over the plate to which the feed is introduced. Let us designate this plate by the suffix ' f '. The feed plate along with related flow, composition and enthalpy terms are shown in Figure 7.16.

Total material balance:

$$F + L + \bar{V} = \bar{L} + V \quad (7.77)$$

Energy balance:

$$FH_F + LH_{L,f-1} + \bar{V}H_{V,f+1} = \bar{L}H_{L,f} + VH_{V,f} \quad (7.78)$$

If we assume that the change in the enthalpy of a phase as it passes through the feed plate is small, we can write (omitting the subscript f),

$$H_{L,f-1} \approx H_{L,f} \approx H_L$$

and $H_{V,f+1} \approx H_{V,f} \approx H_V$ (7.79)

Substituting the relations (7.79) in Eq. (7.78),

$$FH_F + LH_L + \bar{V}H_V = \bar{L}H_L + VH_V$$

i.e. $(\bar{L} - L)H_L = (\bar{V} - V)H_V + FH_F$ (7.80)

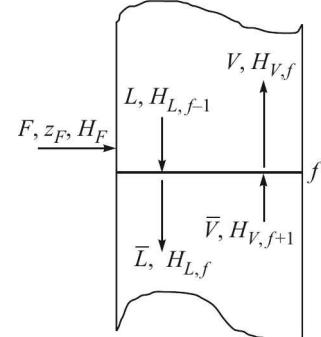


Figure 7.16 The feed plate.

From Eqs. (7.77) and (7.80),

$$\begin{aligned} (\bar{L} - L)H_L &= (\bar{L} - L - F)H_V + FH_F = (\bar{L} - L)H_V + F(H_F - H_V) \\ \Rightarrow & (\bar{L} - L)(H_L - H_V) = F(H_F - H_V) \\ \Rightarrow & \frac{\bar{L} - L}{F} = \frac{H_F - H_V}{H_L - H_V} = \frac{H_V - H_F}{H_V - H_L} = q \text{ (say)} \end{aligned} \quad (7.81)$$

But $\bar{L} - L$ = increase in the liquid flow rate across the feed tray as a result of introduction of the feed = rate of input of liquid with the feed. So q is the fraction of liquid in the feed.

On the basis of Eq. (7.81), the quantity q may also be attributed another physical significance.

$$q = \frac{\text{heat required to convert 1 mole feed to saturated vapour}}{\text{molar heat of vaporization of the saturated liquid}} \quad (7.82)$$

If the feed is a liquid at its bubble point (saturated liquid), $q = 1$; if it is a vapour at dew point (saturated vapour), $q = 0$. If the feed is a two-phase mixture of liquid and vapour, q represents the fraction of liquid in it. So $(1 - q)$ gives a measure of the ‘quality’ of the feed.

The point of intersection of the two operating lines, rectifying section and stripping section, must satisfy Eqs. (7.72) and (7.74). If the point of intersection is (x, y) ,

$$\text{From Eq. (7.72),} \quad Vy = Lx + Dx_D$$

$$\text{From Eq. (7.74),} \quad \bar{V}y = \bar{L}x - Wx_W$$

Subtracting the above equations and using Eq. (7.70),

$$(V - \bar{V})y = (L - \bar{L})x + (Dx_D + Wx_W) = (L - \bar{L})x + Fz_F \quad (7.83)$$

Now, dividing both sides of Eq. (7.77) by F , simplifying, and using the definition of q given by Eq. (7.81),

$$\frac{\bar{V} - V}{F} + 1 = \frac{\bar{L} - L}{F} = q \quad (7.84)$$

Dividing both sides of Eq. (7.83) by F and using the above result,

$$-(q - 1)y = -qx + z_F \quad \Rightarrow \quad y = \frac{q}{q-1}x - \frac{z_F}{q-1} \quad (7.85)$$

The above equation represents a straight line passing through (i) the point (z_F, z_F) on the diagonal (recall that z_F is the overall mole fraction of A in the feed) and (ii) the point of intersection of the operating lines. The line has a slope $q/(q - 1)$, where q is the quality of the feed as stated before [Eq. (7.82)]. Since the line given by Eq. (7.85) is completely described by the state (quality) and concentration of the feed, it is called the *feed line*.

The stripping section operating line can be drawn by taking the help of the feed line. The upper operating line and the feed line are drawn on the $x-y$ plane and their point of intersection is located. The line joining this point of intersection and the point (x_W, x_W) is the stripping section operating line. The following characteristics of the feed line may be noted (also see Example 7.14).

- (a) If the feed is a saturated liquid, $q = 1$; and the slope of the feed line is infinite. So the feed line is a vertical line through (z_F, z_F) .
- (b) If the feed is a saturated vapour, $q = 0$; and the slope of the feed line is zero. So the feed line is a horizontal line through (z_F, z_F) .
- (c) If the feed is a mixture of liquid and vapour or a superheated vapour or a subcooled liquid, the slope of the feed line can be calculated from the enthalpy data and Eq. (7.81).

Drawing of feed lines under different thermal conditions of the feed is illustrated in Example 7.14.

EXAMPLE 7.14 (Drawing the feed line for different feed conditions) A mixture of benzene and toluene containing 58 mole% benzene is to be separated in a continuous column operating at 1 atm total pressure. Draw the feed line for the following feed conditions: (a) saturated liquid, (b) saturated vapour, (c) 65 mass% vapour, (d) vapour at 120°C, and (e) liquid at 50°C.

The other relevant data are given as follows: Benzene: average specific heat of liquid = 146.5 kJ/kmol·K, of vapour = 97.6 kJ/kmol·K; heat of vaporization = 30,770 kJ/kmol. Toluene: average specific heat of liquid = 170 kJ/kmol·K, of vapour = 124.3 kJ/kmol·K; heat of vaporization = 32,120 kJ/kmol.

Solution

The feed line is given by Eq. (7.85). To draw the line, we need to know the value of q . The feed line must pass through the point $F(z_F, z_F)$, i.e. (0.58, 0.58) which lies on the diagonal on the x - y plane. We consider the cases given.

- (a) The feed is a *saturated liquid*. So, q = the fraction of liquid in the feed = 1.

Therefore, the slope of the feed line = $q/(q - 1) = 1/0 = \infty$. The feed line is a vertical line through the point F . This is line I on Figure 7.17.

- (b) The feed is a *saturated vapour*, i.e. $q = 0$ and the slope of the feed line is zero. The feed line is a horizontal line through the point F (line II).

(c) The feed is 65 mass% vapour. So on the average, the feed contains 35 mole% liquid (in this case mass% and mole% can be used interchangeably). So $q = 0.35$ and the slope of the feed line = $0.35/(0.35 - 1) = -0.538$ and its intercept on the y -axis = $-z_F/(q - 1) = -(0.58)/(0.35 - 1) = 0.892$. The line is drawn through the point (0.58, 0.58) on the x - y plane and is marked III on Figure 7.17.

(d) The feed is a superheated vapour at 120°C. In this case the value of q has to be calculated from Eq. (7.81). The values of the enthalpy terms H_F , H_V and H_L are required. In order to calculate the enthalpies, a reference state is to be selected. Using the Antoine constants given in Table 7.2, the bubble point of a solution having 58% benzene can be calculated (assuming that the solution is ideal). The bubble point is 90°C (the calculation of the bubble point is left as an exercise). We take pure liquids at 90°C as the reference state for convenience. The *heat of solution* (ΔH_s) is assumed to be zero.

Enthalpy of the liquid: For the solution at its bubble point ($T = 90^\circ\text{C}$), put $T_0 = 90$ and $\Delta H_s = 0$ in Eq. (7.18) $\Rightarrow H_L = 0$.

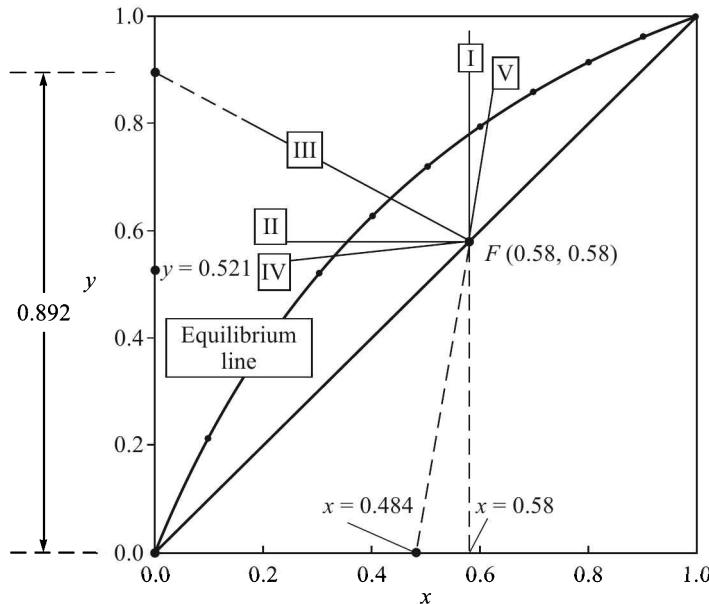


Figure 7.17 Feed lines for different conditions of the feed: (I) saturated liquid, (II) saturated vapour, (III) two-phase mixture, (IV) superheated vapour, and (V) subcooled liquid.

Enthalpy of the vapour: The mole fraction of benzene in the saturated vapour in equilibrium with a liquid with $x = 0.58$ is $y^* = 0.78$. Putting $y^* = 0.78$, T (vapour temp.) = 90°C, T_0 (ref. temp.) = 90°C, $M_A \lambda_A = 30,770$ kJ/kmol, and $M_B \lambda_B = 32,120$ kJ/kmol in Eq. (7.19), the enthalpy of the saturated vapour is

$$H_V = (0.78)(30,770) + (1 - 0.78)(32,120) = 31,067 \text{ kJ/kmol}$$

Enthalpy of the feed: We imagine that 0.58 kmol of benzene and 0.42 kmol of toluene are vaporized separately at 90°C, the vapours are heated to 120°C and then mixed to get one kmole of the feed.

$$\begin{aligned} H_F &= [(0.58)(30,770) + (0.58)(97.6)(120 - 90)] \\ &\quad \text{latent heat} \qquad \qquad \qquad \text{sensible heat} \\ &+ [(0.42)(32,120) + (0.42)(124.3)(120 - 90)] = 34,601 \\ &\quad \text{latent heat} \qquad \qquad \qquad \text{sensible heat} \end{aligned}$$

$$\text{Then, } q = \frac{H_V - H_F}{H_V - H_L} = \frac{31,067 - 34,601}{31,067 - 0} = -0.114$$

To draw the feed line in this case, it will be more convenient to use the intercept on the y-axis, i.e.

$$-z_F/(q - 1) = -0.58/(-0.114 - 1) = 0.521$$

The feed line is marked IV on Figure 7.17.

- (e) The feed is a subcooled liquid at 50°C. We imagine that 0.58 kmol of benzene and 0.42 kmol of toluene are separately cooled from the reference temperature ($T_0 = 90^\circ\text{C}$) to $T = 50^\circ\text{C}$ and then mixed to get one mole of the subcooled feed.

The enthalpy of the feed,

$$H_F = (0.58)(146.5)(50 - 90) + (0.42)(170)(50 - 90) = -6240 \text{ kJ/kmol} \text{ (the heat of mixing is neglected).}$$

$$q = \frac{H_V - H_F}{H_V - H_L} = \frac{31,067 - (-6240)}{31,067 - 0} = 1.2$$

From Eq. (7.85), the intercept on the x -axis = $z_F/q = 0.58/1.2 = 0.58/1.2 = 0.484$.

The feed line is drawn through (0.58, 0.58) with this intercept on the x -axis. It is marked V on Figure 7.17.

Feed tray location and the number of ideal trays

The next step of graphical construction is to determine the number of equilibrium trays (or ideal trays) required for a specified degree of separation (i.e. for specified values of x_D and x_W) and to locate the feed tray. This is illustrated in Example 7.15 and Figure 7.18(a). The rectifying section operating line DE is drawn through the point D (x_D, x_D) with an intercept $x_D/(R + 1)$ on the y -axis. If the feed is a saturated liquid, the feed line FN is a vertical line through the point F (z_F, z_F). The feed line FN intersects the rectifying section operating line DE at M . The point W (x_W, x_W) is located on the diagonal. WM is joined to give the stripping section operating line. The line WM , when extended, intersects the equilibrium curve at S'' , and the line DE , when extended, intersects the equilibrium curve at S' .

The number of equilibrium trays is determined by step or staircase construction between the equilibrium curve and the operating lines (see Example 7.15). The basis of such construction has been described in Section 4.6.2. The point (x_n, y_n) lies on the equilibrium curve whereas the point (x_n, y_{n+1}) lies on the operating line. Construction may start from either end, i.e. from D (the top tray) or W (the bottom tray). When the feed line is crossed in course of construction, a changeover from one operating line to the other is necessary. This means a transition from the rectifying to the stripping section (or vice versa). For example, starting the stage construction from the point D in Figure 7.18(a), we should make a changeover from the upper operating line to the lower after tray number 5 from the top. The step construction should thereafter proceed along the lower operating line MW . In this way we take the advantage of maximum possible change in the concentration in each tray. So the sixth tray from the top is the *optimum feed tray*. The stage construction (solid line) shows that the number of ideal stages required is 7.8. If the graphical construction does not give an integral number of trays (in fact, it rarely does), it is customary to report the number of ideal trays as a mixed fraction. The idea behind this is that the integral number of real trays is determined after considering tray efficiency. Usually, the reboiler partly vaporizes the liquid from the lowest tray. Because equilibrium vaporization in the reboiler is quite a reasonable assumption, the reboiler also acts as a tray. So the number of ideal trays in the construction shown in Figure 7.18(a) is 7.8 *including the reboiler*; i.e. 6.8 number of trays and a reboiler are required for the desired separation.

The above discussion does not mean that the feed has to be introduced always on the 'optimum feed tray'. Consider the staircase construction on Figure 7.18(b). The feed is

deliberately introduced on the fifth tray from the top. So a changeover to the lower operating line has been made at the fifth tray from the top, and construction has thereafter been done along WMS' , the stripping section operating line. The number of equilibrium trays required to reach the point W is 8, which is 0.2 ideal trays more than the previous case. This is expected because full advantage of the driving force has not been exploited on a few trays.

However, a changeover from one operating line to the other is possible only in the section $S'S''$. When a new column is designed, the optimum feed tray location is used. But if an existing column with a feed nozzle at a particular tray has to be considered for possible use to separate a mixture, a changeover from one operating line to the other during staircase construction should be done at the tray which is provided with a feed nozzle [see Example 7.15, part (d)]. Complete construction of the steps will tell whether the existing column is suitable for a particular service. If not, further calculations may be done with a different reflux ratio before discarding the possibility of use of the available column.

It is to be noted that a liquid feed is introduced just above the feed tray, but a vapour feed is introduced just below it. If the feed is a mixture of liquid and vapour, it is desirable that it is separated into the vapour and the liquid phases first. The liquid part should enter the column just above the feed tray and the vapour part just below it. However, this is not always done in practice, and a mixed feed is often introduced as a whole over the feed tray.

If a high purity product is required, the graphical construction of the trays may pose a problem. The operating and the equilibrium lines may be too close at the top and the bottom region to allow graphical construction. One way is to draw steps for these regions on separate graphs drawn using expanded scales. Alternatively, the Kremser equation may be used assuming the equilibrium line to be linear at low concentrations. Another technique of plotting the equilibrium and the operating line for McCabe–Thiele construction has been suggested by Ryan (2001).

EXAMPLE 7.15 (*Determination of the number of ideal trays*) A stream of aqueous methanol having 45 mol% CH_3OH is to be separated into a top product having 96 mole% methanol and a bottom liquid with 4% methanol. The feed is at its bubble point and the operating pressure is 101.3 kPa. A reflux ratio of 1.5 is suggested. (a) Determine the number of ideal trays. (b) Find the number of real trays if the ‘overall tray efficiency’ is 40%. On which real tray should the feed be introduced? (c) Plot the temperature profile along the column. (d) A column having twenty-two trays with a feed nozzle at tray number 13 from the top is available in the plant. The trays are presumed to be 40% efficient on the average. Is this column suitable for the above separation?

The equilibrium and bubble point data for the methanol–water system at 101.3 kPa are given below.

x	0	0.02	0.04	0.06	0.08	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95	1.0
y	0	0.134	0.23	0.304	0.365	0.418	0.579	0.665	0.729	0.779	0.825	0.87	0.915	0.958	0.979	1.0
Temp.	100	96.4	93.5	91.2	89.3	87.7	84.4	78.0	75.3	73.1	71.2	69.3	67.6	66	65	64.5

Solution

The equilibrium data are plotted, the diagonal is drawn. Given: $x_D = 0.96$; $x_W = 0.04$ and $z_F = 0.45$. The points $D(0.96, 0.96)$, $W(0.04, 0.04)$ and $F(0.45, 0.45)$ are located on the x – y plane.

(a) Number of ideal trays: The reflux ratio is $R = 1.5$. The intercept of the rectifying section operating line on the y -axis is $x_D/(R + 1) = 0.96/(1.5 + 1) = 0.384$.

The upper operating line is drawn through the point $D(0.96, 0.96)$ with an intercept of 0.384 on the vertical axis [Figure 7.18(a)]. The extended operated line meets the y -axis at E (intercept = 0.384). The feed is a saturated liquid and the feed line is a vertical line through F . The upper operating line meets the feed line at the point M . The points M and W are joined to get the lower or stripping section operating line WM . Now the number of ideal trays is determined by drawing steps between the equilibrium line and the operating lines DM and WM , changing from the upper to the lower operating line as the feed line is crossed. The number of ideal trays is 7.8. It is to be noted that the feed is to be introduced on the 6th ideal tray.

(b) Number of real trays: The number of real trays is obtained by dividing the number of ideal trays by the fractional overall tray efficiency (the given value is 0.4). The number of real trays is $6.8/0.4 = 17$ real trays *plus* the reboiler which is assumed to act like an ideal stage.

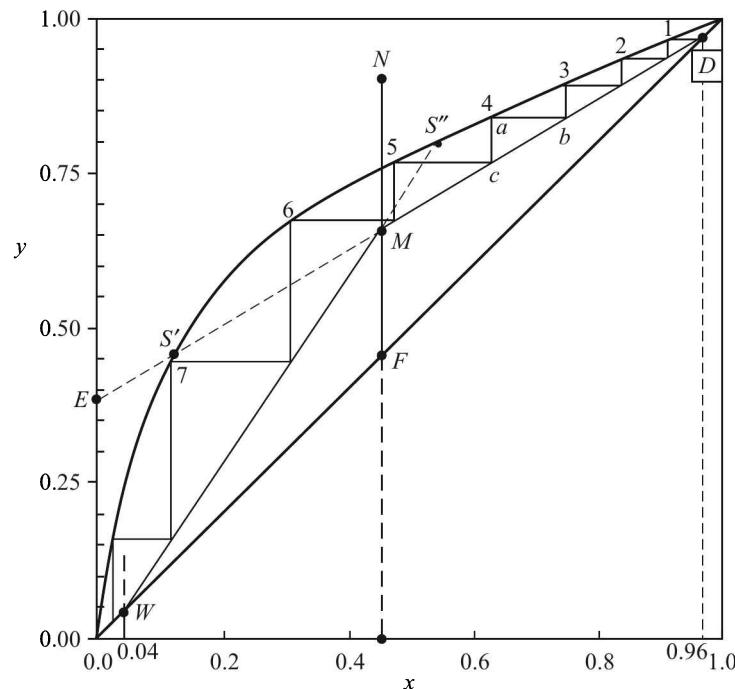


Figure 7.18(a) McCabe-Thiele construction for the number of ideal trays.

(c) The temperature on the n th tray can be obtained from the values x_n , y_n and the given bubble point data. The temperatures on the different ideal trays are given below.

n	1	2	3	4	5	6	7	8
x_n	0.913	0.853	0.773	0.667	0.575	0.35	0.15	0.0405
Temp.	66	66.9	68	70	72.8	76.5	85	94

(d) This part is left as an exercise. Note that now the feed is introduced on the fifth ideal tray from the top [see Figure 7.18(b)].

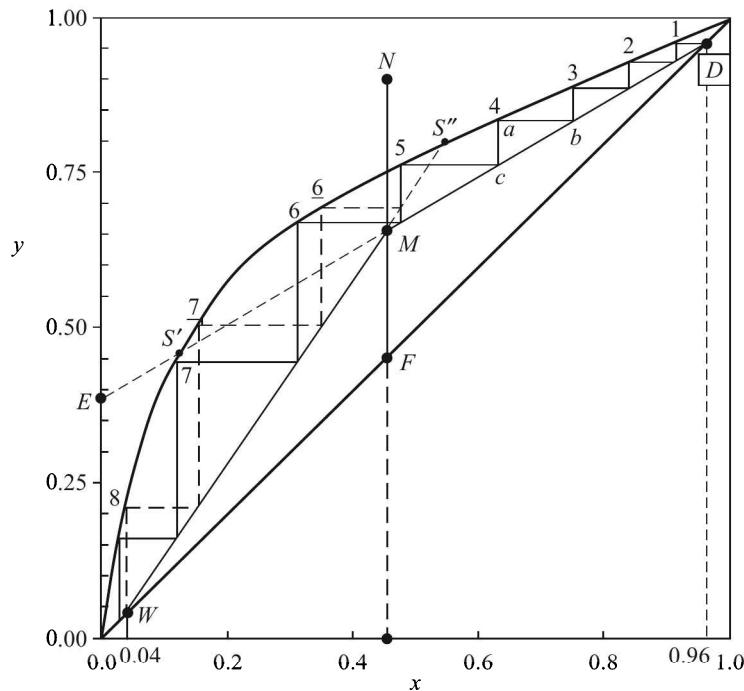


Figure 7.18(b) McCabe-Thiele construction for the number of ideal trays—the feed enters a particular tray.

Analytical determination of the number of ideal stages—Smoker's equation

A simple but elegant equation was derived by Smoker (1938) to *analytically* determine the number of ideal stages required for the separation of a binary mixture if the relative volatility is constant and constant molar overflow (CMO) occurs. Smoker used a simple coordinate transformation that ultimately led to a relation between the liquid concentrations on the top tray and on the n th tray. Smoker's equation reduces to the Fenske equation in the limit $R \rightarrow \infty$. Interested readers are referred to the original classical article or to Sinnott (Coulson–Richardson's *Chemical Engineering*, Vol. 6, Elsevier, 2005, pp. 512–515). Applications of Smoker's equation have been discussed further by Jafarey et al. (1979).

Total reflux

If the liquid from the overhead condenser is totally recycled to the column, i.e. no distillate is removed from the reflux drum ($D = 0$), the column is said to run at 'total reflux'. The reflux ratio becomes $R = L_0/D = L_0/0 = \infty$. No product is drawn from the reboiler either. All the liquid flowing to the reboiler is vaporized and fed back to the column. So, in a column operating at total reflux under steady-state conditions, there should not be any flow of feed into it.

At total reflux, the slope of the rectifying section operating line is $[R/(R + 1)]$ for $R \rightarrow \infty$, i.e. the slope of the line is unity and it passes through the point (x_D, x_D) on the diagonal. Therefore,

the operating line coincides with the diagonal. So does the stripping section operating line. The number of ideal stages is obtained by staircase construction between the equilibrium line and the diagonal. This gives the *theoretical minimum* number of stages to achieve a given separation. The construction is illustrated in Figure 7.19. Total reflux is very often used during the startup of a column till the steady-state condition is reached. After this, continuous feed flow and product withdrawal are started.

Fenske's equation

This equation can be used to theoretically calculate the minimum number of trays if the relative volatility remains reasonably constant. Let N_m be the minimum number of trays in the column. Besides, there is a *total reboiler*. If α_w is the relative volatility of A at the reboiler temperature and pressure, and x_w and y_w are the equilibrium liquid and vapour concentrations in the reboiler, then by definition,

$$\frac{y_w}{1 - y_w} = \alpha_w \frac{x_w}{1 - x_w} \quad (7.86)$$

The vapour leaving the reboiler and entering the lowest tray (tray number N_m in this case) has a mole fraction y_w of the component A. The liquid leaving this tray has a composition x_{Nm} . So the point (x_{Nm}, y_w) lies on the operating line. Because the operating line coincides with the diagonal at total reflux, $x_{Nm} = y_w$. Putting this result in Eq. (7.86),

$$\frac{x_{Nm}}{1 - x_{Nm}} = \alpha_w \frac{x_w}{1 - x_w} \quad (7.87)$$

Applying the same procedure to the case of tray number N_m ,

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

Similarly for tray number $N_m - 1$,

$$\frac{y_{(Nm-1)}}{1 - y_{(Nm-1)}} = \alpha_{(Nm-1)} \frac{x_{(Nm-1)}}{1 - x_{(Nm-1)}} = \alpha_{(Nm-1)} \cdot \alpha_{Nm} \cdot \alpha_w \cdot \frac{x_w}{1 - x_w}$$

[Note that the point (x_{Nm-1}, y_{Nm}) lies on the operating line which coincides with the diagonal; therefore, $x_{Nm-1} = y_{Nm}$]

Continuing the procedure up to the top tray (where $y_1 = x_D$),

$$\begin{aligned} \frac{x_D}{1 - x_D} &= \frac{y_1}{1 - y_1} = \alpha_1 \alpha_2 \dots \alpha_{Nm} \cdot \alpha_w \cdot \frac{x_w}{1 - x_w} \\ \Rightarrow \quad \frac{x_D}{1 - x_D} &= (\alpha_{av})^{N_m+1} \cdot \frac{x_w}{1 - x_w} \\ \text{i.e.} \quad N_m + 1 &= \frac{\log \frac{x_D(1 - x_w)}{x_w(1 - x_D)}}{\log \alpha_{av}} \end{aligned} \quad (7.88)$$

Here α_{av} is the average relative volatility of the more volatile component. The above equation is called *Fenske's equation*, which is useful for the calculation of the minimum number of trays.

EXAMPLE 7.16 (Number of theoretical plates at total reflux) A mixture of benzene and toluene having 40% benzene is to be separated at a rate of 200 kmol/h into a top product containing 95% benzene and a bottom product with 4% of it. It is a common practice to run a column at total reflux for some time for the purpose of stabilization during startup. Determine the number of ideal trays required for this separation if the column is operated at total reflux (no feed input at this time). Also calculate the same using the Fenske equation if the average relative volatility of benzene in the mixture is 2.5. Vapour–liquid equilibrium data for this system at the operating pressure of 1 atm are also given in Example 7.13.

Solution

At total reflux, the reflux ratio is infinite ($R = \infty$) and the slope of the rectifying section operating line is $R/(R + 1) = 1$. So both the operating lines should coincide with the 45° line (i.e. the diagonal). Given: top product composition, $x_D = 0.95$; bottom liquid composition, $x_W = 0.04$.

The equilibrium data are plotted on the x – y plane in Figure 7.19. The points $D(0.95, 0.95)$ and $W(0.04, 0.04)$ are located on the diagonal. The number of ideal trays is obtained by construction of steps between the equilibrium line and the diagonal, starting at one end (say at D) and terminating at the other. The number of trays is 7.

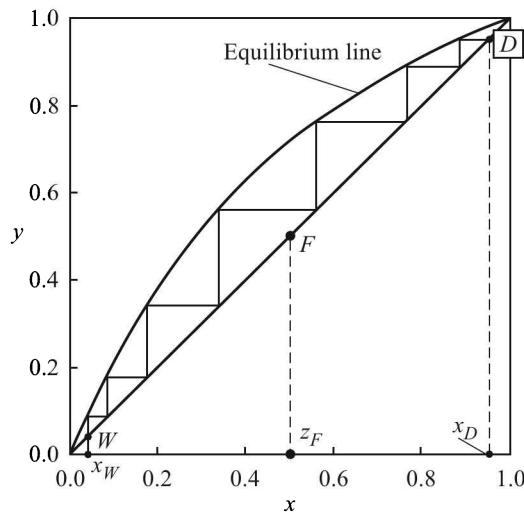


Figure 7.19 Number of plates for operation at total reflux (the minimum number of plates).

Use of the Fenske equation: Put the values of x_D , x_W and α_{av} (= 2.5) in Eq. (7.88). The total number of trays is

$$N_m + 1 = \frac{\log \frac{x_D(1 - x_W)}{x_W(1 - x_D)}}{\log \alpha_{av}} = \frac{\log \frac{(0.95)(1 - 0.04)}{(0.04)(1 - 0.95)}}{\log 2.5} = 6.7$$

This is very close to the number of ideal trays determined graphically. One of the reasons of the small difference is the assumption of an average value of the relative volatility.

Note: For operation at total reflux, sufficient amount of feed is charged into the reboiler and flow of steam (to the reboiler) and of cooling water (to the condenser) are started. The entire

condensate is fed back as reflux. The rate, the concentration and the thermal state of the feed are not relevant for a column operated at total reflux since there is no feed input at all.

Minimum reflux ratio

In Section 6.4, we discussed the method of determination of the minimum liquid rate for gas absorption by identifying the pinch point for a given system. The determination of the minimum reflux ratio for distillation is also based on identifying the pinch point. Let us refer to Figure 7.20 in which the equilibrium curve and the feed line are shown; $D(x_D, x_D)$ and $W(x_W, x_W)$ are the terminal points of the operating lines. For a particular reflux ratio (R_1 , say), DE_1 is the enriching section operating line having a slope $R_1/(R_1 + 1)$. It intersects the feed line at the point M_1 ; WM_1 is the stripping section operating line. The ordinate of the point E_1 gives the intercept of the upper operating line on the y -axis. The number of theoretical trays required is obviously finite. As the reflux ratio R_1 decreases to R_2 , the slope of the upper operating line decreases, but the intercept increases, i.e. the point E_1 moves to E_2 (say). The upper operating line is DM_2 ; the stripping section operating line is WM_2 ; and they intersect at M_2 on the feed line. Now the driving force is less at all the points and the number of theoretical trays will be more. If the reflux ratio is gradually reduced, a situation will appear when the upper operating line DE_3 intersects the feed line at the point M_3 that lies on the equilibrium curve. The driving force is zero at the point M_3 . It is the *pinch point*. The number of theoretical trays required to achieve the given separation becomes infinite. This operating line DM_3 corresponds to the minimum reflux ratio, because if the reflux ratio is further reduced, the operating line will intersect the feed line at a point M_4 above the equilibrium curve. This is impossible. To determine the minimum reflux ratio R_m , for the kind of equilibrium line shown in Figure 7.20, the steps given below should be followed.

- Locate the points $D(x_D, x_D)$ and $F(z_F, z_F)$ on the diagonal on the $x-y$ plane.
- Draw the feed line through F from the known feed composition z_F , and the feed quality (given by q); locate the point M_3 .
- Join DM_3 and extend to intersect the y -axis at E_3 . Find out the ordinate of E_3 and equate it to $x_D/(R_{m+1})$. Calculate the minimum reflux ratio, R_m .

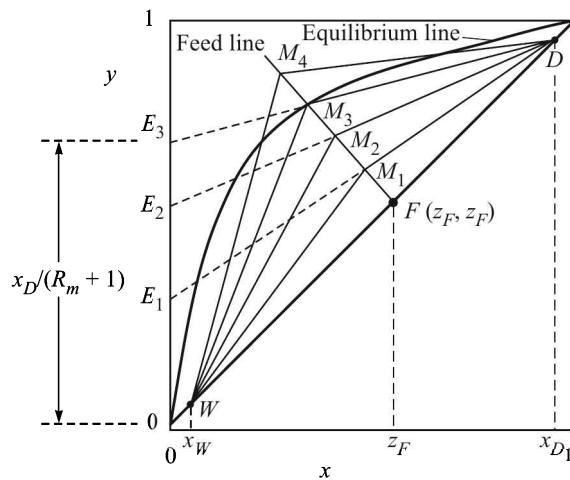


Figure 7.20 Operating lines for changing reflux ratios and for the minimum reflux (R_m).

The above strategy fails for some other shapes of the equilibrium curve. Examples are shown in Figure 7.21 and Figure 7.22. Because of the typical curvature, the pinch point does not occur at the intersection of the feed line and the equilibrium curve. As the reflux ratio is reduced, at a certain value of it the pinch point K occurs at the point of tangency of the rectifying section operating line (Figure 7.21) or the stripping section operating line (Figure 7.22) and the equilibrium line. The location of the point of tangency depends upon the shape of the equilibrium line. This type of pinch point and the minimum reflux ratio can be determined only graphically. Example 7.17 illustrates the procedure.

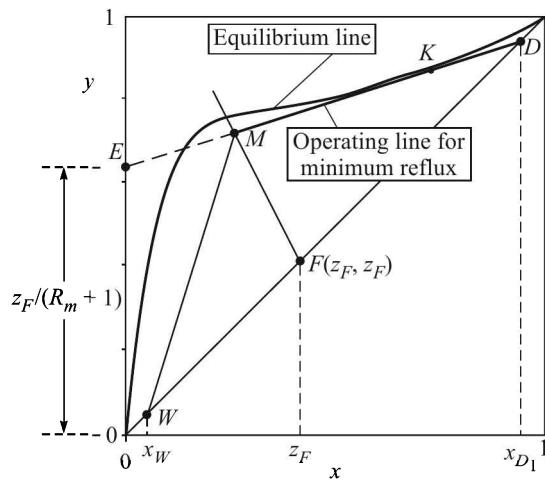


Figure 7.21 A pinch point (K) on the operating line for the rectifying section.

EXAMPLE 7.17 (*Determination of the minimum reflux ratio*) A binary solution of 60 mol% A and 40 mol% B is to be separated into a top product having 96 mol% A and a bottom product with 6 mol% A . The feed is a two-phase mixture containing 72% liquid. Determine the minimum reflux ratio for this separation. The equilibrium data for the system at the operating condition of the column are given below.

x	0	0.05	0.07	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50	0.60	0.70	0.80	0.90	1.0
y	0	0.07	0.10	0.14	0.205	0.29	0.39	0.55	0.67	0.75	0.86	0.93	0.96	0.98	0.99	1.0

Solution

Given: $x_D = 0.96$; $x_W = 0.06$; $z_F = 0.60$; fraction of liquid in the feed, $q = 0.72$.

The equilibrium diagram is plotted and the points $D(0.96, 0.96)$, $W(0.06, 0.06)$ and $F(0.6, 0.6)$ are located on the x - y plane (Figure 7.22). The feed line is drawn through the point F with an intercept of $z_F/q = 0.6/0.72 = 0.833$ on the x -axis. It meets the equilibrium line at the point M . The points W and M are joined, but the corresponding line WM in the stripping section cannot be an operating line since WM (shown as a dotted line) cuts the lower part of the equilibrium line at two points. So the point M cannot be a *pinch point*. This happens because the lower part of the equilibrium line is convex downwards.

To determine the true pinch point, we draw a tangent to the equilibrium line through the point W . This line meets the feed line at the point M_1 . Join DM_1 and produce it to meet the y -axis at

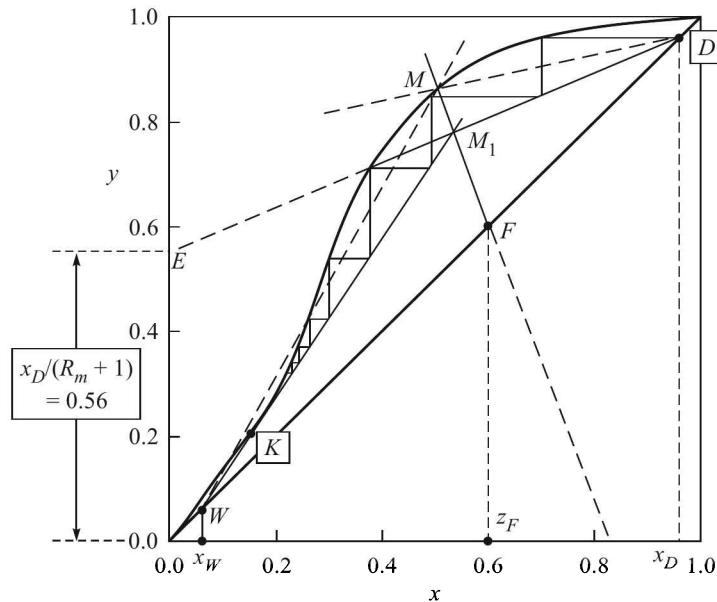


Figure 7.22 A pinch point on the operating line for the stripping section.

E. The point of tangency is K . If we make step construction starting at D , it is seen that as we approach the pinch point K , the step size becomes progressively smaller, and it is not possible to reach K by drawing a finite number of plates. The situation corresponds to the minimum reflux and DE is the rectifying section operating line for minimum reflux. If R_m is the minimum reflux, the ordinate of the point E is

$$0.56 = x_D/(R_m + 1) = 0.96/(R_m + 1) \Rightarrow R_m = (0.96/0.56) - 1 = 0.174$$

Open steam

While separating an aqueous solution, if the residue or bottom product consists of water and traces of the solute, sometimes it may be convenient to feed live steam at the bottom of the tower. No reboiler is necessary. The arrangement is shown in Figure 7.23.

The operating line equation for the rectifying section remains the same as Eq. (7.73), but that for the stripping section is obviously different. The material balance of component A over the envelope shown in Figure 7.23 is [assume that the inlet steam is saturated]

$$\bar{L} x_m + \bar{V} \cdot (0) = \bar{V} y_{m+1} + W x_W \quad (7.89)$$

Since there is no reboiler, $\bar{L} = W$. Therefore,

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

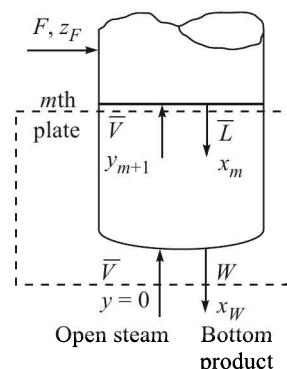


Figure 7.23 A distillation column using open steam.

$$\Rightarrow \frac{\bar{L}}{\bar{V}} = \frac{y_{m+1}}{x_m - x_W} = \text{slope of the lower operating line} \quad (7.90)$$

Also, by definition, the point $(x_W, 0)$ lies on the lower operating line. The determination of the number of ideal plates in a column using open steam is illustrated in Example 7.18. When open steam is used, one or two more ideal trays are required for a separation, but there is no reboiler cost.

There may be other practical situations which are not covered in the above discussion. Cases may arise when heat loss from the column wall may occur causing some condensation of the vapour, or the overhead vapour may be partially condensed and the top product may be withdrawn as a vapour. In any such case, the operating lines have to be drawn on the basis of appropriate mass and energy balance equations.

EXAMPLE 7.18 (Use of open steam in distillation) An aqueous solution containing 40 mol% methanol is to be separated at a rate of 300 kmol per hour using open steam as the source of heat energy. The top product must have 96 mol% methanol and the bottom product must not have more than 4 mol% of it. The feed enters the column 50% vaporized. A reflux ratio of 2.25 is suitable. Determine (a) the equation of the stripping section operating line, (b) the slope of the feed line, (c) the number of ideal plates required for this separation, (d) the steam rate, and (e) the condenser heat load. The following enthalpy data for 96 mol% methanol solution at 1 atm are available: saturated vapour, $H_V = 9725 \text{ kcal/kmol}$; saturated liquid, $H_L = 1260 \text{ kcal/kmol}$ (reference state: pure liquids at 15°C; see Example 7.4).

Hints: Given: reflux ratio, $R = 2.25$; Top product concentration, $x_D = 0.96$.

Operating line for the rectifying section: intercept on the y -axis = $x_D/(R + 1) = 0.96/3.25 = 0.295$

Feed line: $q = \text{fraction of liquid in the vapour-liquid mixture} = 0.5$; feed concentration, $z_F = 0.4$.

$$\text{Slope of the feed line} = q/(q - 1) = 0.5/(0.5 - 1) = \boxed{-1}$$

[this is the answer to part (b) of the problem]

$$\text{Intercept of the feed line on the } x\text{-axis} = -z_F/(q - 1) = -0.4/(0.5 - 1) = 0.8$$

The stripping section operating line passes through $W(0.04, 0)$.

The equilibrium data [see Example 7.15] are plotted on the x - y plane and the diagonal is drawn. The points $D(0.96, 0.96)$, $W(0.04, 0)$ and the feed point $F(0.4, 0.4)$ are located on the x - y plane. The feed line is drawn through F with an intercept of 0.8 on the x -axis (it is more convenient to draw the line using this intercept rather than the slope). The rectifying section operating line is drawn through D with an intercept of 0.295 on the y -axis. This line intersects the feed line at the point D_1 . Join WD_1 which is the stripping section operating line.

Equation of the stripping section operating line, WD_1 : $y = 1.944x - 0.078$ [answer to part (a)].

Draw steps between the equilibrium line and the operating lines (we start from the end D) changing from the upper to the lower operating line as the feed line is crossed. The number of ideal stages is $\boxed{7}$ [answer to part (c)]. The graphical construction is left as an exercise.

In order to calculate the steam rate we have to use the following material balance equations.

$$\text{Total material balance: } F + \bar{V} = D + W \Rightarrow 300 + \bar{V} = D + W \quad (\text{i})$$

$$\text{Methanol balance: } Fz_F + \bar{V}(0) = Dx_D + Wx_W \Rightarrow (300)(0.4) = D(0.96) + W(0.04) \quad (\text{ii})$$

Liquid flow rate in the stripping section, $\bar{L} = W$ (because there is no reboiler).

$$\text{Slope of the operating line of this section} = \bar{L}/\bar{V} = W/\bar{V} = 1.944 \Rightarrow \bar{V} = 0.514W \quad (\text{iii})$$

Solving Eqs. (i), (ii) and (iii),

$$D = 108.6 \text{ kmol}, W = 394.3 \text{ and } \bar{V} = 202.9 \text{ kmol/h} = \boxed{3652 \text{ kg steam per hour}}$$

[Answer to part (d)];

The condenser heat load [part (e)]: The vapour (96 mol% methanol) leaving the top tray is condensed to the saturated liquid. Condenser heat load

$$= V_1(H_V - H_L) = D(R + 1)(H_V - H_L)$$

$$= 108.6(2.25 + 1)(9725 - 1260) = \boxed{2.987 \times 10^6 \text{ kcal/h}}$$

Use of reflux below its bubble point

The vapour from the top tray may sometimes be condensed and then cooled below its bubble point (*subcooled*) in the condenser. This is ‘cold reflux’. On entering the top tray, the ‘cold reflux’ reaches its bubble point very quickly. The required energy is supplied by condensation of some of the vapour on the top tray. Thus, the vapour flow rate V_1 from the top tray will be less than that at the lower trays, and the liquid flow rate L in the rectifying section (Figure 7.24) will be larger than the reflux L_0 fed to the column from the condenser. As a result, the ‘internal reflux ratio’, R' ($= L/D$), will be greater than the ‘external reflux ratio’, R ($= L_0/D$). In order to calculate the internal reflux ratio R' , we need to know the liquid flow rate L .

If θ_r is the temperature of the *cold reflux*, and θ_{rb} is its bubble point, energy required for heating the reflux,

$$Q = L_0 c_{pr} M_r (\theta_{rb} - \theta_r); \quad \text{vapour condensed} = \frac{Q}{M_r \lambda} = \frac{L_0 c_{pr} M_r (\theta_{rb} - \theta_r)}{M_r \lambda}$$

where

c_{pr} = specific heat of the reflux ($\text{kJ/kg}\cdot^\circ\text{C}$)

M_r = its average molecular weight (this is the same as that of the vapour from the top tray)

λ = latent heat of condensation of the vapour (kJ/kg). Then the internal liquid flow rate,

$$L = L_0 + \frac{L_0 (c_{pr} M_r) (\theta_{rb} - \theta_r)}{M_r \lambda}; \quad R' = L/D \quad (7.91)$$

$$\text{The equation of the rectifying section operating line: } y_{n+1} = \frac{R'}{R'+1} x_n + \frac{x_D}{R'+1} \quad (7.92)$$

The rest of the graphical construction is pretty much the same as described before. This is illustrated in Example 7.19.

Use of murphree efficiency in graphical construction of stages

One more case deserves attention. Trays are never ideal. As discussed in Chapter 6, tray efficiency is an indicator of how good the mass transfer performance of a tray is. If an overall fractional tray efficiency is given, the number of real trays is calculated by simply dividing the number of ideal trays by the fractional tray efficiency. The Murphree tray efficiency E_M is given as

$$E_M = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \quad (7.93)$$

Note that the actual enrichment of the vapour over the n th tray is $(y_n - y_{n+1}) = E_M(y_n^* - y_{n+1})$; the theoretically possible enrichment is $(y_n^* - y_{n+1})$, which is the vertical distance between the operating line and the equilibrium line. A *pseudo-equilibrium line* is drawn (see also Section 6.8.2) such that its vertical distance from the operating line is E_M -times the distance between the operating line and the equilibrium curve. Staircase construction between the pseudo-equilibrium curve and the operating lines gives the number of real plates. This is illustrated in Example 7.19.

EXAMPLE 7.19 (*Number of real trays—cold reflux; the Murphree efficiency is given*) An aqueous methanol having 45 mol% of the alcohol at 40°C is to be separated into a top product with 96 mol% methanol and a bottom stream with not more than 4% of methanol. The vapour leaving the tower is condensed and cooled. The reflux is returned to the column at 50°C and the external reflux ratio is 2.25. It is required to determine (a) the number of real trays for this separation if the Murphree efficiency is 60%, and (b) the heat duty of the reboiler and of the condenser.

The following data are supplied: Enthalpy values (reference states—pure liquids at 0°C): saturated feed (45 mol% methanol, 74°C): 1390 kcal/kmol; saturated reflux (96 mol% methanol, 66°C): 1253 kcal/kmol; saturated ‘vaporized’ feed (45 mol% methanol): 10,630 kcal/kmol; heat of vaporization of the top product (96% methanol): 8470 kcal/kmol; c_p of water: 18 kcal/kmol·°C, c_p of methanol: 19.4 kcal/kmol·°C (average values over the temperature range).

Solution

Enthalpy values of the ‘cold’ feed at 40°C and of the ‘cold reflux’ at 50°C are required for the calculations. These can be obtained from the given enthalpies of the streams at the ‘saturated’ condition. For this purpose we need the heat capacities of these solutions. We assume that the heat capacity of a solution is a linear function of its concentration.

Heat capacity of the feed (45 mol% methanol),

$$c_{pf} = (0.45)(19.4) + (0.55)(18) = 18.62 \text{ kcal/kmol}\cdot^\circ\text{C}$$

Heat capacity of the reflux (96 mol% methanol),

$$c_{pr} = (0.96)(19.4) + (0.04)(18) = 19.3 \text{ kcal/kmol}\cdot^\circ\text{C}$$

The feed line: Enthalpy of the feed is 1390 kcal/kmol, if saturated (74°C). Its value at 40°C, $H_F = 1390 - (18.62)(74 - 40) = 757 \text{ kcal/kmol}$.

Similarly, the enthalpy of the ‘cold reflux’ (50°C),

$$\begin{aligned} H_r &= 1253 - (19.3)(66 - 50) = 944.2 \text{ kcal/kmol} \\ \Rightarrow q &= \frac{H_V - H_F}{H_V - H_L} = \frac{10,630 - 757}{10,630 - 1390} = 1.068 \end{aligned}$$

The intercept of the feed line on the x -axis = $z_F/q = 0.45/1.068 = 0.421$. The feed line can be drawn.

Internal reflux ratio: This can be calculated from Eq. (7.91). The external reflux ratio, $R = L_0/D = 2.25$.

$$R' = \frac{L}{D} = \frac{L_0}{D} \left[1 + \frac{c_{pr} M_r (\theta_{rb} - \theta_r)}{M_r \lambda} \right] = (2.25) \left[1 + \frac{19.3(66 - 50)}{8470} \right] = 2.33$$

The intercept of the rectifying section operating line on the y -axis = $x_D/(R' + 1) = (0.96/3.33) = 0.284$.

Determination of the number of trays: Given: $x_D = 0.96$, $x_W = 0.04$, $z_F = 0.45$. The equilibrium data are plotted on the $x-y$ plane and the diagonal line is drawn. The points $D(0.96, 0.96)$, $W(0.04, 0.04)$, and $F(0.45, 0.45)$ are located. The feed line is drawn through F with an intercept of 0.421 on the x -axis. The operating line for the rectifying section is drawn through the point D with an intercept of 0.284. The feed line and the upper operating line meet at the point E_1 . The points W and E_1 are joined to get the lower operating line. The graphical construction is shown in Figure 7.24.

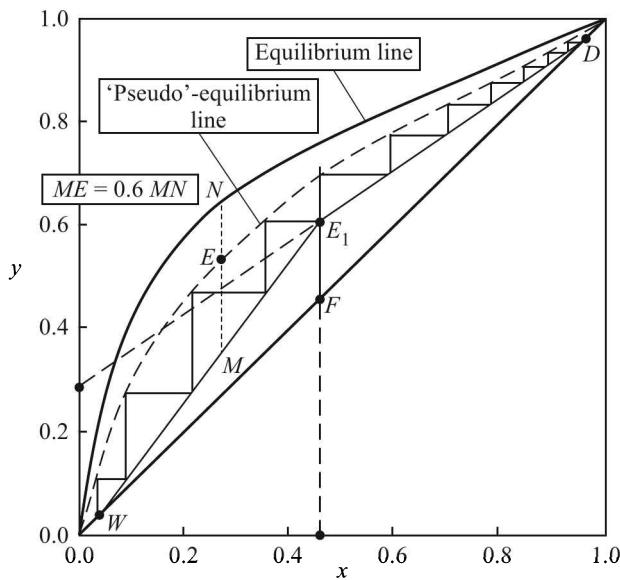


Figure 7.24 McCabe-Thiele construction of real trays for a given Murphree tray efficiency.

The Murphree efficiency is given as 60%. We draw the ‘pseudo-equilibrium line’ which is the locus of a point E located at 60% of the height of a vertical line segment MN between the operating line and the equilibrium line. Now steps are constructed between the operating line and the pseudo-equilibrium line (we started from the end D). The total number of real stages = 11.

Multiple feed or product withdrawal

If two feeds of different compositions are to be treated in a column, each should normally be introduced on the tray of matching composition. Similarly, a product stream of any intermediate

composition may be withdrawn from the appropriate tray. Withdrawal of side streams is done frequently in refinery columns. Developing the equations of the operating lines and the determination of the number of plates in such a column is discussed in Example 7.20.

A column with two feeds and one side stream is shown in Figure 7.25(a). We may consider the column as consisting of four sections on the basis of the flow rates of the liquid and the vapour phases. (As stated before, a section means a part of the column between two input or output points.) The number of such sections in a column is one less than the total number of input and output streams. The liquid and vapour flow rates vary from one section to another. The operating line for each section has a different slope. So, there will be as many operating lines as the number of sections.

Determination of the minimum reflux ratio for such a column is a bit tricky. The pinch point may occur at the intersection of a feed line, or a side stream line, and the equilibrium curve. If the equilibrium curve has any unusual curvature, a pinch point may have to be found out by drawing an operating line that touches the equilibrium curve.

EXAMPLE 7.20 (*McCabe–Thiele construction—multiple feed and product withdrawal*) A distillation column receives two feeds: (i) 200 kmol/h, 80% liquid and 20% vapour, with 42.86 mole% methanol on the average; (ii) 100 kmol/h, saturated liquid, with 17.65 mole% methanol. The top product must have a purity of 96.1 mole% and the bottoms must not have more than 3.1 mole% of the alcohol. A liquid side stream having 66.67 mole% methanol is to be withdrawn at a rate of 35 kmol/h. The reflux is returned to the top tray as a saturated liquid at a reflux ratio of 2.0. (a) Determine the equations of the operating lines. (b) Find the number of ideal trays required for the separation. (c) Identify the feed trays and also the tray from which the side stream should be withdrawn. Vapour–liquid equilibrium data at the operating pressure of 1 atm is given in Example 7.15.

Solution

Basis of calculation: 1 hour operation. The column is sketched in Figure 7.25(a). *Given:* Feed 1: $F_1 = 200$ kmol; feed 2: $F_2 = 100$ kmol; side stream, $S = 35$ kmol. Reflux ratio, $R = 2$. A sketch of the column with the various streams is shown in Figure 7.25(a). There are two feeds and one side stream. So, as discussed earlier, there are four operating lines of the four sections of the column. In order to find out the equations of the operating lines, the liquid and vapour flow rates in all the sections are to be calculated. The material balance calculations are done first.

Material balance: Total material balance:

$$F_1 + F_2 = D + S + W \Rightarrow 200 + 100 = D + 35 + W \quad (\text{i})$$

Methanol balance: $F_1 z_{F1} + F_2 z_{F2} = D x_D + S x_S + W x_W$

$$\Rightarrow (200)(0.4286) + (100)(0.1765) = (0.961)x_D + (35)(0.6667) + (0.031)x_W$$

$$\Rightarrow (0.961)x_D + (0.031)x_W = 84.3 \quad (\text{ii})$$

Solving Eqs. (i) and (ii), $D = 77.25$ kmol/h; $W = 187.75$ kmol/h.

The equilibrium diagram and the diagonal are drawn in Figure 7.25(b). The points $D(x_D, x_D)$, $W(x_W, x_W)$, $S(x_S, x_S)$, $F_1(z_{F1}, z_{F1})$ and $F_2(z_{F2}, z_{F2})$ are located on the x – y plane.

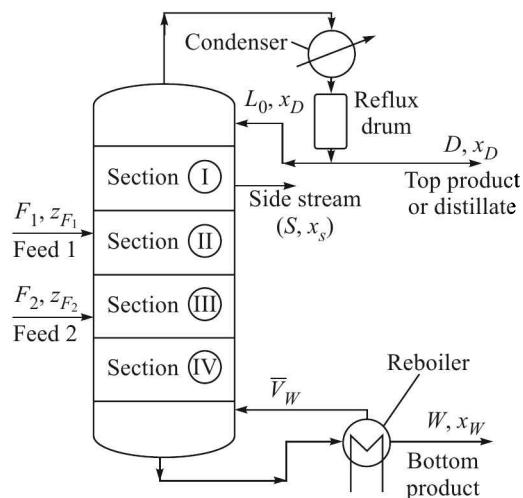


Figure 7.25(a) A distillation column with two feeds and one side stream withdrawal.

Operating lines: The liquid flow rate of Section I decreases by an amount of $S = 35$ kmol as the liquid enters Section II (because of side stream withdrawal). Because of addition of the feed 1 (which is 80% liquid and 20% vapour), the liquid flow rate increases by $(0.8)(2000) = 160$ kmol/h in Section III, and again by 100 kmol/h in Section IV (because the second feed is a saturated liquid).

The liquid rate in Section I, $L_0 = RD = (2)(77.25) = 154.5$.

(a) Vapour rate, $V_1 = V = (R + 1)D = (2 + 1)(77.25) = 231.75$. This value remains constant in Section I.

The flow rates of the streams in different sections and the equations of the operating lines are given below.

Section	Liquid rate	Vapour rate	Slope of the operating line	Equation of the operating line
I	$L(I) = L_0 = 154.5$	$V = 231.75$	$L_0/V = 0.6667$	$y = 0.6667x + 0.3203$
II	$L(II) = L(I) - S = 119.5$	$V = 231.75$	$L(II)/V = 0.5156$	$y = 0.5156x + 0.421$
III	$L(III) = L(II) + 0.8F_1$ $= 119.5 + (0.8)(200) = 279.5$	$V = 231.75 - 0.2F_1$ $= 231.75 - 40$ $= 191.75$	$L(III)/V = 1.4576$	$y = 1.4576x + 0.06176$
IV	$L(IV) = L(III) + F_2$ $= 279.5 + 100 = 379.5$	$V = 191.75$	$L(IV)/V = 1.9791$	$y = 1.9791x - 0.03028$

Some details of the calculations are given here. Operating line I starts at $D(x_D, x_D)$, i.e. $(0.961, 0.961)$ and has an intercept $= x_D/(R + 1) = 0.961/(2 + 1) = 0.3203$. Its equation is $y = 0.6667x + 0.3203$.

Operating line II starts at the point E_1 [see Figure 7.25(b)] having coordinates $(0.6667, 0.7647)$ which is the point of intersection of the vertical ‘side stream line’, $x = 0.6667$ and $y = 0.6667x + 0.3203$. Also the operating line II has a slope 0.5156. Its equation is $y = 0.5156x + 0.421$.

(Note: The ‘side stream line’ is vertical as the side stream is drawn as a saturated liquid.)

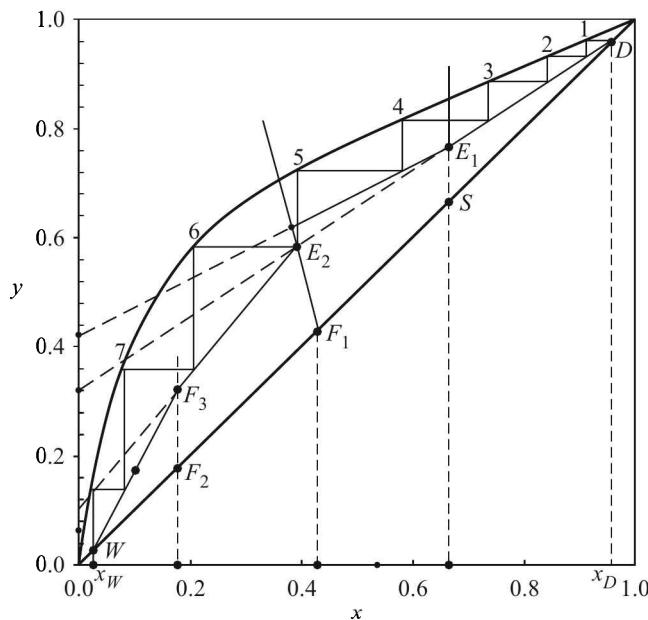


Figure 7.25(b) McCabe–Thiele construction of the number of ideal trays for multiple feed and product withdrawal.

Feed-1 has 80% liquid in it, i.e. $q = 0.8$. Feed line-1 has a slope of $q/(q - 1) = -4$. It passes through (z_{F1}, z_{F1}) , i.e. $(0.4286, 0.4286)$ on the diagonal. Its equation is $y = -4x + 2.143$. The point of intersection of the feed line-1 and the operating line II is $E_2(0.3813, 0.6176)$.

The operating line III starts at $E_2(0.3813, 0.6176)$ and has a slope of 1.4576. Its equation is $y = 1.4576x + 0.0618$. This line meets the feed line-2 (it is a vertical line since this feed is a saturated liquid) at E_3 . Join E_3W to get the operating line IV.

(b) The operating lines are drawn and the steps are constructed between the equilibrium line and the four operating lines as shown in Figure 7.25(b). The number of ideal trays is 7.8.

(c) From Figure 7.25(b), the side stream is drawn from tray no. 4, the feed-1 enters the tray no. 5 and the other feed enters the tray no. 7.

7.7 MULTISTAGE BATCH DISTILLATION WITH REFLUX

In single-stage batch distillation (Rayleigh distillation), the purity of the product is practically governed by the concentration of the feed and the fraction distilled out. However, if a batch of liquid is distilled in a multistage column with reflux, a significantly higher product purity as well as higher fractional recovery of the product can be achieved. A schematic of a multistage batch distillation unit is shown in Figure 7.26.

In the theoretical analysis given below we assume that: (a) constant molar overflow occurs, i.e. the vapour rate V and the liquid rate L remain constant in the column; (b) liquid holdup on the plates is negligible; (c) although batch distillation is an unsteady state process, we assume that pseudo-steady state condition prevails; this means that the liquid and the vapour concentration profiles in the column at any moment are the same as the steady-state profiles achievable under identical conditions.

It is easy to understand that if the reflux ratio is held constant, the distillate concentration will decrease as the distillation proceeds. So the column may be operated till the distillate quality remains within the acceptable limit. This is called the *constant reflux operation*. Alternatively, the reflux ratio is continuously increased so that the product concentration remains constant for some time. This is called the *variable reflux operation*. In practice, the constant reflux operation is more common.

7.7.1 Constant Reflux Operation

Let the amount of liquid in the stillpot of the multistage unit at any moment be W mole at a concentration x_W . Over a small time, dD mole of distillate is withdrawn and the amount of liquid in the stillpot decreases by dW mole. Following Eq. (7.47),

$$-d(Wx_W) = x_D dD \Rightarrow -Wdx_W - x_W dW = -x_D dW \quad (\text{since } dD = -dW) \quad (7.94)$$

$$\Rightarrow \frac{dW}{W} = \frac{dx_W}{x_D - x_W} \quad (7.95)$$

If W_i and W_f are the initial and final amounts of liquid in the stillpot, then on integration,

$$\ln \frac{W_i}{W_f} = \int_{x_{Wf}}^{x_{Wi}} \frac{dx_W}{x_D - x_W} \quad (7.96)$$

As distillation proceeds, x_D and x_W both keep on changing. This is shown in Figure 7.27(a) for a batch column having two ideal trays and a stillpot (equilibrium vaporization occurs in the stillpot). An operating line of slope $= R/(R + 1)$, for the constant reflux ratio R , is drawn. Three stages are constructed starting from (x_D, x_D) on the diagonal. A value of x_W ($x_{Wf} \leq x_W \leq x_{Wi}$) is reached at the end of three stages. A set of such operating lines are drawn to yield a set of (x_D, x_W) values. The integral in Eq. (7.96) can now be evaluated graphically. Of the four quantities— W_i , W_f , x_{Wi} , x_{Wf} —any one can be calculated by this way if the others are known. The accumulated distillate composition can be found out by material balance.

$$x_{D,\text{av}} = \frac{W_i x_{Wi} - W_f x_{Wf}}{W_i - W_f} \quad (7.97)$$

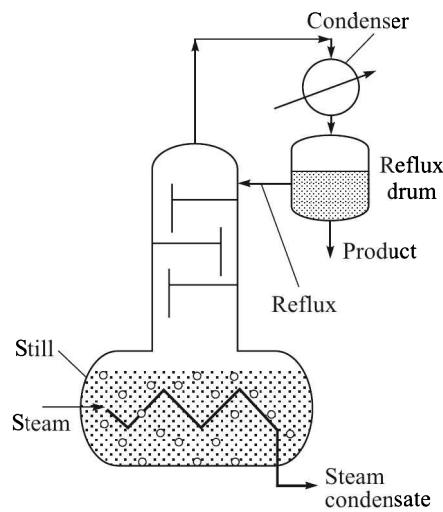


Figure 7.26 Schematic of a multistage batch distillation setup.

EXAMPLE 7.21 (Batch distillation with constant reflux) Forty kilomoles of an equimolar mixture of benzene and chlorobenzene is to be batch-distilled at 1 atm total pressure in a column consisting of a stillpot, two ideal trays and a total condenser. Reflux is returned to the top tray as a saturated liquid and the reflux ratio is 1.0. Distillation is to be continued until the benzene concentration of the liquid in the stillpot becomes 6 mol%. Calculate the amount and purity of the collected distillate, the amount of liquid left in the stillpot, and the fractional recovery of benzene. Liquid holdup on the trays is assumed to be rather small. Vapour–liquid equilibrium data for the system are given below.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0
y	0	0.314	0.508	0.640	0.734	0.806	0.862	0.905	0.943	1.0

Solution

Here the batch still is operated at constant reflux. As a result, the concentration of the vapour from the top tray will decrease gradually. Our procedure will be: (i) select a number of values of x_D on the diagonal and to draw the corresponding operating lines (since the reflux rate is constant, the operating lines will be parallel); (ii) for each value of x_D , determine the value of x_W by drawing three stages (two trays and the stillpot) between the operating line and the equilibrium line. Thus, we shall have a set of values of x_D and x_W within the concentration range $x_{W_i} = 0.5$ (initial) and $x_{W_f} = 0.06$ (final). The integral in Eq. (7.96) can then be evaluated graphically.

Reflux ratio, $R = 1.0$; constant slope of the operating lines $= R/(R + 1) = 0.5$

The equilibrium line, the two operating lines and the graphical construction are shown in Figure 7.27(a). The values of x_D , x_W and $(x_D - x_W)^{-1}$ obtained from the graph are as follows:

x_D	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.50	0.40	0.30
x_W	0.50	0.35	0.28	0.245	0.205	0.175	0.15	0.135	0.105	0.090	0.056
$(x_D - x_W)^{-1}$	2.222	1.818	1.754	1.802	1.835	1.905	2.0	2.151	2.532	3.226	4.10

$(x_D - x_W)^{-1}$ is plotted versus x_W in Figure 7.27(b) and the area under the curve from $x_{W_f} = 0.06$ to $x_{W_i} = 0.50$ is 0.9065.

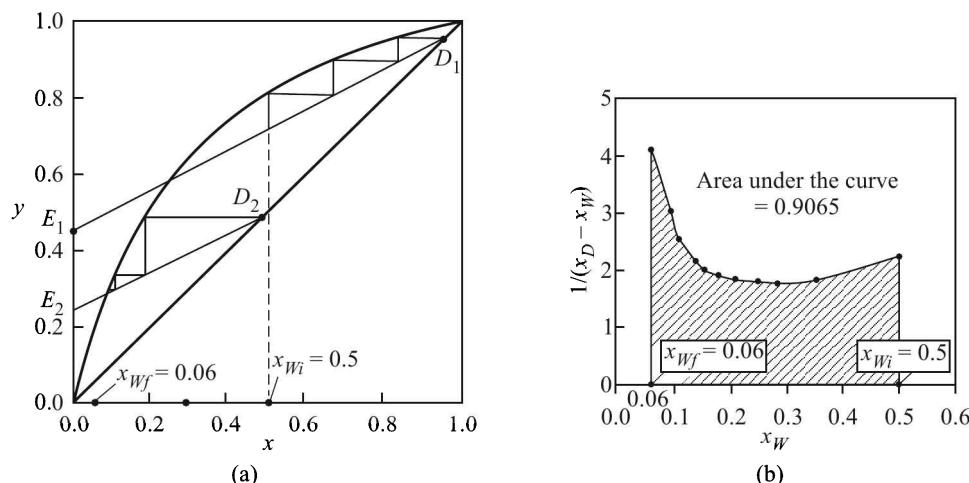


Figure 7.27 (a) Parallel operating lines and three ideal stages for constant reflux batch distillation, and (b) graphical evaluation of the integral in Eq. (7.96).

Also the initial amount of liquid, $W_i = 40$ kmol. From Eq. (7.96),

$$\ln \frac{W_i}{W_f} = \int_{x_{wf}}^{x_{wi}} \frac{dx_W}{x_D - x_W} \Rightarrow \ln(40/W_f) = 0.9065$$

$$\Rightarrow W_f = 16.16 \text{ kmol} \quad \text{and} \quad D = W_i - W_f = 23.84 \text{ kmol}$$

By benzene balance, we get the concentration of the accumulated distillate, $(x_D)_{av}$.

Use Eq. (7.97) to get

$$(x_D)_{av} = \frac{(40)(0.5) - (16.16)(0.06)}{23.84} = 0.8$$

Amount of distillate collected = 23.84 kmol, its purity = 80 mol% benzene;

liquid left = 16.16 kmol.

Fractional recovery of benzene = $(23.84)(0.8)/(40)(0.5) = 0.954$.

EXAMPLE 7.22 (*Simple batch distillation, graphical/numerical evaluation of the integral*) Consider that the separation of the mixture in Example 7.21 (40 moles feed with 50 mol% benzene) is to be done in a simple batch distillation unit in which the vapour from the stillpot is condensed to get the distillate (see Figure 7.13). If the amount of accumulated distillate is the same as in Example 7.21, calculate the composition of the distillate and the fractional recovery of benzene. Also, approximately calculate the ratio of the energy requirements in the two cases.

Solution

The working equation is Eq. (7.50) which may be written in the form

$$\ln \frac{W_i}{W_f} = \int_{x_f}^{x_i} \frac{dx}{y^* - x}$$

Given: $W_i = 40$ kmol; $D = 23.84$ (as calculated in Example 7.21); $W_f = 40 - 23.84 = 16.16$; $x_i = 0.5$; $\ln(W_i/W_f) = \ln(40/16.16) = 0.9065$; $x_f = ?$

A set of values of x is selected starting from $x = 0.5$. The equilibrium vapour composition y^* is obtained from the plot of the equilibrium data. A plot of $1/(y^* - x)$ versus x is prepared. The value of x_f is obtained from the plot such that the area under the curve is 0.9036. The tabulated values are given below and the plot is shown in Figure 7.28.

x	0.50	0.45	0.40	0.35	0.30	0.25	0.20	0.15	0.10
y^*	0.81	0.773	0.734	0.69	0.64	0.581	0.508	0.415	0.314
$1/(y^* - x)$	3.226	3.096	2.994	2.941	2.941	3.021	3.247	3.773	4.673

From Figure 7.28, $x_f = 0.21$ = concentration of the liquid left in the stillpot. The product composition is obtained by material balance.

$$(40)(0.5) = (16.16)(0.21) + (23.84)(x_D)_{av} \Rightarrow (x_D)_{av} = 0.696$$

Fractional recovery of benzene = $(23.84)(0.696)/(40)(0.5) = \boxed{0.83}$. (Compare with the value of 0.954 obtained in Example 7.21.)

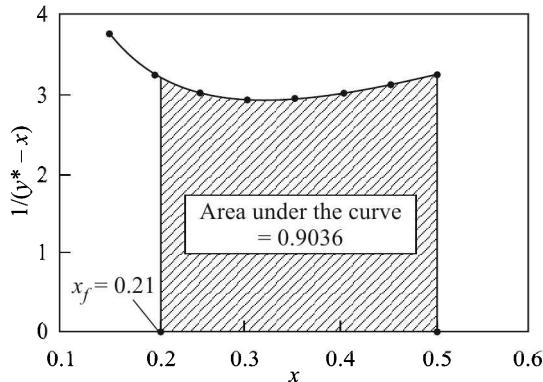


Figure 7.28 Graphical integration.

In Example 7.21, the reflux ratio was $R = 1.0$. The total amount of vapour generated, $V = (R + 1)(23.84) = (2)(23.84) = 47.68$, which is double the amount of vapour generated in simple batch distillation. So the energy consumption is about twice the value of that in Example 7.21.

7.7.2 Variable Reflux Operation

In a variable reflux operation, the reflux ratio is continuously increased in such a manner that the distillate concentration remains unchanged despite the fall in concentration of the more volatile in the stillpot. If dV , dL and dD are the changes in the rates of vapour flow, liquid flow and distillate withdrawal,

$$dV = dL + dD \quad (7.98)$$

$$\Rightarrow dD = [1 - (dL/dV)]dV \quad (7.99)$$

By material balance,

$$Wx_W = W_i x_{Wi} - (W_i - W)x_D \quad [x_D = \text{constant}] \quad \Rightarrow \quad W = W_i \left(\frac{x_{Wi} - x_D}{x_W - x_D} \right) \quad (7.100)$$

Substituting for dD and W from Eqs. (7.99) and (7.100), in the material balance Eq. (7.98) and noting that $dD = -dW$,

$$dV = \frac{W_i(x_{Wi} - x_D)dx_W}{(x_D - x_W)^2(1 - dL/dV)}$$

Total amount of vapour generated,

$$V = \int_{x_{Wi}}^{x_{Wf}} \frac{W_i(x_{Wi} - x_D)dx_W}{(x_D - x_W)^2(1 - dL/dV)} = W_i(x_D - x_{Wi}) \int_{x_{Wf}}^{x_{Wi}} \frac{dx_W}{(x_D - x_W)^2(1 - dL/dV)} \quad (7.101)$$

For a given number of ideal trays, a bunch of operating lines of different slopes ($dL/dV = L/V$ = slope of the operating line) can be drawn, and the plates can be constructed to get the x_W value. This allows graphical integration of Eq. (7.101) and calculation of any relevant quantity. Example 7.23 illustrates a practical batch distillation problem with variable reflux.

EXAMPLE 7.23 (Batch distillation with variable reflux) Ten kilomoles of acetone has been pumped by mistake into a storage vessel of ethanol containing 10 kilomoles of ethanol. It is decided to separate the mixture by batch distillation. Ten mole% of alcohol in the top product and 12 mole% acetone in the bottom product are acceptable. A column having six theoretical plates, a reboiler and a condenser is available. The operation is to be carried out at essentially atmospheric pressure and the reflux is to be returned at its bubble point.

(a) Calculate the amounts of top and bottom products. (b) What initial and final reflux ratios should be used? (c) Determine the total moles of vapour to be generated to achieve the separation. (d) If steam is supplied to the coils in the still at such a rate that 6 kmol of vapour is generated per hour, calculate the time required for distillation. The vapour–liquid equilibrium data for the acetone–ethanol system are given below.

x	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
y	0.16	0.25	0.42	0.51	0.60	0.67	0.72	0.79	0.87	0.93	1.00

Solution

(a) The quantities of the top and the bottom products can be calculated from material balances. *Total material balance:*

$$F = D + W \Rightarrow 20 = D + W; \quad D = \text{moles distillate}; \quad W = \text{moles residue}.$$

Acetone balance:

$$Fx_F = Dx_D + Wx_W \Rightarrow (20)(0.50) = D(0.9) + W(0.12)$$

$$\Rightarrow D = \boxed{9.74}; \quad W = \boxed{10.26}$$

(b) and (c) This is a case of operating a batch still with variable reflux. The concentration of the more volatile (acetone) in the still decreases gradually. But the reflux ratio has to be increased continuously until the bottom liquid concentration (x_{Wf}) drops down to 12 mol% acetone while seven ideal trays (six plates and a reboiler) are fitted between the operating line and the equilibrium line. The overhead vapour concentration should always be 90 mol% acetone. The steps are:

- (i) Draw the equilibrium line on the x – y plane.
- (ii) Locate the point (x_D, x_D) where $x_D = 0.90$.
- (iii) Draw a bunch of operating lines emanating from $(0.9, 0.9)$ and having varying slopes.
- (iv) In each case, fit seven ideal stages between the operating line and the equilibrium line and determine the bottom concentration, x_W .
- (v) Using the (x_D, x_W) data as well as the slopes of the bunch of operating lines drawn, evaluate the integral in Eq. (7.101) numerically to get the total moles of vapour generated during distillation.

The equilibrium line and only two operating lines (DE_1 at the beginning of the operation, and DE_2 at the end; a few other operating lines were drawn for calculations but are not shown) are shown in Figure 7.29(a). The graphical construction of seven ideal stages is also shown. The calculated data for graphical evaluation of the integral in Eq. (7.101) are given below. Graphical integration is shown in Figure 7.29(b).

$dL/dV = (L/V)$	0.733	0.787	0.833	0.905	0.919
x_W	0.5	0.335	0.21	0.13	0.12
$\frac{1}{(x_D - x_W)^2 (1 - L/V)}$	23.4	14.7	12.96	17.75	20.3

The initial reflux ratio is $R_i = 0.733$ and the end reflux ratio is $R_f = 0.919$.

The area under the curve in Figure 7.29(b) is 6.04.

Total quantity of vapour generated [Eq. (7.101)],

$$V_{\text{tot}} = W_i(x_D - x_{W_i})I = (20)(0.9 - 0.5)(6.04) = 48.32 \text{ kmol}$$

(d) Rate of vapour generation = 6 kmol/h. Time of distillation = $48.32/6 = 8.05 \text{ h}$

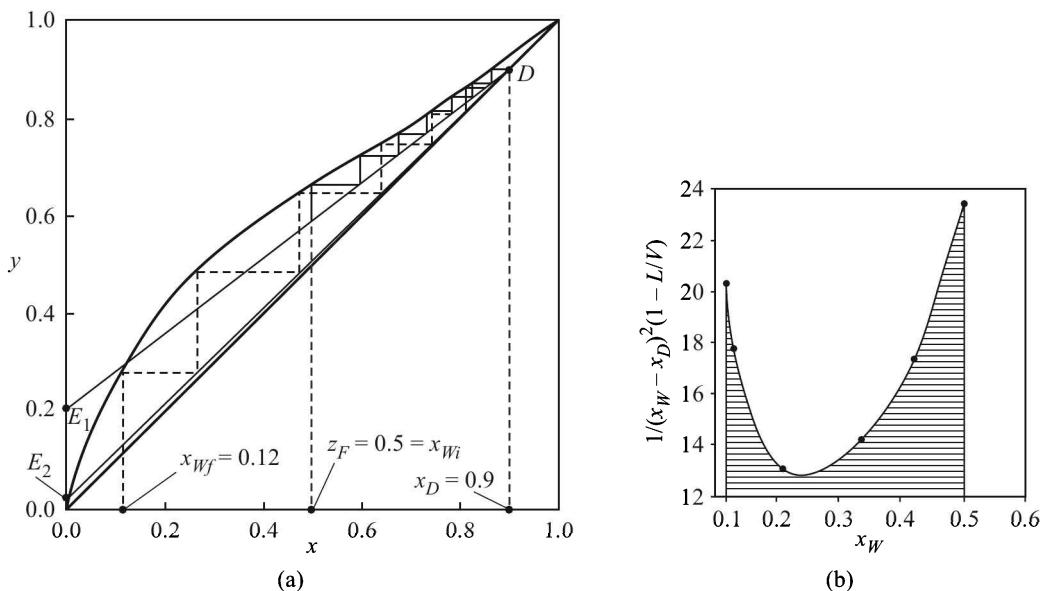


Figure 7.29 (a) Graphical construction of stages for variable reflux batch distillation (the two extreme operating lines only are shown), and (b) graphical integration.

Another strategy of operation of a multistage batch distillation column, called the ‘optimal reflux’ operation has been described by Divekar (1995).

7.8 THE PONCHON-SAVARIT METHOD

This method was developed by Ponchon and Savarit independently in 1921–22. It is a more rigorous method and is free from the assumption of ‘constant molar overflow’. So the use of this method is suggested if the enthalpy of a stream appreciably depends upon its composition. The Ponchon–Savarit method is also a graphical method of solution of the material and energy balance equations as well as the equilibrium relation taken together.

The rectifying section: Refer to Figure 7.14(a). Consider the material and energy balance Eqs. (7.64) and (7.65) taken over envelope [2]:

$$V_{n+1}y_{n+1} = L_nx_n + (V_{n+1} - L_n)z_D \Rightarrow \frac{L_n}{V_{n+1}} = \frac{z_D - y_{n+1}}{z_D - x_n} \quad (7.102)$$

[Note: Here we assume that the reflux may be a sub-cooled liquid (i.e. below its bubble point) in general and z_D is the mole fraction of the more volatile in it.]

The energy balance Equation (7.65) is rewritten as

$$V_{n+1}H_{V,n+1} = L_nH_{Ln} + D\left(H_D + \frac{Q_C}{D}\right) = L_nH_{Ln} + DQ'_d \quad (7.103)$$

Here $Q'_d = H_D + Q_C/D$ = thermal energy removed from the top section of the column per mole of distillate. Putting $D = V_{n+1} - L_n$ [see Eq. (7.63)] in the above equation,

$$V_{n+1}H_{V,n+1} = L_nH_{Ln} + (V_{n+1} - L_n)Q'_d \Rightarrow \frac{L_n}{V_{n+1}} = \frac{Q'_d - H_{V,n+1}}{Q'_d - H_{Ln}} \quad (7.104)$$

[The quantity L_n/V_{n+1} is the *internal reflux ratio*.]

From Eqs. (7.102) and (7.104),

$$\frac{z_D - y_{n+1}}{z_D - x_n} = \frac{Q'_d - H_{V,n+1}}{Q'_d - H_{Ln}} \Rightarrow \frac{Q'_d - H_{Ln}}{z_D - x_n} = \frac{Q'_d - H_{V,n+1}}{z_D - y_{n+1}} \quad (7.105)$$

Refer to Figure 7.30 on which the liquid and vapour enthalpy–concentration curves (x – H_L and y – H_V) are plotted. A point on this diagram represents the composition and enthalpy of a phase (liquid, vapour or mixed), and we denote this point by a term that also represents the flow rate of the particular phase (this convention has been used before). Thus, the point L_n represents the liquid phase leaving the n th plate (and entering the $(n+1)$ th plate) at a rate L_n mole/h with enthalpy H_{Ln} and concentration x_n .

The right side of Eq. (7.105) is the slope of a line through the points $(y_{n+1}, H_{V,n+1})$ and (z_D, Q'_d) , and the left side is the slope of a line through the points (x_n, H_{Ln}) and (z_D, Q'_d) on the concentration–enthalpy plane. So the points (x_n, H_{Ln}) , $(y_{n+1}, H_{V,n+1})$ and (z_D, Q'_d) are collinear. The point (z_D, Q'_d) can be viewed as a phase obtained by subtracting L_n from V_{n+1} (see the discussion in the last para of Section 7.2). We represent this point by D' in Figure 7.30. The flow rate of the phase D' is also denoted by $D' = V_{n+1} - L_n$. However, none of the phases can have the concentration z_D and enthalpy $Q'_d = H_D + Q_C/D$. So this stream D' is a “fictitious stream” defined solely for the purpose of graphical construction.

The point $D(z_D, H_D)$ and $D'(z_D, Q'_d)$ are located on the enthalpy–concentration diagram, D' lying vertically above D (because they have the same abscissa, z_D). In Figure 7.30, the point D

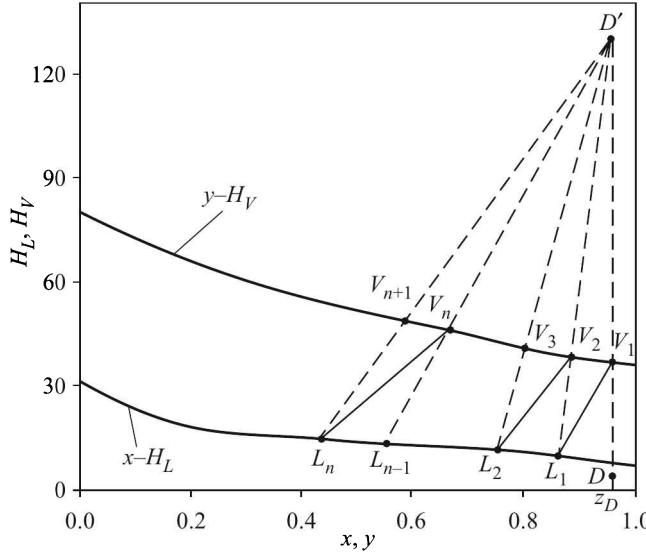


Figure 7.30 Ponchon-Savarit construction for the rectifying section of a distillation column.

lies below the x - H_L curve. So, the reflux is a sub-cooled liquid here. If we put $n = 0$ in Eq. (7.105), it appears that the vertical line joining the points D and D' should intersect the y - H_V curve at (y_1, H_{V1}) because these points are collinear. The point (y_1, H_{V1}) is denoted by V_1 according to our convention. The point $L_1(x_1, H_{L1})$ is now located by drawing a tie line through V_1 , because x_1 and y_1 are in equilibrium for an ideal tray. Next, L_1D' is joined to get the point V_2 . The graphical construction now proceeds from one tray to the next.

Now we consider Eq. (7.104), again. Inverting both sides and putting $n = 0$,

$$\begin{aligned} \frac{V_1}{L_0} &= \frac{Q'_d - H_{L0}}{Q'_d - H_{V1}}; \quad \text{we note that } H_{L0} = H_D; V_1 = L_0 + D \\ \Rightarrow \frac{V_1}{L_0} &= \frac{L_0 + D}{L_0} = 1 + \frac{D}{L_0} = \frac{Q'_d - H_D}{Q'_d - H_{V1}} \\ \Rightarrow R &= \frac{L_0}{D} = \frac{Q'_d - H_{V1}}{H_{V1} - H_D} = \frac{\text{vertical distance } V_1D'}{\text{vertical distance } DV_1} \end{aligned} \quad (7.106)$$

If the reflux ratio is given, Eq. (7.106) can be used directly to locate the point D' . First the point $D(z_D, H_D)$ is located from the known state (concentration z_D , and enthalpy H_D). A vertical line through z_D intersects the y - H_V curve at V_1 . Then obtain D' so that Eq. (7.106) is satisfied.

The stripping section: The material and energy balance equations for the stripping section (envelope 3, Figure 7.14(a) are given by Eqs. (7.66) through (7.68). Putting $W = \bar{L}_m - \bar{V}_{m+1}$ from Eq. (7.66) in Eq. (7.67),

$$\bar{L}_m x_m = \bar{V}_{m+1} y_{m+1} + (\bar{L}_m - \bar{V}_{m+1}) x_W \quad (7.107)$$

$$\Rightarrow \frac{\bar{L}_m}{\bar{V}_{m+1}} = \frac{y_{m+1} - x_W}{x_m - x_W} \quad (7.108)$$

We may write the energy balance Equation (7.68) as

$$\begin{aligned} \bar{L}_m H_{Lm} - \bar{V}_{m+1} H_{V,m+1} &= WH_W - Q_B = W(H_W - Q_B/W) \\ \Rightarrow \quad \bar{L}_m H_{Lm} - \bar{V}_{m+1} H_{V,m+1} &= WQ'_W; \quad Q'_W = H_W - Q_B/W \end{aligned} \quad (7.109)$$

Putting $W = \bar{L}_m - \bar{V}_{m+1}$,

$$\bar{L}_m H_{Lm} - \bar{V}_{m+1} H_{V,m+1} = (\bar{L}_m - \bar{V}_{m+1})Q'_W \Rightarrow \frac{\bar{L}_m}{\bar{V}_{m+1}} = \frac{H_{V,m+1} - Q'_W}{H_{Lm} - Q'_W} \quad (7.110)$$

$$\text{From Eqs. (7.108) and (7.110), } \frac{H_{V,m+1} - Q'_W}{y_{m+1} - x_W} = \frac{H_{Lm} - Q'_W}{x_m - x_W} \quad (7.111)$$

Extending the arguments put forward in the analysis of the rectifying section, we can say:

- (a) The points $\bar{V}_{m+1}(y_{m+1}, H_{V,m+1})$, $\bar{L}_m(x_m, H_{Lm})$, and $W'(x_W, Q'_W)$, are collinear
- (b) The point W' denotes a “fictitious stream” of concentration x_W , enthalpy $Q'_W = H_W - Q_B/W$ (= the rate of enthalpy removal at the bottom, per mole of the bottom product), and flow rate $W' = \bar{L}_m - \bar{V}_{m+1}$.

Now, let us see how to proceed with the graphical construction of stages for the stripping section (Figure 7.31). The points $W(x_W, H_W)$ and $W'(x_W, Q'_W)$, are located on the enthalpy-concentration plane. The output stream or the bottom product, W , leaving the partial reboiler is in equilibrium with the vapour generated in the reboiler and entering the bottom tray. If there is a total of N trays in the column, we may call the reboiler the $(N + 1)$ th tray. So the flow rate as well as the state

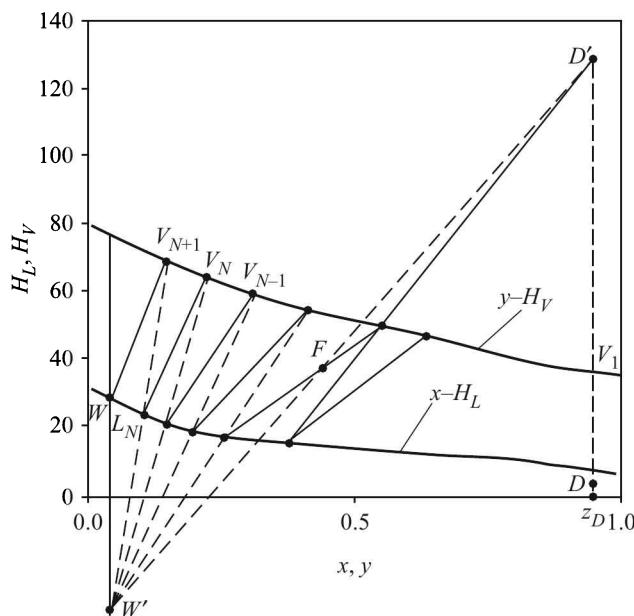


Figure 7.31 Ponchon-Savarit construction for the stripping section of a distillation column.

of the vapour from the reboiler is denoted by \bar{V}_{N+1} ; \bar{V}_{N+1} should lie on the $y-H_V$ curve at the end of the tie line through W . The line connecting \bar{V}_{N+1} and W' intersects the $x-H_L$ curve at \bar{L}_N by virtue of the collinearity condition given by Eq. (7.111). The tie line through \bar{L}_N identifies \bar{V}_N on $y-H_V$ curve and thus the construction for trays in the stripping proceeds.

The feed line: The procedures of graphical construction of ideal trays for the rectifying and for the stripping sections have been discussed above. However, a changeover from one section to the other is necessary at the feed tray and for this purpose we have to draw the ‘feed line’. Consider the material and energy balance equations over envelope 4 of the column in Figure 7.14(a) as given by Eqs. (7.69) through (7.71). Substituting for F from Eq. (7.69) in Eq. (7.70),

$$(D + W)z_F = Dz_D + Wx_W \quad (7.112)$$

[Note: We use z_D to denote the reflux or distillate concentration because these may be subcooled liquids; the notation x_D may be used if the streams are at bubble point.]

$$\Rightarrow \frac{D}{W} = \frac{z_F - x_W}{z_D - z_F} \quad (7.113)$$

Similarly, from Eqs. (7.69) and (7.71),

$$\begin{aligned} & (D + W)H_F + Q_B = DH_D + WH_W + Q_C \\ \Rightarrow & DH_F + WH_F = D(H_D + Q_C/D) + W(H_W - Q_B/W) \\ \Rightarrow & \frac{D}{W} = \frac{H_F - (H_D + Q_C/D)}{(H_W - Q_B/W) - H_F} = \frac{H_F - Q'_W}{Q'_d - H_F} \end{aligned} \quad (7.114)$$

From Eqs. (7.113) and (7.114),

$$\frac{H_F - Q'_W}{z_F - x_W} = \frac{Q'_d - H_F}{z_D - z_F} \quad (7.115)$$

The above equation shows that the points $W'(x_W, Q'_W)$, $F(z_F, H_F)$, and $D'(z_D, Q'_d)$ are collinear. The intermediate point $F(z_F, H_F)$ denotes the state of the feed in terms of composition and enthalpy. It lies on the line joining W' and D' . As stated before, W' represents a fictitious stream of flow rate $W' = \bar{L}_m - \bar{V}_{m+1} = W$, and D' is another fictitious stream of flow rate $D' = \bar{V}_{n+1} - \bar{L}_n = D$.

$$\Rightarrow F = D + W = D' + W' \quad (7.116)$$

So, F , a real stream, can be viewed as a stream obtained by mixing the two fictitious streams W' and D' . The line $W'D'$ is called the *feed line*. On the basis of graphical construction described above, the steps to be followed for the determination of the number of ideal stages are:

- (a) We assume that the concentrations, the enthalpies, and the flow rates of the distillate and the bottom product as also the reflux ratio are given (or sufficient data are supplied for the calculation of these quantities by material and/or energy balance). Then the points D and D' are located on the $H-x,y$ diagram.

- (b) The feed point $F(z_F, H_F)$ is located.
- (c) $D'F$ is joined and extended to meet the vertical line through $W(x_W, H_W)$ at the point W' .
- (d) Construction of stages may proceed either from D' or from W' . A changeover has to be done after the feed line is crossed. The tray at which the changeover is made is the feed tray. Construction proceeds till the other point is reached.

It is possible (and perhaps more convenient) to construct the stages on the x - y plane rather than on the H - x , y plane. The steps of such construction are given below.

- (a) Draw the equilibrium curve using separate axes below the H - x - y curves with matching scales.
- (b) Locate (z_D, z_D) and (x_W, x_W) on the diagonal.
- (c) It is obvious from Eq. (7.105) that any line emanating from D' (or W') intersects the H - x and H - y curves at x_n and y_{n+1} respectively. The point (x_n, y_{n+1}) is a point on the operating line in the lower diagram (see Figure 7.32). Several lines are now drawn from D' and W' and for each such line, the point (x_n, y_{n+1}) is located on the x - y plane. All such points are joined by two continuous curves. These two curves are the two operating lines. Because the flow rates in any of the sections are not constant (since constant molar overflow is not applicable), the operating lines are not straight. Staircase construction between the equilibrium line and the operating lines gives the number of ideal stages. The procedure is illustrated in Example 7.24.

Minimum reflux ratio (R_m)

If the reflux ratio is minimum, there must be a pinch point on the diagram. If a line through D' or W' coincides with a tie line, the corresponding (x, y) values give the pinch point. The expression for the reflux ratio given by Eq. (7.106) indicates that the smaller the distance V_1D' (or the nearer the point D' is to the concentration axis), the smaller is the reflux ratio. For many liquid mixtures this happens when the line $D'W'$ coincides with the tie line through the feed point (compare with Figure 7.20). But for some highly non-ideal mixtures, it so happens that a tie line through a point other than F intersects the vertical line through z_D at the smallest distance. This gives the true pinch point. The minimum reflux ratio is calculated by Eq. (7.106) once the point $(D')_{\min}$ is identified.

EXAMPLE 7.24 (*Determination of the number of ideal trays using the Ponchon–Savarit method*) An aqueous solution of ethanol (30 mass% ethanol) is to be enriched into a top product having 88 mass% alcohol. The bottom product must not contain more than 4 mass% alcohol. The feed enters the column at 40°C at a rate of 5000 kg per hour. The reflux is at its bubble point and the reflux ratio is 1.0. Determine (a) the number of ideal trays required using the Ponchon–Savarit method and (b) the heat duty of the condenser and of the reboiler. The enthalpy–concentration (kJ/kmol; reference states: pure liquids at 0°C) and the vapour–liquid equilibrium data at the operating pressure of 1 atm are given below.

x, y	0	0.0417	0.0891	0.1436	0.207	0.281	0.37	0.477	0.61	0.779	1.0
H_L	7540	7125	6880	6915	7097	7397	7750	8105	8471	8945	9523
H_V	48150	48250	48300	48328	48436	48450	48450	48631	48694	48950	

<i>x</i>	0	0.00792	0.016	0.0202	0.0417	0.0891	0.1436	0.281	0.37	0.477
<i>y</i>	0	0.0850	0.1585	0.191	0.304	0.427	0.493	0.568	0.603	0.644
<i>x</i>	0.61	0.641	0.706	0.779	0.86	0.904	0.95	1.0		
<i>y</i>	0.703	0.72	0.756	0.802	0.864	0.902	0.9456	1.0		

Given: enthalpy of the feed = 4790 kJ/kmol.

Solution

Molecular weights: ethanol = 46; water = 18. The concentrations of the feed z_F , the top and the bottom products (x_D and x_W) in mole fraction units and mol. wt. of the feed M_F are given by

$$z_F = \frac{30/46}{(30/46) + (70/18)} = 0.1436; \quad x_D = 0.7416; \quad x_W = 0.01604$$

$$M_F = \frac{100}{(30/46) + (70/18)} = 22.02$$

$$\text{Feed rate, } F = 5000/22.02 = 227 \text{ kmol/h}$$

$$\text{Total material balance equation: } F = D + W \Rightarrow 227 = D + W \quad (\text{i})$$

$$\text{Ethanol balance: } Fz_F = Dx_D + Wx_W \Rightarrow (227)(0.1436) = D(0.7416) + W(0.01604) \quad (\text{ii})$$

Solving Eqs. (i) and (ii), $D = 39.9 \text{ kmol/h}$; $W = 187.1 \text{ kmol/h}$

Enthalpy values of the feed (H_F), the top and the bottom products (H_D and H_W):

Enthalpy of the feed at 40°C, $H_F = 4790 \text{ kJ/kmol}$ (given).

The other enthalpy values can be obtained by interpolation of the given data.

Enthalpy of the top vapour ($y_1 = 0.7416$), $H_{V1} = 48,680 \text{ kJ/kmol}$; enthalpy of the distillate ($x_D = 0.7416$), $H_D = 8850 \text{ kJ/kmol}$; enthalpy of the bottom product, $H_W = 7380 \text{ kJ/kmol}$.

(a) Graphical construction of the number of ideal trays

- (i) The given enthalpy-concentration data are plotted in Figure 7.32(a).
- (ii) The points $F(z_F, H_F) \rightarrow (0.1436, 4790)$, $D(x_D, H_D) \rightarrow (0.7416, 8850)$, and $W(x_W, H_W) \rightarrow (0.01604, 7380)$ are located on the enthalpy-concentration plane.
- (iii) Next the difference point, $\Delta D'(x_D, Q'_d)$, is to be located; Q'_d is related to the reflux ratio as given in Eq. (7.106). The reflux ratio is $R = 1.0$ (given).

$$R = \frac{Q'_d - H_{V1}}{H_{V1} - H_D} \Rightarrow 1 = \frac{Q'_d - 48,680}{48,680 - 8850}$$

$$\Rightarrow Q'_d = 88,510 \text{ kJ/kmol}; \Delta D' \rightarrow (0.7416, 88,510)$$

- (iv) A vertical line is drawn through the point W ; $\Delta D'F$ is joined and extended to meet this vertical line through W at $\Delta W'$ [$\Delta D'$ and $\Delta W'$ are the same as D' and W' in Figures 7.30 and 7.31].
- (v) The number of ideal trays or stages can be determined by drawing tie lines and operating lines (through $\Delta D'$) as described in Section 7.8. However, it is more convenient to adopt the following procedure.

Draw a number of lines from the point $\Delta D'$ on the right side of the feed point F [Figure 7.32(a)]. Consider one such line $\Delta D'MM_1$ (M is on the saturated vapour line and M_1 is

on the saturated liquid line). The abscissa of the point M_1 (i.e. the liquid composition x) and the abscissa of the point M (i.e. the vapour composition y) give the coordinates of the point P on the x - y diagram drawn below the enthalpy–concentration diagram [Figure 7.32(b)]. A set of such points on the x - y plane are joined to get the operating line for the rectifying section.

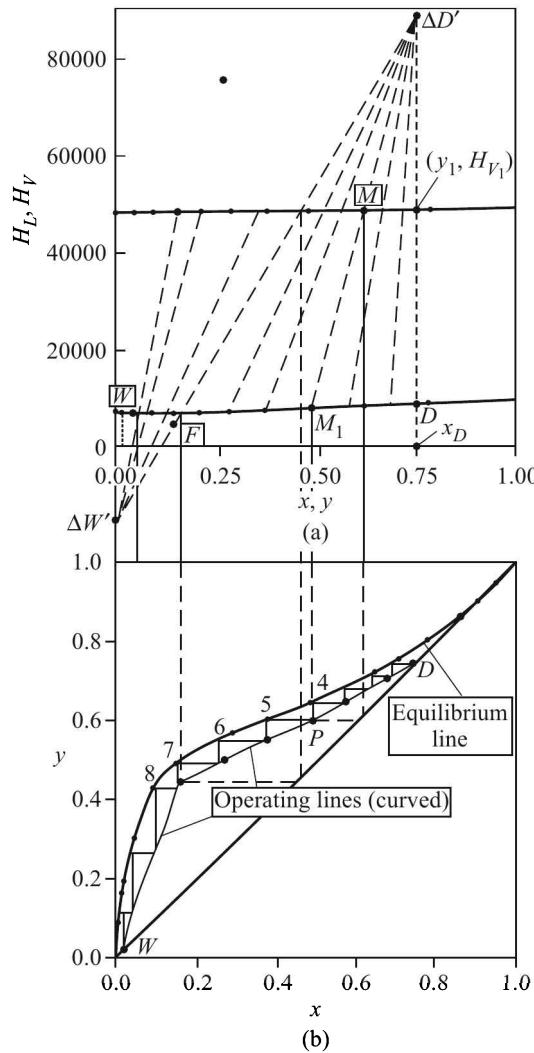


Figure 7.32 Construction of plates using the Ponchon–Savarit method: (a) enthalpy–conc. diagram, and (b) plate.

Similarly, a set of lines are drawn from the point $\Delta W'$ on the left side of the feed point F . The points of intersection of such lines and the enthalpy–concentration curves are used to draw the operating line for the stripping section on the x - y plane. Now steps are drawn between the operating lines and the equilibrium curve on the x - y plane starting from the top or the bottom end. The number of ideal trays is found to be 10 . The intersection of the operating lines is crossed at tray number 7 from the top. So the 7th tray is the optimum feed tray.

(b) Calculation of heat duties of the reboiler and condenser: To calculate the condenser heat duty, use the following equation:

$$Q'_d = H_D + Q_C/D \Rightarrow 88,510 = 8850 + Q_C/39.9 \Rightarrow Q_C = [3.16 \times 10^6 \text{ kJ/h}]$$

To calculate the reboiler heat duty, first use Eq. (7.115).

$$\begin{aligned} \frac{H_F - Q'_W}{z_F - x_W} &= \frac{Q'_d - H_F}{z_D - z_F} \\ \Rightarrow \frac{4790 - Q'_W}{0.1436 - 0.01604} &= \frac{88,510 - 4790}{0.7416 - 0.1436} \\ \Rightarrow Q'_W &= -13,068 \text{ kJ/h} \\ \text{Now use Eq. (7.109).} \quad Q'_W &= H_W - Q_B/W \\ \Rightarrow -13,068 &= 7380 - Q_B/187.1 \\ \Rightarrow Q_B &= [3.826 \times 10^6 \text{ kJ/h}] \end{aligned}$$

Total reflux

Here the reflux ratio is infinite and the points D' and W' lie at infinity. So all the lines through D' and W' are vertical lines. The construction involves drawing alternate tie lines and vertical lines starting at V_1 to obtain the number of plates at total reflux. This gives the minimum number of plates too. However, it is easier to find it by drawing steps between the equilibrium curve and the diagonal on the x - y plane.

Optimum reflux ratio

While designing a new column (or even for using an existing column) for a given separation, the designer has to choose a reflux ratio. From the foregoing discussion, it is clear that the number of plates required decreases as the reflux ratio is increased. The column height decreases as a result. However, at a higher reflux, both the liquid and vapour flow rates are higher. This increases the column diameter. But, on the whole, the cost of the column decreases with increasing reflux ratio. On the other hand, a larger reflux ratio demands higher heat duty of both the reboiler (more heat supply to the reboiler is necessary to maintain a larger supply of the vapour) and the condenser (more heat is to be removed in the condenser). So the size, and therefore the capital cost, of these equipment will be more. The operating cost will also be higher because of larger heat duty of the reboiler and the condenser. So there are a number of opposing factors that govern the different types of cost. A simplified approach to determine the optimum reflux ratio is to plot the fixed cost of the equipment taken together and also the operating cost versus the reflux ratio as shown in Figure 7.33. The plot of the total cost shows a minimum which gives the optimum reflux ratio.

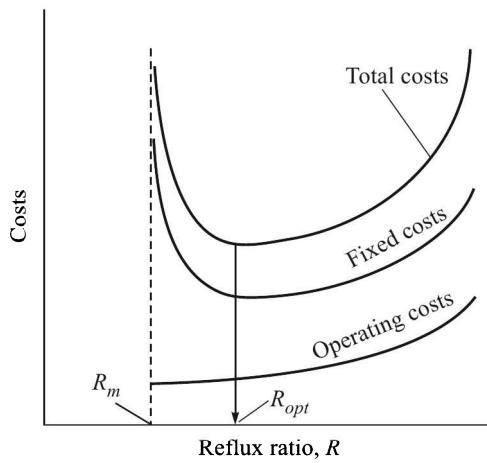


Figure 7.33 Optimum reflux ratio in distillation.

An important point needs attention in this context. The fixed cost has the unit of rupees, dollars, etc. but the operating cost is based on unit time (rupee/year, dollar/year, etc.). How to calculate the total cost, then? Without going into details, we can divide the fixed cost by the estimated "life" of the equipment and then estimate the 'total annual cost'. A more realistic calculation should take into account the interest rate on various cost items, if necessary. In actual practice, a reflux ratio of 1.2 to 1.5 times the minimum is common.

7.9 DISTILLATION IN A PACKED TOWER

Distillation of a liquid mixture in a packed tower is preferred in the following cases: (a) vacuum or low pressure operation, (b) low capacity or feed rate, (c) small allowable pressure drop, and (d) corrosive service. A packed tower for distillation is essentially similar to the one used for gas absorption. However, the tower should be provided with a distributor for the feed at an appropriate location (this is in addition to the distributor of the reflux at the top), besides a condenser, a reflux drum and a reboiler.

There are two methods for the determination of the height of packing: (a) from the height and number of transfer units (H_G and N_G) and (b) from the HETP. To derive the design equations for the calculation of the packed height based on H_G and N_G , refer to Figure 7.34. Let us consider the rectifying section first. Constant molar overflow is assumed. The vapour and liquid flow rates remain constant over a section. Let the flow rates (based on unit

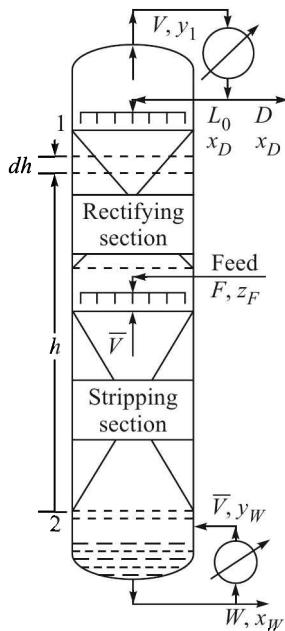


Figure 7.34 Schematic of a packed distillation tower.

cross-section of the tower) be V' and L' kmol/h·m². The individual mass transfer coefficient are k'_x and k'_y , and the specific interfacial area is \bar{a} . It is to be noted that equimolar counterdiffusion of the components occurs. If N_A is the local flux at a height h from the bottom of the packed section, we may write the following differential mass balance equations for the more volatile component.

$$\text{Vapour phase: } \bar{a} \cdot dh \cdot N_A = d(V'y) = V'dy \Rightarrow k'_y \bar{a} (y_i - y) dh = V'dy \quad (7.117)$$

$$\text{Liquid phase: } \bar{a} \cdot dh \cdot N_A = d(L'x) = L'dx \Rightarrow k'_x \bar{a} (x - x_i) dh = L'dx \quad (7.118)$$

Note that transport of the more volatile component occurs from the liquid to the vapour phase and its concentration in the vapour as well as in the liquid phase increases with h . Rearranging Eq. (7.117) and integrating over the rectifying section [from $y = y_F$ (at the feed point) to $y = y_1$ (top of the tower)],

$$\begin{aligned} dh &= \frac{V'dy}{k'_y \bar{a} (y_i - y)} \Rightarrow \int_0^{h_r} dh = \int_{y_F}^{y_1} \frac{V'dy}{k'_y \bar{a} (y_i - y)} \\ \Rightarrow h_r &= \frac{V'}{k'_y \bar{a}} \int_{y_F}^{y_1} \frac{dy}{y_i - y} \Rightarrow h_r = H_G N_G \end{aligned} \quad (7.119)$$

Here h_r is the packed height of the rectifying section. The value of H_G can be calculated if the individual volumetric mass transfer coefficient, $k'_y \bar{a}$, is known; N_G can be obtained by numerical or graphical evaluation of the integral in Eq. (7.119). The interfacial vapour concentrations, y_i , for a set of values of y ($y_F < y < y_1$) are required for the numerical integration. The procedure described in Section 6.4.1 can be followed for this purpose. From Eqs. (7.117) and (7.118), we can write

$$-\frac{k'_x \bar{a}}{k'_y \bar{a}} = \frac{y - y_i}{x - x_i} \quad [\text{Compare with Eq. (4.10)}] \quad (7.120)$$

The equation for the operating line for the rectifying section can be written for a given reflux ratio, R . We take a point (x, y) on the operating line and draw a line of slope $-k'_x \bar{a}/k'_y \bar{a}$; this line meets the equilibrium curve at (x_i, y_i) . If the individual coefficients remain constant over a section (this is quite reasonable because the flow rates do not vary over a section), such lines emanating from different points on the operating line are parallel. Thus, for a set of points (x, y) , the corresponding interfacial concentrations (x_i, y_i) required for integration can be obtained. The procedure is illustrated in Example 7.25.

Similar design equations can be written for the height and the number of individual liquid phase transfer units.

$$\begin{aligned} dh &= \frac{L'dx}{k'_x \bar{a} (x - x_i)} \Rightarrow \int_0^{h_r} dh = \int_{x_F}^{x_1} \frac{L'dx}{k'_x \bar{a} (x - x_i)} \\ \Rightarrow h_r &= \frac{L'}{k'_x \bar{a}} \int_{x_F}^{x_1} \frac{dx}{x - x_i} \Rightarrow h_r = H_L N_L \end{aligned} \quad (7.121)$$

The packed height can also be determined using the overall coefficients ($K'_y \bar{a}$ and $K'_x \bar{a}$). The design equations can be obtained by putting $N_A = K'_y(y^* - y)$ in Eq. (7.117) or $N_A = K'_x(x - x^*)$ in Eq. (7.118).

$$h = H_{OG} \int_{y_F}^{y_1} \frac{dy}{y^* - y} = H_{OL} \int_{x_F}^{x_1} \frac{dx}{x - x^*};$$

$$H_{OG} = \frac{V'}{K'_y \bar{a}} \quad \text{and} \quad H_{OL} = \frac{L'}{K'_x \bar{a}} \quad (7.122)$$

We assume that the heights of overall transfer units, H_{OG} and H_{OL} , remain reasonably constant over the section. The number of overall gas-phase or liquid-phase transfer units are to be determined by graphical integration. Corresponding to a point (x, y) on the operating line, y^* is the ordinate of the point vertically above it on the equilibrium curve; x^* is the abscissa of a point on the equilibrium line horizontally left to (x, y) . Thus the values of y^* for a set of values of y ($y_F < y < y_1$) can be obtained and N_{OG} can be evaluated graphically or numerically.

Mass exchange between the vapour and the liquid phases in distillation is mostly controlled by the vapour phase resistance. Thus, for the sake of accuracy, it is advisable to calculate the packed height using the 'gas-phase coefficient'.

Following the procedure described in Section 6.4.3, it is possible to combine the heights of individual transfer units to obtain the height of an overall transfer unit. Thus,

$$H_{OG} = H_G + \lambda H_L; \quad \lambda = mV'/L', \quad (m = \text{slope of the equilibrium line}) \quad (7.123)$$

It is obvious that the slope of the equilibrium line varies with composition. Even if H_G and H_L remain constant over a section, H_{OG} and H_{OL} are liable to variation. However, an average value can be used. A similar procedure is used to determine the packed height for the stripping section.

EXAMPLE 7.25 (*Determination of packed height of a distillation column*) A mixture of diethylamine (1) and triethylamine (2) containing 40 mol% of the higher amine is to be separated in a packed distillation column (dia = 0.75 m) at a rate of 2000 kg/h and at a total pressure of 113.3 kPa. The top product should have 97 mol% of diethylamine and the bottom product, 96 mol% triethylamine. The feed is at its bubble point and the reflux ratio used is twice the minimum. The individual volumetric mass transfer coefficients are:

Rectifying section: $k'_x \bar{a} = 600$ and $k'_y \bar{a} = 170 \text{ kmol}/\text{h} \cdot \text{m}^3$

Stripping section: $k'_x \bar{a} = 750$ and $k'_y \bar{a} = 200 \text{ kmol}/\text{h} \cdot \text{m}^3$

The equilibrium data for the system at the given pressure are available [Bittrich, H.J., and E. Kruer: *Z. Physik. Chem.* (Leipzig), 219 (3/4), 1962, p. 224].

x	0	0.02	0.104	0.227	0.342	0.424	0.522	0.79	0.923	0.969	1.0
y	0	0.052	0.231	0.451	0.60	0.674	0.755	0.91	0.978	0.988	1.0

Solution

Molecular weights: $M_1 = 73.09$; $M_2 = 101.1$

Average mol. wt. = $(0.6)(73.09) + (0.4)(101.1) = 84.3$

Molar feed rate, $F = 2000/84.3 = 23.72 \text{ kmol/h}$

Total material balance: $F = D + W \Rightarrow 23.72 = D + W$

Component 1 balance: $Fz_F = Dx_D + Wx_W \Rightarrow (23.72)(0.6) = D(0.97) + W(0.04)$

Solving, $D = 14.3 \text{ kmol/h}$; $W = 9.42 \text{ kmol/h}$

The minimum reflux ratio, $R_m = 0.796$ [this can be obtained by the usual procedure].

Actual reflux ratio (2 times the minimum), $R = (2)(0.796) = 1.592$; vapour rate at the top tray, $V = D(R + 1) = (14.3)(1.592 + 1) = 37.06 \text{ kmol/h}$; reflux rate, $L_0 = DR = (14.3)(1.592) = 22.76 \text{ kmol/h}$.

The feed is a saturated liquid. Vapour rate in the stripping section, $\bar{V} = V = 37.06$; liquid rate in the stripping section, $\bar{L} = L + F = 22.76 + 23.72 = 46.48 \text{ kmol/h}$.

Rectifying section operating line:

$$y = \frac{R}{R+1}x + \frac{x_D}{R+1} \Rightarrow y = \frac{1.592}{1+1.592}x + \frac{0.97}{1+1.592} = 0.614x + 0.374$$

Stripping section operating line: It passes through $W(0.04, 0.04)$ and the intersection of the feed line ($x = 0.6$) and the rectifying section operating line $\Rightarrow y = 1.255x - 0.01$

The number of gas-phase transfer units N_G can be obtained by evaluation of the integral in Eq. (7.119). A set of values of $(y_i - y)$ is required for this purpose.

A set of lines of slope $-k'_x \bar{a} / k'_y \bar{a} = -600/170 = -3.75$ are drawn between the operating line and the equilibrium lines for the rectifying section to get a set of values of y and y_i and hence of $y_i - y$. Similarly, another set of lines of slope $-k'_x \bar{a} / k'_y \bar{a} = -750/200 = -3.53$ are drawn between the operating line and the equilibrium line for the stripping section. A few such lines are shown in Figure 7.35(a) and several values of $y_i - y$ are given below.

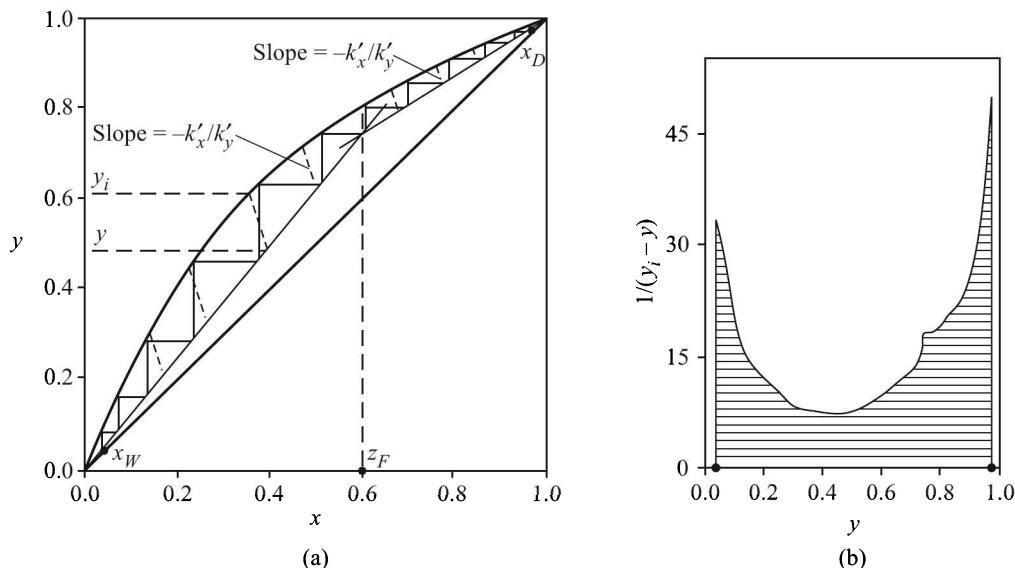


Figure 7.35 (a) Determination of the interfacial concentrations y_i in a packed distillation column. A set of (dotted) lines of slope k'_x/k'_y is shown. Step construction for ideal trays is also shown. (b) Graphical integration.

y	0.97	0.95	0.895	0.835	0.77	0.725	0.615	0.49	0.365	0.168	0.04
y_i	0.99	0.977	0.935	0.885	0.828	0.792	0.713	0.625	0.495	0.263	0.07
$1/(y_i - y)$	50	37.04	25	20.83	18.2	14.3	10.2	7.41	7.7	13.2	33.3

The integral for N_G is obtained by graphical integration as shown in Figure 7.35(b). The areas under the curves are:

Rectifying section: $N_G = 5.02$ units; stripping section: $N_G = 8.7$ units

The values of H_G for both the sections are required in order to find out the column height. It is to be noted that the vapour flow rates are the same in both the sections, but the volumetric vapour phase mass transfer coefficients vary. The column dia is 0.75 m; its cross-section is 0.442 m².

Vapour flow rate = $V' = 37.06/0.442 = 83.85 \text{ kmol/h} \cdot \text{m}^2 = \bar{V}'$ (for the stripping section)

$$(H_G)_{\text{recti}} = V'/k'_y \bar{a} = 83.85/170 = \boxed{0.49 \text{ m}}; (H_G)_{\text{strip}} = \bar{V}'/k'_y \bar{a} = 83.85/200 = \boxed{0.42 \text{ m}}$$

$$\text{Total packed height of the two sections} = (0.49 \text{ m})(5.02) + (0.42 \text{ m})(8.7) = \boxed{6.1 \text{ m}}$$

Eleven theoretical plates are required for the separation as shown in Figure 7.35(a). The average height of a theoretical plate (HETP) for the packing under the given conditions is

$$\text{HETP} = 6.1/11 = 0.55 \text{ m}$$

The concept of HETP (see also Chapter 6) is widely used in packed tower design. Experimental data on the performance of a particular packing are sometimes expressed in terms of HETP rather than the volumetric mass transfer coefficients. If the HETP value is known, the packed height can be determined from the calculated number of theoretical trays required for the separation. The diameter of a packed column is calculated from flooding considerations as usual. As the flow rates differ in the two sections, it is advisable to estimate the diameter based on the larger flow rates for a safer design.

NOTATIONS

c_{pA}	: specific heat of component A (liquid)
D	: rate of withdrawal of the distillate at the top of a column, kmol/h
E_M	: Murphree efficiency, Eq. (7.93)
F	: feed rate, kmol/h
H_G	: height of a vapour-phase mass transfer unit, m
H_L	: height of a liquid-phase mass transfer unit, m
H_L	: enthalpy of liquid, kcal/kmol
H_V	: enthalpy of vapour, kcal/kmol
H_s	: heat of solution, kcal/kmol

K_i	: equilibrium vaporization ratio of component i in a mixture, Eq. (7.14)
L	: liquid flow rate, kmol/h (in the rectifying section of a continuous column)
\bar{L}	: liquid flow rate in the stripping section of a column, kmol/h
M_A	: molecular weight of component A
N_m	: minimum number of trays (at total reflux)
p_A	: partial pressure of A in a vapour mixture, kPa/bar/atm
P	: total pressure, kPa/bar/atm
P_A^v	: vapour pressure of pure component A
q	: a parameter indicating the quality of the feed, Eq. (7.82)
Q	: rate of heat input to the column/chamber, kcal/h
Q_B	: heat load of the reboiler, kcal/h
Q_C	: heat load of the condenser, kcal/h
R	: reflux ratio ($= L_0/V$)
T_A	: boiling point of pure component A
T_B	: boiling point of pure B ; bubble point of a mixture
V	: vapour flow rate, kmol/h (in the rectifying section of a continuous column)
\bar{V}	: vapour flow rate in the stripping section of a column, kmol/h
W	: rate of withdrawal of bottom product from a column, kmol/h
x	: liquid-phase mole fraction of a component (the more volatile component in a binary) in a mixture
x_D	: mole fraction of the more volatile in the distillate
x_n	: mole fraction of the more volatile of a binary in the liquid leaving the n th plate
x_W	: mole fraction of the more volatile in the bottom product
y	: vapour-phase mole fraction of a component (the more volatile component in a binary) in a mixture
y^*	: vapour-phase mole fraction of a component in equilibrium with the liquid at mole fraction x
y_n	: mole fraction of the more volatile of a binary in the vapour leaving the n th plate
z_F	: mole fraction of the more volatile in a binary feed mixture
z_i, z_{Fi}	: mole fraction of component i in the feed
α	: relative volatility, Eqs. [7.8(a)] and (7.10)
λ_A	: heat of vaporization of pure component A , kcal/kmol

SHORT AND MULTIPLE CHOICE QUESTIONS

1. The relative volatility of A in a mixture with B is $\alpha_{AB} = 2.0$. The equilibrium vaporization ratio of B is $K_B = 0.7$. (a) What is the value of α_{BA} ?
 - (i) 2.0
 - (ii) 0.5
 - (iii) 1.0
 (b) What is the value of K_A ?
 - (i) 1.4
 - (ii) 0.35
 - (iii) 2.7
2. Consider equilibrium in the ternary system of benzene (1), toluene (2) and *o*-xylene (3). Given: $T = 393$ K, $P = 1.2$ bar and $x_3 = 0.2$. Is the system completely defined?
3. What are the major sources of error in the experimental determination of vapour–liquid equilibrium using a liquid recirculation type still?
4. (a) The overall mole fraction of benzene in a mixture of benzene and toluene is $z_F = 0.3$ at 1 atm total pressure and 95°C. Then the mixture is
 - (i) a liquid
 - (ii) a vapour
 - (iii) a two-phase mixture.
 (b) What is the minimum temperature at which a vapour of this composition can exist at 1 atm total pressure?
 - (i) 370 K
 - (ii) 376.8 K
 - (iii) 382.7 K

[Ideal solution; vapour pressure equation in Table 7.2]
5. Water (1) and formic acid (2) form a higher-boiling azeotrope. At 1 atm total pressure, the azeotropic composition is $x = 0.409$. Then which of the following is correct?
 - (i) $\alpha_{12} = 1$, at $x = 0.409$
 - (ii) $\alpha_{12} > 1$, at $x = 0.617$
 - (iii) $\alpha_{12} < 1$, at $x = 0.803$
 - (iv) $\alpha_{12} < 1$, at $x = 0.205$.
6. The relative volatility of A in a mixture of A and B is $\alpha_{AB} = 1.5$. What is the mole fraction of B in the first droplet of liquid condensed from an equimolar saturated vapour mixture of A and B ?
 - (i) 0.5
 - (ii) 0.6
 - (iii) 0.4
7. A binary totally miscible mixture forms a maximum boiling azeotrope at $x = x_a$. Two sets of equilibrium data points for the system are (x_1, y_1^*) and (x_2, y_2^*) . If $x_1 < x_a < x_2$, identify the correct inequalities.
 - (i) $x_1 < y_1^*$
 - (ii) $x_2 < y_2^*$
 - (iii) $y_1^* > y_2^*$
8. A given mixture of *n*-pentane and *n*-octane is heated and flashed when one mole liquid having a mole fraction $x = 0.15$ of *n*-pentane and two moles of vapour are generated. At the temperature of the flash drum, the relative volatility of *n*-octane with respect to *n*-pentane is 0.216. The solution is ideal. Calculate the composition of the original mixture.
9. A mixture of compounds A and B forms a higher-boiling azeotrope at $x = 0.75$ at 1 atm

total pressure. A solution of this composition has a bubble point T_b and a vapour of the same composition has a dew point T_d . Then:

- (i) $T_b > T_d$ (ii) $T_b = T_d$ (iii) $T_b < T_d$

10. Consider a mixture of 40 mole% benzene (1), 40% toluene (2) and 20% *p*-xylene (3). The solution is approximately ideal. The following relative volatility values are known at 1 atm total pressure: $\alpha_{12} = 2.4$ and $\alpha_{32} = 0.43$. Then (a) the value of α_{31} is
(i) 0.18 (ii) 1.03 (iii) 5.58
(b) And the mole fraction of toluene in the equilibrium vapour at 100°C is
(i) 0.688 (ii) 0.277 (iii) 0.743
(c) Given the values $K_1 = 1.67$ and $K_2 = 0.688$, the value of K_3 is
(i) 1.15 (ii) 2.43 (iii) 0.296
11. One mole of a solution of *A* and *B* (enthalpy = 900 kcal/kmol; $x = 0.4$) is mixed with two moles of another solution of the components (enthalpy = 1200 kcal/kmol, $x = 0.8$). Calculate the enthalpy and composition of the mixture.
12. A ternary solution of *n*-hexane (20 mole%), *n*-heptane (40 mole%) and *n*-octane may be considered to be ideal. The equilibrium vaporization ratios are: $K_1 = 2.25$, $K_2 = 1.02$, and $K_3 = 0.6$ at 1 atm total pressure. The solution is
(i) below its bubble point
(ii) saturated
(iii) above its bubble point.
13. A student was asked to do flash calculation of an ideal mixture of four components having an overall composition (in mole fraction) of $w_1 = 0.2$, $w_2 = 0.15$, and $w_3 = 0.40$. At the condition of the flash drum, the equilibrium vaporization ratios were: $K_1 = 2.1$, $K_2 = 1.02$, $K_3 = 0.6$, and $K_4 = 0.2$. The student reported that 38 mole% of the feed vaporized on flashing. (a) Was the calculation reasonably correct? (b) What was the value of relative volatility α_{43} ?
(i) 0.33 (ii) 3.1 (iii) 0.4
14. An essential oil, virtually immiscible with water, is steam-distilled by passing live steam at 107°C through a mixture of the oil and water (one mol of the oil per 200 mol water). The vapour pressure of water at 107°C is 1.3 bar and that of the essential oil is 6.55 mm Hg. How much steam is necessary to recover 80% of the essential oil? Neglect condensation of steam.
15. What are the important factors that determine the selection of a batch distillation column for the separation of a liquid mixture?
16. A mixture of benzene and *p*-xylene is batch distilled at atmospheric pressure. The rate of heat input to the still is 4000 kcal/h. Individual heats of vaporization are: benzene = 100 kcal/kg, *p*-xylene = 85 kcal/kg, and the relative volatility of benzene in the mixture is 5.6. Calculate the instantaneous rate of vaporization of *p*-xylene when the liquid in the still has 40 mole% benzene in it.
17. One thousand kilograms of an equimolar mixture of benzene and nitro-benzene is being separated by batch distillation. After an hour of operation, 500 kg of the mixture remains

in the still. The operator takes a sample of the accumulated condensate and reports that it has 70 mole% benzene in it. The relative volatility of benzene in the mixture can be taken as 7. Is the reported concentration of the distillate reasonably accurate?

18. A quaternary solution is being distilled in a batch still. Over a period of time, 30 mol% of component 1 is distilled out. The following relative volatility values are given: $\alpha_{31} = 0.2$; $\alpha_{23} = 1.8$; $\alpha_{43} = 0.7$. What fraction of component 3 is distilled out over this period?
19. Given: $x_D = 0.95$, $x_W = 0.05$, $\alpha = 2$, $z_F = 0.5$ and the feed is saturated. Algebraically, calculate the theoretical minimum slope of the rectifying section operating line for distillation of the binary mixture. Does it differ from the theoretical minimum slope of the stripping section operating line?
20. At a particular section of a packed distillation column, the bulk liquid concentration in a binary mixture is $x = 0.7$. Given: internal reflux ratio = 0.9, $\alpha = 2.5$, $H_G = 0.42$ m, $H_L = 0.15$ m. What is the height of an overall vapour phase transfer unit, H_{OG} ?
(i) 0.52 (ii) 0.38 (iii) 0.65
21. The stripping section operating line for a binary distillation problem is $y = 1.4x - 0.02$. The relative volatility is $\alpha = 2.6$. On a particular tray the liquid composition is $x = 0.2$. What is the composition of the vapour leaving the tray if the Murphree tray efficiency is 0.7?
(i) 0.32 (ii) 0.354 (iii) 0.26
22. What happens if a column heated by open steam is operated at total reflux for a long time?
23. The stripping section operating line of a distillation column receiving saturated open steam for the separation of an aqueous solution is $y = 1.1x - 0.022$.
 - (a) If $\alpha = 2.7$, what is the bottom product composition?
(i) 0.22 (ii) 0.022 (iii) 0.02
 - (b) What is the enrichment of the vapour across the bottom tray?
(i) 0.052 (ii) 0.022 (iii) 0.011
24. A column receives saturated steam at the bottom for heat supply. If the feed ($z_F = 0.5$) is a mixture of 40 mole% liquid and 60 mole% vapour, calculate the slope of the stripping section operating line corresponding to the minimum reflux. Given: $\alpha = 2.6$, and $x_W = 0.03$ mole fraction.
25. A column has to separate a mixture of *A* and *B* to yield a top product of $x_D = 0.97$ and a bottom product of $x_W = 0.04$. Calculate the minimum number of ideal trays required to achieve this separation, Given: $\alpha_{AB} = 1.8$ at the bottom condition and $\alpha_{AB} = 2.0$ at the top condition.
26. The following concentrations of the vapour at two consecutive trays in the rectifying section of a column have been measured: $y_3 = 0.94$ and $y_4 = 0.925$. The equation of the operating line is $y = 0.6667x + 0.32$. The relative volatility at the liquid composition on the third tray is $\alpha = 1.85$. Calculate the Murphree efficiency of the tray.
27. A column receives a ‘cold reflux’, and the ‘external reflux ratio’ is 2.0. For each mole

- of the cold reflux, 0.05 mole of the vapour condenses at the top tray. What is the true slope of the rectifying section operating line?
- (i) 0.677 (ii) 0.5 (iii) 1.0
28. A saturated equimolar mixture of vapours of *A* and *B* enters a partial condenser at a rate of 1 kmol/h. The vapour leaves the condenser at a rate of 0.6 kmol/h. If the relative volatility of *B* with respect to *A* is 0.3, calculate the composition of the vapour and the liquid leaving the partial condenser.
29. A mixture (40 mole% vapour, the rest liquid) of aniline and nitrobenzene (80 mole% aniline) is separated into a distillate having 98 mole% aniline and a bottom product with 3 mole% aniline. The reflux ratio used is 2.2. (a) Determine the equations of the operating lines and of the feed line. (b) Write down the same equations if the column operates at total reflux.
30. A column is designed to operate at a reflux ratio of 1.3 (saturated reflux). In actual operation the reflux is well below its bubble point. What reflux ratio would you suggest qualitatively?
- (i) $R > 1.3$ (ii) $R < 1.3$ (iii) $R = 1.3$
31. The equation of the rectifying section operating line for distillation of a mixture of *A* and *B* in a packed column is $y = 0.6x + 0.376$. The relative volatility of *A* with respect to *B* is $\alpha_{AB} = 2.0$. At a point in the rectifying section, $x = 0.8$. Given: $k'_x \bar{a} = 400 \text{ kmol}/(\text{m}^3)(\text{h})(\Delta x)$, and $k'_y \bar{a} = 170 \text{ kmol}/(\text{m}^3)(\text{h})(\Delta y)$.
- (a) What is the reflux ratio?
- (i) 0.5 (ii) 1.0 (iii) 1.5
- (b) What is the top product mole fraction?
- (i) 0.49 (ii) 0.94 (iii) 0.98
- (c) What are the concentrations of the more volatile at the vapour–liquid interface?
32. A column for distillation of a mixture of *A* and *B* operates at total reflux. The liquid concentration of the fifth tray from the top is $x = 0.4$. If the relative volatility is $\alpha_{AB} = 1.8$, what are the concentrations of vapour streams (i) entering the tray and (ii) leaving the tray?
33. In order to reduce energy supply to a tray column for the separation of a binary mixture of *A* and *B*, it is planned to retrofit it with the Intalox high performance structured packing. The column receives a saturated liquid feed having 60 mol% *A*. The top product purity is 98 mol% *A* and the relative volatility is $\alpha_{AB} = 2.0$. The plant engineer suggests reduction of the reflux ratio from the present value of 1.8 to 1.5. Is the suggestion practicable?
34. If the relative volatility of *A* in a binary mixture of *A* and *B* is constant, show that the product of the terminal slopes of the equilibrium curve (i.e. $[dy/dx]_{x=0} \cdot [dy/dx]_{x=1}$) is unity.
35. The relative volatility of *A* with respect to *B* is $\alpha_{AB} = 2$. At what concentration of a mixture of *A* and *B* is the slope of the equilibrium line unity?

- 36.** For distillation of an equimolar binary mixture of *A* and *B*, the equations of the operating lines are:
- Rectifying section: $y = 0.663x + 0.32$
- Stripping section: $y = 1.329x - 0.01317$
- What is the condition of the feed?
- 37.** A binary distillation column separating *A* and *B* is being operated at total reflux in the startup period. The relative volatility of *A* with respect to *B* is $\alpha_{AB} = 2.0$. If the vapour entering the top tray has 95 mole% *A*, what is the mole fraction of *A* in the liquid leaving the tray?
- (i) 0.95 (ii) 0.5 (iii) 0.475
- 38.** Write down the equations of the operating lines of the column (that runs under total reflux) described in Problem 37.
- 39.** Prepare sketches of typical energy-concentration diagram of binary liquid and vapour mixtures of *A* and *B* if constant molar overflow (i) occurs and (ii) does not occur in the distillation column. Explain the sketches.
- 40.** An aqueous solution of ethanol [30 mole% ethanol (1) and 70 mole% water (2)] at 75°C exerts an equilibrium total pressure of 592 mm Hg. Given $P_1^v = 661$ mm Hg, $P_2^v = 289.5$ mm Hg, $\gamma_1 = 1.765$, and $\gamma_2 = 1.195$, calculate the equilibrium vaporization ratios K_1 and K_2 .

PROBLEMS

[Note: To calculate vapour pressures, use the Antoine equation constants given in Table 7.2.]

- 7.1** (*Equilibrium in a binary mixture*)¹ Mixtures of *n*-hexane and *n*-octane form essentially ideal solutions. (a) Prepare the bubble point, dew point and equilibrium curves (T - x - y and x - y plots) at 1 atm total pressure. (b) Calculate the values of the relative volatility of *n*-hexane and *n*-octane in mixtures containing 10 mole% and 90 mole% hexane using vapour pressure equations given in Table 7.2. Do these values suggest that the solutions may be ideal? (c) A solution of concentration $x = 0.2$ is slowly heated. What is the composition of the initial vapour formed if the total pressure is (i) 1 atm, (ii) 2 atm? (d) If a vapour of composition as in part (c) (ii) above is cooled at 2 atm total pressure and a differential amount of vapour is formed from the condensate, calculate its composition. How can the quantities be calculated using the T - x - y and x - y data?
- 7.2** (*Bubble point/dew point calculation, ternary mixture*)³ Calculate the bubble point of a mixture of 30% methanol, 30% ethanol and 40% *n*-propanol (all in mole%) at 1 atm total pressure. Also calculate the dew point of a vapour of the above composition at 1.5 atm total pressure. Assume ideal behaviour of the solution.
- 7.3** (*Equilibrium in a multicomponent heterogeneous system*)³ A heterogeneous mixture containing benzene (0.025 gmol), toluene (0.025 gmol) and water (0.05 gmol) is heated slowly at 1 atm total pressure. The vapour generated remains in equilibrium with the

liquid. Calculate (a) the temperature at which boiling starts, (b) the composition of the initial vapour, and (c) the temperature at which vaporization is complete.

- 7.4 (Binary flash distillation—yield vs composition)¹** Ethanol forms a nearly ideal solution with *iso*-butanol and has a relative volatility 2.2. A heated feed containing 40 mole% ethanol and 60 mole% *iso*-butanol enters a flash drum at a rate of 50 kmol/h. Prepare a plot of the fractional yield of the distillate versus its composition. What fraction of the feed should be vaporized in order to have a bottom product containing not more than 10% ethanol?
- 7.5 (Two-stage flash distillation)²** Consider Problem 7.4 again. Now there is a second flash drum that receives the bottom product from the first drum. If 60% of the feed is vaporized in each drum, find the vapour and the liquid flow rates from each chamber as well as their composition.
- 7.6 (Two-stage flash distillation)³** A mixture of acetone and phenol (40 mass% acetone) is flashed consecutively in a cascade consisting two flash drums at 1 atm. The feed enters at a rate of 3000 kg/h and half of it is flashed in the first flash drum. The liquid from the first drum is heated and flashed again in the second drum. What fraction of the feed entering the second drum should be vaporized so that the residue contains not more than 1 mass % acetone? The vapour–liquid equilibrium data of the acetone–phenol system are given below.
- | x | 0.01 | 0.04 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 0.96 | 0.99 |
|---|------|-------|-------|------|------|-------|------|------|-------|-------|-------|-------|--------|
| y | 0.67 | 0.776 | 0.852 | 0.91 | 0.94 | 0.962 | 0.98 | 0.99 | 0.991 | 0.994 | 0.997 | 0.999 | 0.9996 |
- 7.7 (Heat requirement for a simple flash distillation)²** Components A and B form approximately ideal solutions and the relative volatility is $\alpha_{AB} = 3.0$. One kilomol of a mixture ($x = 0.5$) at 40°C is passed through a heat exchanger and then flashed to get equal amounts of liquid and vapour products. The temperature in the flash drum is 80°C. The molar specific heats are $c_{pA} = 20 \text{ kcal/kmol}$, $c_{pB} = 30 \text{ kcal/kmol}$. The molar heats of vaporization are $\lambda_A = 1250 \text{ kcal/kmol}$, $\lambda_B = 1700 \text{ kcal/kmol}$. Calculate the heat absorbed by the liquid in the heat exchanger.
- 7.8 (Use of enthalpy-concentration relations)¹** The molar enthalpies of saturated liquid and vapour mixtures of A and B at 1 atm total pressure (reference temp. = 5°C) may be expressed as: $H_L = 9000 + 1000x \text{ kJ/kmol}$; $H_V = 35,000 + 8000y \text{ kJ/kmol}$. The relative volatility is $\alpha_{AB} = 1.8$. (a) Calculate the molar heats of condensation of saturated pure vapours of compounds A and B at 1 atm. (b) We have one kmol of a liquid ($x = 0.3$, $H_L = 8500 \text{ kJ/kmol}$), and one kmol of a vapour ($y = 0.5$, $H_V = 40,000 \text{ kJ/kmol}$). What is the condition of the liquid (subcooled, saturated or superheated) and the condition of the vapour (saturated or superheated)?
- 7.9 (Ternary flash distillation)²** A mixture of 38 mol% propane, 22.5 mol% *iso*-butane, and 39.5 mol% *n*-butane is flashed in a drum. If 50 mol% of the feed vaporizes, estimate the compositions of the liquid and the vapour phases. The K-values at the given conditions are as follows: Propane—1.42; *iso*-butane—0.86 and *n*-butane—0.72.
- 7.10 (Bubble point of a heterogeneous mixture)²** Liquids A and B are miscible in all proportions and $P_A^v = 1.75P_B^v$ at all temperatures. The vapour pressure of B is given by

$\ln P_B^v(\text{mm Hg}) = 14.243 - 2570/(\theta, ^\circ\text{C} + 232.5)$. At what temperature does an equimolar mixture of A and B boil if the total pressure is 1.5 bar? Write down the Antoine equation for A.

Neither A or B is miscible with water. If some water is added to the mixture, at what temperature should it boil if the total pressure remains unchanged? The vapour pressure relation for water is given in Table 7.2.

- 7.11 (Binary batch distillation)¹** Ten kmol of a feed having 65 mole% benzene and 35 mole% toluene is batch distilled at 1 atm pressure. Calculate the moles of distillate produced and the composition of the bottom product if distillation is done until (a) 75 mole% of the feed benzene leaves with the vapour; (b) the stillpot contains 35 mol% benzene; (c) 50 mole% of the feed is vaporized; (d) the accumulated distillate contains 75 mole% of benzene. Take $\alpha = 2.51$.
- 7.12 (Partial condensation of a vapour)²** The vapour (containing 85 mole% methanol and 15 mole% water) from the top tray of a methanol distillation column enters a partial condenser at a rate of 70 kmol/h at 1 atm pressure. (a) If 70 mole% of the vapour is condensed, calculate the composition of the uncondensed vapour. (b) If the uncondensed vapour leaving the condenser has 91.5 mole% methanol in it, how much condensate leaves the condenser per hour? The vapour–liquid equilibrium data are given in Example 7.15.
- 7.13 (Steam distillation)¹** Two kg charge of geraniol (mol. wt. = 154.1) is to be steam-distilled at a temperature of 108°C. The steam is saturated and it is passed at a rate of 50 kg/h. Calculate the time for distillation of 95% of the material. The vaporization efficiency is 0.90. Vapour pressure at 108°C: water—1.34 bar; geraniol—8.65 mm Hg.
- 7.14 (Steam distillation in presence of an impurity)²** Twenty kg charge containing 40 mass% of an essential oil (mol. wt. = 170) and the rest a non-volatile impurity (mol. wt. = 282) having complete mutual miscibility but both immiscible with water, is being steam-distilled. The steam supplied is saturated at 108°C. Calculate the rate of volatilization of the oil when 50% of it has been removed. The vaporization efficiency is 0.85. The vapour pressure of the substance at the given temperature is 6.5 mm Hg.
- 7.15 (McCabe–Thiele construction for ideal trays)¹** A feed mixture of A and B (45 mole% A and 55 mole% B) is to be separated into a top product containing 96 mole% A and a bottom product having 95 mole% B. The feed is 50% vapour and the reflux ratio is 1.5 times the minimum. What is the equation of the feed line? Determine the number of ideal trays required and the location of the feed tray. Given: $\alpha_{AB} = 2.8$.
- 7.16 (Use of the McCabe–Thiele method)¹** A mixture of di- and tri-ethylamines containing 55 mole% of the former is fed to a distillation column at a rate of 40 kmol/h. The feed is at its bubble point. The column is to operate at atmospheric pressure and the top product should not have more than 2.5 mol% of the less volatile. Also, not more than 2% of the diethylamine in the feed should be allowed to leave at the bottom. The reflux to the column is a saturated liquid. Determine (a) the minimum reflux ratio, (b) the number of theoretical plates if the actual reflux ratio is 1.4 times the minimum, (c) the slopes of the two operating lines, and (d) the number of theoretical plates if the reflux

is a subcooled liquid at such a temperature that one mole of vapour is condensed for twenty moles of reflux. The equilibrium data in terms of the more volatile are:

x	0.02	0.039	0.052	0.065	0.09	0.092	0.14	0.215	0.43	0.601	0.782	0.853	0.932	0.985
y	0.042	0.085	0.124	0.153	0.225	0.243	0.316	0.449	0.678	0.802	0.910	0.948	0.970	0.993

- 7.17 (Use of the McCabe-Thiele method)²** Styrene, a tonnage organic chemical used in the production of moulding resins and rubbers, is produced by catalytic dehydrogenation of ethylbenzene followed by separation of the product by distillation. A fractionating column receives an equimolar mixture of styrene and ethylbenzene at a rate of 120 kmol/h. The purity of the top product (ethylbenzene) and that of the bottom product (styrene) must not be less than 98% and 99.5% respectively. Determine (a) the minimum external reflux ratio, (b) the minimum number of ideal trays required for the above separation, (c) the number of ideal trays and the feed-tray location if the actual reflux ratio is twice the minimum and the feed is a saturated liquid, and (d) the vapour load in the condenser. It will be convenient to use the Kremser equation to determine the number ideal trays near the top and bottom ends. The column operates at 20 mm pressure and the equilibrium data at this pressure are given below (x , y are for ethylbenzene).

x	0.0	0.0555	0.0782	0.115	0.139	0.2405	0.2715	0.335	0.460	0.545	0.755	0.874	0.965	1.0
y	0.0	0.090	0.120	0.162	0.201	0.318	0.355	0.4055	0.535	0.630	0.825	0.910	0.975	1.0

In industrial practice too, styrene is purified by distillation under vacuum. How are the column parameters (diameter, tray spacing, number of trays) affected if a mixture is distilled under vacuum rather than at atmospheric pressure?

- 7.18 (Calculation of the minimum reflux)²** A saturated vapour feed containing benzene (30 mole%) and chlorobenzene is to be separated into a top product having 98 mol% benzene and a bottom product having 99 mol% chlorobenzene. Calculate the minimum reflux ratio algebraically. What is the corresponding boil-up ratio? The relative volatility of benzene in the mixture is 4.12.
- 7.19 (Effects of operating parameters on column performance)³** A distillation column provided with a partial reboiler and a total condenser separates a mixture of A and B to yield products of compositions x_D (top) and x_W (bottom). (a) How can the purity of the distillate be increased without changing its quantity and without the addition of extra trays? How is the purity of the bottom product affected as a result? (b) If the rate of withdrawal of distillate is increased (without making any changes in the reboiler heat input), identify the consequent changes. (c) If the pressure of the saturated steam fed to the reboiler undergoes a step change and no other change occurs to the parameters, how is the performance of the column affected?
- 7.20 (Algebraic calculations for a tray column)²** A mixture of 60 mole% A and 40 mole% B is separated in a column to yield 96 mole% A as the top product. Also, 97% of A entering the tower must be recovered in the distillate. The feed is a saturated vapour. The following concentrations have been measured by analyzing the liquid and vapour samples around the 6th tray: $x_6 = 0.55$, $y_6 = 0.72$, $y_7 = 0.63$. (a) What is the local value of the relative volatility of A with respect to B ? (b) How many ideal trays does the column have? Assume that the relative volatility remains constant.

- 7.21 (A stripping column having a given number of trays)³** A saturated liquid mixture of benzene and toluene having 70 mole% benzene is fed continuously at a rate of 40 kmol/h to the top tray of a column having six theoretical trays. There is no reflux at the top. The rate of vapour generation in the reboiler is 30 kmol/h. Determine the equation of the operating line and the rates and compositions of the product. (*Note:* This column may be called a ‘stripping column’.)
- 7.22 (Algebraic calculation of the vapour/liquid concentrations in a tray column)³** A distillation column separates a saturated feed containing 25 mole% A and 75 mole% B. The relative volatility is $\alpha_{AB} = 2.51$. The liquid concentration on the 5th tray is $x_5 = 0.54$. The distillate has 98 mole% A and the reflux ratio is 3.0. (a) Determine the concentration of the vapour (i) entering the 5th tray from the top, and (ii) leaving the 5th tray. (b) Which section of the column (rectifying or stripping) does the 5th tray belong to? (c) Calculate the enrichment of the vapour across the 4th tray. (d) If 97% of A present in the feed goes to the top product, calculate the moles of liquid vaporized in the reboiler per mole of distillate and also the boil-up ratio. Assume that the trays are ideal. Solve the problem algebraically (i.e. without any graphical construction).
- 7.23 (High purity product; use of Kremser equation)³** An equimolar mixture of A and B is to be separated in a tray tower. A top product having 95 mol% A is acceptable. However, a very pure bottom product having not more than 0.1 mol% A is required. The feed is liquid at its bubble point. A reflux ratio of 2.0 is suggested. The relative volatility of A with respect to B is $\alpha_{AB} = 2.2$. Determine the number of ideal stages.
- The graphical construction of stages is difficult at low concentration and an algebraic method is convenient. Use the McCabe–Thiele method to make stage construction up to about 5 mol% of A. Then use the Kremser equation to determine the number of trays required to reach the stipulated value of 0.1 mol% A in the bottom product.
- 7.24 (A stripping column with a given number of trays)³** The vapour phase alkylation of phenol is carried out by a selective zeolite catalyst to yield a mixture of 35 mole% *p*-cresol and the rest phenol. The mixture which is at its bubble point is to be separated at 1 atm pressure in a stripping column having nine ideal trays and a partial reboiler at a rate of 50 kmol/h to yield 95% *p*-cresol as the bottom product. The relative volatility of phenol in the mixture is 1.76. Calculate (a) the composition of the top product and (b) the boil-up rate, \bar{V}/W , where \bar{V} is the vapour rate and W is the rate removal of the bottom product.
- 7.25 (Performance of a column with an additional number of trays)³** A column having 16 trays of 25% overall efficiency separates a mixture of 60 mole% benzene and 40 mole% toluene available as a saturated vapour. The overhead product is 85 mole% benzene and the bottom product is 20 mole% benzene. It is possible to add a section having eight trays of the same efficiency to the column. If all process conditions remain unchanged, calculate the percentage saving in steam fed to the reboiler that can be achieved by this increase in the number of trays. On which tray of the modified column should the feed be introduced? Equilibrium data for the system is given under Example 7.13.
- 7.26 (Given the number of trays and efficiency, to determine the product composition)³** A distillation column has five plates that are 60% efficient. The heat input to the stillpot is

100,800 kcal/h and the condenser load is 280,000 kcal/h. The reflux is at 37°C below the boiling point. A feed, an equimolar mixture of benzene and toluene, enters the column at a rate of 50 kmol/h. Also the feed is 55% vapour. Latent heat of vaporization of the liquid can be taken as 7000 kmol/kmol irrespective of the composition. The specific heat of liquid is 38 Btu/(lb)(mol)(°F). Find the compositions of the top and the bottom products.

- 7.27 (McCabe-Thiele construction—feed is not supplied at the optimum location)³** A distillation column receives an equimolar saturated liquid mixture of benzene and toluene ($\alpha = 2.51$). The top product has 95 mol% benzene, the bottom product contains 95 mol% toluene, and the reflux ratio is 2.0. (a) Determine the feed tray and the number of ideal trays if the feed is supplied to the optimum location. (b) How many more trays would be required for this separation if the feed is supplied at the ninth ideal tray from the top? (c) Determine the number of real trays if the Murphree efficiency is 60% and the feed enters the optimum position in the column.
- 7.28 (McCabe-Thiele method, number of trays given, Murphree efficiency given)²** A distillation column which separates pinene and limonene consists of a reboiler, 15 theoretical plates and a total condenser. The feed is at its bubble point and has 72% pinene in it. The overhead product contains 95 mole% pinene and the bottom product has 94% limonene. Determine (a) the reflux ratio to be maintained, (b) the location of the feed plate, (c) the number of ideal stages required for the above separation for total reflux. *Given:* $\alpha = 1.71$.
- 7.29 (A column receiving two feeds)³** A distillation column for separation of methanol from water receives two feeds—100 kmol/h saturated liquid having 30 mol% methanol, and 100 kmol/h 20% vaporized feed having 60 mol% methanol. The top product should have 96 mol% methanol, and the bottom must not contain more than 3 mol% of it. If an external reflux ratio of 1.45 is used, calculate the amounts of the top and bottom products, and determine the number of ideal trays required for the separation. The vapour–liquid equilibrium data are given in Example 7.15.
- 7.30 (Withdrawal of a side stream from a distillation column)²** A saturated liquid feed having 45 mole% methanol is distilled at a rate of 200 kmol/h in a column to yield a top product, 96% methanol, a bottom product, 97% water, and a liquid side stream, 20 kmol/h, having 70 mole% methanol, from the appropriate tray. Determine the number of ideal trays required. From which tray should the side stream be withdrawn? A reflux ratio of 1.5 may be used.
- 7.31 (A column with an arrangement for heat supply to a particular tray)³** A distillation column separates an equimolar mixture of methanol and water at its bubble point to a top product having 95% methanol and a bottom product with 95% water.
- How many trays should be used to achieve this separation if the column is operated at total reflux?
 - Determine the number of theoretical trays required and the location of the feed tray if a reflux ratio of 1.5 is used.
 - It is planned to install a heating coil on the third tray from the top so as to vaporize 10% of the liquid it receives. What will be the number of trays for this arrangement?

- 7.32 (A column receiving two feeds; feeds supplied to the wrong plates)³** A column receives two feeds—20 kmol/h, 40 mole% benzene, and 40 kmol/h, 60 mole% benzene, both liquid at the respective bubble points. The top product rate is 30 kmol/h with 94% benzene, and the reflux ratio is 1.5. After an annual shutdown, the feed pipe connections got interchanged inadvertently. Can you predict the top product composition at this condition? The reflux ratio remains unchanged.
- 7.33 (Side stream withdrawal from a column—algebraic calculations)³** A continuous distillation column receives a saturated liquid feed ($z_F = 0.45$). It produces a distillate of $x_D = 0.98$ and a bottom product of $x_W = 0.015$. A side stream amounting to 25% of the downflowing liquid ($x_S = 0.75$) is withdrawn as a saturated liquid from the appropriate tray. The rectifying section operating line for the part of the column above the point of side stream withdrawal is $y = 0.821x + 0.175$. Determine the equations of the operating lines for the middle and the last sections of the column. What fraction of the feed is drawn as the bottom product?
- 7.34 (Binary batch distillation)¹** A charge of 15 kmol of an equimolar mixture of methanol and water is batch-distilled to recover 85% of the alcohol. Calculate the amount of distillate and its composition. Equilibrium data are available under Example 7.15.
- 7.35 (Multicomponent batch distillation)²** A mixture containing 2 kmol each of *n*-hexane, *n*-heptane and *n*-octane is batch-distilled at 1 atm pressure to remove 80% of hexane. Taking *K*-values from Figure 7.8, calculate the amount and composition of the distillate. What fraction of heptane remains in the still?
- 7.36 (Batch distillation with constant reflux)³** A batch distillation column having a stillpot and one ideal tray separates a mixture of benzene and toluene. At the beginning there is 10 kmol of liquid in the still with 40 mole% benzene. The rate of vapour generation is 15 kmol/h and a reflux ratio of 3.0 is used. Determine the concentration of the overhead vapour and the instantaneous rate of removal of benzene. The relative volatility of benzene is 2.51.
- 7.37 (Batch distillation with variable reflux)³** Fifty kilomols of aqueous methanol (60 mole% methanol) is charged into a batch still having a reboiler and five ideal trays. The reflux ratio is continuously increased so that the distillate always contains 90 mol% methanol. If distillation is stopped after the reflux ratio required to maintain the stipulated top product concentration exceeds 8.0, calculate the fractional recovery of methanol.
- 7.38 (Batch distillation)³** Twenty kilomoles of a mixture of *A* and *B* ($x_F = 0.45$) is charged in the stillpot of a batch distillation unit. A constant vaporization rate of 5.0 kmol/h is maintained and there is a total condenser. (a) What is the concentration of the distillate after one hour? (b) At the end of one hour, it is planned to start withdrawal of the condensate from the receiver at a rate equal to that of the rate of vaporization. Thus the amount of condensate in the receiver remains constant (it is also assumed to be well-mixed all the time). Calculate the concentration of the distillate in the receiver at the end of two hours of operation. The equilibrium vaporization constants at the operating condition are: $K_A = 2.6$, and $K_B = 0.9$.

- 7.39 (Batch distillation in a unit having a partial condenser)²** The vapour from a batch still flows to a partial condenser in which 50 mole% of the vapour is condensed. The condensate is fed back to the still and the uncondensed part flows to a second total condenser and gets accumulated in a receiver vessel (Figure 7.36). The still is charged with 10 kmol of a mixture of A and B and batch distillation continues. What is the composition of the accumulated distillate after 5 kmols of the charge is distilled out? The relative volatility is $\alpha_{AB} = 2.8$.

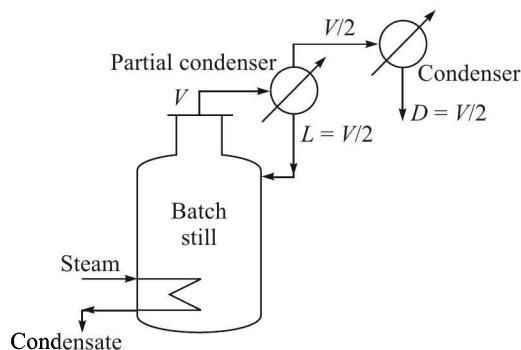


Figure 7.36 A batch still with a partial condenser.

- 7.40 (Continuous distillation using open steam)²** An aqueous solution of ethanol with 25 mole% of the alcohol is to be distilled in a tray column at a rate of 200 kmol/h to get a distillate with 80 mol% ethanol. The feed is at its bubble point. If 95% recovery of the alcohol in the distillate is required, and saturated *open steam* at 1 atm is fed to the bottom of the column, calculate the number of ideal trays required for the separation. A reflux ratio of 2.2 is suggested. Constant molar overflow may be assumed. (The VLE data is given under Example 7.24.)

- 7.41 (Use of the Ponchon–Savarit method)³** A dilute aqueous solution of ethanol is to be concentrated from 20 mass% to 85 mass% alcohol in a tray tower at 1 atm pressure. The feed rate is 8000 kg/h at its bubble point. The bottom product must not contain more than 3.5 mass% ethanol. Determine (a) the minimum reflux ratio, (b) the number of ideal trays, and (c) the reboiler and condenser heat duties. The enthalpy–concentration and the equilibrium data are given under Example 7.24.

- 7.42 (Use of the Ponchon–Savarit method)³** An aqueous solution of ammonia is continuously generated in the absorption column for its recovery from the ammonia reactor bleed stream. Ammonia is separated from this aqueous solution by distillation at around 20 atm pressure. A distillation unit is to be designed for treating 5000 kg/h of a solution containing 25 mass% ammonia. The top product should have 97 mass% ammonia and the bottom must not have more than 1.5% of it. A reflux ratio of 1.6 may be used.

If the feed is at its bubble point, determine (a) the number of ideal trays, (b) the location of the feed tray, and (c) the number of ideal trays if constant molar overflow is assumed.

x or y	0	0.1053	0.2094	0.312	0.414	0.514	0.614	0.712	0.809	0.905
H_L , kcal/kmol	0	-500	-970	-1310	-1540	-1650	-1580	-1400	-960	-520
H_V , kcal/kmol	8430	7955	7660	7495	7210	6920	6620	6300	5980	5470
x or y	0.923	0.942	0.962	0.981	1.00					
H_L , kcal/kmol	-430	-310	-210	-110	0.0					
H_V , kcal/kmol	5350	5240	5050	4870	4250					

[Reference states: pure liquids at their boiling points at 20 atm pressure]

- 7.43 (Calculation of the packed height)²** A saturated aqueous feed (20 mole% ethanol; 50 kmol/h) is to be distilled in a packed tower filled with 1-inch metal Pall ring. The top product should have 80 mole% ethanol and the bottom not more than 2 mole% of it. A reflux ratio of $R = 1.7$ may be used. (a) If a vapour flow rate of 70% of flooding velocity is maintained, determine the tower diameter. (b) Given the following values of heights of individual transfer units— $H_{tG} = 0.4$ m and $H_{tL} = 0.25$ for the enriching section; $H_{tG} = 0.28$ m and $H_{tL} = 0.11$ for the enriching section—calculate the packed height required.
- 7.44 (Packed height and HETP)²** An aqueous solution of methanol (30 mol% methanol; 2000 kg/h) is to be separated in a 0.7 m diameter packed tower to yield a distillate having 97% methanol and a bottom product having 4% methanol. The following values of the volumetric mass transfer coefficients are supplied.

Rectifying section

$$k'_x \bar{a} = 800 \quad k'_y \bar{a} = 170 \quad k'_x \bar{a} = 1250 \quad k'_y \bar{a} = 255 \text{ kmol/(m}^3\text{)(h)(}\Delta x \text{ or } \Delta y\text{)}$$

A reflux ratio of 1.4 times the minimum may be used. Calculate the height of the packed section. Also determine the HEPT of the packing.

- 7.45 (Relation between the reflux ratio and the boil-up ratio)¹** If the relative volatility remains constant, show that the reflux ratio R and the boil-up ratio R_v , are related as follows (Stichlmair and Fair, 1998) for distillation of a binary mixture.

$$R_v = \frac{(D/F)(R+1)-(1-q)}{(1-D/F)}$$

- 7.46 (The minimum reflux ratio if the relative volatility is constant)¹** If the relative volatility is constant and the feed is a saturated liquid, show that the minimum reflux ratio is given by the following expression.

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

- 7.47 (A column receiving cold reflux)²** A saturated liquid feed containing 50 mol% A and 50 mol% B enters a distillation column at a rate of 100 kmol/h. The top product must have 95 mol% A, and 4% of A should leave at the bottom. An external reflux ratio of $R = 2$ is maintained. However, the reflux is subcooled having an enthalpy of 4,000 kJ/kmol of reflux. Given the following relations for enthalpies (kJ/kmol) of saturated liquid and vapour, calculate (a) the equations of the top and the bottom operating lines, and (b) the boil-up ratio.

$$\text{Saturated liquid: } H_L = 9000 - 3000x$$

$$\text{Saturated vapour: } H_L = 40,000 - 3000y$$

- 7.48 (A column receiving open steam)³** An equimolar mixture of methanol and water is to be separated at a rate of 200 kmol/h in a tray tower to yield a top product having 96 mol% methanol. At least 97% of the total methanol is to be recovered. A small reboiler that can generate 150 kmol/h vapour hour is available and will be used. Any additional heat supply necessary will be met by injecting live steam at the bottom. If a reflux ratio of 2.0 is used, determine the amount of live steam to be supplied per hour and the number of ideal trays required. The column operates at essentially atmospheric pressure.
- 7.49 (A leaking batch still)²** Forty kilomols of a mixture of methanol and water (40 mol% methanol) was charged in a still for batch distillation to yield 15 kmol of distillate over a period of 1 hour. Immediately after distillation started, the drainage valve at the bottom of the still was found leaking. The liquid that had leaked out over the period of 1 hour is found to be 5 kmol. Both the rate of distillation and the leakage at the valve occurred at uniform rates. If the relative volatility of methanol is approximately taken as 3.0, calculate the distillate composition and the amount of methanol that had leaked out.
- 7.50 (The minimum reflux ratio for multistage batch distillation)²** An equimolar mixture of A and B having 50 mol% A is to be batch-distilled in a multistage column maintaining a constant reflux ratio. It is desired that the initial distillate should have 90 mol% of A. If the relative volatility of A with respect to B is 3.0, what is the minimum reflux ratio required?
- 7.51 (A packed column operated at total reflux)²** A packed distillation column for separation of benzene and toluene is operated at total reflux. The benzene concentration in the distillate is 97 mol% and that in the bottoms is 2 mol%. If the relative volatility of benzene in the mixture is $\alpha = 2.51$, calculate the number of *overall gas-phase transfer units*.
- 7.52 (A multistage batch distillation unit having a large number of trays)³** It is an interesting exercise to theoretically calculate the separation capability of a multistage batch column having an *infinite number of trays* (see Bauerle and Sandall, *AICHE J.*, June 1987, 1034–1036). An equimolar mixture of A and B ($\alpha_{AB} = 3.5$) is to be batch distilled in a column having a very large number of trays at a constant reflux ratio of 2.5. If one-third of the liquid is distilled out, calculate the composition of the accumulated distillate.
- 7.53 (Number of trays given, get the reflux ratio)³** An equimolar mixture of iso-pentane and benzene is to be separated into a top product having 96 mole% iso-pentane and a bottom product with 95% benzene. The feed rate is 100 kmol/h, saturated vapour. A column of suitable diameter having twenty trays of 40% efficiency and a partial reboiler is available. If saturated liquid reflux is fed back to the column, what reflux ratio should be used to get the desired separation in the column. The average relative volatility is 2.5. (The problem can be solved algebraically as well as by *tray-by-tray* calculation.)
- 7.54 (Stripping of an aqueous solution using open steam)²** Ethanol is to be steam-stripped from a dilute aqueous waste stream in a tray tower using open steam. The feed that has 2.5 mass% ethanol in it is heated to its bubble point before it enters into the column. The

steam rate is 0.25 mole per mole of the feed. At this low concentration, the equilibrium relation is approximately linear, $y = 8.5x$. Determine the number of ideal trays required if 95% of the ethanol is to be removed.

- 7.55 (A column with side streams)³** A distillation column should separate 200 kmol/h of a saturated liquid feed containing 45 mole% methanol and 55 mole%. The top product should have 97 mole% methanol and the bottom, 96 mole% water. The reflux is saturated liquid and a reflux ratio of 2.0 is suggested. A vapour side stream containing 80 mole% methanol is to be withdrawn at a rate of 50 kmol/h from the appropriate tray and condensed in a heat exchanger. Half of it should be taken as an intermediate product and the rest returned into the column as an additional reflux stream. Determine (a) the number of ideal stages required, (b) the feed tray, (c) the tray from which the side stream should be withdrawn, and (d) the tray that should receive the additional reflux.

REFERENCES

- Billet, R., *Distillation Engineering*, Chemical Publishing, 1979.
- Billet, R., *Packed Towers in Processing and Environmental Engineering*, VCH, 1995.
- Divekar, U.M., *Batch Distillation*, Taylor and Francis, 1995.
- Eubank, P.T. et al., ‘Simplify flash calculations’, *Chem. Eng.*, Nov. 2000, 125–130.
- Fair, J.R., ‘Distillation, whither, not whether’, *Chem. Eng. Res. & Des.*, 66(July 1988) 363–370.
- Forbes, R.J., *Short History of the Art of Distillation*, E.J. Brill, Leiden, 1948.
- Hala, M. et al., *Computer-aided Data Book of Vapor-Liquid Equilibria*, Kodansa, Tokyo, 1975.
- Jafarey, A., J.M. Douglas, and T.J. McAvoy, ‘Shortcut techniques for distillation column design and control column design’, *Ind Eng. Chem. Proc. Des. Dev.*, 18(1979) 197–202.
- Kister, H.Z., *Distillation Operation*, McGraw-Hill, New York, 1989.
- Kister, H.Z., *Distillation Design*, McGraw-Hill, New York, 1992.
- Kunesh, J.G. et al., ‘Distillation: still towering over other options’, *Chem. Eng. Progr.*, Oct. 1995, 43–54.
- Lewis, W.K., ‘The efficiency and design of rectifying columns for binary mixtures,’ *Ind. Eng. Chem.*, 14(1922) 492.
- Porter, K.E., ‘Why research is needed in distillation’, *Trans. Inst. Chem. Engrs.*, 73 (Part A), May 1995, 357–362.
- Ryan, J.M., ‘Replotting the McCabe-Thiele diagram’, *Chem. Eng.*, May 2001, 109–113.
- Smoker, E.H., ‘Analytic determination of plates in fractionating columns’, *Trans. AIChE*, 34(1938) 165–172.
- Sorel, E., *La Rectification de l’Alcohol*, Gauthiers Villars, Paris, 1893.
- Stichlmair, J.G., and J.R. Fair, *Distillation—Principles and Practice*, Wiley-VCH, New York, 1998.
- Yuan, K.S., and B.C.-Y. Lu, ‘Vapour-liquid equilibria,’ *J. Chem. Eng. Data*, 8(Oct. 1963) 549.

8

Liquid–Liquid Extraction

Liquid–liquid extraction (sometimes abbreviated LLX) is a mass transfer operation in which a solution (called the *feed* which is a mixture of a solute and a carrier liquid) is brought into intimate contact with a second immiscible or slightly miscible liquid (called the *solvent*) in order to achieve transfer of the solute(s) from the feed to the solvent. The two liquid phases that have different densities are then separated. The solute-rich phase (this is the solvent stream, now enriched with the solute) is called the *extract*; the residual feed stream that may have a little of the solute left in it is called the *raffinate*. If the carrier in the feed and the solvent are partly miscible, the raffinate will also have a little solvent dissolved in it, and the extract phase will contain a little dissolved carrier. The solute is separated from the extract phase in an acceptably pure form, and the solvent dissolved in the raffinate is recovered. An extraction process generally involves four major steps.

- (a) Bringing the feed and the solvent into intimate contact by dispersing one phase into the other as droplets.
- (b) Separation of the extract and the raffinate phases that have different densities.
- (c) Removal and recovery of the solute from the extract phase in a relatively pure form (by distillation, evaporation, crystallization, etc.).
- (d) Removal and recovery of the solvent from each phase, usually by distillation.

Separation of a liquid mixture or solution by distillation is operationally simpler than extraction. For example, a binary liquid mixture having components of different volatilities can, in principle, be separated into two relatively pure products (a ‘distillate’ and a ‘residue’) in a single column. But separation of the same mixture by extraction requires *at least* one distillation column in addition to the extractor. Very often more than one distillation column is used for the recovery of the solvent from the raffinate (called *raffinate clean-up*) and for separation of the carrier liquid from the extract phase (Figure 8.1). Phase separation of the extract and the raffinate may not be rapid if the difference in their densities is small and the interfacial tension is low. Loss of solvent may also occur in some cases. In its totality, solvent extraction is a more elaborate technique than distillation. In a typical liquid–liquid extraction process, only about 15% of the capital cost goes towards the extractor and the remaining 85% goes towards the distillation