Transport Processes and Separation Process Principles

(INCLUDES UNIT OPERATIONS)

FOURTH EDITION

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Chapter 11. Vapor–Liquid Separation Processes

VAPOR–LIQUID EQUILIBRIUM RELATIONS

Phase Rule and Raoult's Law

As in the gas–liquid systems, the equilibrium in vapor–liquid systems is restricted by the phase rule, Eq. (10.2-1). As an example we shall use the ammonia–water, vapor–liquid system. For two components and two phases, F from Eq. (10.2-1) is 2 degrees of freedom. The four variables are temperature, pressure, and the composition y_A of NH_3 in the vapor phase and x_A in the liquid phase. The composition of water (B) is fixed if y_A or x_A is specified, since $y_A + y_B = 1.0$ and $x_A + x_B = 1.0$. If the pressure is fixed, only one more variable can be set. If we set the liquid composition, the temperature and vapor composition are automatically set.

An ideal law, *Raoult's law,* can be defined for vapor–liquid phases in equilibrium:

Equation 11.1-1.

$$p_A = P_A x_A$$

where p_A is the partial pressure of component A in the vapor in Pa (atm), P_A is the vapor pressure of pure A in Pa (atm), and x_A is the mole fraction of A in the liquid. This law holds only for ideal solutions, such as benzene–toluene, hexane–heptane, and methyl alcohol– ethyl alcohol, which are usually substances very similar to each other. Many systems that are ideal or nonideal solutions follow Henry's law in dilute solutions.

Boiling-Point Diagrams and *x*-*y* Plots

Often the vapor–liquid equilibrium relations for a binary mixture of A and B are given as a boiling-point diagram, shown in Fig. 11.1-1 for the system benzene (A)–toluene (B) at a total pressure of 101.32 kPa. The upper line is the saturated vapor line (the *dew-point line*) and the lower line is the saturated liquid line (the *bubble-point line*). The two-phase region is in the region between these two lines.

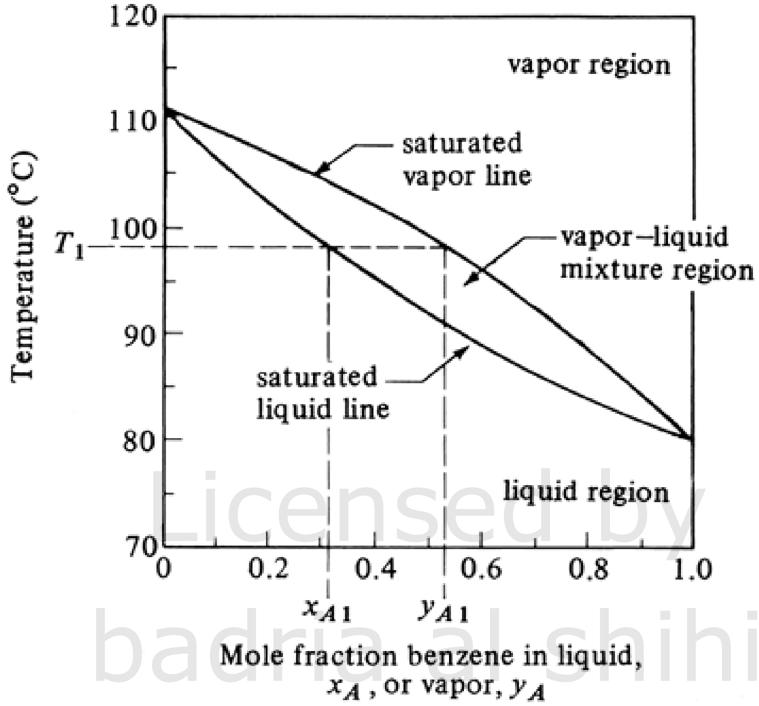

Figure 11.1-1. Boiling point diagram for benzene (A)–toluene (B) at 101.325 kPa (1 atm) total pressure.

In Fig. 11.1-1, if we start with a cold liquid mixture of $x_{A1} = 0.318$ and heat the mixture, it will start to boil at 98°C (371.2 K), and the composition of the first vapor in equilibrium is $y_{A1} = 0.532$. As we continue boiling, the composition x_A will move to the left since y_A is richer in A.

The system benzene–toluene follows Raoult's law, so the boiling-point diagram can be calculated from the pure vapor-pressure data in Table 11.1-1 and the following equations:

Equation 11.1-2.

$$p_A + p_B = P$$

Equation 11.1-3.

$$P_A x_A + P_B(1 - x_A) = P$$

Equation 11.1-4.

$$y_A = \frac{p_A}{P} = \frac{P_A x_A}{P}$$

Table 11.1-1. Vapor-Pressure and Equilibrium-Mole-Fraction Data for Benzene–Toluene System

Temperature		Vapor Pressure Benzene		Toluene		Mole Fraction Benzene at 101.325 kPa	
K	°C	kPa	mm Hg	kPa	mm Hg	x_A	y_A
353.3	80.1	101.32	760			1.000	1.000
358.2	85	116.9	877	46.0	345	0.780	0.900
363.2	90	135.5	1016	54.0	405	0.581	0.777
368.2	95	155.7	1168	63.3	475	0.411	0.632
373.2	100	179.2	1344	74.3	557	0.258	0.456

Temperature		*Vapor Pressure*				*Mole Fraction Benzene at 101.325 kPa*	
		Benzene		*Toluene*			
K	*°C*	*kPa*	*mm Hg*	*kPa*	*mm Hg*	x_A	y_A
378.2	105	204.2	1532	86.0	645	0.130	0.261
383.8	110.6	240.0	1800	101.32	760	0	0

EXAMPLE 11.1-1. Use of Raoult's Law for Boiling-Point Diagram

Calculate the vapor and liquid compositions in equilibrium at 95°C (368.2 K) for benzene–toluene using the vapor pressure from Table 11.1-1 at 101.32 kPa.

Solution: At 95°C from Table 11.1-1 for benzene, P_A = 155.7 kPa and P_B = 63.3 kPa. Substituting into Eq. (11.1-3) and solving,

$$155.7(x_A) + 63.3(1 - x_A) = 101.32 \text{ kPa } (760 \text{ mm Hg})$$

Hence, $x_A = 0.411$ and $x_B = 1 - x_A = 1 - 0.411 = 0.589$. Substituting into Eq. (11.1-4),

$$y_A = \frac{P_A x_A}{P} = \frac{155.7(0.411)}{101.32} = 0.632$$

A common method of plotting the equilibrium data is shown in Fig. 11.1-2, where y_A is plotted versus x_A for the benzene–toluene system. The 45° line is given to show that y_A is richer in component *A* than is x_A.

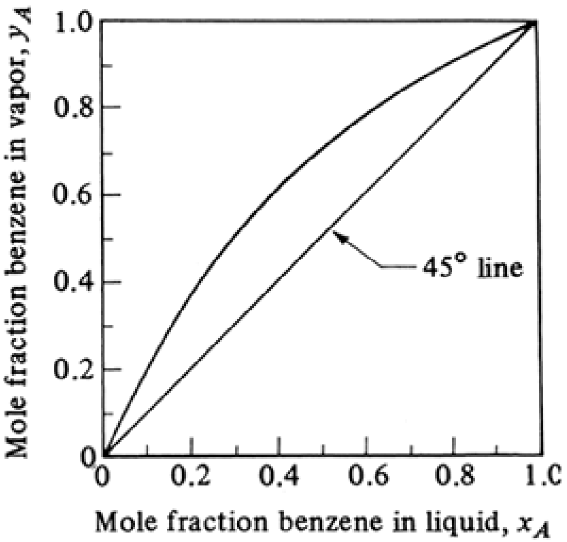

Figure 11.1-2. Equilibrium diagram for system benzene (A)–toluene (B) at 101.32 kPa (1 atm).

The boiling-point diagram in Fig. 11.1-1 is typical of an ideal system following Raoult's law. Nonideal systems differ considerably. In Fig. 11.1-3a the boiling-point diagram is shown for a maximum-boiling azeotrope. The maximum temperature T_{max} corresponds to a concentration x_{Az} and $x_{Az} = y_{Az}$ at this point. The plot of y_A versus x_A would show the curve crossing the 45° line at this point. Acetone–chloroform is an example of such a system. In Fig. 11.1-3b a minimum-boiling azeotrope is shown with $y_{Az} = x_{Az}$ at T_{min}. Ethanol–water is such a system.

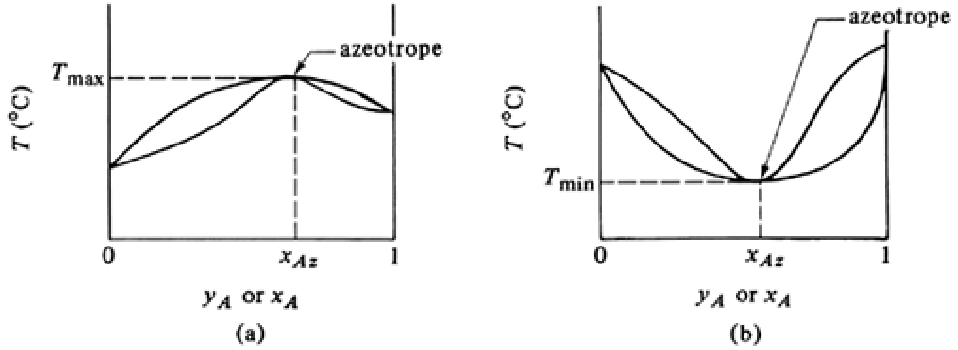

Figure 11.1-3. Equilibrium boiling-point diagrams: (a) maximum-boiling azeotrope, (b) minimum-boiling azeotrope.

SINGLE-STAGE EQUILIBRIUM CONTACT FOR VAPOR–LIQUID SYSTEM

If a vapor–liquid system is being considered, where the stream V_2 is a vapor and L_0 is a liquid, and the two streams are brought into contact in a single equilibrium stage which is quite similar to Fig. 10.3-1, the boiling point or the *x-y* equilibrium diagram must be used, because an equilibrium relation similar to Henry's law is not available. Since we are considering only two components, *A* and *B*, only Eqs. (10.3-1) and (10.3-2) are used for the material balances. If sensible heat effects are small and the latent heats of both compounds are the same, then when 1 mol of *A* condenses, 1 mol of *B* must vaporize. Hence, the total moles of vapor V_2 entering will equal V_1 leaving. Also, moles $L_0 = L_1$. This case is called one of *constant molal overflow.* An example is the benzene–toluene system.

EXAMPLE 11.2-1. Equilibrium Contact of Vapor–Liquid Mixture

A vapor at the dew point and 101.32 kPa containing a mole fraction of 0.40 benzene (*A*) and 0.60 toluene (*B*) and 100 kg mol total is brought into contact with 110 kg mol of a liquid at the boiling point containing a mole fraction of 0.30 benzene and 0.70 toluene. The two streams are contacted in a single stage, and the outlet streams leave in equilibrium with each other. Assume constant molal overflow. Calculate the amounts and compositions of the exit streams.

***Solution*:** The process flow diagram is the same as in Fig. 10.3-1. The given values are V_2 = 100 kg mol, y_{A2} = 0.40, L_0 = 110 kg mol, and x_{A0} = 0.30. For constant molal overflow, $V_2 = V_1$ and $L_0 = L_1$. Substituting into Eq. (10.3-2) to make a material balance on component *A*,

Equation 10.3-2.

$$L_0 x_{A0} + V_2 y_{A2} = L_1 x_{A1} + V_1 y_{A1}$$

Equation 11.2-1.

$$110(0.30) + 100(0.40) = 110x_{A1} + 100y_{A1}$$

To solve Eq. (11.2-1), the equilibrium relation between y_{A1} and x_{A1} in Fig. 11.1-1 must be used. This is by trial and error, since an analytical expression is not available that relates y_A and x_A.

First, we assume that x_{A1} = 0.20 and substitute into Eq. (11.2-1) to solve for y_{A1}:

$$110(0.30) + 100(0.40) = 110(0.20) + 100y_{A1}$$

Solving, y_{A1} = 0.51. The equilibrium relations for benzene–toluene are plotted in Fig. 11.2-1. It is evident that y_{A1} = 0.51 and x_{A1} = 0.20 do not fall on the curve. This point is plotted on the graph. Next, assuming that x_{A1} = 0.40 and solving, y_{A1} = 0.29. This point is also plotted in Fig. 11.2-1. Assuming that x_{A1} = 0.30, y_{A1} = 0.40. A straight line is drawn between these three points which represents Eq. (11.2-1). At the intersection of this line with the equilibrium curve, y_{A1} = 0.455 and x_{A1} = 0.25, which agree with Eq. (11.2-1).

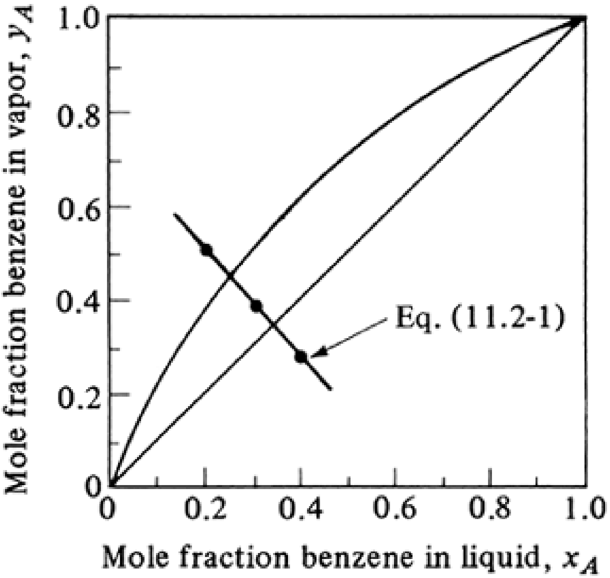

Figure 11.2-1. Solution to Example 11.2-1.

SIMPLE DISTILLATION METHODS

Introduction

The separation process known as distillation is a method for separating the various components of a liquid solution which depends upon the distribution of these components between a vapor phase and a liquid phase. All components are present in both phases. The vapor phase is created from the liquid phase by vaporization at the boiling point.

The basic requirement for the separation of components by distillation is that the composition of the vapor be different from the composition of the liquid with which it is in equilibrium at the boiling point of the liquid. Distillation is concerned with solutions where all components are appreciably volatile, such as ammonia–water or ethanol–water solutions, where both components will be in the vapor phase. In evaporation, by contrast, of a solution of salt and water, for example the water is vaporized but the salt is not. The process of absorption differs from distillation in that one of the components in absorption is essentially insoluble in the liquid phase. An example is absorption of ammonia from air by water, where air is insoluble in the water–ammonia solution.

Relative Volatility of Vapor–Liquid Systems

In Fig. 11.1-2, the equilibrium diagram for a binary mixture of *A* and *B*, the greater the distance between the equilibrium line and the 45° line, the greater the difference between the vapor composition y_A and liquid composition x_A. Hence, the separation is more easily made. A numerical measure of this separation is the relative volatility α_{AB}. This is defined as the ratio of the concentration of *A* in the vapor to the concentration of *A* in the liquid divided by the ratio of the concentration of *B* in the vapor to the concentration of *B* in the liquid:

Equation 11.3-1.

$$\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A/x_A}{(1 - y_A)/(1 - x_A)}$$

where α_{AB} is the relative volatility of *A* with respect to *B* in the binary system.

If the system obeys Raoult's law, as does the benzene–toluene system,

Equation 11.3-2.

$$y_A = \frac{P_A x_A}{P} \qquad y_B = \frac{P_B x_B}{P}$$

Substituting Eq. (11.3-2) into (11.3-1) for an ideal system,

Equation 11.3-3.

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

Equation (11.3-1) can be rearranged to give

Equation 11.3-4.

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A}$$

where $\alpha = \alpha_{AB}$. When the value of α is above 1.0, a separation is possible. The value of α may change as concentration changes. When binary systems follow Raoult's law, the relative volatility often varies only slightly over a large concentration range at constant total pressure.

EXAMPLE 11.3-1. Relative Volatility for Benzene–Toluene System

Using the data from Table 11.1-1, calculate the relative volatility for the benzene–toluene system at 85°C (358.2 K) and 105°C (378.2 K).

Solution: At 85°C, substituting into Eq. (11.3-3) for a system following Raoult's law,

$$\alpha = \frac{P_A}{P_B} = \frac{116.9}{46.0} = 2.54$$

Similarly at 105°C,

$$\alpha = \frac{204.2}{86.0} = 2.38$$

The variation in α is about 7%.

Equilibrium or Flash Distillation

Introduction to distillation methods

Distillation can be carried out by either of two main methods in practice. The first method of distillation involves the production of a vapor by boiling the liquid mixture to be separated in a single stage and recovering and condensing the vapors. No liquid is allowed to return to the single-stage still to contact the rising vapors. The second method of distillation involves the returning of a portion of the condensate to the still. The vapors rise through a series of stages or trays, and part of the condensate flows downward through the series of stages or trays countercurrent to the vapors. This second method is called *fractional distillation, distillation with reflux,* or *rectification.*

There are three important types of distillation that occur in a single stage or still and that do not involve rectification. The first of these is equilibrium or flash distillation, the second is simple batch or differential distillation, and the third is simple steam distillation.

Equilibrium or flash distillation

In *equilibrium* or *flash distillation,* which occurs in a single stage, a liquid mixture is partially vaporized. The vapor is allowed to come to equilibrium with the liquid, and the vapor and liquid phases are then separated. This can be done batchwise or continuously.

In Fig. 11.3-1 a binary mixture of components *A* and *B* flowing at the rate of *F* mol/h into a heater is partially vaporized. Then the mixture reaches equilibrium and is separated. The composition of *F* is x_F mole fraction of *A*. A total material balance on component *A* is as follows:

Equation 11.3-5.

$$Fx_F = Vy + Lx$$

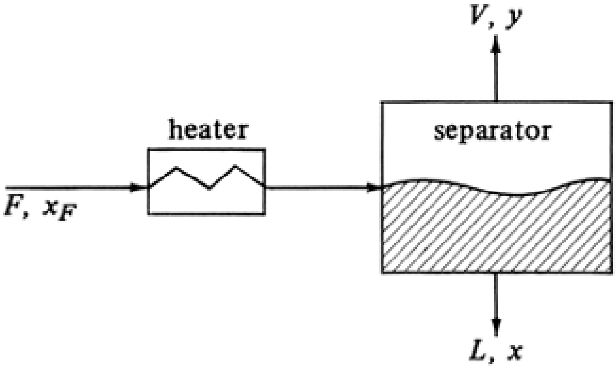

Figure 11.3-1. Equilibrium or flash distillation.

Since $L = F - V$, Eq. (11.3-5) becomes

Equation 11.3-6.

$$Fx_F = Vy + (F - V)x$$

Usually, the moles per hour of feed *F*, moles per hour of vapor *V*, and moles per hour of *L* are known or set. Hence, there are two unknowns *x* and *y* in Eq. (11.3-6). The other relationship needed in order to solve Eq. (11.3-6) is the equilibrium line. A convenient method to use is to plot Eq. (11.3-6) on the *x*-*y* equilibrium diagram. The intersection of the equation and the equilibrium line is the desired solution. This is similar to Example 11.2-1 and shown in Fig. 11.2-1.

Simple Batch or Differential Distillation

In *simple batch* or *differential distillation,* liquid is first charged to a heated kettle. The liquid charge is boiled slowly and the vapors are withdrawn as rapidly as they form to a condenser, where the condensed vapor (distillate) is collected. The first portion of vapor condensed will be richest in the more volatile component *A*. As vaporization proceeds, the vaporized product becomes leaner in *A*.

In Fig. 11.3-2 a simple still is shown. Originally, a charge of L_1 moles of components *A* and *B* with a composition of x_1 mole fraction of *A* is placed in the still. At any given time, there are *L* moles of liquid left in the still with composition *x*, and the composition of the vapor leaving in equilibrium is *y*. A differential amount *dL* is vaporized.

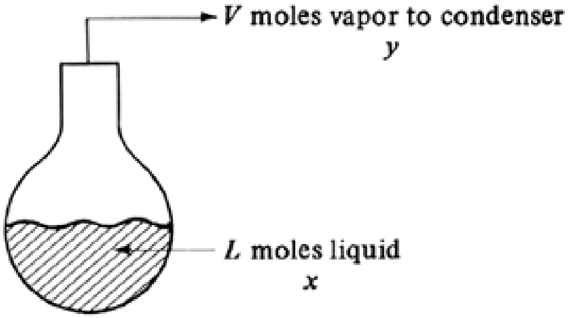

Figure 11.3-2. Simple batch or differential distillation.

The composition in the still pot changes with time. In deriving the equation for this process, we assume that a small amount of dL is vaporized. The composition of the liquid changes from x to $x - dx$ and the amount of liquid from L to $L - dL$. A material balance on A can be made, where the original amount = the amount left in the liquid + the amount of vapor:

Equation 11.3-7.

$$xL = (x - dx)(L - dL) + y\,dL$$

Multiplying out the right side,

Equation 11.3-8.

$$xL = xL - x\,dL - L\,dx + dx\,dL + y\,dL$$

Neglecting the term $dx\,dL$ and rearranging,

Equation 11.3-9.

$$\frac{dL}{L} = \frac{dx}{y - x}$$

Integrating,

Equation 11.3-10.

$$\int_{L_2}^{L_1} \frac{dL}{L} = \ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{dx}{y - x}$$

where L_1 is the original moles charged, L_2 the moles left in the still, x_1 the original composition, and x_2 the final composition of liquid.

The equilibrium curve gives the relationship between y and x. The integration of Eq. (11.3-10) can be done by calculating values of $f(x) = 1/(y - x)$ and numerically or graphically integrating Eq. (11.3-10) between x_1 and x_2. Equation (11.3-10) is known as the *Rayleigh equation.* The average composition of total material distilled, y_{av}, can be obtained by material balance:

Equation 11.3-11.

$$L_1x_1 = L_2x_2 + (L_1 - L_2)y_{av}$$

EXAMPLE 11.3-2. Simple Differential Distillation

A mixture of 100 mol containing 50 mol % *n*-pentane and 50 mol % *n*-heptane is distilled under differential conditions at 101.3 kPa until 40 mol is distilled. What is the average composition of the total vapor distilled and the composition of the liquid left? The equilibrium data are as follows, where x and y are mole fractions of *n*-pentane:

x	y	x	y	x	y
1.000	1.000	0.398	0.836	0.059	0.271
0.867	0.984	0.254	0.701	0	0
0.594	0.925	0.145	0.521		

Solution. The given values to be used in Eq. (11.3-10) are L_1 = 100 mol, x_1 = 0.50, L_2 = 60 mol, and V (moles distilled) = 40 mol. Substituting into Eq. (11.3-10),

Equation 11.3-12.

$$\ln \frac{100}{60} = 0.510 = \int_{x_2}^{x_1=0.5} \frac{dx}{y-x}$$

The unknown is x_2, the composition of the liquid L_2 at the end of the differential distillation. To solve this by numerical integration, equilibrium values of y versus x are plotted so values of y can be obtained from this curve at small intervals of x. Alternatively, instead of plotting, the equilibrium data can be fitted to a polynomial function. For x = 0.594, the equilibrium value of y = 0.925. Then $f(x) = 1/(y - x) = 1/(0.925 - 0.594) = 3.02$. Other values of $f(y)$ are similarly calculated.

The numerical integration of Eq. (11.3-10) is performed from x_1 = 0.5 to x_2 such that the integral = 0.510 by Eq. (11.3-12) in Fig. 11.3-3. Hence, x_2 = 0.277. Substituting into Eq. (11.3-11) and solving for the average composition of the 40 mol distilled,

$$100(0.50) = 60(0.277) + 40(y_{\text{av}})$$

$$y_{\text{av}} = 0.835$$

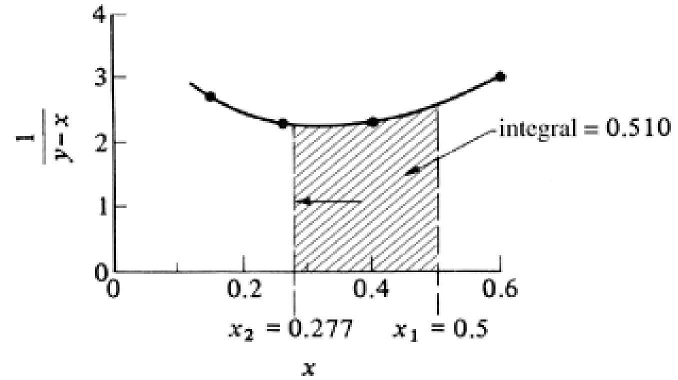

Figure 11.3-3. Numerical integration for Example 11.3-2.

Simple Steam Distillation

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

If a layer of liquid water (A) and an immiscible high-boiling component (B) such as a hydrocarbon are boiled at 101.3 kPa abs pressure, then, by the phase rule, Eq. (10.2-1), for three phases and two components,

$$F = 2 - 3 + 2 = 1 \text{ degree of freedom}$$

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

Equation 11.3-13.

$$P_A + P_B = P$$

where P_A is vapor pressure of pure water A and P_B is vapor pressure of pure B. Then the vapor composition is

Equation 11.3-14.

$$y_A = \frac{P_A}{P} \qquad y_B = \frac{P_B}{P}$$

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

Note that by steam distillation, as long as liquid water is present, the high-boiling component B vaporizes at a temperature well below its normal boiling point without using a vacuum. The vapors of water (A) and high-boiling component (B) are usually condensed in a condenser and the resulting two immiscible liquid phases separated. This method has the disadvantage that large amounts of heat must be used to evaporate the water simultaneously with the high-boiling compound.

The ratio moles of B distilled to moles of A distilled is

Equation 11.3-15.

$$\frac{n_B}{n_A} = \frac{P_B}{P_A}$$

Steam distillation is sometimes used in the food industry for the removal of volatile taints and flavors from edible fats and oils. In many cases vacuum distillation is used instead of steam distillation to purify high-boiling materials. The total pressure is quite low so that the vapor pressure of the system reaches the total pressure at relatively low temperatures.

Van Winkle (V1) derives equations for steam distillation where an appreciable amount of a nonvolatile component is present with the high-boiling component. This involves a three-component system. He also considers other cases for binary batch, continuous, and multicomponent batch steam distillation.

DISTILLATION WITH REFLUX AND McCABE–THIELE METHOD

Introduction to Distillation with Reflux

Rectification (fractionation) or stage distillation with reflux, from a simplified point of view, can be considered to be a process in which a series of flash-vaporization stages are arranged in a series in such a manner that the vapor and liquid products from each stage flow counter current to each other. The liquid in a stage is conducted or flows to the stage below and the vapor from a stage flows upward to the stage above. Hence, in each stage a vapor stream V and a liquid stream L enter, are mixed and equilibrated, and a vapor and a liquid stream leave in equilibrium. This process flow diagram was shown in Fig. 10.3-1 for a single stage and an example given in Example 11.2-1 for a benzene–toluene mixture.

For the countercurrent contact with multiple stages in Fig. 10.3-2, the material-balance or operating-line equation (10.3-13) was derived, which relates the concentrations of the vapor and liquid streams passing each other in each stage. In a distillation column the stages (referred to as *sieve plates* or *trays*) in a distillation tower are arranged vertically, as shown schematically in Fig. 11.4-1.

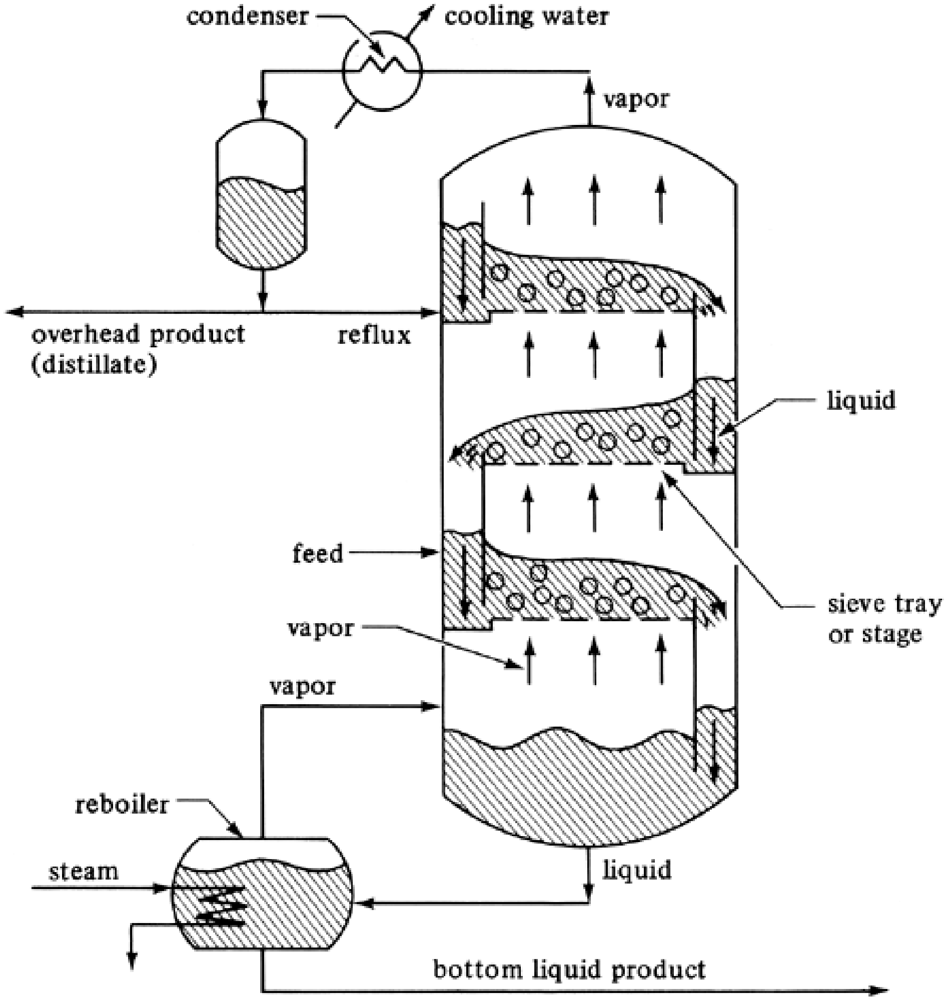

Figure 11.4-1. Process flow of a fractionating tower containing sieve trays.

The feed enters the column in Fig. 11.4-1 somewhere in the middle of the column. If the feed is liquid, it flows down to a sieve tray or stage. Vapor enters the tray and bubbles through the liquid on this tray as the entering liquid flows across. The vapor and liquid leaving the tray are essentially in equilibrium. The vapor continues up to the next tray or stage, where it is again contacted with a downflowing liquid. In this case the concentration of the more volatile component (the lower-boiling component *A*) is being increased in the vapor from each stage going upward and decreased in the liquid from each stage going downward. The final vapor product coming overhead is condensed in a condenser and a portion of the liquid product (distillate) is removed, which contains a high concentration of *A*. The remaining liquid from the condenser is returned (refluxed) as a liquid to the top tray.

The liquid leaving the bottom tray enters a reboiler, where it is partially vaporized, and the remaining liquid, which is lean in *A* or rich in *B*, is withdrawn as liquid product. The vapor from the reboiler is sent back to the bottom stage or tray. Only three trays are shown in the tower of Fig. 11.4-1. In most cases the number of trays is much greater. In the sieve tray the vapor enters through an opening and bubbles up through the liquid to provide intimate contact between the liquid and vapor on the tray. In a theoretical tray the vapor and liquid leaving are in equilibrium. The reboiler can be considered as a theoretical stage or tray.

McCabe–Thiele Method of Calculation for Number of Theoretical Stages

Introduction and assumptions

A mathematical–graphical method for determining the number of theoretical trays or stages needed for a given separation of a binary mixture of *A* and *B* has been developed by McCabe and Thiele. The method uses material balances around certain parts of the tower, which give operating lines somewhat similar to Eq. (10.3-13), and the *x*-*y* equilibrium curve for the system.

The main assumption made in the McCabe–Thiele method is that there must be equimolar overflow through the tower between the feed inlet and the top tray and the feed inlet and bottom tray. This is shown in Fig. 11.4-2, where liquid and vapor streams enter a tray, are equilibrated, and leave. A total material balance gives

Equation 11.4-1.

$$V_{n+1} + L_{n-1} = V_n + L_n$$

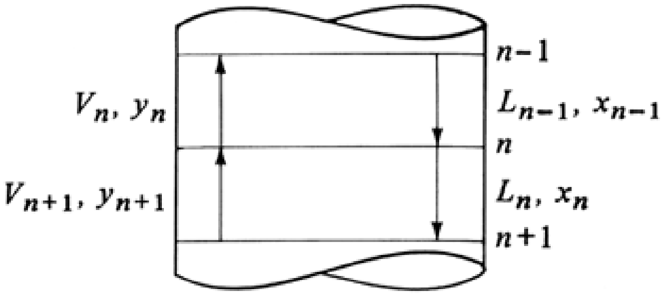

Figure 11.4-2. Vapor and liquid flows entering and leaving a tray.

A component balance on *A* gives

Equation 11.4-2.

$$V_{n+1}y_{n+1} + L_{n-1}x_{n-1} = V_n y_n + L_n x_n$$

where V_{n+1} is mol/h of vapor from tray $n + 1$, L_n is mol/h liquid from tray n, y_{n+1} is mole fraction of A in V_{n+1}, and so on. The compositions y_n and x_n are in equilibrium and the temperature of the tray n is T_n. If T_n is taken as a datum, it can be shown by a heat balance that the sensible heat differences in the four streams are quite small if heats of solution are negligible. Hence, only the latent heats in streams V_{n+1} and V_n are important. Since molar latent heats for chemically similar compounds are almost the same, $V_{n+1} = V_n$ and $L_n = L_{n-1}$. Therefore, we have constant molal overflow in the tower.

Equations for enriching section

In Fig. 11.4-3 a continuous-distillation column is shown, with feed being introduced to the column at an intermediate point and an overhead distillate product and a bottoms product being withdrawn. The upper part of the tower above the feed entrance is called the *enriching section,* since the entering feed of binary components A and B is enriched in this section, so that the distillate is richer in A than the feed. The tower is at steady state.

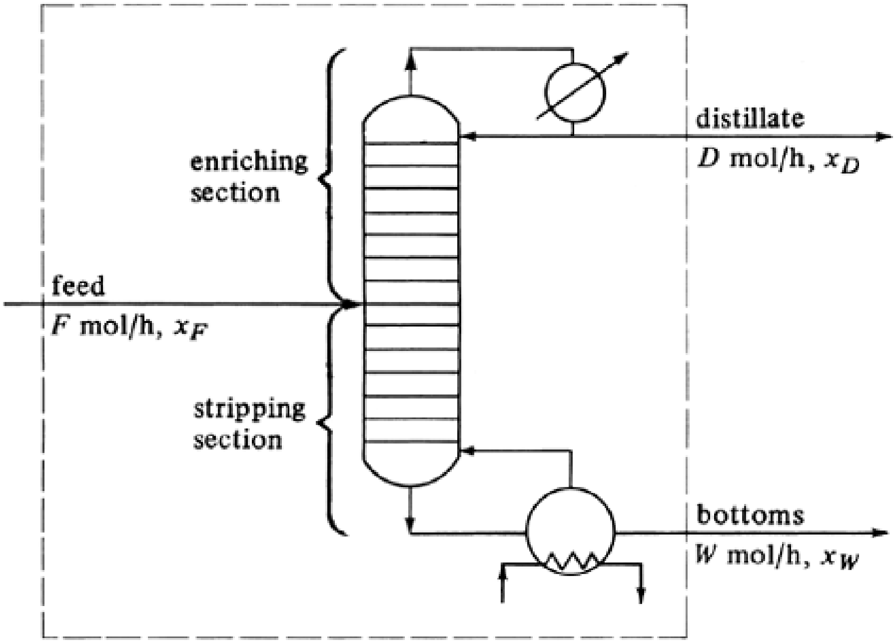

Figure 11.4-3. Distillation column showing material-balance sections for McCabe–Thiele method.

An overall material balance around the entire column in Fig. 11.4-3 states that the entering feed of F mol/h must equal the distillate D in mol/h plus the bottoms W in mol/h:

Equation 11.4-3.

$$F = D + W$$

A total material balance on component A gives

Equation 11.4-4.

$$Fx_F = Dx_D + Wx_W$$

In Fig. 11.4-4a the distillation-tower section above the feed, the enriching section, is shown schematically. The vapor from the top tray having a composition y_1 passes to the condenser, where it is condensed so that the resulting liquid is at the boiling point. The reflux stream L mol/h and distillate D mol/h have the same composition, so $y_1 = x_D$. Since equimolal overflow is assumed, $L_1 = L_2 = L_n$ and $V_1 = V_2 = V_n = V_{n+1}$.

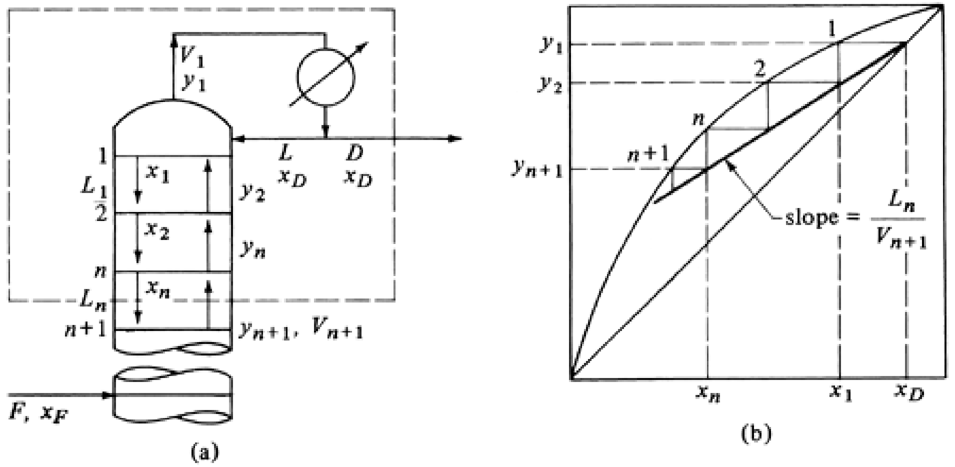

Figure 11.4-4. Material balance and operating line for enriching section: (a) schematic of tower, (b) operating and equilibrium lines.

Making a total material balance over the dashed-line section in Fig. 11.4-4a,

Equation 11.4-5.

$$V_{n+1} = L_n + D$$

Making a balance on component *A*,

Equation 11.4-6.

$$V_{n+1} y_{n+1} = L_n x_n + D x_D$$

Solving for y_{n+1}, the enriching-section operating line is

Equation 11.4-7.

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{D x_D}{V_{n+1}}$$

Since $V_{n+1} = L_n + D$, $L_n/V_{n+1} = R/(R + 1)$ and Eq. (11.4-7) becomes

Equation 11.4-8.

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$$

where $R = L_n/D$ = reflux ratio = constant. Equation (11.4-7) is a straight line on a plot of vapor composition versus liquid composition. It relates the compositions of two streams passing each other and is plotted in Fig. 11.4-4b. The slope is L_n/V_{n+1} or $R/(R + 1)$, as given in Eq. (11.4-8). It intersects the $y = x$ line (45° diagonal line) at $x = x_D$. The intercept of the operating line at $x = 0$ is $y = x_D/(R + 1)$.

The theoretical stages are determined by starting at x_D and stepping off the first plate to x_1. Then y_2 is the composition of the vapor passing the liquid x_1. In a similar manner, the other theoretical trays are stepped off down the tower in the enriching section to the feed tray.

Equations for stripping section

Making a total material balance over the dashed-line section in Fig. 11.4-5a for the stripping section of the tower below the feed entrance,

Equation 11.4-9.

$$V_{m+1} = L_m - W$$

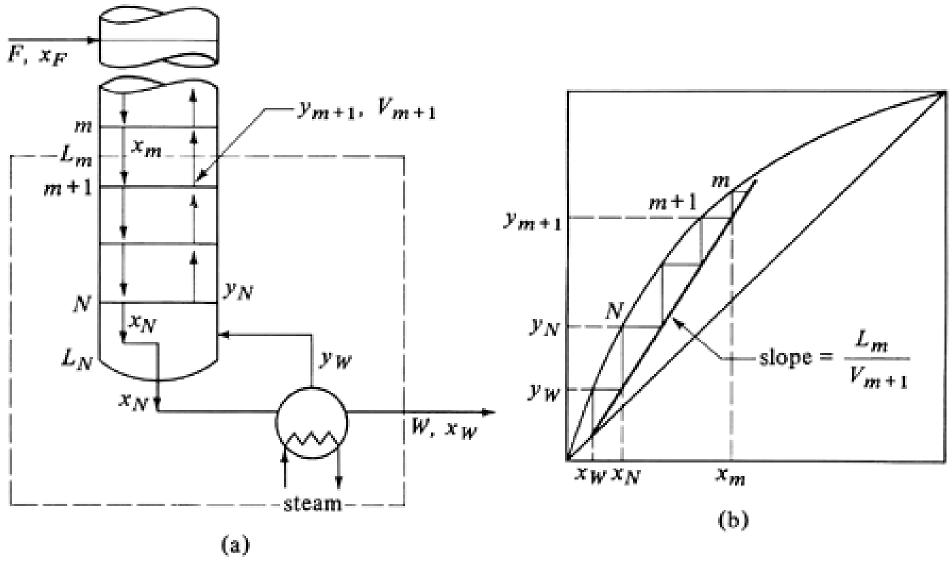

Figure 11.4-5. Material balance and operating line for stripping section: (a) schematic of tower, (b) operating and equilibrium lines.

Making a balance on component *A*,

Equation 11.4-10.

$$V_{m+1} y_{m+1} = L_m x_m - W x_W$$

Solving for y_{m+1}, the stripping-section operating line is

Equation 11.4-11.

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{W x_W}{V_{m+1}}$$

Again, since equimolal flow is assumed, $L_m = L_N$ = constant and $V_{m+1} = V_N$ = constant. Equation (11.4-11) is a straight line when plotted as *y* versus *x* in Fig. 11.4-5b, with a slope of L_m/V_{m+1}. It intersects the $y = x$ line at $x = x_W$. The intercept at $x = 0$ is $y = -Wx_W/V_{m+1}$.

Again the theoretical stages for the stripping section are determined by starting at x_W, going up to y_W, and then across to the operating line, and so on.

Effect of feed conditions

The condition of the feed stream *F* entering the tower determines the relation between the vapor V_m in the stripping section and V_n in the enriching section as well as between L_m and L_n. If the feed is part liquid and part vapor, the vapor will add to V_m to give V_n.

For convenience, we represent the condition of the feed by the quantity *q*, which is defined as

Equation 11.4-12.

$$q = \frac{\text{heat needed to vaporize 1 mol of feed at entering conditions}}{\text{molar latent heat of vaporization of feed}}$$

If the feed enters at its boiling point, the numerator of Eq. (11.4-12) is the same as the denominator, and $q = 1.0$. Equation (11.4-12) can also be written in terms of enthalpies:

Equation 11.4-13.

$$q = \frac{H_V - H_F}{H_V - H_L}$$

where H_V is the enthalpy of the feed at the dew point, H_L the enthalpy of the feed at the boiling point (bubble point), and H_F the enthalpy of the feed at its entrance conditions. If the feed enters as vapor at the dew point, $q = 0$. For cold liquid feed $q > 1.0$, for superheated vapor $q < 0$, and for the feed being part liquid and part vapor, q is the fraction of feed that is liquid.

We can also look at q as the number of moles of saturated liquid produced on the feed plate by each mole of feed added to the tower. In Fig. 11.4-6 a diagram shows the relationship between flows above and below the feed extrance. From the definition of q, the following equations hold:

Equation 11.4-14.

$$L_m = L_n + qF$$

Equation 11.4-15.

$$V_n = V_m + (1 - q)F$$

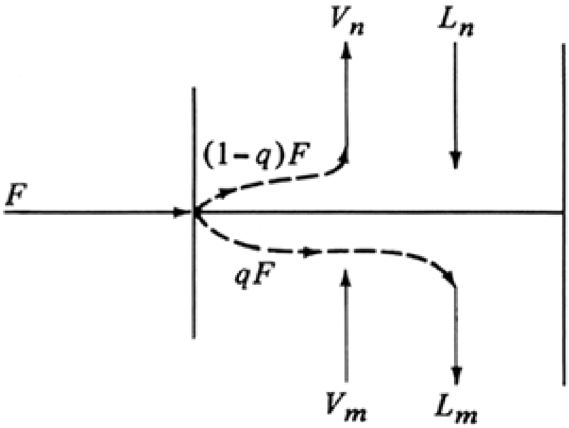

Figure 11.4-6. Relationship between flows above and below the feed entrance.

The point of intersection of the enriching and the stripping operating-line equations on an x-y plot can be derived as follows. Rewriting Eqs. (11.4-6) and (11.4-10) as follows without the tray subscripts:

Equation 11.4-16.

$$V_n y = L_n x + D x_D$$

Equation 11.4-17.

$$V_m y = L_m x - W x_W$$

where the y and x values are the point of intersection of the two operating lines. Subtracting Eq. (11.4-16) from (11.4-17),

Equation 11.4-18.

$$(V_m - V_n)y = (L_m - L_n)x - (D x_D + W x_W)$$

Substituting Eqs. (11.4-4), (11.4-14), and (11.4-15) into Eq. (11.4-18) and rearranging,

Equation 11.4-19.

$$y = \frac{q}{q-1}x - \frac{x_F}{q-1}$$

This equation is the q-line equation and is the locus of the intersection of the two operating lines. Setting $y = x$ in Eq. (11.4-19), the intersection of the q-line equation with the 45° line is $y = x = x_F$, where x_F is the overall composition of the feed.

In Fig. 11.4-7 the q line is plotted for various feed conditions given below the figure. The slope of the q line is $q/(q - 1)$. For example, for the liquid below the boiling point, $q > 1$, and the slope is >1.0, as shown. The enriching and operating lines are plotted for the case of a feed of part liquid and part vapor, and the two lines intersect on the q line. A convenient way to locate the stripping operating line is to first plot the enriching operating line and the q line. Then draw the stripping line between the intersection of the q line and enriching operating line and the point $y = x = x_W$.

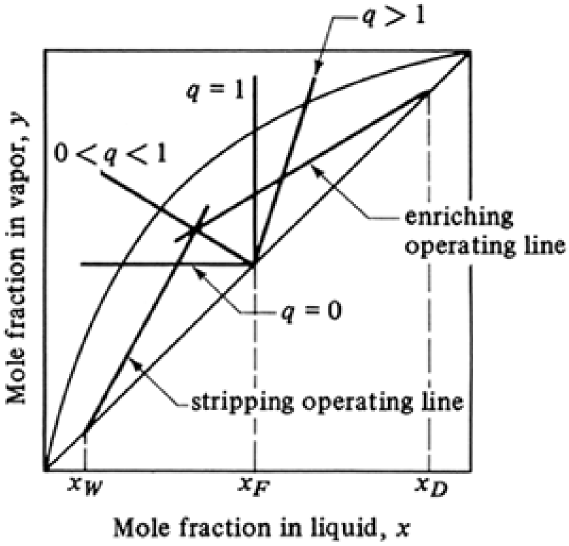

Figure 11.4-7. Location of the q line for various feed conditions: liquid below boiling point (q > 1), liquid at boiling point (q = l), liquid + vapor (0 < q < 1), saturated vapor (q = 0).

Location of the feed tray in a tower and number of trays

To determine the number of theoretical trays needed in a tower, the stripping and operating lines are drawn to intersect on the q line, as shown in Fig. 11.4-8. Starting at the top at x_D, the trays are stepped off. For trays 2 and 3, the steps can go to the enriching operating line, as shown in Fig. 11.4-8a. At step 4 the step goes to the stripping line. A total of about 4.6 theoretical steps are needed. The feed enters on tray 4.

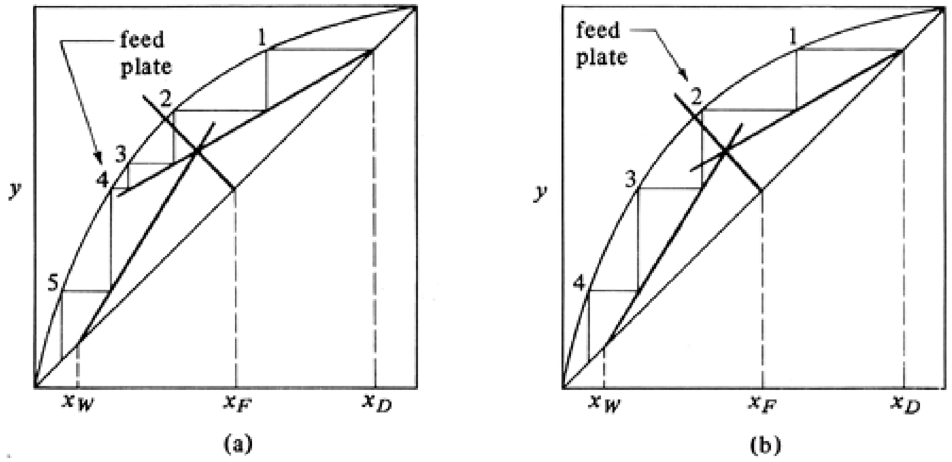

Figure 11.4-8. Method of stepping off number of theoretical trays and location of feed plate: (a) improper location of feed on tray 4, (b) proper location of feed on tray 2 to give minimum number of steps.

For the correct method, the shift is made on step 2 to the stripping line, as shown in Fig. 11.4-8b. A total of only about 3.7 steps are needed, with the feed on tray 2. To keep the number of trays to a minimum, the shift from the enriching to the stripping operating line should be made at the first opportunity after passing the operating-line intersection.

In Fig. 11.4-8b the feed is part liquid and part vapor, since $0 < q < 1$. Hence, in adding the feed to tray 2, the vapor portion of the feed is separated and added beneath plate 2 and the liquid added to the liquid from above entering tray 2. If the feed is all liquid, it should be added to the liquid flowing to tray 2 from the tray above. If the feed is all vapor, it should be added below tray 2 and join the vapor rising from the plate below.

Since a reboiler is considered a theoretical step, when the vapor y_W is in equilibrium with x_W, as in Fig. 11.4-5b, the number of theoretical trays in a tower is equal to the number of theoretical steps minus one.

EXAMPLE 11.4-1. Rectification of a Benzene–Toluene Mixture

A liquid mixture of benzene–toluene is to be distilled in a fractionating tower at 101.3 kPa pressure. The feed of 100 kg mol/h is liquid, containing 45 mol % benzene and 55 mol % toluene, and enters at 327.6 K (130°F). A distillate containing 95 mol % benzene and 5 mol % toluene and a bottoms containing 10 mol % benzene and 90 mol % toluene are to be obtained. The reflux ratio is 4:1. The average heat capacity of the feed is 159 kJ/kg mol · K (38 btu/lb mol · °F) and the average latent heat 32 099 kJ/kg mol (13 800 btu/lb mol). Equilibrium data for this system are given in Table 11.1-1 and Fig. 11.1-1. Calculate the kg moles per hour distillate, kg moles per hour bottoms, and the number of theoretical trays needed.

***Solution*:** The given data are $F = 100$ kg mol/h, $x_F = 0.45$, $x_D = 0.95$, $x_W = 0.10$, and $R = L_n/D = 4$. For the overall material balance substituting into Eq. (11.4-3),

Equation 11.4-3.

$$F = D + W$$

$$100 = D + W$$

Substituting into Eq. (11.4-4) and solving for D and W,

Equation 11.4-4.

$$Fx_F = Dx_D + Wx_W$$

$$100(0.45) = D(0.95) + (100 - D)(0.10)$$

$$D = 41.2 \text{ kg mol/h} \qquad W = 58.8 \text{ kg mol/h}$$

For the enriching operating line, using Eq. (11.4-8),

$$y_{n+1} = \frac{R}{R+1}x_n + \frac{x_D}{R+1} = \frac{4}{4+1}x_n + \frac{0.95}{4+1} = 0.800x_n + 0.190$$

The equilibrium data from Table 11.1-1 and the enriching operating line above are plotted in Fig. 11.4-9.

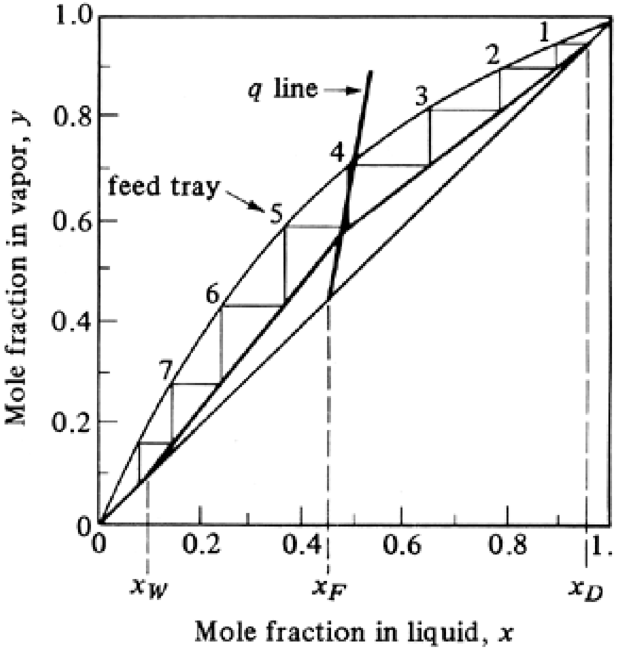

Figure 11.4-9. McCabe–Thiele diagram for distillation of benzene–toluene for Example 11.4-1.

Next, the value of q is calculated. From the boiling-point diagram, Fig. 11.1-1, for $x_F = 0.45$ the boiling point of the feed is 93.5°C or 366.7 K (200.3°F). From Eq. (11.4-13),

Equation 11.4-13.

$$q = \frac{H_V - H_F}{H_V - H_L}$$

The value of $H_V - H_L$ = latent heat = 32 099 kJ/kg mol. The numerator of Eq. (11.4-13) is

Equation 11.4-20.

$$H_V - H_F = (H_V - H_L) + (H_L - H_F)$$

Also,

Equation 11.4-21.

$$H_L - H_F = c_{pL}(T_B - T_F)$$

where the heat capacity of the liquid feed c_{pL} = 159 kJ/kg mol · K, T_B = 366.7 K (boiling point of feed), and T_F = 327.6 K (inlet feed temperature). Substituting Eqs. (11.4-20) and (11.4-21) into (11.4-13),

Equation 11.4-22.

$$q = \frac{(H_V - H_L) + c_{pL}(T_B - T_F)}{H_V - H_L}$$

Substituting the known values into Eq. (11.4-22),

$$q = \frac{32\,099 + 159(366.7 - 327.6)}{32\,099} = 1.195 \qquad \text{(SI)}$$

$$q = \frac{13\,800 + 38(200.3 - 130)}{13\,800} = 1.195 \qquad \text{(English)}$$

From Eq. (11.4-19), the slope of the *q* line is

$$\frac{q}{q-1} = \frac{1.195}{1.195 - 1} = 6.12$$

The *q* line is plotted in Fig. 11.4-9 starting at the point $y = x_F = 0.45$ with a slope of 6.12.

The stripping operating line is drawn connecting the point $y = x = x_W = 0.10$ with the intersection of the *q* line and the enriching operating line. Starting at the point $y = x = x_D$, the theoretical steps are drawn in, as shown in Fig. 11.4-9. The number of theoretical steps is 7.6, or 7.6 steps minus a reboiler, which gives 6.6 theoretical trays. The feed is introduced on tray 5 from the top.

Total and Minimum Reflux Ratio for McCabe–Thiele Method

Total reflux

In distillation of a binary mixture *A* and *B*, the feed conditions, distillate composition, and bottoms composition are usually specified and the number of theoretical trays are to be calculated. However, the number of theoretical trays needed depends upon the operating lines. To fix the operating lines, the reflux ratio $R = L_n/D$ at the top of the column must be set.

One of the limiting values of reflux ratio is that of total reflux, or $R = \infty$. Since $R = L_n/D$ and, by Eq. (11.4-5),

Equation 11.4-5.

$$V_{n+1} = L_n + D$$

then L_n is very large, as is the vapor flow V_n. This means that the slope $R/(R + 1)$ of the enriching operating line becomes 1.0 and the operating lines of both sections of the column coincide with the 45° diagonal line, as shown in Fig. 11.4-10.

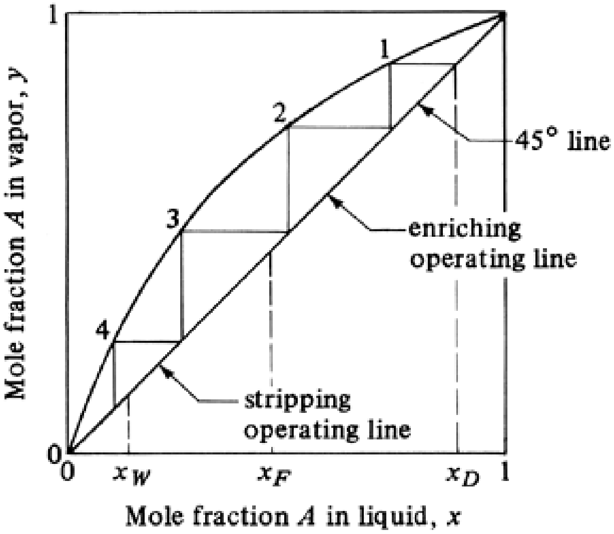

Figure 11.4-10. Total reflux and minimum number of trays by McCabe–Thiele method.

The number of theoretical trays required is obtained as before by stepping off the trays from the distillate to the bottoms. This gives the minimum number of trays that can possibly be used to obtain the given separation. In actual practice, this condition can be realized by returning all the overhead condensed vapor V_1 from the top of the tower back to the tower as reflux, that is, total reflux. Also, all the liquid in the bottoms is reboiled. Hence, all the products distillate and bottoms are reduced to zero flow, as is the fresh feed to the tower.

This condition of total reflux can also be interpreted as requiring infinite sizes of condenser, reboiler, and tower diameter for a given feed rate.

If the relative volatility α of the binary mixture is approximately constant, the following analytical expression by Fenske can be used to calculate the minimum number of theoretical steps N_m when a total condenser is used:

Equation 11.4-23.

$$N_m = \frac{\log\left(\frac{x_D}{1 - x_D}\frac{1 - x_W}{x_W}\right)}{\log \alpha_{av}}$$

For small variations in α, $\alpha_{av} = (\alpha_1 \alpha_W)^{1/2}$, where α_1 is the relative volatility of the overhead vapor and α_W is the relative volatility of the bottoms liquid.

Minimum reflux ratio

The minimum reflux ratio can be defined as the reflux ratio R_m that will require an infinite number of trays for the given desired separation of x_D and x_W. This corresponds to the minimum vapor flow in the tower, and hence the minimum reboiler and condenser sizes. This case is shown in Fig. 11.4-11. If R is decreased, the slope of the enriching operating line $R/(R + 1)$ is decreased, and the intersection of this line and the stripping line with the q line moves farther from the 45° line and closer to the equilibrium line. As a result, the number of steps required to give a fixed x_D and x_W increases. When the two operating lines touch the equilibrium line, a "pinch point" at y' and x' occurs, where the number of steps required becomes infinite. The slope of the enriching operating line is as follows from Fig. 11.4-11, since the line passes through the points x', y', and x_D ($y = x_D$):

Equation 11.4-24.

$$\frac{R_m}{R_m + 1} = \frac{x_D - y'}{x_D - x'}$$

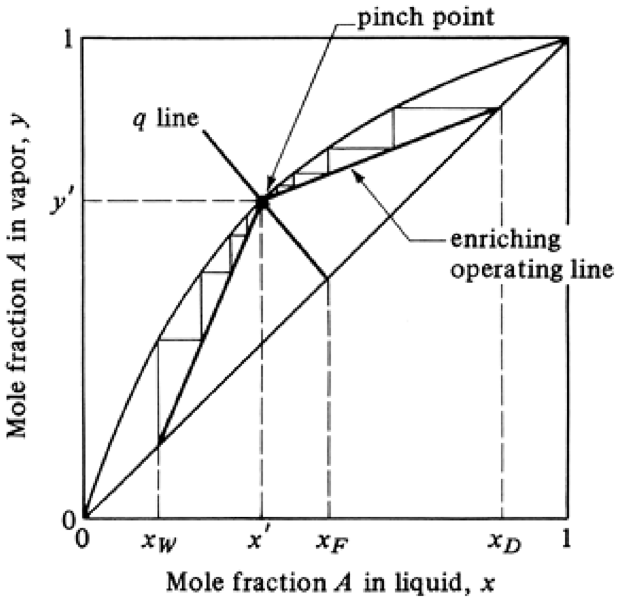

Figure 11.4-11. Minimum reflux ratio and infinite number of trays by McCabe–Thiele method.

In some cases, where the equilibrium line has an inflection in it as shown in Fig. 11.4-12, the operating line at minimum reflux will be tangent to the equilibrium line.

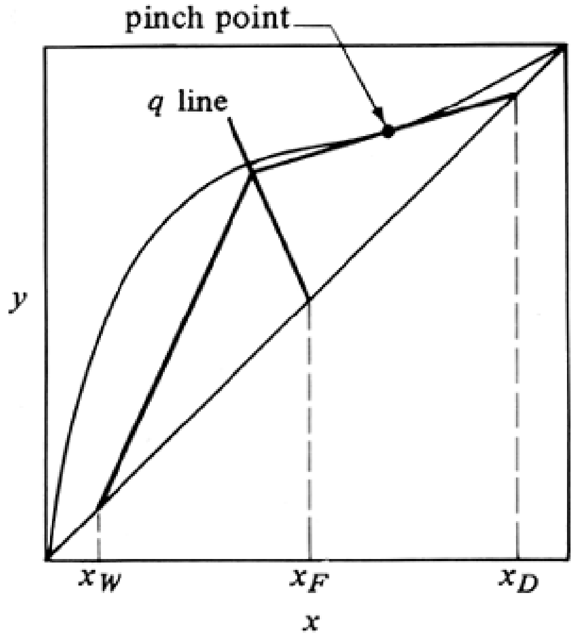

Figure 11.4-12. Minimum reflux ratio and infinite number of trays when operating line is tangent to equilibrium line.

Operating and optimum reflux ratio

For the case of total reflux, the number of plates is a minimum, but the tower diameter is infinite. This corresponds to an infinite cost of tower as well as steam and cooling water. This is one limit in the tower operation. Also, for minimum reflux, the number of trays is infinite, which again gives an infinite cost. These are the two limits in operation of the tower.

The actual operating reflux ratio to use lies between these two limits. To select the proper value of R requires a complete economic balance on the fixed costs of the tower and operating costs. The optimum reflux ratio to use for lowest total cost per year is between the minimum R_m and total reflux. This has been shown for many cases to be at an operating reflux ratio between $1.2R_m$ and $1.5R_m$.

EXAMPLE 11.4-2. Minimum Reflux Ratio and Total Reflux in Rectification

For the rectification in Example 11.4-1, where a benzene–toluene feed is being distilled to give a distillate composition of $x_D = 0.95$ and a bottoms composition of $x_W = 0.10$, calculate the following:

a. Minimum reflux ratio R_m.

b. Minimum number of theoretical plates at total reflux.

Solution: For part (a), the equilibrium line is plotted in Fig. 11.4-13 and the q-line equation is also shown for $x_F = 0.45$. Using the same x_D and x_W as in Example 11.4-1, the enriching operating line for minimum reflux is plotted as a dashed line and intersects the equilibrium line at the same point at which the q line intersects. Reading off the values of $x' = 0.49$ and $y' = 0.702$, substituting into Eq. (11.4-24), and solving for R_m,

$$\frac{R_m}{R_m + 1} = \frac{x_D - y'}{x_D - x'} = \frac{0.95 - 0.702}{0.95 - 0.49}$$

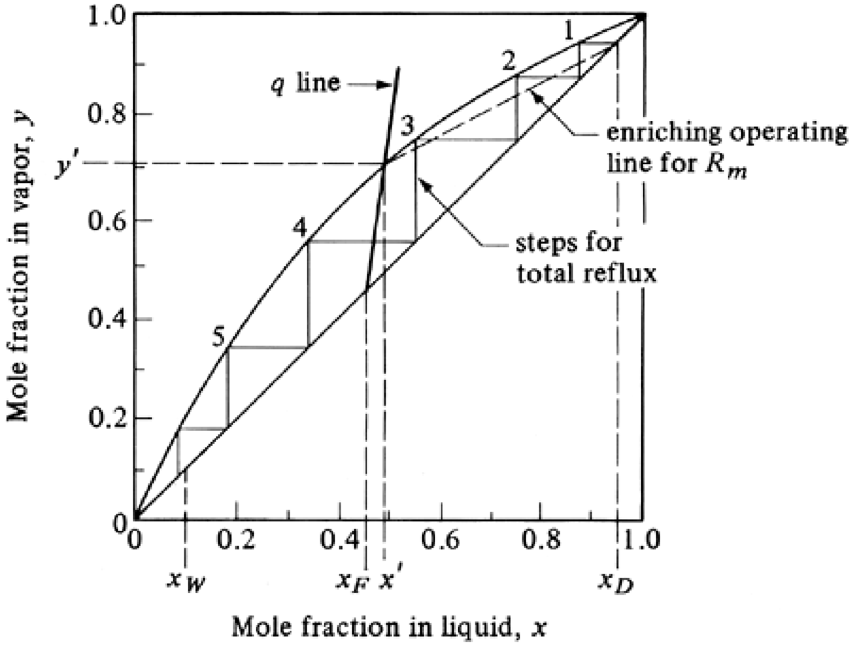

Figure 11.4-13. Graphical solution for minimum reflux ratio R_m and total reflux for Example 11.4-2.

Hence, the minimum reflux ratio $R_m = 1.17$.

For the case of total reflux in part (b), the theoretical steps are drawn as shown in Fig. 11.4-13. The minimum number of theoretical steps is 5.8, which gives 4.8 theoretical trays plus a reboiler.

Special Cases for Rectification Using McCabe–Thiele Method

Stripping-column distillation

In some cases the feed to be distilled is not supplied to an intermediate point in a column but is added to the top of the stripping column, as shown in Fig. 11.4-14a. The feed is usually a saturated liquid at the boiling point, and the overhead product V_D is the vapor rising from the top plate, which goes to a condenser with no reflux or liquid returned to the tower.

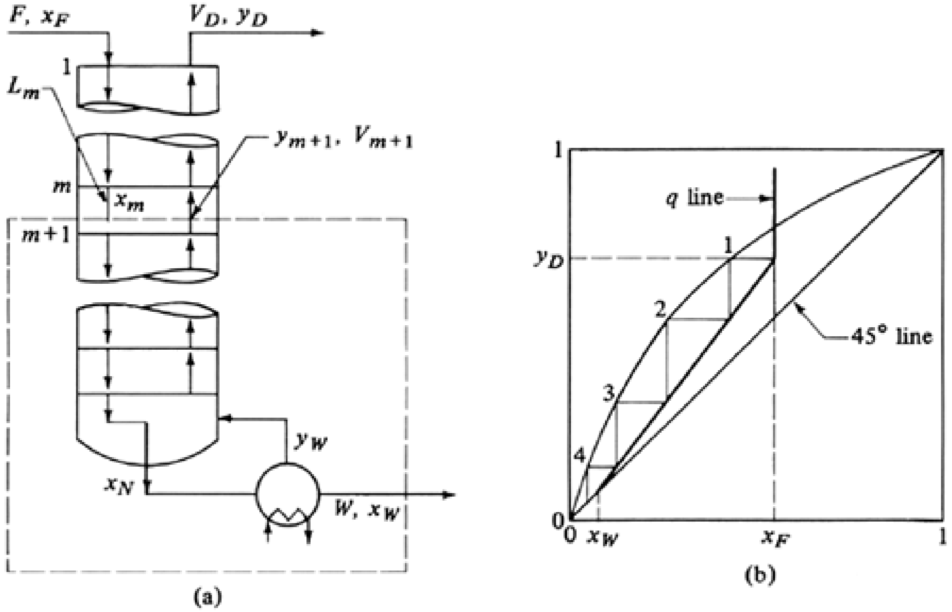

Figure 11.4-14. Material balance and operating line for stripping tower: (a) flows in tower, (b) operating and equilibrium line.

The bottoms product W usually has a high concentration of the less volatile component B. Hence, the column operates as a stripping tower, with the vapor removing the more volatile A from the liquid as it flows downward. Assuming constant molar flow rates, a material balance of the more volatile component A around the dashed line in Fig. 11.4-14a gives, on rearrangement,

Equation 11.4-25.

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{W x_W}{V_{m+1}}$$

This stripping-line equation is the same as the stripping-line equation for a complete tower given as Eq. (11.4-11). It intersects the $y = x$ line at $x = x_W$, and the slope is constant at L_m / V_{m+1}.

If the feed is saturated liquid, then $L_m = F$. If the feed is cold liquid below the boiling point, the q line should be used and $q > 1$:

Equation 11.4-26.

$$L_m = qF$$

In Fig. 11.4-14 the stripping operating-line equation (11.4-25) is plotted and the q line, Eq. (11.4-19), is also shown for $q = 1.0$. Starting at x_F, the steps are drawn down the tower.

EXAMPLE 11.4-3. Number of Trays in Stripping Tower

A liquid feed at the boiling point of 400 kg mol/h containing 70 mol % benzene (*A*) and 30 mol % toluene (*B*) is fed to a stripping tower at 101.3 kPa pressure. The bottoms product flow is to be 60 kg mol/h containing only 10 mol % *A* and the rest *B*. Calculate the kg mol/h overhead vapor, its composition, and the number of theoretical steps required.

Solution. Referring to Fig. 11.4-14a, the known values are $F = 400$ kg mol/h, $x_F = 0.70$, $W = 60$ kg mol/h, and $x_W = 0.10$. The equilibrium data from Table 11.1-1 are plotted in Fig. 11.4-15. Making an overall material balance,

$$F = W + V_D$$

$$400 = 60 + V_D$$

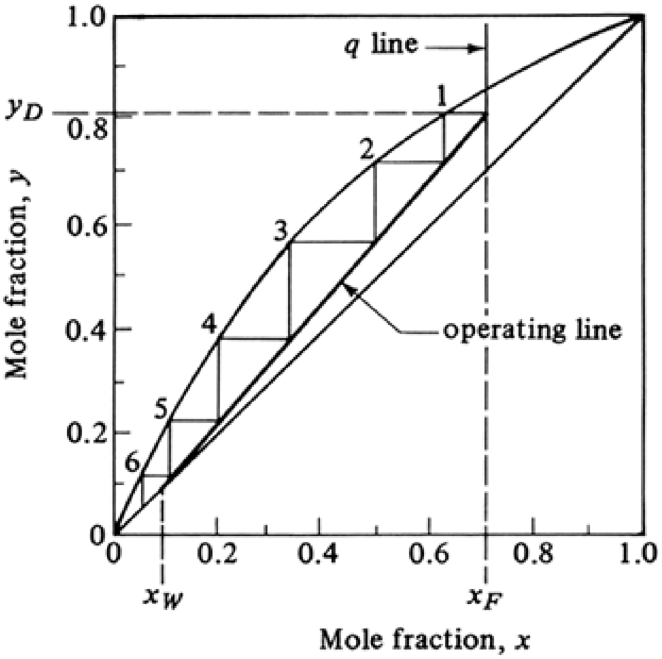

Figure 11.4-15. Stripping tower for Example 11.4-3.

Solving, $V_D = 340$ kg mol/h. Making a component *A* balance and solving,

$$Fx_F = Wx_W + V_D y_D$$

$$400(0.70) = 60(0.10) + 340(y_D)$$

$$y_D = 0.806$$

For a saturated liquid, the *q* line is vertical and is plotted in Fig. 11.4-15. The operating line is plotted through the point $y = x_W = 0.10$ and the intersection of $y_D = 0.806$ with the *q* line. Alternatively, Eq. (11.4-25) can be used, with a slope of $L_m/V_{m+1} = 400/340$. Stepping off the trays from the top, 5.3 theoretical steps or 4.3 theoretical trays plus a reboiler are needed.

Enriching-column distillation

Enriching towers are also used at times, where the feed enters the bottom of the tower as a vapor. The overhead distillate is produced in the same manner as in a complete fractionating tower and is usually quite rich in the more volatile component *A*. The liquid bottoms is usually comparable to the feed in composition, being slightly leaner in component *A*. If the feed is saturated vapor, the vapor in the tower $V_n = F$. Enriching-line equation (11.4-7) holds, as does the *q*-line equation (11.4-19).

Rectification with direct steam injection

Generally, the heat to a distillation tower is applied to one side of a heat exchanger (reboiler) and the steam does not come into direct contact with the boiling solution, as shown in Fig. 11.4-5. However, when an aqueous solution of more volatile *A* and water *B* is being distilled, the heat required may be provided by the use of open steam injected directly at the bottom of the tower. The reboiler exchanger is then not needed.

The steam is injected as small bubbles into the liquid in the tower bottom, as shown in Fig. 11.4-16a. The vapor leaving the liquid is then in equilibrium with the liquid if sufficient contact is obtained. Making an overall balance on the tower and a balance on *A*,

Equation 11.4-27.

$$F + S = D + W$$

Equation 11.4-28.

$$Fx_F + Sy_S = Dx_D + Wx_W$$

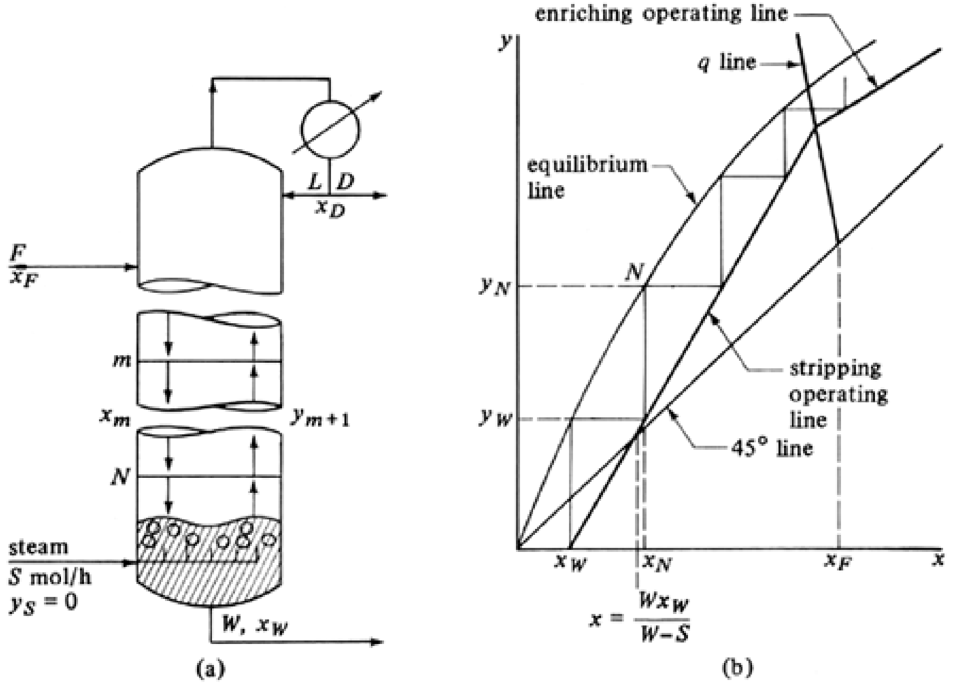

Figure 11.4-16. Use of direct steam injection: (a) schematic of tower, (b) operating and equilibrium lines.

where S = mol/h of steam and $y_S = 0$ = mole fraction of *A* in steam. The enriching operating-line equation is the same as for indirect steam.

For the stripping-line equation, an overall balance and a balance on component *A* are as follows:

Equation 11.4-29.

$$L_m + S = V_{m+1} + W$$

Equation 11.4-30.

$$L_m x_m + S(0) = V_{m+1} y_{m+1} + W x_W$$

Solving for y_{m+1} in Eq. (11.4-30),

Equation 11.4-31.

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{W x_W}{V_{m+1}}$$

For saturated steam entering, $S = V_{m+1}$ and hence, by Eq. (11.4-29), $L_m = W$. Substituting into Eq. (11.4-31), the stripping operating line is

Equation 11.4-32.

$$y_{m+1} = \frac{W}{S} x_m - \frac{W}{S} x_W$$

When $y = 0$, $x = x_W$. Hence, the stripping line passes through the point $y = 0$, $x = x_W$, as shown in Fig. 11.4-16b, and is continued to the x axis. Also, for the intersection of the stripping line with the 45° line, when $y = x$ in Eq. (11.4-32), $x = Wx_W/(W - S)$.

For a given reflux ratio and overhead distillate composition, the use of open steam rather than closed requires an extra fraction of a stage, since the bottom step starts below the $y = x$ line (Fig. 11.4-16b). The advantage of open steam lies in simpler construction of the heater, which is a sparger.

Rectification tower with side stream

In certain situations, intermediate product or side streams are removed from sections of the tower between the distillate and the bottoms. The side stream may be vapor or liquid and may be removed at a point above the feed entrance or below, depending on the composition desired.

The flows for a column with a liquid side stream removed above the feed inlet are shown in Fig. 11.4-17. The top enriching operating line above the liquid side stream and the stripping operating line below the feed are found in the usual way. The equation for the q line is also unaffected by the side stream and is found as before. The liquid side stream alters the liquid rate below it, and hence the material balance or operating line in the middle portion between the feed and liquid side stream plates as well.

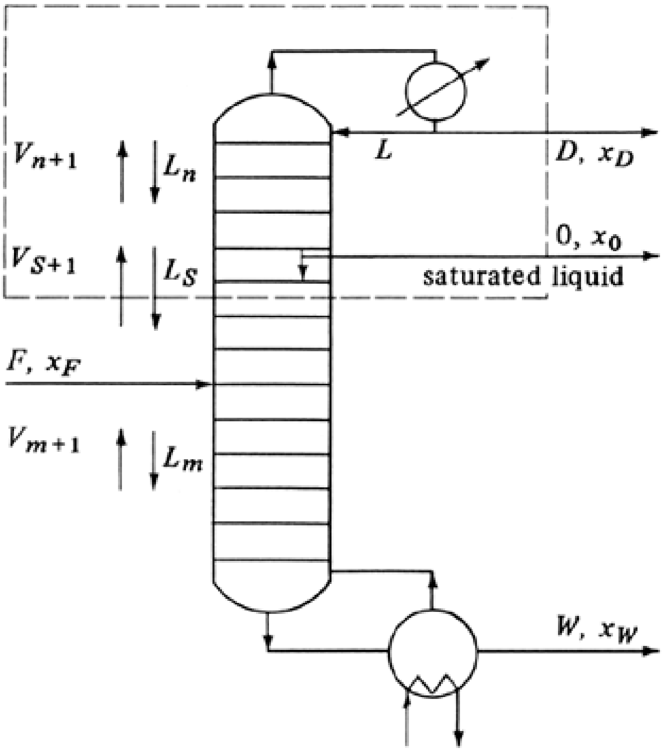

Figure 11.4-17. Process flow for a rectification tower with a liquid side stream.

Making a total material balance on the top portion of the tower, as shown in the dashed-line box in Fig. 11.4-17,

Equation 11.4-33.

$$V_{S+1} = L_S + O + D$$

where O is mol/h saturated liquid removed as a side stream. Since the liquid side stream is saturated,

Equation 11.4-34.

$$L_n = L_S + O$$

Equation 11.4-35.

$$V_{S+1} = V_{n+1}$$

Making a balance on the most volatile component,

Equation 11.4-36.

$$V_{S+1}y_{S+1} = L_S x_S + O x_O + D x_D$$

Solving for y_{S+1}, the operating line for the region between the side stream and the feed is

Equation 11.4-37.

$$y_{S+1} = \frac{L_S}{V_{S+1}} x_S + \frac{O x_O + D x_D}{V_{S+1}}$$

The slope of this line is L_S/V_{S+1}. The line can be located as shown in Fig. 11.4-18 by the q line, which determines the intersection of the stripping line and Eq. (11.4-37), or it may be fixed by the specification of x_O, the side-stream composition. The step on the McCabe–Thiele diagram must be at the intersection of the two operating lines at x_O in an actual tower. If this does not occur, the reflux ratio can be altered slightly to change the steps.

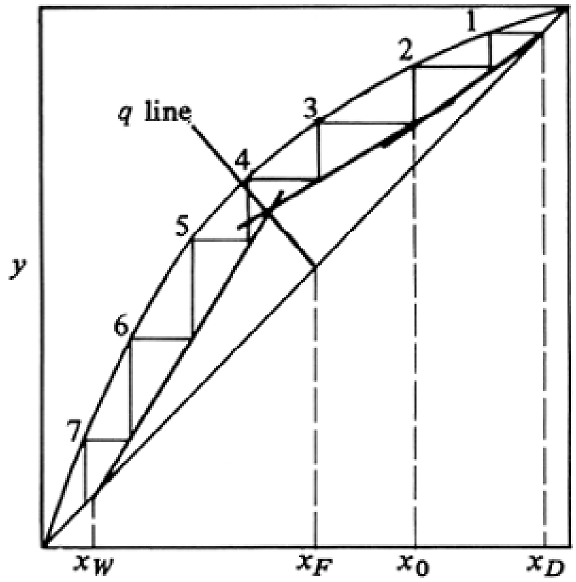

Figure 11.4-18. McCabe–Thiele plot for a tower with a liquid side stream above the feed.

Partial condensers

In a few cases it may be desired to remove the overhead distillate product as a vapor instead of a liquid. This can also occur when the low boiling point of the distillate makes complete condensation difficult. The liquid condensate in a partial condenser is returned to the tower as reflux and the vapor removed as product, as shown in Fig. 11.4-19.

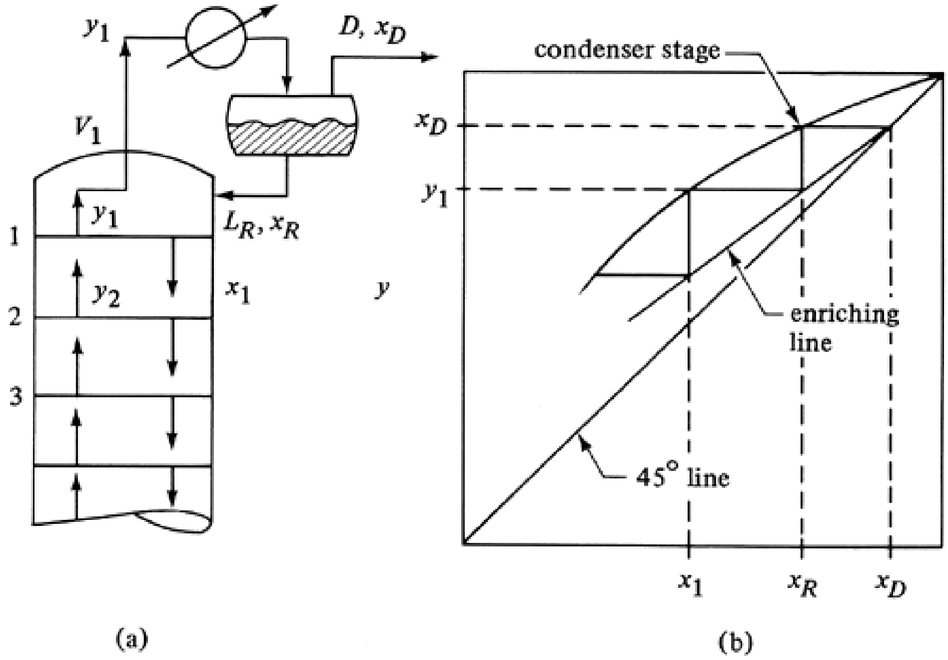

Figure 11.4-19. Partial condenser where the vapor and liquid leave in equilibrium: (a) process flow diagram, (b) McCabe-Thiele plot.

If the time of contact between the vapor product and the liquid is sufficient, the partial condenser is a theoretical stage. Then the composition x_R of the liquid reflux is in equilibrium with the vapor composition y_D, where $y_D = x_D$. If the cooling in the condenser is rapid and the vapor and liquid do not reach equilibrium, only a partial stage separation is obtained.

DISTILLATION AND ABSORPTION EFFICIENCIES FOR TRAY AND PACKED TOWERS

Tray Efficiencies

In all the previous discussions of theoretical trays or stages in distillation, we assumed that the vapor leaving a tray was in equilibrium with the liquid leaving. However, if the time of contact and the degree of mixing on the tray are insufficient, the streams will not be in equilibrium. As a result the efficiency of the stage or tray will not be 100%. This means that we must use more actual trays for a given separation than the theoretical number of trays determined by calculation. The discussions in this section apply to both absorption and distillation tray towers.

Three types of tray or plate efficiency are used: *overall tray efficiency* E_O, *Murphree tray efficiency* E_M, and point or local tray efficiency E_{MP} (sometimes called *Murphree point efficiency*). These will be considered individually.

Types of Tray Efficiencies

Overall tray efficiency

The *overall tray* or *plate efficiency* E_O concerns the entire tower and is simple to use, but it is the least fundamental. It is defined as the ratio of the number of theoretical or ideal trays needed in an entire tower to the number of actual trays used:

Equation 11.5-1.

$$E_O = \frac{\text{number of ideal trays}}{\text{number of actual trays}}$$

For example, if eight theoretical steps are needed and the overall efficiency is 60%, the number of theoretical trays is eight minus a reboiler, or seven trays. The actual number of trays is 7/0.60, or 11.7 trays.

Murphree tray efficiency

The *Murphree tray efficiency* E_M is defined as follows:

Equation 11.5-2.

$$E_M = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}}$$

where y_n is the average actual concentration of the mixed vapor leaving the tray n as shown in Fig. 11.5-1, y_{n+1} the average actual concentration of the mixed vapor entering tray n, and y_n^* the concentration of the vapor that would be in equilibrium with the liquid of concentration x_n leaving the tray to the downcomer.

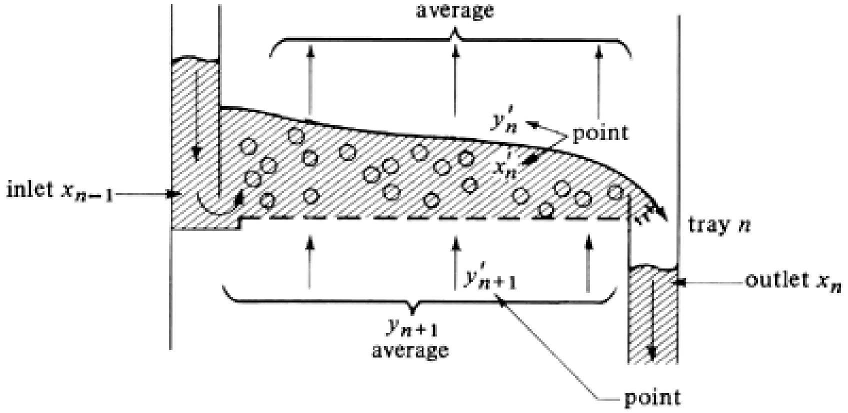

Figure 11.5-1. Vapor and liquid compositions on a sieve tray and tray efficiency.

The liquid entering the tray has a concentration of x_{n-1}; as it travels across the tray, its concentration drops to x_n at the outlet. Hence, there is a concentration gradient in the liquid as it flows across the tray. The vapor entering the tray comes in contact with liquid of different concentrations, and the outlet vapor will not be uniform in concentration.

Point efficiency

The *point* or *local efficiency* E_{MP} on a tray is defined as

Equation 11.5-3.

$$E_{MP} = \frac{y'_n - y'_{n+1}}{y_n^* - y'_{n+1}}$$

where y'_n is the concentration of the vapor at a specific point in plate *n* as shown in Fig. 11.5-1, y'_{n+1} the concentration of the vapor entering the plate *n* at the same point, and y'^{*}_n the concentration of the vapor that would be in equilibrium with x'_n at the same point. Since y'_n cannot be greater than y'^{*}_n, the local efficiency cannot be greater than 1.00 or 100%.

In small-diameter towers, the vapor flow sufficiently agitates the liquid so that it is uniform on the tray. Then the concentration of the liquid leaving is the same as that on the tray. Then $y'_n = y_n$, $y'_{n+1} = y_{n+1}$ and $y'^{*}_n = y^{*}_n$. The point efficiency then equals the Murphree tray efficiency, or $E_M = E_{MP}$.

In large-diameter columns, incomplete mixing of the liquid occurs on the trays. Some vapor will contact the entering liquid x_{n-1}, which is richer in component *A* than x_n. This will give a richer vapor at this point than at the exit point, where x_n leaves. Hence, the tray efficiency E_M will be greater than the point efficiency E_{MP}. The value of E_M can be related to E_{MP} by integration of E_{MP} over the entire tray.

Relationship Between Tray Efficiencies

The relationship between E_{MP} and E_M can be derived mathematically if the amount of liquid mixing is specified together with the amount of vapor mixing. Derivations for three different sets of assumptions are given by Robinson and Gilliland (R1). However, experimental data are usually needed to obtain amounts of mixing. Semitheoretical methods for predicting E_{MP} and E_M are summarized in detail by Van Winkle (V1).

When the Murphree tray efficiency E_M is known or can be predicted, the overall tray efficiency E_O can be related to E_M by several methods. In the first method, an analytical expression is as follows when the slope *m* of the equilibrium line is constant as well as the slope *L*/*V* of the operating line:

Equation 11.5-4.

$$E_O = \frac{\log[1 + E_M(mV/L - 1)]}{\log(mV/L)}$$

If the equilibrium and operating lines of the tower are not straight, a graphical method employing the McCabe–Thiele diagram can be used to determine the actual number of trays when the Murphree tray efficiency is known. In Fig. 11.5-2 a diagram is given for an actual plate as compared with an ideal plate. The triangle *acd* represents an ideal plate and the smaller triangle *abe* the actual plate. For the case shown, the Murphree efficiency $E_M = 0.60 = ba/ca$. The dashed line going through point *b* is drawn so that *ba*/*ca* for each tray is 0.60. The trays are stepped off using this efficiency, and the total number of steps gives the actual number of trays needed. The reboiler is considered to be one theoretical tray, so the true equilibrium curve is used for this tray, as shown. In Fig. 11.5-2, 6.0 actual trays plus a reboiler are obtained.

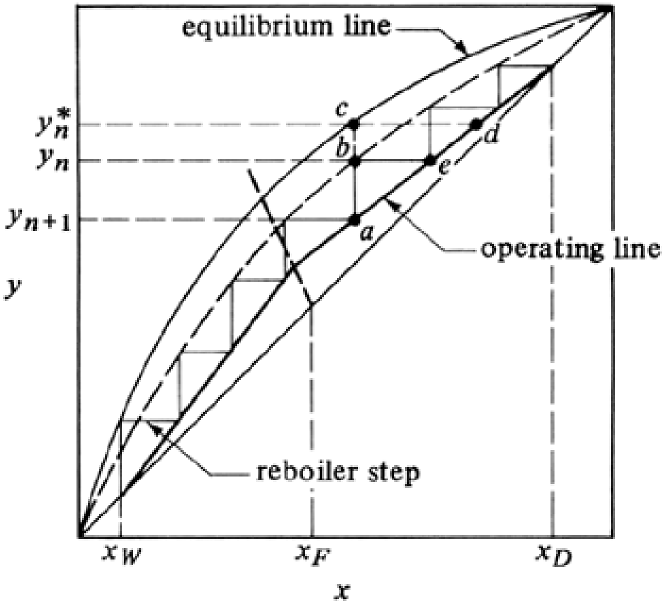

Figure 11.5-2. Use of Murphree plate efficiency to determine actual number of trays.

Efficiency of Random-Packed and Structured Packed Towers

In tray towers, a theoretical tray is defined as a tray in which equilibrium is attained between the gas or vapor leaving and the liquid leaving the tray. In random-packed or structured packed towers, the same approach is used, where the HETP in m (ft) is defined as the height of the packed column necessary to give a separation equal to one theoretical plate. The design of mass-transfer towers requires evaluation of the number of theoretical stages or transfer units. Hence, the height of packing H in m (ft) required to perform a given separation is

Equation 11.5-5.

$$H = n(\text{HETP})$$

where n is the number of theoretical stages needed. Using the number-of-transfer-units method, the height H is

Equation 11.5-6.

$$H = H_{OG}N_{OG}$$

where H_{OG} is the overall height of a transfer unit in m (ft) and N_{OG} is the number of transfer units.

The HETP and overall height of a transfer unit H_{OG} can be related by the following equation, which is the same as Eq. (10.6-55):

Equation 11.5-7.

$$\text{HETP} = H_{OG}\frac{\ln[m/(L/V)]}{m/(L/V) - 1}$$

where m is the slope of the equilibrium line in mole fraction units and L and V are molar flow rates. If the operating line and equilibrium line are parallel, then HETP = H_{OG}. In distillation, the operating and equilibrium lines diverge below the feed point and converge above, so that the average mV/L is about 1.0 and HETP ≅ HTU for distillation. This is usually not true for absorption or stripping towers. Although the HETP concept lacks a sound theoretical basis, unlike the mass-transfer and H_{OG} concepts, it is simple and easy to use in computer equilibrium stage-to-stage calculations in distillation and is widely used to estimate packing height (S3). It is especially useful in multicomponent systems.

For a tray tower, the HETP can be defined as

Equation 11.5-8.

$$\text{HETP} = \frac{T}{E_0}$$

where E_0 is the overall tray efficiency and T is the tray spacing, which varies from about 0.3 m for a 0.5-m-diameter tower, 0.6 m for a 1.0-m-diameter tower, to about 0.8 m (2.6 ft) for much larger towers over 4 m in diameter.

Estimation of Efficiencies of Tray and Packed Towers

In order to design the number of trays or packing heights needed, efficiencies must be obtained.

Efficiency of tray towers

For estimating the overall tray efficiency of bubble-tray towers for distillation, the O'Connell (O1) correlation can be used (K2) with about a ±10% error. The following equation for these data from Lockett (L1) can be used for sieve and valve trays as well, but predictions will be slightly conservative:

Equation 11.5-9.

$$E_0 = 0.492(\mu_L \alpha)^{-0.245}$$

where E_0 is fraction efficiency, α is relative volatility of the two key components at the average tower temperature, and μ_L is the molar average viscosity in cp of the liquid feed at the average tower temperature of the top and the bottom. Most typical efficiencies are between 40 and 80%.

To estimate the overall tray efficiency for absorption towers, the O'Connell correlation (O1) can be used. This correlation is represented by the equation (S3)

Equation 11.5-10.

$$\log E_0 = 1.597 - 0.199 \log(mM_L\mu_L/\rho_L) - 0.0896[\log(mM_L\mu_L/\rho_L)]^2$$

where E_0 is overall average % tray efficiency, M_L is the average molecular weight of the liquid, m is the slope of the equilibrium line in mole fraction units, ρ_L is the liquid density in lb_m/ft^3, and μ_L is molar average liquid viscosity in cp at the average tower temperature. The average deviation of the data is ±16.3% and the maximum is 157%. This can be used for bubble-cap, sieve, and valve-type trays. Note that these tray efficiencies are quite low and in the range of 1% to 50%, with typical values of 10 to 30%.

Efficiency of random-packed towers

For estimates for random packing, Eq. (11.5-11) can be used to determine the HETP for second- and third-generation packings only (S2):

Equation 11.5-11.

$$\text{HETP} = 0.0180 d_p \qquad \text{(SI)}$$

$$\text{HETP} = 1.5 d_p \qquad \text{(English)}$$

where HETP is in m and d_p is packing diameter in mm. In English units, HETP is in ft and d_p is in in. Also, for small-diameter towers, where the tower diameter D is less than 0.60 m (2 ft), HETP = D, but not less than 0.3 m (1 ft).

For vacuum service (S3),

Equation 11.5-12.

$$\text{HETP} = 0.0180 d_p + 0.15 \qquad \text{(SI)}$$

$$\text{HETP} = 1.5 d_p + 0.50 \qquad \text{(English)}$$

The above equations are useful for low-viscosity liquids. For absorption with high-viscosity liquids, the values of HETP are much greater, with values of 1.5 to 1.8 m (5 to 6 ft).

Efficiency of structured packing in towers

For approximate estimates of the efficiency of structured packings at low to moderate pressure with low viscosity liquids (K4),

Equation 11.5-13.

$$\text{HETP} = 100/a + 0.10 \qquad \text{(SI)}$$

$$\text{HETP} = 100/a + 0.33 \qquad \text{(English)}$$

where HETP is in m and a is surface area in m^2/m^3. In English units, HETP is in ft and a in ft^2/ft^3. The value added of 0.10 m gives the estimate a conservative bias (K4). Values of HETP range from about 0.3 to 0.6 m (1.0 to 2.0 ft). For wire mesh (gauze), structured-packing values range from 0.1 to 0.3 m (0.3 to 1.0 ft).

EXAMPLE 11.5-1. Estimation of Tray and Packing Efficiencies and Tower Height

A liquid feed of benzene–toluene is being distilled under the same conditions as in Ex. 11.4-1. The number of theoretical steps needed is calculated as 7.6. The feed composition $x_F = 0.45$, $x_D = 0.95$, and $x_W = 0.10$. Do as follows:

a. Using valve trays, calculate the overall efficiency E_0 and the tower height. Assume a tray spacing T of 0.6 m.
b. Using 2-in. metal Pall rings, calculate the HETP and the tower height.
c. Using Flexipac No. 2 structured packing, calculate the tower height.

Solution: For part (a), from Fig. 11.1-1 at 1 atm abs and $x_W = 0.10$, the boiling temperature is 106.5°C. At the top, for $x_D = 0.95$, the dew point is 82.3°C. The average is (106.5 + 82.3)/2 or 94.4°C.

Using Table A.3-12 and Fig. A.3-4 at 94.4°C, the viscosity of benzene is 0.26 cp, and of toluene, 0.295 cp. The molar average viscosity is $\mu_L = 0.45(0.26) + 0.55(0.295) = 0.279$ cp.

From Table 11.1-1, the vapor pressure of benzene P_A at 94.4°C is 153.3 kPa, and for toluene, $P_B = 62.2$ kPa. Hence, the average relative volatility $\alpha = 153.3/62.2 = 2.465$.

Using Eq. (11.5-9), $E_0 = 0.492(\mu_L\alpha)^{-0.245} = 0.492\,(0.279 \times 2.465)^{-0.245} = 0.539$. Using Eq. (11.5-8), HETP = $T/E_0 = 0.6/0.539 = 1.113$ m/theoretical steps. The number of tray theoretical steps = 7.6 − 1 step for the reboiler, or 6.6 steps. Hence, tower tray height $H = 1.113(6.6) = 7.35$ m.

For part (b), for 2-in. (25.4 × 2 mm) Pall rings, Eq. (11.5-11) gives

$$\text{HETP} = 0.0180 d_p = 0.0180(25.4 \times 2) = 0.914 \text{ m}$$

For 6.6 theoretical steps, tower height $H = 0.914(6.6) = 6.03$ m.

For part (c), for Flexipac No. 2 structured packing and using Table 10.6-1, $a = 223\ m/m^2$. From Eq. (11.5-13),

$$\text{HETP} = 100/a + 0.10 = 100/223 + 0.10 = 0.548 \text{ m}$$

$$\text{Tower height } H = 0.548(6.6) = 3.617 \text{ m}$$

Flooding Velocity and Diameter of Tray Towers

In tray towers the maximum vapor velocity can be limited either by entrainment of small liquid droplets or by the liquid handling capacity of the tray downcomer whereby the liquid in the downcomer backs up to the next tray. The general basis for design uses the allowable-vapor-velocity concept. The equation by Fair (F1) for estimating the maximum allowable vapor velocity for sieve, bubble-cap, or valve trays is

Equation 11.5-14.

$$v_{\max} = K_v\left(\frac{\sigma}{20}\right)^{0.2}\sqrt{\frac{\rho_L - \rho_V}{\rho_V}}$$

where $v_{\max}$ is the allowable vapor velocity in ft/s based on the total cross-sectional area minus the area of one downcomer, σ is the surface tension of the liquid in dyn/cm (mN/m), and ρ_L and ρ_V are liquid and gas densities, kg/m^3 or lb$_m$/ft^3. The value of K_v in ft/s is obtained from Fig. 11.5-3, where L and V are total flow rates in kg/h or lb$_m$/h. As a rule-of-thumb, the value of K_v should be multiplied by a factor of 0.91 to account for the downspout area of 9% of the tray (T2).

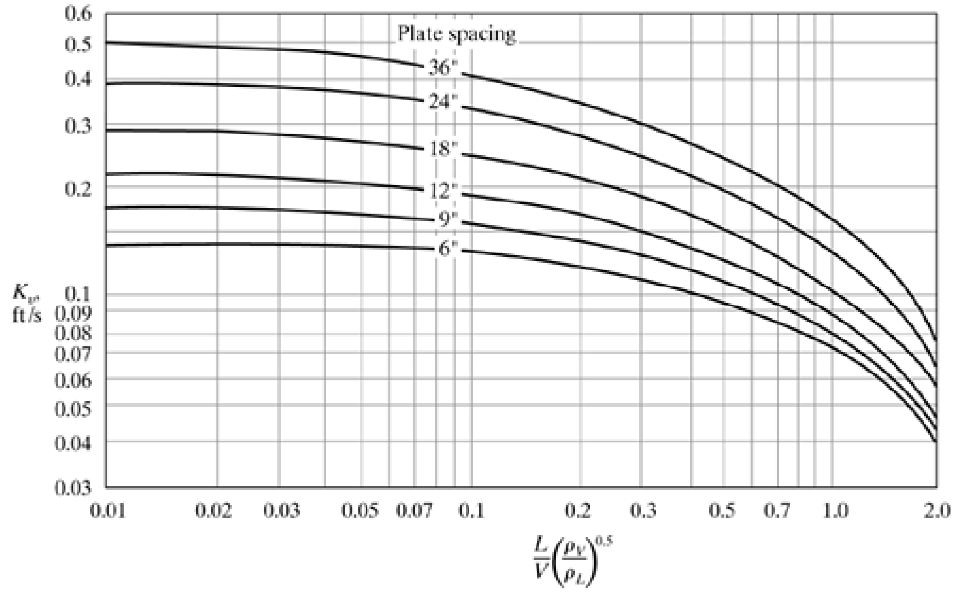

*Figure 11.5-3. Estimation of K_v value for allowable vapor velocity. (From Fair, J. R., Petro/Chem. Eng., **33**(10), 45 (1961). With permission.)*

The Eq. (11.5-14) holds for nonfoaming systems. For many absorbers the K_v should be multiplied by 0.90 or so to account for foaming (S3). For the final design the above $v_{\max}$ should be multiplied by 0.80 to be 20% below flooding. For organic liquids a typical value of σ is about 20–25 dyn/cm. For water with a surface tension of about 72 dyn/cm, the flooding velocity is larger by a factor of about $(72/22.5)^{0.20}$, or 1.26/1.

EXAMPLE 11.5-2. Tray Diameter of a Valve-Tray Absorption Tower

A valve-tray absorption tower is being used to absorb and recover ethyl alcohol vapor in air by pure water. The tower operates at 30°C and a pressure of 110 kPa abs. The entering gas contains 2.0 mol % ethyl alcohol in water, and 95% of the alcohol is recovered in the outlet water. The inlet pure aqueous flow is 186 kg mol/h and the inlet gas flow is 211.7 kg mol/h. Calculate the required tower diameter. A tray spacing of 0.610 m (2.0 ft) will be assumed. Use a factor of 0.95 for possible foaming.

***Solution*:** The molecular weight of the entering air at the tower bottom where the flow rates are the greatest is

$$M = 0.98(29.0) + 0.02(46.1) = 29.34 \text{ kg/kg mol}$$

The density of the vapor is

$$\rho_V = \frac{29.34 \text{ kg/kg mol}}{(22.414 \text{ m}^3\text{/kg mol})} \frac{(273.2)(110)}{(273.2 + 30)(101.325)}$$

$$= 1.280 \text{ kg/m}^3$$

The mass flow rate of the gas is $V = 211.7(29.34) = 6211$ kg/h. Moles ethyl alcohol absorbed = 0.95(0.02)(211.7) = 4.02. The outlet aqueous flow rate $L = 186.0 + 4.02 = 190.02$ kg mol/h. The liquid mass flow rate is

$$L = 186.0(18) + 4.02(46.1) = 3533 \text{ kg/h}$$

The outlet water density, assuming a dilute solution at 30°C, from Appendix A.2-3 is $\rho_L = 0.995(1000) = 995$ kg/m^3. Then,

$$\frac{L}{V}\left(\frac{\rho_V}{\rho_L}\right)^{0.5} = \frac{(3533)}{(6211)}\left(\frac{1.280}{995}\right)^{0.5} = 0.02040$$

Using Fig. 11.5-3 for a 24-in. tray spacing, $K_v = 0.385$ ft/s. Substituting into Eq. (11.5-14) and using a surface tension of 70 (slightly less than water),

$$v_{\max} = 0.385\left(\frac{70}{20}\right)^{0.2}\sqrt{\frac{995 - 1.280}{1.280}} = 13.78 \text{ ft/s}$$

Multiplying the above by 0.91 to account for downspout area, by 0.95 for foaming, and by 0.80 for 80% of flooding,

$$v_{\text{design}} = 13.78(0.91)(0.95)(0.80)$$

$$= 9.531 \text{ ft/s} \quad \text{or} \quad 2.905 \text{ m/s}$$

The tower cross-section equals

$$\frac{(6211 \text{ kg/h})}{(3600 \text{ s/h})} \frac{1}{(1.28 \text{ kg/m}^3)} \frac{1}{(2.905 \text{ m/s})} = 0.464 \text{ m}^2$$

Solving for the diameter, $\pi D^2/4 = 0.464$. Then, $D = 0.7686$ m (2.522 ft).

FRACTIONAL DISTILLATION USING ENTHALPY–CONCENTRATION METHOD

Enthalpy–Concentration Data

Introduction

In Section 11.4B the McCabe–Thiele method was used to calculate the number of theoretical steps or trays needed for a given separation of a binary mixture of *A* and *B* by rectification or fractional distillation. The main assumptions in the method are that the latent heats are equal, sensible heat differences are negligible, and constant molal overflow occurs in each section of the distillation tower. In this section we shall consider fractional distillation using enthalpy–concentration data where the molal overflow rates are not necessarily constant. The analysis will be made using enthalpy as well as material balances.

Enthalpy–concentration data

An enthalpy–concentration diagram for a binary vapor– liquid mixture of *A* and *B* takes into account latent heats, heats of solution or mixing, and sensible heats of the components of the mixture. The following data are needed to construct such a diagram at a constant pressure: (1) heat capacity of the liquid as a function of temperature, composition, and pressure; (2) heat of solution as a function of temperature and composition; (3) latent heats of vaporization as a function of composition and pressure or temperature; and (4) boiling point as a function of pressure, composition, and temperature.

The diagram at a given constant pressure is based on arbitrary reference states of liquid and temperature, such as 273 K (32°F). The saturated liquid line in enthalpy *h* kJ/kg (btu/lb_m) or kJ/kg mol is calculated by

Equation 11.6-1.

$$h = x_A c_{pA}(T - T_0) + (1 - x_A)c_{pB}(T - T_0) + \Delta H_{\text{sol}}$$

where x_A is wt or mole fraction *A, T* is boiling point of the mixture in K (°F) or °C, T_0 is reference temperature, K, c_{pA} is the liquid heat capacity of the component *A* in kJ/kg · K (btu/lb_m · °F) or kJ/kg mol · K, c_{pB} is heat capacity of *B*, and ΔH_{sol} is heat of solution at T_0 in kJ/kg (btu/lb_m) or kJ/kg mol. If heat is evolved on mixing, the ΔH_{sol} will be a negative value in Eq. (11.6-1). Often, the heats of solution are small, as in hydrocarbon mixtures, and are neglected.

The saturated vapor enthalpy line of *H* kJ/kg (btu/lb_m) or kJ/kg mol of a vapor composition y_A is calculated by

Equation 11.6-2.

$$H = y_A[\lambda_A + c_{py_A}(T - T_0)] + (1 - y_A)[\lambda_B + c_{py_B}(T - T_0)]$$

where c_{py_A} is the vapor heat capacity for *A* and c_{py_B} for *B*. The latent heats λ_A and λ_B are the values at the reference temperature T_0. Generally, the latent heat is given as λ_{Ab} at the normal boiling point T_{bA} of the pure component *A* and λ_{Bb} for *B*. Then to correct this to the reference temperature T_0 for use in Eq. (11.6-2),

Equation 11.6-3.

$$\lambda_A = c_{pA}(T_{bA} - T_0) + \lambda_{Ab} - c_{py_A}(T_{bA} - T_0)$$

Equation 11.6-4.

$$\lambda_B = c_{pB}(T_{bB} - T_0) + \lambda_{Bb} - c_{py_B}(T_{bB} - T_0)$$

In Eq. (11.6-3) the pure liquid is heated from T_0 to T_{bA}, vaporized at T_{bA}, and then cooled as a vapor to T_0. Similarly, Eq. (11.6-4) also holds for λ_B. For convenience, the reference temperature T_0 is often taken as equal to the boiling point of the lower-boiling component *A*. This means $\lambda_A = \lambda_{Ab}$. Hence, only λ_{Bb} must be corrected to λ_B.

EXAMPLE 11.6-1. Enthalpy–Concentration Plot for Benzene–Toluene

Prepare an enthalpy–concentration plot for benzene–toluene at 1 atm pressure. Equilibrium data are given in Table 11.1-1 and Figs. 11.1-1 and 11.1-2. Physical property data are given in Table 11.6-1.

Table 11.6-1. Physical Property Data for Benzene and Toluene

		Heat Capacity, (kJ/kg mol · K)		
Component	*Boiling Point, (°C)*	*Liquid*	*Vapor*	*Latent Heat of Vaporization (kJ/kg mol)*
Benzene (*A*)	80.1	138.2	96.3	30 820
Toluene (*B*)	110.6	167.5	138.2	33 330

Solution: A reference temperature of T_0 = 80.1°C will be used for convenience so that the liquid enthalpy of pure benzene (x_A = 1.0) at the boiling point will be zero. For the first point, we will select pure toluene (x_A = 0). For liquid toluene at the boiling point of 110.6°C, using Eq. (11.6-1) with zero heat of solution and data from Table 11.6-1,

Equation 11.6-5.

$$h = x_A c_{pA}(T - 80.1) + (1 - x_A)c_{pB}(T - 80.1) + 0$$

$$h = 0 + (1 - 0)(167.5)(110.6 - 80.1) = 5109 \text{ kJ/kg mol}$$

For the saturated vapor enthalpy line, Eq. (11.6-2) is used. However, we must first calculate λ_B at the reference temperature T_0 = 80.1°C, using Eq. (11.6-4):

Equation 11.6-4.

$$\begin{aligned}\lambda_B &= c_{pB}(T_{bB} - T_0) + \lambda_{Bb} - c_{pyB}(T_{bB} - T_0)\\ &= 167.5(110.6 - 80.1) + 33\,330 - 138.2(110.6 - 80.1)\\ &= 34\,224 \text{ kJ/kg mol}\end{aligned}$$

To calculate *H*, Eq. (11.6-2) is used, and y_A = 0:

Equation 11.6-2.

$$\begin{aligned}H &= y_A[\lambda_A + c_{pyA}(T - T_0)] + (1 - y_A)[\lambda_B + c_{pyB}(T - T_0)]\\ &= 0 + (1.0 - 0)[34\,224 + 138.2(110.6 - 80.1)]\\ &= 38\,439 \text{ kJ/kg mol}\end{aligned}$$

For pure benzene, x_A = 1.0 and y_A = 1.0. Using Eq. (11.6-5), since $T = T_0$ = 80.1, h = 0. For the saturated vapor enthalpy, using Eq. (11.6-2) and T = 80.1,

$$H = 1.0[30\,820 + 96.3(80.1 - 80.1)] + 0 = 30\,820$$

Selecting x_A = 0.50, the boiling point T_b = 92°C and the temperature of saturated vapor for y_A = 0.50 is 98.8°C from Fig. 11.1-1. Using Eq. (11.6-5) for the saturated liquid enthalpy at the boiling point,

$$h = 0.5(138.2)(92 - 80.1) + (1 - 0.5)(167.5)(92 - 80.1) = 1820$$

Using Eq. (11.6-2) for $y_A = 0.5$, the saturated vapor enthalpy at 98.8°C is

$$H = 0.5[30\,820 + 96.3(98.8 - 80.1)] + (1 - 0.5)[34\,224 + 138.2(98.8 - 80.1)] = 34\,716$$

Selecting $x_A = 0.30$ and $y_A = 0.30$, $h = 2920$ and $H = 36\,268$. Also, for $x_A = 0.80$ and $y_A = 0.80$, $h = 562$ and $H = 32\,380$. These values are tabulated in Table 11.6-2 and plotted in Fig. 11.6-1.

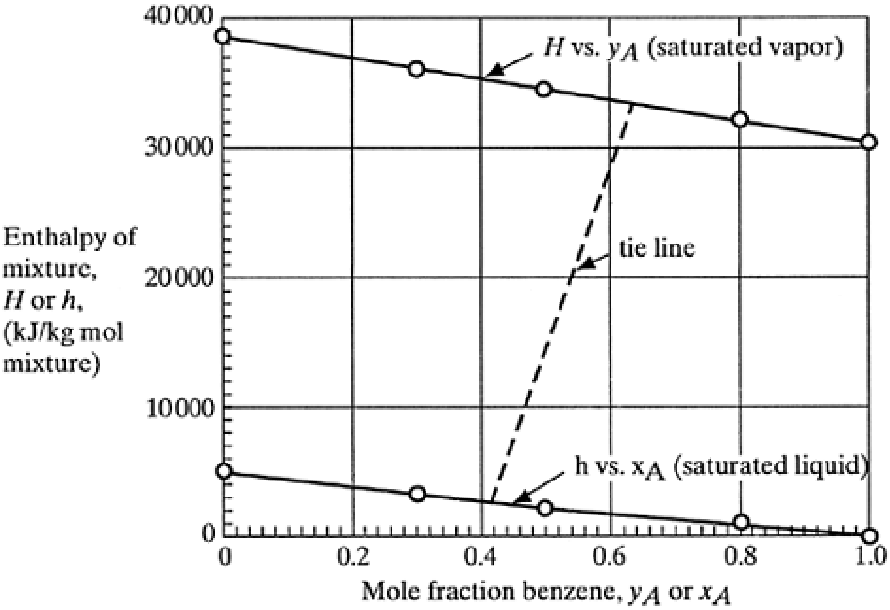

Figure 11.6-1. Enthalpy-concentration plot for benzene-toluene mixture at 1.0 atm abs.

Table 11.6-2. Enthalpy–Concentration Data for Benzene–Toluene Mixtures at 101.325 kPa (1 atm) Total Pressure

Saturated Liquid		*Saturated Vapor*	
Mole fraction, x_A	*Enthalpy, h, (kJ/kg mol)*	*Mole fraction, y_A*	*enthalpy, H, (kJ/kg mol)*
0	5109	0	38 439
0.30	2920	0.30	36 268
0.50	1820	0.50	34 716
0.80	562	0.80	32 380
1.00	0	1.00	30 820

Some properties of the enthalpy–concentration plot are as follows. The region in between the saturated vapor line and the saturated liquid line is the two-phase liquid–vapor region. From Table 11.1-1, for $x_A = 0.411$, the vapor in equilibrium is $y_A = 0.632$. These two points are plotted in Fig. 11.6-1; this tie line represents the enthalpies and compositions of the liquid and vapor phases in equilibrium. Other tie lines can be drawn in a similar manner. The region below the h-versus-x_A line represents liquid below the boiling point.

Distillation in Enriching Section of Tower

To analyze the enriching section of a fractionating tower using enthalpy–concentration data, we make an overall and a component balance in Fig. 11.6-2:

Equation 11.6-6.

$$V_{n+1} = L_n + D$$

Equation 11.6-7.

$$V_{n+1}\,y_{n+1} = L_n x_n + D x_D$$

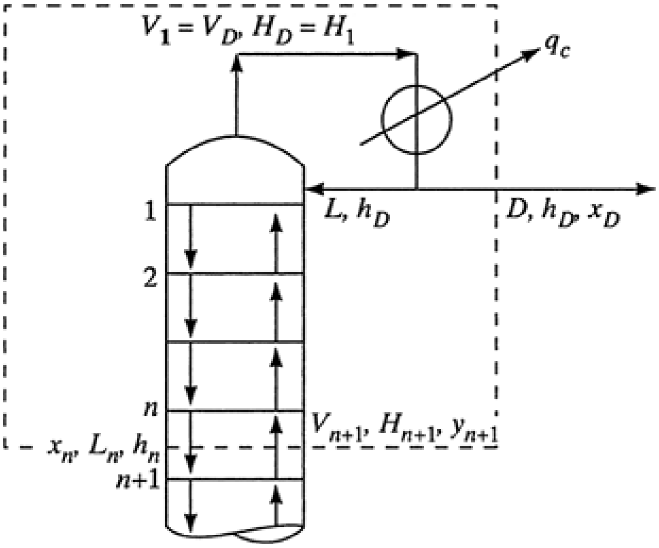

Figure 11.6-2. Enriching section of distillation tower.

Equation (11.6-7) can be rearranged to give the enriching-section operating line:

Equation 11.6-8.

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{D x_D}{V_{n+1}}$$

This is the same as Eq. (11.4-7) for the McCabe–Thiele method, but now the liquid and vapor flow rates V_{n+1} and L_n may vary throughout the tower, and Eq. (11.6-8) will not be a straight line on an *x-y* plot.

Making an enthalpy balance,

Equation 11.6-9.

$$V_{n+1} H_{n+1} = L_n h_n + D h_D + q_c$$

where q_c is the condenser duty, kJ/h or kW (btu/h). An enthalpy balance can be made just around the condenser:

Equation 11.6-10.

$$q_c = V_1 H_1 - L h_D - D h_D$$

By combining Eqs. (11.6-9) and (11.6-10) to eliminate q_c, an alternative form is obtained:

Equation 11.6-11.

$$V_{n+1} H_{n+1} = L_n h_n + V_1 H_1 - L h_D$$

Substituting the value of L_n from Eq. (11.6-6) into (11.6-11),

Equation 11.6-12.

$$V_{n+1}H_{n+1} = (V_{n+1} - D)h_n + V_1H_1 - Lh_D$$

Equations (11.6-8) and (11.6-12) are the final working equations for the enriching section.

In order to plot the operating line Eq. (11.6-8), the terms V_{n+1} and L_n must be determined from Eq. (11.6-12). If the reflux ratio is set, V_1 and L are known. The values H_1 and h_D can be determined by means of Eqs. (11.6-1) and (11.6-2) or from an enthalpy–concentration plot. If a value of x_n is selected, it is a trial-and-error solution to obtain H_{n+1}, since y_{n+1} is not known. The steps to follow are given below:

1. Select a value of x_n. Assume $V_{n+1} = V_1 = L + D$ and $L_n = L$. Then using these values in Eq. (11.6-8), calculate an approximate value for y_{n+1}. This assumes a straight operating line.
2. Using this y_{n+1}, obtain H_{n+1}, and obtain h_n using x_n. Substitute these values into Eq. (11.6-12) and solve for V_{n+1}. Obtain L_n from Eq. (11.6-6).
3. Substitute into Eq. (11.6-8) and solve for y_{n+1}.
4. If the calculated value of y_{n+1} does not equal the assumed value of y_{n+1}, repeat steps 2–3. Generally, a second trial is not needed. Assume another value of x_n and repeat steps 1–4.
5. Plot the curved operating line for the enriching section. Generally, only a few values for the flows L_n and V_{n+1} are needed to determine the operating line, which is slightly curved.

Distillation in Stripping Section of Tower

To analyze the stripping section of a distillation tower, an overall and a component material balance are made on Fig. 11.4-5a:

Equation 11.6-13.

$$L_m = W + V_{m+1}$$

Equation 11.6-14.

$$L_m x_m = W x_W + V_{m+1} y_{m+1}$$

Equation 11.6-15.

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{W x_W}{V_{m+1}}$$

Making an enthalpy balance with q_R kJ/h or kW(btu/h) entering the reboiler in Fig. 11.4-5a, and substituting ($V_{m+1} + W$) for L_m from Eq. (11.6-13),

Equation 11.6-16.

$$V_{m+1}H_{m+1} = (V_{m+1} + W)h_m + q_R - Wh_W$$

Making an overall enthalpy balance in Fig. 11.4-3,

Equation 11.6-17.

$$q_R = Dh_D + Wh_W + q_c - Fh_F$$

The final working equations to use are Eqs. (11.6-15)–(11.6-17).

Using a method similar to that for the enriching section to solve the equations, select a value of y_{m+1} and calculate an approximate value for x_m from Eq. (11.6-15), assuming constant molal overflow. Then calculate V_{m+1} and L_m from Eqs. (11.6-16) and (11.6-13). Then use Eq. (11.6-15) to determine x_m. Compare this calculated value of x_m with the assumed value.

EXAMPLE 11.6-2. Distillation Using Enthalpy–Concentration Method

A liquid mixture of benzene–toluene is being distilled under the same conditions as in Example 11.4-1, except that a reflux ratio of 1.5 times the minimum reflux ratio is to be used. The value R_m = 1.17 from Example 11.4-2 will be used. Use enthalpy balances to calculate the flow rates of the liquid and vapor at various points in the tower and plot the curved operating lines. Determine the number of theoretical stages needed.

Solution: The given data are as follows: F = 100 kg mol/h, x_F = 0.45, x_D = 0.95, x_W = 0.10, $R = 1.5R_m = 1.5(1.17) = 1.755$, D = 41.2 kg mol/h, W = 58.8 kg mol/h. The feed enters at 54.4°C and q = 1.195. The flows at the top of the tower are calculated as follows:

$$\frac{L}{D} = 1.755; \qquad L = 1.755(41.2) = 72.3;$$

$$V_1 = L + D = 72.3 + 41.2 = 113.5$$

From Fig. 11.1-1, the saturation temperature at the top of the tower for $y_1 = x_D = 0.95$ is 82.3°C. Using Eq. (11.6-2),

$$H_1 = 0.95[30\,820 + 96.3(82.3 - 80.1)] + (1 - 0.95)[34\,224 + 138.2(82.3 - 80.1)] = 31\,206$$

This value of 31 206 could also have been obtained from the enthalpy–concentration plot, Fig. 11.6-1. The boiling point of the distillate D is obtained from Fig. 11.1-1 and is 81.1°C. Using Eq. (11.6-5),

$$h_D = 0.95(138.2)(81.1 - 80.1) + (1 - 0.95)(167.5)(81.1 - 80.1) = 139$$

Again, this value could have been obtained from Fig. 11.6-1.

Following the procedure outlined for the enriching section for step 1, a value of x_n = 0.55 is selected. Assuming a straight operating line for Eq. (11.6-8), an approximate value of y_{n+1} is obtained:

$$y_{n+1} = \frac{72.3}{113.5}x_n + \frac{41.2}{113.5}(0.95) = 0.637(x_n) + 0.345$$

$$= 0.637(0.55) + 0.345 = 0.695$$

Starting with step 2 and using Fig. 11.6-1, for x_n = 0.55, h_n = 1590, and for y_{n+1} = 0.695, H_{n+1} = 33 240. Substituting into Eq. (11.6-12) and solving,

$$V_{n+1}(33\,240) = (V_{n+1} - 41.2)1590 + 113.5(31\,206) - 72.3(139)$$

$$V_{n+1} = 109.5$$

Using Eq. (11.6-6),

$$109.5 = L_n + 41.2 \quad \text{or} \quad L_n = 68.3$$

For step 3, substituting into Eq. (11.6-8),

$$y_{n+1} = \frac{68.3}{109.5}(0.55) + \frac{41.2}{109.5}(0.95) = 0.700$$

This calculated value of y_{n+1} = 0.700 is sufficiently close to the approximate value of 0.695 that no further trials are needed.

Selecting another value for x_n = 0.70 and using Eq. (11.6-8), an approximate value of y_{n+1} is calculated:

$$y_{n+1} = \frac{72.3}{113.5}(0.70) + \frac{41.2}{113.5}(0.95) = 0.791$$

Using Fig. 11.6-1 for x_n = 0.70, h_n = 1000, and for y_{n+1} = 0.791, H_{n+1} = 32 500. Substituting into Eq. (11.6-12) and solving,

$$V_{n+1}(32\,500) = (V_{n+1} - 41.2)1000 + 113.5(31\,206) - 72.3(139)$$

$$V_{n+1} = 110.8$$

Using Eq. (11.6-6),

$$L_n = 110.8 - 41.2 = 69.6$$

Substituting into Eq. (11.6-8),

$$y_{n+1} = \frac{69.6}{110.8}(0.70) + \frac{41.2}{110.8}(0.95) = 0.793$$

In Fig. 11.6-3, the points for the curved operating line in the enriching section are plotted. This line is approximately straight and is very slightly above that for constant molal overflow.

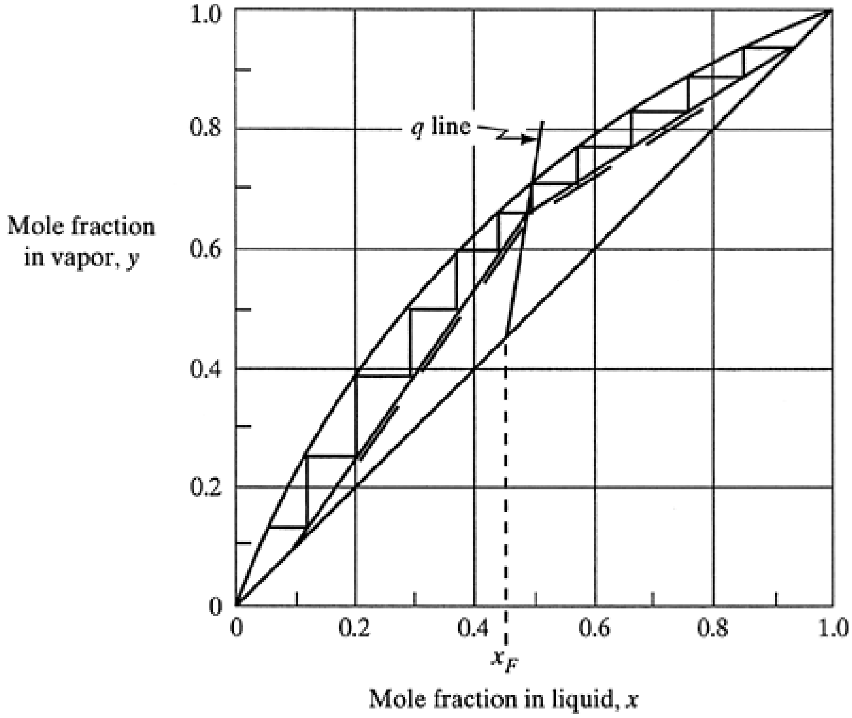

Figure 11.6-3. Plot of curved operating lines using enthalpy–concentration method for Example 11.6-2. Solid lines are for enthalpy–concentration method and dashed lines for constant molal overflow.

Using Eq. (11.6-10), the condenser duty is calculated:

$$q_c = 113.5(31\,206) - 72.3(139) - 41.2(139)$$
$$= 3\,526\,100 \text{ kJ/h}$$

To obtain the reboiler duty q_R, values for h_W and h_F are needed. Using Fig. 11.6-1 for x_W = 0.10, h_W = 4350. The feed is at 54.5°C. Using Eq. (11.6-5),

$$h_F = 0.45(138.2)(54.5 - 80.1) + (1 - 0.45)(167.5)(54.5 - 80.1)$$
$$= -3929$$

Using Eq. (11.6-17),

$$q_R = 41.2(139) + 58.8(4350) + 3\,526\,100 - 100(-3929)$$
$$= 4\,180\,500 \text{ kJ/h}$$

Using Fig. 11.4-5 and making a material balance below the bottom tray and around the reboiler,

Equation 11.6-18.

$$L_N = W + V_W$$

Rewriting Eq. (11.6-16) for this bottom section,

Equation 11.6-19.

$$V_W H_W = (V_W + W)h_N + q_R - Wh_W$$

From the equilibrium diagram, Fig. 11.1-2, for $x_W = 0.10$, $y_W = 0.207$, which is the vapor composition leaving the reboiler.

For equimolal overflow in the stripping section, using Eqs. (11.4-14) and (11.4-15),

Equation 11.4-14.

$$L_m = L_n + qF = 72.3 + 1.195(100) = 191.8$$

Equation 11.4-15.

$$V_{m+1} = V_{n+1} - (1 - q)F$$
$$= 113.5 - (1 - 1.195)100 = 133.0$$

Selecting $y_{m+1} = y_W = 0.207$, and using Eq. (11.6-15), an approximate value of $x_m = x_N$ is obtained:

Equation 11.6-15.

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{Wx_w}{V_{m+1}}$$

$$0.207 = \frac{191.8}{133.0}(x_N) - \frac{58.8}{133.0}(0.10)$$

Solving, $x_N = 0.174$. From Fig. (11.6-1), for $x_N = 0.174$, $h_N = 3800$, and for $y_W = 0.207$, $H_W = 37\,000$. Substituting into Eq. (11.6-19),

$$V_W(37\,000) = (V_W + 58.8)(3800) + 4\,180\,500 - 58.8(4350)$$

Solving, $V_W = 125.0$. Using Eq. (11.6-18), $L_N = 183.8$. Substituting into Eq. (11.6-15) and solving for x_N,

$$0.207 = \frac{183.8}{125.0}(x_N) - \frac{58.8}{125.0}(0.10)$$
$$x_N = 0.173$$

This value of 0.173 is quite close to the approximate value of 0.174.

Assuming a value of $y_{m+1} = 0.55$ and using Eq. (11.6-15), an approximate value of x_m is obtained:

$$y_{m+1} = 0.55 = \frac{191.8}{133.0}(x_m) - \frac{58.8}{133.0}(0.10)$$

$$x_m = 0.412$$

From Fig. (11.6-1), for $x_m = 0.412$, $h_m = 2300$, and for $y_{m+1} = 0.55$, $H_m = 34\,400$. Substituting into Eq. (11.6-16),

$$V_{m+1}(34\,400) = (V_{m+1} + 58.8)(2300) + 4\,180\,500 - 58.8(4350)$$

Solving, $V_{m+1} = 126.5$. Using Eq. (11.6-13),

$$L_m = W + V_{m+1} = 58.8 + 126.5 = 185.3$$

Substituting into Eq. (11.6-15) and solving for x_m,

$$y_{m+1} = 0.55 = \frac{185.3}{126.5}x_m - \frac{58.8}{126.5}(0.1)$$

$$x_m = 0.407$$

This value of 0.407 is sufficiently close to the approximate value of 0.412 that no further trials are needed. The two points calculated for the stripping section are plotted in Fig. 11.6-3. This stripping line is also approximately straight and is very slightly above the operating line for constant molal overflow.

Using the operating line for the enthalpy balance method, the number of theoretical steps is 10.4. Using the equimolal method, 9.9 steps are obtained. This difference would be larger if the reflux ratio of 1.5 times R_m were decreased to, say, 1.2 or 1.3. At larger reflux ratios, this difference in number of steps would be less.

Note that in Example 11.6-2, in the stripping section the vapor flow increases slightly from 125.0 to 126.5 in going from the reboiler to near the feed tray. These values are lower than the value of 133.0 obtained assuming equimolal overflow. Similar conclusions hold for the enriching section. The enthalpy–concentration method is useful in calculating the internal vapor and liquid flows at any point in the column. These data are then used in sizing the trays. Also, calculations of q_c and q_R are used in designing the condenser and reboiler. This method is very applicable to design using a computer solution for binary and multicomponent mixtures to make tray-to-tray mass and enthalpy balances for the whole tower. The more restrictive Ponchon–Savarit graphical method for only binary mixtures is available (K3, T2).

DISTILLATION OF MULTICOMPONENT MIXTURES

Introduction to Multicomponent Distillation

In industry many of the distillation processes involve the separation of more than two components. The general principles of design for multicomponent distillation towers are the same in many respects as those described for binary systems. There is one mass balance for each component in the multicomponent mixture. Enthalpy or heat balances are made which are similar to those for the binary case. Equilibrium data are used to calculate boiling points and dew points. The concepts of minimum reflux and total reflux as limiting cases are also used.

Number of distillation towers needed

In binary distillation, one tower was used to separate the two components *A* and *B* into relatively pure components, with *A* in the overhead and *B* in the bottoms. However, in a multicomponent mixture of *n* components, $n - 1$ fractionators will be required for separation. For example, for a three-component system of components *A, B*, and *C*, where *A* is the most volatile and *C* the least volatile, two columns will be needed, as shown in Fig. 11.7-1. The feed of *A, B*, and *C* is distilled in column 1, and *A* and *B* are removed in the overhead and *C* in the bottoms. Since the separation in this column is between *B* and *C*, the bottoms containing *C* will contain a small amount of *B* and often a negligible amount of *A* (often called trace component). The amount of the trace component *A* in the bottoms can usually be neglected if the relative volatilities are reasonably large. In column 2 the feed of *A* and *B* is distilled, with *A* in the distillate containing a small amount of component *B* and a much smaller amount of *C*. The bottoms containing *B* will also be contaminated with a small amount of *C* and *A*. Alternately, column 1 could be used to remove *A* overhead, with *B* plus *C* being fed to column 2 for separation of *B* and *C*.

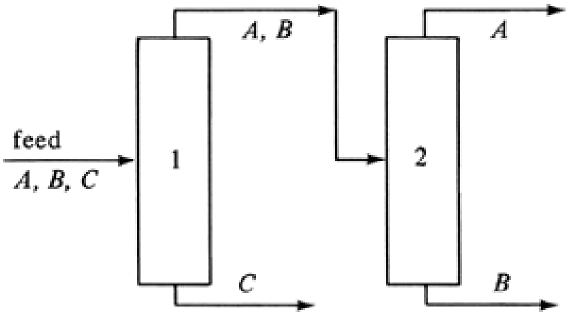

Figure 11.7-1. Separation of a ternary system of A, B, and C.

Design calculation methods

In multicomponent distillation, as in binary, ideal stages or trays are assumed in the stage-to-stage calculations. Using equilibrium data, equilibrium calculations are used to obtain the boiling point and equilibrium vapor composition from a given liquid composition or the dew point and liquid composition from a given vapor composition. Material balances and heat balances similar to those described in Section 11.6 are then used to calculate the flows to and from the adjacent stages. These stage-to-stage design calculations involve trial-and-error calculations, and high-speed digital computers are generally used to provide rigorous solutions.

In a design the conditions of the feed are generally known or specified (temperature, pressure, composition, flow rate). Then, in most cases, the calculation procedure follows either of two general methods. In the first method, the desired separation or split between two of the components is specified and the number of theoretical trays is calculated for a selected reflux ratio. It is clear that with more than two components in the feed, the complete compositions of the distillate and bottoms are not then known, and trial-and-error procedures must be used. In the second method, the number of stages in the enriching section and stripping section and the reflux ratio are specified or assumed and the separation of the components is calculated using assumed liquid and vapor flows and temperatures for the first trial. This approach is often preferred for computer calculations (H2, P1). In the trial-and-error procedures, the design method of Thiele and Geddes (P1, S1, T1), which is reliable, is often used to calculate resulting distillate and bottoms compositions together with tray temperatures and compositions. Various combinations and variations of the above rigorous calculation methods are available in the literature (H2, P1, S1) and will not be considered further.

The variables in the design of a distillation column are all interrelated, and there are only a certain number of these which may be fixed in the design. For a more detailed discussion of the specification of these variables, see Kwauk (K2).

Shortcut calculation methods

In the remainder of this chapter, shortcut calculation methods for the approximate solution of multicomponent distillation are considered. These methods are quite useful for studying a large number of cases rapidly to help orient the designer, determine approximate optimum conditions, or provide information for a cost estimate. Before discussing these methods, equilibrium relationships and calculation methods of bubble point, dew point, and flash vaporization for multicomponent systems will be covered.

Equilibrium Data in Multicomponent Distillation

For multicomponent systems which can be considered ideal, Raoult's law can be used to determine the composition of the vapor in equilibrium with the liquid. For example, for a system composed of four components, *A*, *B, C*, and *D*,

Equation 11.7-1.

$$p_A = P_A x_A, \qquad p_B = P_B x_B, \qquad p_C = P_C x_C, \qquad p_D = P_D x_D$$

Equation 11.7-2.

$$y_A = \frac{p_A}{P} = \frac{P_A}{P} x_A, \qquad y_B = \frac{P_B}{P} x_B, \qquad y_C = \frac{P_C}{P} x_C, \qquad y_D = \frac{P_D}{P} x_D$$

In hydrocarbon systems, because of nonidealities, the equilibrium data are often represented by

Equation 11.7-3.

$$y_A = K_A x_A, \qquad y_B = K_B x_B, \qquad y_C = K_C x_C, \qquad y_D = K_D x_D$$

where K_A is the vapor–liquid equilibrium constant or distribution coefficient for component *A*. These *K* values for light hydrocarbon systems (methane to decane) have been determined semiempirically and each *K* is a function of temperature and pressure. Convenient *K* factor charts are available from Depriester (D1) and Hadden and Grayson (H1). For light hydrocarbon systems, *K* is generally assumed not to be a function of composition, which is sufficiently accurate for most engineering calculations. Note that for an ideal system, $K_A = P_A/P$, and so on. As an example, data for the hydrocarbons *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane are plotted in Fig. 11.7-2 at 405.3 kPa (4.0 atm) absolute (D1, H1).

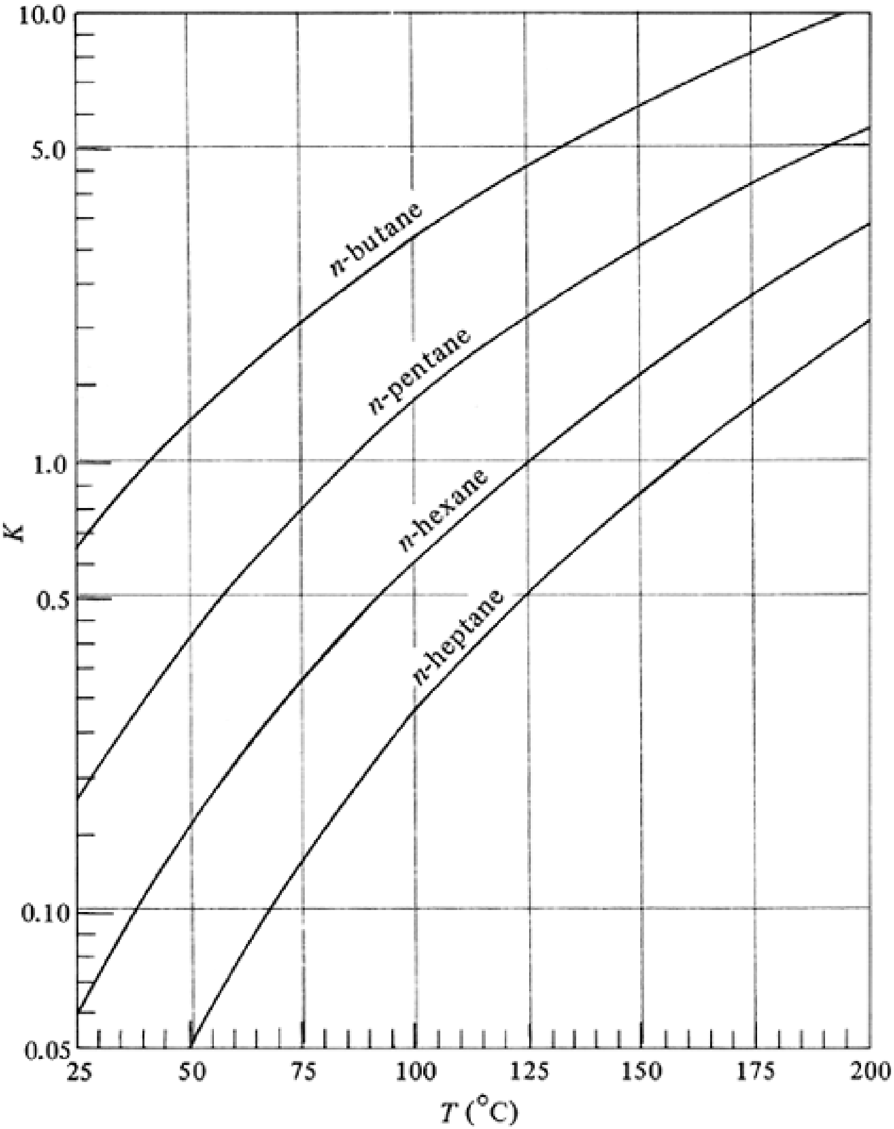

Figure 11.7-2. Equilibrium K values for light hydrocarbon systems at 405.3 kPa (4.0 atm) absolute.

The relative volatility α_i for each individual component in a multicomponent mixture can be defined in a manner similar to that for a binary mixture. If component *C* in a mixture, of *A, B, C*, and *D* is selected as the base component,

Equation 11.7-4.

$$\alpha_i = \frac{K_i}{K_C}, \qquad \alpha_A = \frac{K_A}{K_C}, \qquad \alpha_B = \frac{K_B}{K_C}, \qquad \alpha_C = \frac{K_C}{K_C} = 1.0, \qquad \alpha_D = \frac{K_D}{K_C}$$

The values of K_i will be a stronger function of temperature than the α_i values, since the K_i lines in Fig. 11.7-2 all increase with temperature in a similar manner.

Boiling Point, Dew Point, and Flash Distillation

Boiling point

At a specified pressure, the boiling point or bubble point of a given multicomponent mixture must satisfy the relation Σ $y_i = 1.0$. For a mixture of *A, B, C*, and *D*, with *C* as the base component,

Equation 11.7-5.

$$\sum y_i = \sum K_i x_i = K_C \sum \alpha_i x_i = 1.0$$

The calculation is a trial-and-error process, as follows. First a temperature is assumed and the values of α_i are calculated from the values of K_i at this temperature. Then the value of K_C is calculated from $K_C = 1.0/\sum \alpha_i x_i$. The temperature corresponding to the calculated value of $K_C = 1.0/\sum \alpha_i x_i$. The temperature corresponding to the calculated value of K_C is compared to the assumed temperature. If the values differ, the calculated temperature is used for the next iteration. After the final temperature is known, the vapor composition is calculated from

Equation 11.7-6.

$$y_i = \frac{\alpha_i x_i}{\Sigma\,(\alpha_i x_i)}$$

Dew point

For the dew-point calculation, which is also trial and error,

Equation 11.7-7.

$$\sum x_i = \sum \left(\frac{y_i}{K_i}\right) = \left(\frac{1}{K_C}\right) \sum \left(\frac{y_i}{\alpha_i}\right) = 1.0$$

The value of K_C is calculated from $K_C = 1.0/\sum \alpha_i x_i$. After the final temperature is known, the liquid composition is calculated from

Equation 11.7-8.

$$x_i = \frac{y_i/\alpha_i}{\Sigma\,(y_i/\alpha_i)}$$

EXAMPLE 11.7-1. Boiling Point of a Multicomponent Liquid

A liquid feed to a distillation tower at 405.3 kPa abs is fed to a distillation tower. The composition in mole fractions is as follows: *n*-butane ($x_A = 0.40$), *n*-pentane ($x_B = 0.25$), *n*-hexane ($x_C = 0.20$), *n*-heptane ($x_D = 0.15$). Calculate the boiling point and the vapor in equilibrium with the liquid.

Solution: First a temperature of 65°C is assumed and the values of *K* obtained from Fig. 11.7-2. Using component *C* (*n*-hexane) as the base component, the following values are calculated using Eq. (11.7-5) for the first trial:

	Trial 1 (65°C)				*Trial 3 (70°C) Final*			
Comp.	x_i	K_i	$\frac{K_i}{K_C} = \alpha_i$	$\alpha_i x_i$	K_i	α_i	$\alpha_i x_i$	y_i
A	0.40	1.68	6.857	2.743	1.86	6.607	2.643	0.748
B	0.25	0.63	2.571	0.643	0.710	2.522	0.631	0.178
C	0.20	0.245	1.000	0.200	0.2815	1.000	0.200	0.057

	Trial 1 (65°C)				***Trial 3 (70°C) Final***			
Comp.	x_i	K_i	$\frac{K_i}{K_C} = \alpha_i$	$\alpha_i x_i$	K_i	α_i	$\alpha_i x_i$	y_i
D	0.15	0.093	0.380	0.057	0.110	0.391	0.059	0.017
	1.00			$\sum \alpha_i x_i = 3.643$			$\sum \alpha_i x_i = 3.533$	1.000
$K_C = 1/\sum \alpha_i x_i = 1/3.643 = 0.2745$(69°C)					$K_C = 1/3.533 = 0.2830$ (70°C)			

The calculated value of K_C is 0.2745, which corresponds to 69°C, Fig. 11.7-2. Using 69°C for trial 2, a temperature of 70°C is obtained. Using 70°C for trial 3, the calculations shown give a final calculated value of 70°C, which is the bubble point. Values of y_i are calculated from Eq. (11.7-6).

Flash distillation of multicomponent mixture

For flash distillation, the process flow diagram is shown in Fig. 11.3-1. Defining $f = V/F$ as the fraction of the feed vaporized and $(1 - f) = L/F$ as the fraction of the feed remaining as liquid, and making a component i balance as in Eq. (11.3-6), the following is obtained:

Equation 11.7-9.

$$y_i = \frac{f-1}{f} x_i + \frac{x_{iF}}{f}$$

where y_i is the composition of i in the vapor, in equilibrium with x_i in the liquid after vaporization. For equilibrium, $y_i = K_i x_i = K_C \alpha_i x_i$, where $\alpha_i = K_i/K_C$. Then Eq. (11.7-9) becomes

Equation 11.7-10.

$$y_i = K_C \alpha_i x_i = \frac{f-1}{f} x_i + \frac{x_{iF}}{f}$$

Solving for x_i and summing for all components,

Equation 11.7-11.

$$\sum x_i = \sum \frac{x_{iF}}{f(K_C \alpha_i - 1) + 1} = 1.0$$

This is solved by trial and error by first assuming a temperature if the fraction f vaporized has been set. When the $\sum x_i$ values add up to 1.0, the proper temperature has been chosen. The composition of the vapor y_i can be obtained from $y_i = K_C \alpha_i x_i$ or by a material balance.

Key Components in Multicomponent Distillation

Fractionation of a multicomponent mixture in a distillation tower will allow separation only between two components. For a mixture of *A, B, C, D*, and so on, a separation in one tower can only be made between *A* and *B*, or *B* and *C*, and so on. The components separated are called the *light key,* which is the more volatile (identified by the subscript *L*), and the *heavy key* (*H*). The components more volatile than the light key are called *light components* and will be present in the bottoms in small amounts. The components less volatile than the heavy key are called *heavy components* and will be present in the distillate in small amounts. The two key components are present in significant amounts in both the distillate and bottoms.

Total Reflux for Multicomponent Distillation

Minimum stages for total reflux

Just as in binary distillation, the minimum number of theoretical stages or steps, N_m, can be determined for multicomponent distillation for total reflux. The Fenske equation (11.4-23) also applies to any two components in a multicomponent system. When applied to the heavy key H and the light key L, it becomes

Equation 11.7-12.

$$N_m = \frac{\log[(x_{LD}D/x_{HD}D)(x_{HW}W/x_{LW}W)]}{\log(\alpha_{L,\mathrm{av}})}$$

where x_{LD} is mole fraction of light key in distillate, x_{LW} is mole fraction in bottoms, x_{HD} is mole fraction of heavy key in distillate, and x_{HW} is mole fraction in bottoms. The average value of α_L of the light key is calculated from α_{LD} at the top temperature (dew point) of the tower and α_{LW} at the bottoms temperature:

Equation 11.7-13.

$$\alpha_{L,\mathrm{av}} = \sqrt{\alpha_{LD}\alpha_{LW}}$$

Note that the distillate dew-point and bottoms boiling-point estimation is partially trial and error, since the distribution of the other components in the distillate and bottoms is not known and can affect these values.

Distribution of other components

To determine the distribution or concentration of other components in the distillate and bottoms at total reflux, Eq. (11.7-12) can be rearranged and written for any other component i as follows:

Equation 11.7-14.

$$\frac{x_{iD}D}{x_{iW}W} = (\alpha_{i,\mathrm{av}})^{N_m}\frac{x_{HD}D}{x_{HW}W}$$

These concentrations of the other components determined at total reflux can be used as approximations with finite and minimum reflux ratios. More accurate methods for finite and minimum reflux are available elsewhere (H2, S1, V1).

EXAMPLE 11.7-2. Calculation of Top and Bottom Temperatures and Total Reflux

The liquid feed of 100 mol/h at the boiling point given in Example 11.7-1 is fed to a distillation tower at 405.3 kPa and is to be fractionated so that 90% of the *n*-pentane (*B*) is recovered in the distillate and 90% of the *n*-hexane (*C*) in the bottoms. Calculate the following:

a. Moles per hour and composition of distillate and bottoms.
b. Top temperature (dew point) of distillate and boiling point of bottoms.
c. Minimum stages for total reflux and distribution of other components in the distillate and bottoms.

Solution: For part (a), material balances are made for each component, with component *n*-pentane (*B*) being the light key (*L*) and *n*-hexane (*C*) the heavy key (*H*). For the overall balance,

Equation 11.7-15.

$$F = D + W$$

For component *B*, the light key,

Equation 11.7-16.

$$x_{BF}F = 0.25(100) = 25.0 = y_{BD}D + x_{BW}W$$

Since 90% of *B* is in the distillate, $y_{BD}D = (0.90)(25) = 22.5$. Hence, $x_{BW}W = 2.5$. For component *C*, the heavy key,

Equation 11.7-17.

$$x_{CF}F = 0.20(100) = 20.0 = y_{CD}D + x_{CW}W$$

Also, 90% of *C* is in the bottoms, and $x_{CW}W = 0.90(20) = 18.0$. Then, $y_{CD}D = 2.0$. For the first trial, it is assumed that no component *D* (heavier than the heavy key *C*) is in the distillate and no light *A* in the bottoms. Hence, moles *A* in distillate = $y_{AD}D = 0.40(100) = 40.0$. Also, moles *D* in bottoms = $x_{DW}W = 0.15(100) = 15.0$. These values are tabulated below.

	Feed, *F*		**Distillate, *D***		**Bottoms, *W***	
Comp.	x_F	$x_F F$	$y_D = x_D$	$y_D D$	x_W	$x_W W$
A	**0.40**	**40.0**	**0.620**	**40.0**	**0**	**0**
***B* (lt key *L*)**	**0.25**	**25.0**	**0.349**	**22.5**	**0.070**	**2.5**
***C* (hy key *H*)**	**0.20**	**20.0**	**0.031**	**2.0**	**0.507**	**18.0**
D	**0.15**	**15.0**	**0**	**0**	**0.423**	**rowsep="1" 15.0**
	1.00	$F = 100.0$	**1.000**	$D = 64.5$	**1.000**	$W = 35.5$

For the dew point of the distillate (top temperature) in part (b), a value of 67°C will be estimated for the first trial. The *K* values are read from Fig. 11.7-2 and the α values calculated. Using Eqs. (11.7-7) and (11.7-8), the following values are calculated:

Comp.	y_{iD}	K_i(67°C)	α_i	y_i/α_i	x_i
A	0.620	1.75	6.73	0.0921	0.351
B (*L*)	0.349	0.65	2.50	0.1396	0.531
C (*H*)	0.031	0.26	1.00	0.0310	0.118
D	0	0.10	0.385	0	0
	1.000			$\sum y_i/\alpha_i = 0.2627$	1.000
	$K_C = \sum y_i/\alpha_i = 0.2627$				

The calculated value of K_C is 0.2627, which corresponds very closely to 67°C, which is the final temperature of the dew point.

For the bubble point of the bottoms, a temperature of 135°C is assumed for trial 1 and Eqs. (11.7-5) and (11.7-6) used for the calculations. A second trial using 132°C gives the final temperature as shown below:

Comp.	x_{iW}	K_i	α_i	$\alpha_i x_i$	y_i
A	0	5.00	4.348	0	0
B (*L*)	0.070	2.35	2.043	0.1430	0.164
C (*H*)	0.507	1.15	1.000	0.5070	0.580
D	0.423	0.61	0.530	0.2242	0.256
	1.000			$\sum \alpha_i x_i = 0.8742$	1.000
	$K_C = 1/0.8742 = 1.144$				

The calculated value of K_C is 1.144, which is close to the value at 132°C.

For part (c) the proper α values of the light key *L* (*n*-pentane) to use in Eq. (11.7-13) are as follows:

Equation 11.7-13.

$$\alpha_{LD} = 2.50 \qquad (t = 67°\text{C at the column top})$$

$$\alpha_{LW} = 2.04 \qquad (t = 132°\text{C at the column bottom})$$

$$\alpha_{L,\text{av}} = \sqrt{\alpha_{LD}\alpha_{LW}} = \sqrt{2.50(2.04)} = 2.258$$

Substituting into Eq. (11.7-12),

$$N_m = \frac{\log[(0.349 \times 64.5/0.031 \times 64.5)(0.507 \times 35.5/0.070 \times 35.5)]}{\log(2.258)}$$

$$= 5.404 \text{ theoretical stages (4.404 theoretical trays)}$$

The distribution or compositions of the other components can be calculated using Eq. (11.7-14). For component *A*, the average α value to use is

Equation 11.7-14.

$$\alpha_{A,\text{av}} = \sqrt{\alpha_{AD}\alpha_{AW}} = \sqrt{6.73 \times 4.348} = 5.409$$

$$\frac{x_{AD}D}{x_{AW}W} = (\alpha_{A,\text{av}})^{N_m}\frac{x_{HD}D}{x_{HW}W} = (5.409)^{5.404}\frac{0.031(64.5)}{0.507(35.5)} = 1017$$

Making an overall balance on *A*,

Equation 11.7-18.

$$x_{AF}F = 40.0 = x_{AD}D + x_{AW}W$$

Substituting $x_{AD}D = 1017x_{AW}W$ from Eq. (11.7-14) into (11.7-18) and solving,

$$x_{AW}W = 0.039, \qquad x_{AD}D = 39.961$$

For the distribution of component *D*, $\alpha_{D,av}$ = $\alpha_{D,\text{av}} = \sqrt{0.385 \times 0.530} = 0.452$ = 0.452.

$$\frac{x_{DD}D}{x_{DW}W} = (\alpha_{D,\text{av}})^{N_m}\frac{x_{HD}D}{x_{HW}W} = (0.452)^{5.404}\frac{0.031(645)}{0.507(355)} = 0.001521$$

$$x_{DF}F = 15.0 = x_{DD}D + x_{DW}W$$

Solving, $x_{DD}D = 0.023$, $x_{DW}W = 14.977$.

The revised distillate and bottoms compositions are as follows:

	Distillate, *D*		**Bottoms, *W***	
Comp.	$y_D = x_D$	$x_D D$	x_W	$x_W W$
A	**0.6197**	**39.961**	**0.0011**	**0.039**
***B* (*L*)**	**0.3489**	**22.500**	**0.0704**	**2.500**
***C* (*H*)**	**0.0310**	**2.000**	**0.5068**	**18.000**
D	**0.0004**	**0.023**	**0.4217**	**14.977**
	1.0000	***D* = 64.484**	**1.0000**	***W* = 35.516**

Hence, the number of moles of *D* in the distillate is quite small, as is the number of moles of *A* in the bottoms.

Using the new distillate composition, a recalculation of the dew point assuming 67°C gives a calculated value of $K_C = 0.2637$. This is very close to that of 0.2627 obtained when the trace amount of D in the distillate was assumed as zero. Hence, the dew point is 67°C. Repeating the bubble-point calculation for the bottoms assuming 132°C, a calculated value of $K_C = 1.138$, which is close to the value at 132°C. Hence, the bubble point remains at 132°C. If either the bubble- or dew-point temperatures had changed, the new values would then be used in a recalculation of N_m.

Shortcut Method for Minimum Reflux Ratio for Multicomponent Distillation

As in the case of binary distillation, the minimum reflux ratio R_m is that reflux ratio which will require an infinite number of trays for the given separation of the key components.

For binary distillation, only one "pinch point" occurs where the number of steps becomes infinite, and that is usually at the feed tray. For multicomponent distillation, two pinch points or zones of constant composition occur: one in the section above the feed plate and another below the feed tray. The rigorous plate-by-plate stepwise procedure for calculating R_m is trial and error and can be extremely tedious for hand calculations.

Underwood's shortcut method for calculating R_m (U1, U2) uses constant average α values and assumes constant flows in both sections of the tower. This method provides a reasonably accurate value. The two equations to be solved in order to determine the minimum reflux ratio are

Equation 11.7-19.

$$1 - q = \sum \frac{\alpha_i x_{iF}}{\alpha_i - \theta}$$

Equation 11.7-20.

$$R_m + 1 = \sum \frac{\alpha_i x_{iD}}{\alpha_i - \theta}$$

The values of x_{iD} for each component in the distillate in Eq. (11.7-20) are supposed to be the values at the minimum reflex. However, as an approximation, the values obtained using the Fenski total reflux equation are used. Since each α_i may vary with temperature, the average value of α_i to use in the preceding equations is approximated by using α_i at the average temperature of the top and bottom of the tower. Some (P1, S1) have used the average α which is used in the Fenske equation or the α at the entering feed temperature. To solve for R_m, the value of θ in Eq. (11.7-19) is first obtained by trial and error. This value of θ lies between the α value of the light key and the α value of the heavy key, which is 1.0. Using this value of θ in Eq. (11.7-20), the value of R_m is obtained directly. When distributed components appear between the key components, modified methods described by others (S1, T2, V1) can be used.

Shortcut Method for Number of Stages at Operating Reflux Ratio

Number of stages at operating reflux ratio

The determination of the minimum number of stages for total reflux presented in Section 11.7E and the minimum reflux ratio presented in Section 11.7F are useful for setting the allowable ranges for number of stages and flow conditions. These ranges are helpful in selecting the particular operating conditions for a design calculation. The relatively complex rigorous procedures for doing a stage-by-stage calculation at any operating reflux ratio have been discussed in Section 11.7A.

An important shortcut method for determining the theoretical number of stages required for an operating reflux ratio R is the empirical correlation of Erbar and Maddox (E1) given in Fig. 11.7-3. This correlation is somewhat similar to a correlation by Gilliland (G1) and should be considered as an approximate method. In Fig. 11.7-3 the operating reflux ratio R (for flow rates at the column top) is correlated with the minimum R_m obtained using the Underwood method, the minimum number of stages N_m obtained by the Fenske method, and the number of stages N at the operating R.

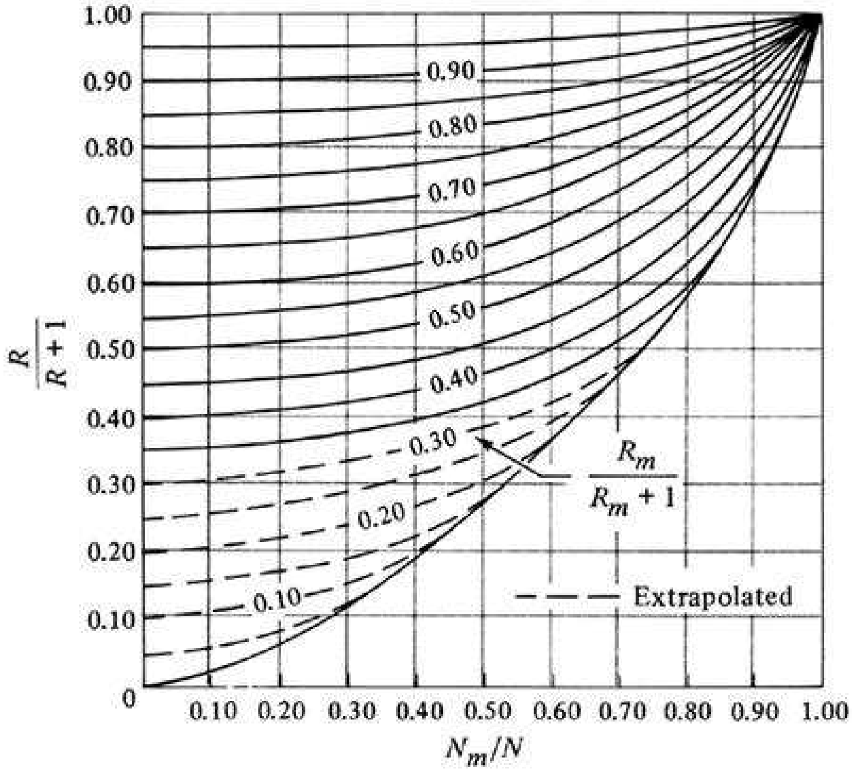

*Figure 11.7-3. Erbar–Maddox correlation between reflux ratio and number of stages (R_m based on Underwood method). [From J. H. Erbar and R. N. Maddox, Petrol. Refiner, **40**(5), 183 (1961). With permission.]*

Estimate of feed-plate location

Kirkbride (K1) has devised an approximate method to estimate the number of theoretical stages above and below the feed which can be used to estimate the feed-stage location. This empirical relation is as follows:

Equation 11.7-21.

$$\log \frac{N_e}{N_s} = 0.206 \log\left[\left(\frac{x_{HF}}{x_{LF}}\right)\frac{W}{D}\left(\frac{x_{LW}}{x_{HD}}\right)^2\right]$$

where N_e is the number of theoretical stages above the feed plate and N_s the number of theoretical stages below the feed plate.

EXAMPLE 11.7-3. Minimum Reflux Ratio and Number of Stages at Operating Reflux Ratio

Using the conditions and results given in Example 11.7-2, calculate the following:

a. Minimum reflux ratio using the Underwood method.

b. Number of theoretical stages at an operating reflux ratio R of $1.5R_m$ using the Erbar–Maddox correlation.

c. Location of feed tray using the method of Kirkbride.

***Solution*:** For part (a), the temperature to use for determining the values of α_i is the average between the top of 67°C and the bottom of 132°C (from Example 11.7-2) and is (67 + 132)/2, or 99.5°C. The K_i values obtained from Fig. 11.7-2 and the α_i values and distillate and feed compositions to use in Eqs. (11.7-19) and (11.7-20) are as follows:

Comp.	x_{iF}	x_{iD}	K_i (99.5°C)	α_i (99.5°C)	x_{iW}
A	0.40	0.6197	3.12	5.20	0.0011
B (*L*)	0.25	0.3489	1.38	2.30	0.0704
C (*H*)	0.20	0.0310	0.60	1.00	0.5068
D	0.15	0.0004	0.28	0.467	0.4217
	1.00	1.0000			1.0000

Substituting into Eq. (11.7-19) with q = 1.0 for feed at the boiling point,

Equation 11.7-22.

$$1 - q = 1 - 1 = 0 = \frac{5.20(0.40)}{5.20 - \theta} + \frac{2.30(0.25)}{2.30 - \theta} + \frac{1.00(0.20)}{1.00 - \theta} + \frac{0.467(0.15)}{0.467 - \theta}$$

This is trial and error, so a value of θ = 1.210 will be used for the first trial (θ must be between 2.30 and 1.00). This and other trials are shown below:

	2.08	**0.575**	**0.200**	**0.070**	
θ *(Assumed)*	**5.2 − θ**	**2.3 − θ**	**1.0 − θ**	**0.467 − θ**	Σ *(Sum)*
1.210	0.5213	0.5275	−0.9524	−0.0942	+0.0022
1.200	0.5200	0.5227	−1.0000	−0.0955	−0.0528
1.2096	0.5213	0.5273	−0.9542	−0.0943	+0.0001

The final value of θ = 1.2096 is substituted into Eq. (11.7-20) to solve for R_m:

$$R_m + 1 = \frac{5.20(0.6197)}{5.20 - 1.2096} + \frac{2.30(0.3489)}{2.30 - 1.2096} + \frac{1.00(0.031)}{1.00 - 1.2096} + \frac{0.467(0.0004)}{0.467 - 1.2096}$$

Solving, R_m = 0.395.

For part (b), the following values are calculated: $R = 1.5R_m = 1.5(0.395) = 0.593$, $R/(R + 1) = 0.593/(0.593 + 1.0) = 0.3723$, $R_m/(R_m + 1) = 0.395/(0.395 + 1.0) = 0.2832$. From Fig. 11.7-3, $N_m/N = 0.49$. Hence, $N_m/N = 0.49 = 5.40/N$. Solving, N = 11.0 theoretical stages in the tower. This gives 11.0 − 1.0 (reboiler), or 10.0 theoretical trays.

For the location of the feed tray in part (c), using Eq. (11.7-21),

$$\log \frac{N_e}{N_s} = 0.206 \log\left[\left(\frac{0.20}{0.25}\right)\frac{35.516}{64.484}\left(\frac{0.0704}{0.0310}\right)^2\right] = 0.07344$$

Hence, N_e/N_s = 1.184. Also, $N_e + N_s = 1.184N_s + N_s = N$ = 11.0 stages.

Solving, N_s = 5.0 and N_e = 6.0. This means that the feed tray is 6.0 trays from the top.

PROBLEMS

11.1-1. ***Phase Rule for a Vapor System.*** For the system NH_3–water and only a vapor phase present, calculate the number of degrees of freedom. What variables can be fixed?

A1: **Ans.** $F = 3$ degrees of freedom; variables T, P, y_A

11.1-2. ***Boiling Point and Raoult's Law.*** For the system benzene–toluene, do as follows, using the data from Table 11.1-1:

a. At 378.2 K, calculate y_A and x_A using Raoult's law.

b. If a mixture has a composition of $x_A = 0.40$ and is at 358.2 K and 101.32 kPa pressure, will it boil? If not, at what temperature will it boil and what will be the composition of the vapor first coming off?

11.1-3. ***Boiling-Point-Diagram Calculation.*** The vapor-pressure data are given below for the system hexane–octane:

		Vapor Pressure			
		n-Hexane		*n-Octane*	
T(°F)	*T(°C)*	*kPa*	*mm Hg*	*kPa*	*mm Hg*
155.7	68.7	101.3	760	16.1	121
175	79.4	136.7	1025	23.1	173
200	93.3	197.3	1480	37.1	278
225	107.2	284.0	2130	57.9	434
258.2	125.7	456.0	3420	101.3	760

a. Using Raoult's law, calculate and plot the x-y data at a total pressure of 101.32 kPa.

b. Plot the boiling-point diagram.

11.2-1. ***Single-Stage Contact of Vapor–Liquid System.*** A mixture of 100 mol containing 60 mol % *n*-pentane and 40 mol % *n*-heptane is vaporized at 101.32 kPa abs pressure until 40 mol of vapor and 60 mol of liquid in equilibrium with each other are produced. This occurs in a single-stage system, and the vapor and liquid are kept in contact with each other until vaporization is complete. The equilibrium data are given in Example 11.3-2. Calculate the composition of the vapor and the liquid.

11.3-1. ***Relative Volatility of a Binary System.*** Using the equilibrium data for the *n*-pentane–*n*-heptane system given in Example 11.3-2, calculate the relative volatility for each concentration and plot α versus the liquid composition x_A.

11.3-2. ***Comparison of Differential and Flash Distillation.*** A mixture of 100 kg mol which contains 60 mol % *n*-pentane (A) and 40 mol % *n*-heptane (B) is vaporized at 101.32 kPa pressure under differential conditions until 40 kg mol are distilled. Use equilibrium data from Example 11.3-2.

a. What is the average composition of the total vapor distilled and the composition of the remaining liquid?

b. If this same vaporization is done in an equilibrium or flash distillation and 40 kg mol are distilled, what is the composition of the vapor distilled and of the remaining liquid?

A6: **Ans.** (a) $x_2 = 0.405$, $y_{av} = 0.892$; (b) $x_2 = 0.430$, $y_2 = 0.854$

11.3-3. ***Differential Distillation of Benzene–Toluene.*** A mixture containing 70 mol % benzene and 30 mol % toluene is distilled under differential conditions at 101.32 kPa (1 atm). A total of one-third of the moles in the feed is vaporized. Calculate the average composition of the distillate and the composition of the remaining liquid. Use equilibrium data from Table 11.1-1.

11.3-4. ***Steam Distillation of Ethylaniline.*** A mixture contains 100 kg of H_2O and 100 kg of ethylaniline (mol wt = 121.1 kg/kg mol), which is immiscible with water. A very slight amount of nonvolatile impurity is dissolved in the organic. To purify the ethylaniline, it is steam-distilled by bubbling saturated steam into the mixture at a total pressure of 101.32 kPa (1 atm). Determine the boiling point of the mixture and the composition of the vapor. The vapor pressure of each of the pure compounds is as follows (T1):

Temperature			
K	**°C**	**PA (water) (kPa)**	**PB (ethylaniline) (kPa)**
353.8	**80.6**	**48.5**	**1.33**
369.2	**96.0**	**87.7**	**2.67**
372.3	**99.15**	**98.3**	**3.04**
386.4	**113.2**	**163.3**	**5.33**

11.3-5. ***Steam Distillation of Benzene.*** A mixture of 50 g mol of liquid benzene and 50 g mol of water is boiling at 101.32 kPa pressure. Liquid benzene is immiscible in water. Determine the boiling point of the mixture and the composition of the vapor. Which component will first be removed completely from the still? Vapor-pressure data for the pure components are as follows:

Temperature			
K	**°C**	**P_{water} (mm Hg)**	**$P_{benzene}$ (mm Hg)**
308.5	**35.3**	**43**	**150**
325.9	**52.7**	**106**	**300**
345.8	**72.6**	**261**	**600**
353.3	**80.1**	**356**	**760**

11.4-1. ***Distillation Using McCabe–Thiele Method.*** A rectification column is fed 100 kg mol/h of a mixture of 50 mol % benzene and 50 mol % toluene at 101.32 kPa abs pressure. The feed is liquid at the boiling point. The distillate is to contain 90 mol % benzene and the bottoms 10 mol % benzene. The reflux ratio is 4.52:1. Calculate the kg mol/h distillate, kg mol/h bottoms, and the number of theoretical trays needed using the McCabe–Thiele method.

A10: Ans. D = 50 kg mol/h, W = 50 kg mol/h, 4.9 theoretical trays plus reboiler

11.4-2. ***Rectification of a Heptane–Ethyl Benzene Mixture.*** A saturated liquid feed of 200 mol/h at the boiling point containing 42 mol % heptane and 58% ethyl benzene is to be fractionated at 101.32 kPa abs to give a distillate containing 97 mol % heptane and a bottoms containing 1.1 mol % heptane. The reflux ratio used is 2.5:1. Calculate the mol/h distillate, mol/h bottoms, theoretical number of trays, and the feed tray number. Equilibrium data are given below at 101.32 kPa abs pressure for the mole fraction *n*-heptane x_H and y_H:

Temperature				**Temperature**			
K	°C	x_H	y_H	K	°C	x_H	y_H
409.3	136.1	0	0	383.8	110.6	0.485	0.730
402.6	129.4	0.08	0.230	376.0	102.8	0.790	0.904
392.6	119.4	0.250	0.514	371.5	98.3	1.000	1.000

A11: **Ans.** *D* = 85.3 mol/h, *W* = 114.7 mol/h, 9.5 trays + reboiler, feed on tray 6 from top

11.4-3. ***Graphical Solution for Minimum Reflux Ratio and Total Reflux.*** For the rectification given in Problem 11.4-1, where an equimolar liquid feed of benzene and toluene is being distilled to give a distillate of composition x_D = 0.90 and a bottoms of composition x_W = 0.10, calculate the following using graphical methods:

a. Minimum reflux ratio R_m.
b. Minimum number of theoretical plates at total reflux.

A12: **Ans.** (a) R_m = 0.91; (b) 4.0 theoretical trays plus a reboiler

11.4-4. ***Minimum Number of Theoretical Plates and Minimum Reflux Ratio.*** Determine the minimum reflux ratio R_m and the minimum number of theoretical plates at total reflux for the rectification of a mixture of heptane and ethyl benzene as given in Problem 11.4-2. Do this by using the graphical methods of McCabe–Thiele.

11.4-5. ***Rectification Using a Partially Vaporized Feed.*** A total feed of 200 mol/h having an overall composition of 42 mol % heptane and 58 mol % ethyl benzene is to be fractionated at 101.3 kPa pressure to give a distillate containing 97 mol % heptane and a bottoms containing 1.1 mol % heptane. The feed enters the tower partially vaporized so that 40 mol % is liquid and 60 mol % vapor. Equilibrium data are given in Problem 11.4-2. Calculate the following:

a. Moles per hour distillate and bottoms.
b. Minimum reflux ratio R_m.
c. Minimum steps and theoretical trays at total reflux.
d. Theoretical number of trays required for an operating reflux ratio of 2.5:1. Compare with the results of Problem 11.4-2, which uses a saturated liquid feed.

11.4-6. ***Distillation Using a Vapor Feed.*** Repeat Problem 11.4-1 but use a feed that is saturated vapor at the dew point. Calculate the following:

a. Minimum reflux ratio R_m.
b. Minimum number of theoretical plates at total reflux.
c. Theoretical number of trays at an operating reflux ratio of 1.5(R_m).

11.4-7. ***Enriching Tower for Benzene–Toluene.*** An enriching tower is fed 100 kg mol/h of a saturated vapor feed containing 40 mol % benzene (*A*) and 60 mol % toluene (*B*) at 101.32 kPa abs. The distillate is to contain 90 mol % benzene. The reflux ratio is set at 4.0:1. Calculate the kg mol/h distillate *D* and bottoms *W* and their compositions. Also, calculate the number of theoretical plates required.

A16: **Ans.** *D* = 20 kg mol/h, *W* = 80 kg mol/h, x_W = 0.275

11.4-8. ***Stripping Tower.*** A liquid mixture containing 10 mol % *n*-heptane and 90 mol % *n*-octane is fed at its boiling point to the top of a stripping tower at 101.32 kPa abs. The bottoms are to contain 98 mol % *n*-octane. For every 3 mol of feed, 2 mol of vapor is withdrawn as product. Calculate the composition of the vapor and the number of theoretical plates required. The equilibrium data below are given as mole fraction *n*-heptane.

x	y	x	y
0.284	0.459	0.039	0.078
0.097	0.184	0.012	0.025
0.067	0.131		

11.4-9. ***Stripping Tower and Direct Steam Injection.*** A liquid feed at the boiling point contains 3.3 mol % ethanol and 96.7 mol % water and enters the top tray of a stripping tower. Saturated steam is injected directly into liquid in the bottom of the tower. The overhead vapor which is withdrawn contains 99% of the alcohol in the feed. Assume equimolar overflow for this problem. Equilibrium data for mole fraction of alcohol are as follows at 101.32 kPa abs pressure (1 atm abs):

x	y	x	y
0	0	0.0296	0.250
0.0080	0.0750	0.033	0.270
0.020	0.175		

a. For an infinite number of theoretical steps, calculate the minimum moles of steam needed per mole of feed. (*Note:* Be sure to plot the q line.)

b. Using twice the minimum moles of steam, calculate the number of theoretical steps needed, the composition of the overhead vapor, and the bottoms composition.

A18: **Ans.** (a) 0.121 mol steam/mol feed; (b) 5.0 theoretical steps, x_D = 0.135, x_W = 0.00033

11.5-1. ***Murphree Efficiency and Actual Number of Trays.*** For the distillation of heptane and ethyl benzene in Problem 11.4-2, the Murphree tray efficiency is estimated as 0.55. Determine the actual number of trays needed by stepping off the trays using the tray efficiency of 0.55. Also, calculate the overall tray efficiency E_O.

11.5-2. ***Packing and Tray Efficiencies for Absorption Tower.*** An absorber in a petroleum refinery uses a lean oil to absorb butane from a natural gas stream. The composition of the key component butane in the gas phase is related to its composition in the liquid phase at equilibrium by $y = mx = 0.7x$. At the tower bottom, where the flows are largest, $\rho_L = 57.9\ \text{lb}_m/\text{ft}^3$ (927 kg/m^3). At the average tower temperature, μ_L = 1.4 cp and the average molecular weight of the liquid is M_L = 245. Estimate the efficiency for a valve-tray tower and the HETP for Norton Intalox 2T structured packing.

11.5-3. ***Estimation of Tower Diameter of Sieve Tray.*** A distillation sieve-tray tower is being used to distill a hydrocarbon feed. The vapor flow rate at the tower bottom is 21 000 kg/hr and the liquid flow rate is 19 500 kg/hr. The density of the liquid ρ_L = 673 kg/m^3 and ρ_V = 3.68 kg/m^3. Assume a tray spacing of 24 in. (0.610 m). Calculate the tower diameter assuming the tower operates at 80% of flooding. Assume σ = 22.5 dyn/cm.

A21: **Ans.** K_v = 0.35, D = 1.372 m (4.50 ft)

11.6-1. ***Use of Enthalpy–Concentration Method to Distill an Ethanol–Water Solution.*** A mixture of 50 wt % ethanol and 50 wt % water which is saturated liquid at the boiling point is to be distilled at 101.3 kPa pressure to give a distillate containing 85 wt % ethanol and a bottoms containing 3 wt % ethanol. The feed rate is 453.6 kg/h and a reflux ratio of 1.5 is to be used. Use equilibrium and enthalpy data from Appendix A.3. Note that the data are given in wt fraction and kJ/kg. Use these consistent units in plotting the enthalpy–concentration data and equilibrium data. Do as follows:

a. Calculate the amount of distillate and bottoms.
b. Calculate the number of theoretical trays needed.
c. Calculate the condenser and reboiler loads.

A22: **Ans.** (a) D = 260.0 kg/h, W = 193.6 kg/h (b) 3.9 trays plus a reboiler (c) q_c = 698 750 kJ/h, q_R = 704 770 kJ/h

11.6-2. ***Distillation of Ethanol–Water Solution Using Enthalpy–Concentration Method.*** Repeat Problem 11.6-1 but use a reflux ratio of 2.0 instead of 1.5.

A23: **Ans.** 3.6 theoretical trays plus reboiler

11.6-3. ***Minimum Reflux and Theoretical Number of Trays.*** A feed of ethanol–water containing 60 wt % ethanol is to be distilled at 101.32 kPa pressure to give a distillate containing 85 wt % ethanol and a bottoms containing 2 wt % ethanol. The feed rate is 10 000 kg/h and its enthalpy is 116.3 kJ/kg (50 btu/lb$_m$). Use consistent units of kg/h, weight fraction, and kJ/kg.

a. Calculate the amount of distillate and bottoms.
b. Determine the minimum reflux ratio using enthalpy–concentration data from Appendix A.3.
c. Using 2.0 times the minimum reflux ratio, determine the theoretical number of trays needed.
d. Calculate the condenser and reboiler heat loads.
e. Determine the minimum number of theoretical plates at total reflux.

A24: **Ans.** (b) R_m = 0.373 (c) 4.4 theoretical trays plus reboiler (d) q_c = 3634 kW, q_R = 4096 kW (e) 2.8 theoretical trays plus reboiler

11.6-4. ***Distillation of Benzene–Toluene Feed Using Enthalpy–Concentration Method.*** A liquid feed of 100 kg mol/h of benzene–toluene at the boiling point contains 55 mol % benzene and 45 mol % toluene. It is being distilled at 101.32 kPa pressure to give a distillate with x_D = 0.98 and a bottoms of x_W = 0.04. Using a reflux ratio of 1.3 times the minimum and the enthalpy-concentration method, do as follows:

a. Determine the theoretical number of trays needed.
b. Calculate the condenser and reboiler heat loads.
c. Determine the minimum number of theoretical trays at total reflux.

11.6-5. ***Use of Enthalpy–Concentration Plot.*** For the system benzene–toluene do as follows:

a. Plot the enthalpy–concentration data using values from Table 11.6-2. For a value of $x = 0.60 = y$, calculate the saturated liquid enthalpy h and the saturated vapor enthalpy H and plot these data on the graph.
b. A mixture contains 60 mol of benzene and 40 mol of toluene. This mixture is heated so that 30 mol of vapor are produced. The mixture is in equilibrium. Determine the enthalpy of this overall mixture and plot this point on the enthalpy–concentration diagram.

11.7-1. ***Flash Vaporization of Multicomponent Feed.*** For the feed to the distillation tower of Example 11.7-1, calculate the following:

a. Dew point of feed and composition of liquid in equilibrium. (*Note:* The boiling point of 70°C has already been calculated.)
b. The temperature and composition of both phases when 40% of the feed is vaporized in a flash distillation.

A27: **Ans.** (a) 107°C, $x_A = 0.114$, $x_B = 0.158$, $x_C = 0.281$, $x_D = 0.447$; (b) 82°C, $x_A = 0.260$, $x_B = 0.254$, $x_C = 0.262$, $x_D = 0.224$; $y_A = 0.610$, $y_B = 0.244$, $y_C = 0.107$, $y_D = 0.039$

11.7-2. ***Boiling Point, Dew Point, and Flash Vaporization.*** Following is the composition of a liquid feed in mole fraction: *n*-butane ($x_A = 0.35$), *n*-pentane ($x_B = 0.20$), *n*-hexane ($x_C = 0.25$), *n*-heptane ($x_D = 0.20$). At a pressure of 405.3 kPa calculate the following.

a. Boiling point and composition of the vapor in equilibrium.
b. Dew point and composition of the liquid in equilibrium.
c. The temperature and composition of both phases when 60% of the feed is vaporized in a flash distillation.

11.7-3. ***Vaporization of Multicomponent Alcohol Mixture.*** The vapor-pressure data are given below for the following alcohols:

	Vapor Pressure (mm Hg)			
T(°C)	Methanol	Ethanol	n-Propanol	n-Butanol
50	415	220.0	88.9	33.7
60	629	351.5	148.9	59.2
65	767	438	190.1	77.7
70	929	542	240.6	99.6
75	1119	665	301.9	131.3
80	1339	812	376.0	165.0
85	1593	984	465	206.1
90	1884	1185	571	225.9
100	2598	1706	843	387.6

Following is the composition of a liquid alcohol mixture to be fed to a distillation tower at 101.32 kPa: methyl alcohol ($x_A = 0.30$), ethyl alcohol ($x_B = 0.20$) *n*-propyl alcohol ($x_C = 0.15$), and *n*-butyl alcohol ($x_D = 0.35$). Calculate the following assuming that the mixture follows Raoult's law:

a. Boiling point and composition of vapor in equilibrium.
b. Dew point and composition of liquid in equilibrium.
c. The temperature and composition of both phases when 40% of the feed is vaporized in a flash distillation.

A29: **Ans.** (a) 83°C, $y_A = 0.589$, $y_B = 0.241$, $y_C = 0.084$, $y_D = 0.086$; (b) 100°C, $x_A = 0.088$, $x_B = 0.089$, $x_C = 0.136$, $x_D = 0.687$

11.7-4. ***Total Reflux, Minimum Reflux, Number of Stages.*** The following feed of 100 mol/h at the boiling point and 405.3 kPa pressure is fed to a fractionating tower: *n*-butane ($x_A = 0.40$), *n*-pentane ($x_B = 0.25$), *n*-hexane ($x_C = 0.20$), *n*-heptane ($x_D = 0.15$). This feed is distilled so that 95% of the *n*-pentane is recovered in the distillate and 95% of the *n*-hexane in the bottoms. Calculate the following:

a. Moles per hour and composition of distillate and bottoms.
b. Top and bottom temperature of tower.
c. Minimum stages for total reflux and distribution of other components (trace components) in the distillate and bottoms, that is, moles and mole fractions. [Also correct the compositions and moles in part (a) for the traces.]
d. Minimum reflux ratio using the Underwood method.
e. Number of theoretical stages at an operating reflux ratio of 1.3 times the minimum using the Erbar–Maddox correlation.
f. Location of the feed tray using the Kirkbride method.

A30: **Ans.** (a) $D = 64.75$ mol/h, $x_{AD} = 0.6178$, $x_{BD} = 0.3668$, $x_{CD} = 0.0154$, $x_{DD} = 0$; $W = 35.25$ mol/h, $x_{AW} = 0$, $x_{BW} = 0.0355$, $x_{CW} = 0.5390$, $x_{DW} = 0.4255$; (b) top, 66°C; bottom, 134°C; (c) $N_m = 7.14$ stages; trace compositions, $x_{AW} = 1.2 \times 10^{-4}$, $x_{DD} = 4.0 \times 10^{-5}$; (d) $R_m = 0.504$; (e) $N = 16.8$ stages; (f) $N_e = 9.1$ stages, $N_s = 7.7$ stages, feed 9.1 stages from top

11.7-5. ***Shortcut Design of Multicomponent Distillation Tower.*** A feed of part liquid and part vapor ($q = 0.30$) at 405.4 kPa is fed at the rate of 1000 mol/h to a distillation tower. The overall composition of the feed is *n*-butane ($x_A = 0.35$), *n*-pentane ($x_B = 0.30$), *n*-hexane ($x_C = 0.20$), and *n*-heptane ($x_D = 0.15$). The feed is distilled so that 97% of the *n*-pentane is recovered in the distillate and 85% of the *n*-hexane in the bottoms. Calculate the following:

a. Amount and composition of products and top and bottom tower temperatures.
b. Number of stages at total reflux and distribution of other components in the products.
c. Minimum reflux ratio, number of stages at $1.2R_m$, and feed-tray location.

11.7-6. ***Distillation of Multicomponent Alcohol Mixture.*** A feed of 30 mol % methanol (*A*), 20% ethanol (*B*), 15% *n*-propanol (*C*), and 35% *n*-butanol (*D*) is distilled at 101.32 kPa abs pressure to give a distillate composition containing 95.0 mol % methanol and a residue composition containing 5.0% methanol and the other components as calculated. The feed is below the boiling point, so that $q = 1.1$. The operating reflux ratio is 3.0. Assume that Raoult's law applies and use vapor-pressure data from Problem 11.7-3. Calculate the following:

a. Composition and amounts of distillate and bottoms for a feed of 100 mol/h.

b. Top and bottom temperatures and number of stages at total reflux. (Also, calculate the distribution of the other components.)

c. Minimum reflux ratio, number of stages at $R = 3.00$, and feed-tray location.

A32: **Ans.** (a) $D = 27.778$ mol/h, $x_{AD} = 0.95$, $x_{BD} = 0.05$, $x_{CD} = 0$, $x_{DD} = 0$; $W = 72.222$ mol/h, $x_{AW} = 0.0500$, $x_{BW} = 0.2577$, $x_{CW} = 0.2077$, $x_{DW} = 0.4846$; (b) 65.5°C top temperature, 94.3°C bottom, $N_m = 9.21$ stages, $x_{CD} = 3.04 \times 10^{-5}$, $x_{DD} = 8.79 \times 10^{-7}$ (trace compositions); (c) $R_m = 2.20$, $N = 16.2$ stages, $N_s = 7.6$, $N_e = 8.6$, feed on stage 8.6 from top

11.7-7. ***Shortcut Design Method for Distillation of Ternary Mixture.*** A liquid feed at its bubble point is to be distilled in a tray tower to produce the distillate and bottoms as follows: Feed, $x_{AF} = 0.047$, $x_{BF} = 0.072$, $x_{CF} = 0.881$; distillate, $x_{AD} = 0.1260$, $x_{BD} = 0.1913$, $x_{CD} = 0.6827$; bottoms, $x_{AW} = 0$, $x_{BW} = 0.001$, $x_{CW} = 0.999$. Average α values to use are $\alpha_A = 4.19$, $\alpha_B = 1.58$, $\alpha_C = 1.00$.

a. For a feed rate of 100 mol/h, calculate *D* and *W*, number of stages at total reflux, and distribution (concentration) of *A* in the bottoms.

b. Calculate R_m and the number of stages at $1.25R_m$.

REFERENCES

Bibliography

[ch11biblio01entry01] (D1) C. L. Depriester, *Chem. Eng. Progr. Symp. Ser.*, **49**(7), 1 (1953).

[ch11biblio01entry02] (E1) J. H., Erbar, and R. N. Maddox, *Petrol. Refiner*, **40**(5), 183 (1961).

[ch11biblio01entry03] (F1) J. R. Fair, *Petro/Chem. Eng.*, **33**(10), 45 (1961).

[ch11biblio01entry04] (G1) E. R. Gilliland, *Ind. Eng. Chem.*, **32**, 1220 (1940).

[ch11biblio01entry05] (H1) S. T., Hadden, and H. G. Grayson, *Petrol. Refiner*, **40**(9), 207 (1961).

[ch11biblio01entry06] (H2) C. D. Holland, *Multicomponent Distillation*. Englewood Cliffs, N.J.: Prentice-Hall, 1963.

[ch11biblio01entry07] (K1) C. G. Kirkbride, *Petrol. Refiner*, **23**(9), 321 (1944).

[ch11biblio01entry08] (K2) M. Kwauk, *A.I.Ch.E. J.*, **2**, 240 (1956).

[ch11biblio01entry09] (K3) C. J King,. *Separation Processes*, 2nd ed. New York: McGraw-Hill Book Company, 1980.

[ch11biblio01entry10] (K4) H. Z. Kister, *Distillation Design*. New York: McGraw-Hill Book Company, 1992.

[ch11biblio01entry11] (L1) M. J. Lockett, *Chem. Eng. Progr.*, **86** (Jan.), 19 (1990).

[ch11biblio01entry12] (O1) H. E. O'Connell, *Trans. A.I.Ch.E.*, **42**, 741 (1946).

[ch11biblio01entry13] (P1) R. H., Perry, and D. Green, *Perry's Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill Book Company, 1984.

[ch11biblio01entry14] (R1) C. S., Robinson, and E. R. Gilliland, *Elements of Fractional Distillation*, 4th ed. New York: McGraw-Hill Book Company, 1950.

[ch11biblio01entry15] (S1) B. D. Smith, *Design of Equilibrium Stage Processes*. New York: McGraw-Hill Book Company, 1963.

[ch11biblio01entry16] (S2) P. A. Schweitzer, *Handbook of Separation Techniques for Chemical Engineers*. New York: McGraw-Hill Book Company, 1997.

[ch11biblio01entry17] (S3) J. D., Seader, and E. J. Henley, *Separation Process Principles*. New York: John Wiley & Sons, Inc., 1998.

[ch11biblio01entry18] (T1) E. W., Thiele, and R. L. Geddes, *Ind. Eng. Chem.*, **25**, 289 (1933).

[ch11biblio01entry19] (T2) R. E. Treybal, *Mass Transfer Operations*, 3rd ed. New York: McGraw-Hill Book Company, 1980.

[ch11biblio01entry20] (U1) A. J. V. Underwood, *Chem. Eng. Progr.*, **44**, 603 (1948); **45**, 609 (1949).

[ch11biblio01entry21] (U2) A. J. V. J. Underwood, *Inst. Petrol.*, **32**, 614 (1946).

[ch11biblio01entry22] (V1) M Van Winkle,. *Distillation*. New York: McGraw-Hill Book Company, 1967.