

In this chapter, equipment for conducting distillation operations is discussed and fundamental equilibrium-based and rate-based calculational procedures are developed for binary mixtures. Trayed and packed distillation columns are

identical in most respects to the absorption and stripping columns discussed in the previous chapter. Therefore, where appropriate, reference is made to Chapter 6 and only important differences are discussed in this chapter.

## 7.1 EQUIPMENT AND DESIGN CONSIDERATIONS

Industrial distillation operations are most commonly conducted in trays towers, but packed columns are finding increasing use. Occasionally, distillation columns contain both trays and packing. Types of trays and packings are identical to those used for absorption and stripping, as described in Section 6.1, shown in Figures 6.2 to 6.7, and compared in Tables 6.2 and 6.3.

Factors that influence the design or analysis of a binary-distillation operation include:

1. Feed flow rate, composition, temperature, pressure, and phase condition
2. Desired degree of separation between two components
3. Operating pressure (which must be below the critical pressure of the mixture)
4. Vapor pressure drop, particularly for vacuum operation
5. Minimum reflux ratio and actual reflux ratio
6. Minimum number of equilibrium stages and actual number of equilibrium stages (stage efficiency)
7. Type of condenser (total, partial, or mixed)
8. Degrees of subcooling, if any, of the liquid reflux
9. Type of reboiler (partial or total)
10. Type of contacting (trays or packing or both)
11. Height of the column
12. Feed-entry stage
13. Diameter of the column
14. Column internals.

The phase condition (also called thermal condition) of the feed is determined at the feed-tray pressure by an adiabatic-flash calculation across the feed valve. As the molar fraction of vapor in the feed increases, the required reflux ratio ( $L/D$ ) increases, but the corresponding boilup ratio ( $V/B$ ) decreases. The column operating pressure in the reflux drum should correspond to a distillate temperature somewhat higher (e.g., 10 to 50°F or 6 to 28°C) than the supply temperature of the cooling water used as the coolant in the overhead condenser. However, if this pressure approaches the critical pressure of the more volatile component, then a lower operating pressure must be used and a refrigerant is required as coolant. For example, in Table 7.1, the separation of ethylene/ethane is

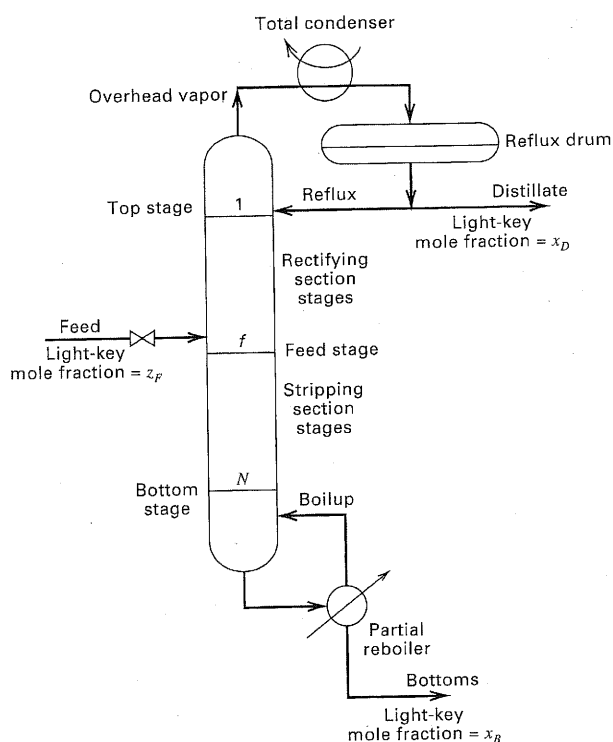
conducted at 230 psia (1,585 kPa), giving a column top temperature of -40°F (233 K), which requires a refrigerant. Water at 80°F (300 K) cannot be used in the condenser because the critical temperature of ethylene is 48.6°F (282 K). If the estimated pressure is less than atmospheric pressure, the operating pressure at the top of the column is often set just above atmospheric pressure to avoid vacuum operation, unless the temperature at the bottom of the column is found to exceed a bottoms temperature limited by decomposition, polymerization, excessive corrosion, or other chemical reaction. In that case, vacuum operation is necessary. In Table 7.1, vacuum operation is required for the separation of ethylbenzene from styrene to maintain a bottoms temperature sufficiently low to prevent polymerization of styrene.

For given (1) feed, (2) desired degree of separation, and (3) operating pressure, a minimum reflux ratio exists that corresponds to an infinite number of theoretical stages; and a minimum number of theoretical stages exists that corresponds to an infinite reflux ratio. A design trade-off is usually made between the number of stages and the reflux ratio. A graphical method for determining the data needed to make this trade-off and to determine the optimal feed-stage location is developed in the next section.

## 7.2 MCCABE-THIELE GRAPHICAL EQUILIBRIUM-STAGE METHOD FOR TRAYED TOWERS

Consider the general countercurrent-flow, multistage, binary-distillation operation shown in Figure 7.2. The operation consists of a column containing the equivalent of  $N$  theoretical stages; a total condenser in which the overhead vapor leaving the top stage is totally condensed to give a liquid distillate product and liquid reflux that is returned to the top stage; a partial reboiler in which liquid from the bottom stage is partially vaporized to give a liquid bottoms product and vapor boilup that is returned to the bottom stage, and an intermediate feed stage. By means of multiple, countercurrent contacting stages arranged in a two-section cascade with reflux and boilup, as discussed in Section 5.4, it is possible to achieve a sharp separation between the two components in the feed unless an azeotrope is formed, in which case one of the two products will approach the azeotropic composition.

The feed, which contains a more-volatile (light) component (the *light key*, LK), and a less-volatile (heavy)



**Figure 7.2** Distillation operation using a total condenser and partial reboiler.

component (the *heavy key*, HK), enters the column at a feed stage,  $f$ . At the feed-stage pressure, the feed may be liquid, vapor, or a mixture of liquid and vapor, with its overall mole-fraction composition with respect to the light component denoted by  $z_F$ . The mole fraction of the light key in the distillate is  $x_D$ , while the mole fraction of the light key in the bottoms product is  $x_B$ . Corresponding compositions with respect to the heavy key are  $1 - z_F$ ,  $1 - x_D$ , and  $1 - x_B$ .

The goal of distillation is to produce from the feed a distillate, rich in the light key (i.e.,  $x_D$  approaching 1.0), and a bottoms product, rich in the heavy key (i.e.,  $x_B$  approaching 0.0). The ease or difficulty with which the separation can be achieved depends on the relative volatility,  $\alpha$ , of the two components (LK = 1 and HK = 2), where

$$\alpha_{1,2} = K_1/K_2 \quad (7-1)$$

Methods for estimating  $K$ -values are discussed in Chapter 2.

If the two components form ideal solutions and follow the ideal-gas law in the vapor phase, Raoult's law applies to give

$$K_1 = P_1^s/P \quad \text{and} \quad K_2 = P_2^s/P$$

and from (7-1), the relative volatility is given simply by the ratio of vapor pressures,  $\alpha_{1,2} = P_1^s/P_2^s$  and thus is a function only of temperature. As discussed in Section 4.2, as the temperature (and therefore the pressure) increases,  $\alpha_{1,2}$

decreases. At the convergence pressure of the mixture,  $\alpha_{1,2} = 1.0$  and a separation cannot be achieved at this or any higher pressure.

The relative volatility can be expressed in terms of equilibrium vapor and liquid compositions from the definition of the  $K$ -value as  $K_i = y_i/x_i$ . For a binary mixture,

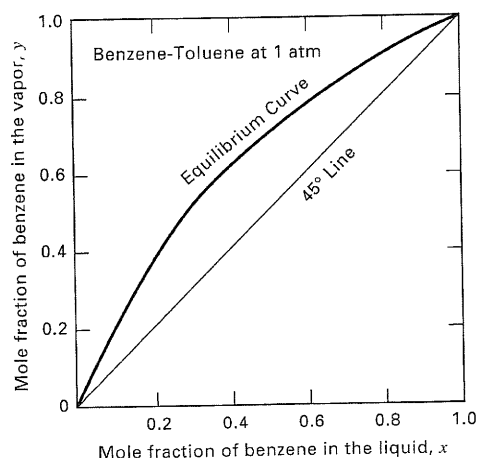
$$\alpha_{1,2} = \frac{y_1/x_1}{y_2/x_2} = \frac{y_1(1-x_1)}{x_1(1-y_1)} \quad (7-2)$$

Solving (7-2) for  $y_1$ ,

$$y_1 = \frac{\alpha_{1,2}x_1}{1 + x_1(\alpha_{1,2} - 1)} \quad (7-3)$$

For ideal binary mixtures of components with close boiling points, the temperature change over the column is small and  $\alpha_{1,2}$  is almost constant. In any case, for a given pressure  $P$  and liquid-phase composition  $x_1$ , the Gibbs phase rule, discussed in Chapter 4, fixes the temperature and equilibrium-vapor composition. An equilibrium curve for the benzene-toluene system is shown in Figure 7.3, where  $y$  and  $x$  correspond to the light key, benzene, and the pressure is 1 atm, at which pure benzene and pure toluene boil at 176 and 231°F, respectively. Thus, these two components are not close-boiling. Using (7-3) with this curve,  $\alpha$  varies from about 2.6 at the bottom of the curve to about 2.35 at the top of the curve. Representative equilibrium curves for some average values of  $\alpha$  are shown in Figure 4.5. The higher the average value of  $\alpha$ , the easier it is to achieve the desired separation. Average values of  $\alpha$  for the distillation operations in Table 7.1 range from 1.16 to 81.2.

In 1925, McCabe and Thiele [5] published an approximate graphical method for combining the equilibrium curve of Figure 7.3 with operating-line curves to estimate, for a given binary-feed mixture and column operating pressure, the number of equilibrium stages and the amount of reflux required for a desired degree of separation of the feed.



**Figure 7.3** Equilibrium curve for benzene-toluene at 1 atm.

Although computer-aided methods, discussed later in Chapter 10, are more accurate and easier to apply, the graphical construction of the McCabe–Thiele method greatly facilitates the visualization of many of the important aspects of multistage distillation, and therefore the effort required to learn the method is well justified.

Typical problem specifications for and results from the McCabe–Thiele method are summarized in Table 7.2. This table applies to a simple, binary-distillation operation, like that in Figure 7.2, for a single feed and two products. The distillate can be a liquid from a total condenser, as shown in Figure 7.2, or a vapor from a partial condenser. The feed phase condition must be known at the column pressure, which is assumed to be uniform throughout the column for the McCabe–Thiele method. The type of condenser and reboiler must be specified, as well as the ratio of reflux to minimum reflux. From the specification of  $x_D$  and  $x_B$  for the light key, the distillate and bottoms flow rates,  $D$  and  $B$ , are fixed by material balance, since

$$Fz_F = x_D D + x_B B$$

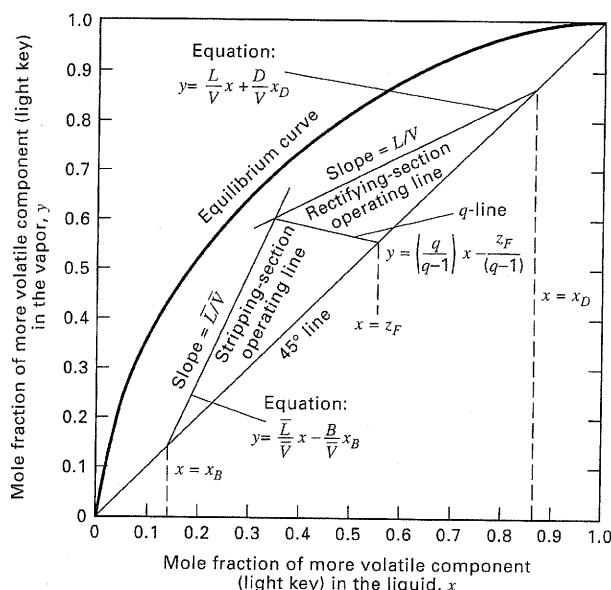
But,  $B = F - D$  and therefore

$$Fz_F = x_D D + x_B (F - D)$$

**Table 7.2** Specifications for and Results from the McCabe–Thiele Method for Binary Distillation

Specifications	
$F$	Total feed rate
$z_F$	Mole-fraction composition of the feed
$P$	Column operating pressure (assumed uniform throughout the column)
	Phase condition of the feed at column pressure
	Vapor–liquid equilibrium curve for the binary mixture at column pressure
	Type of overhead condenser (total or partial)
	Type of reboiler (usually partial)
$x_D$	Mole-fraction composition of the distillate
$x_B$	Mole-fraction composition of the bottoms
$R/R_{\min}$	Ratio of reflux to minimum reflux
Results	
$D$	Distillate flow rate
$B$	Bottoms flow rate
$N_{\min}$	Minimum number of equilibrium stages
$R_{\min}$	Minimum reflux ratio, $L_{\min}/D$
$R$	Reflux ratio, $L/D$
$V_B$	Boilup ratio, $\bar{V}/B$
$N$	Number of equilibrium stages
	Optimal feed-stage location
	Stage vapor and liquid compositions

All mole fraction compositions are for the light key.



**Figure 7.4** Construction lines for McCabe–Thiele method.

or

$$D = F \left( \frac{z_F - x_B}{x_D - x_B} \right)$$

This result requires  $x_B < z_F < x_D$ .

The McCabe–Thiele method determines not only  $N$ , the number of equilibrium stages, but also  $N_{\min}$ ,  $R_{\min}$ , and the optimal stage for feed entry. Following the application of the McCabe–Thiele method, energy balances are applied to estimate condenser and reboiler heat duties.

Besides the equilibrium curve, the McCabe–Thiele method involves a 45° reference line, separate operating lines for the upper *rectifying* (enriching) section of the column and the lower *stripping* (exhausting) section of the column, and a fifth line (the *q-line* or feed line) for the phase or thermal condition of the feed. A typical set of these lines is shown in Figure 7.4. Equations for these lines are derived in the following subsection.

### Rectifying Section

As shown in Figure 7.2, the rectifying section of equilibrium stages extends from the top stage, 1, to just above the feed stage,  $f$ . Consider a top portion of the rectifying stages, including the total condenser. A material balance for the light key over the envelope shown in Figure 7.5a for the total condenser and stages 1 to  $n$  is as follows, where  $y$  and  $x$  refer to vapor and liquid mole fractions, respectively, for the light key:

$$V_{n+1}y_{n+1} = L_n x_n + D x_D \quad (7-4)$$

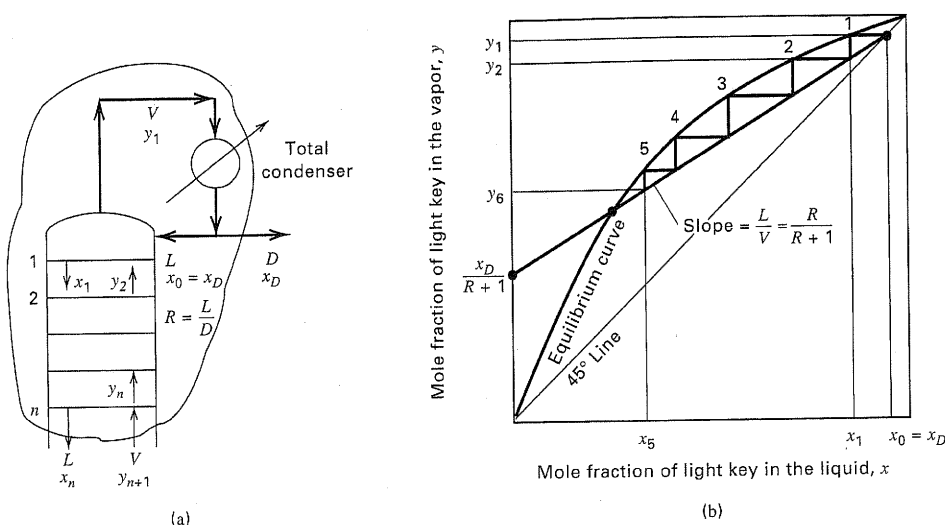


Figure 7.5 McCabe-Thiele operating line for the rectifying section.

Solving for  $y_{n+1}$ :

$$y_{n+1} = \frac{L_n}{V_{n+1}}x_n + \frac{D}{V_{n+1}}x_D \quad (7-5)$$

Equation (7-5) relates the compositions,  $y_{n+1}$  and  $x_n$ , of two passing streams,  $V_{n+1}$  and  $L_n$ , respectively. For (7-5) to plot as a straight line of the form  $y = mx + b$ , which is the locus of compositions of all passing streams in the rectifying section, total molar flow rates  $L$  and  $V$  must not vary from stage to stage. This is the case if:

1. The two components have equal and constant molar enthalpies of vaporization (latent heats).
2. Component sensible-enthalpy changes ( $C_P \Delta T$ ) and heat of mixing are negligible compared to latent heat changes.
3. The column is well insulated so that heat loss is negligible.
4. The pressure is uniform throughout the column (no pressure drop).

These assumptions are referred to as the *McCabe-Thiele assumptions* leading to the condition of *constant molar overflow* in the rectifying section, which refers to a molar liquid flow rate that remains constant as the liquid overflows each weir from one stage to the next. Since a total material balance for the rectifying-section envelope in Figure 7.5a gives  $V_{n+1} = L_n + D$ , if  $L$  is constant, then  $V$  is also constant for a particular value of  $D$ . Thus, (7-5) can be rewritten as

$$y = \frac{L}{V}x + \frac{D}{V}x_D \quad (7-6)$$

as shown in Figure 7.4. Thus, the slope of the operating line is  $L/V$ , which is constant. Because  $V > L$ ,  $L/V < 1$  in the rectifying section, as seen in Figure 7.5b.

For constant molar overflow, it is not necessary to consider energy balances in either the rectifying or stripping

sections; only material balances and a vapor-liquid equilibrium curve are required. However, energy balances are needed to determine condenser and reboiler duties, as discussed later.

The liquid entering the top stage is the external reflux rate,  $L_0$ , and its ratio to the distillate rate,  $L_0/D$ , is the reflux ratio,  $R$ . Because of the assumption of constant molar overflow,  $R$  is a constant in the rectifying section, equal to  $L/D$ . Since  $V = L + D$ , the slope of the operating line is readily related to the reflux ratio:

$$\frac{L}{V} = \frac{L}{L + D} = \frac{L/D}{L/D + D/D} = \frac{R}{R + 1} \quad (7-7)$$

Similarly,

$$\frac{D}{V} = \frac{D}{L + D} = \frac{1}{R + 1} \quad (7-8)$$

Combining (7-6), (7-7), and (7-8) produces the most useful form of the operating line for the rectifying section:

$$y = \left( \frac{R}{R + 1} \right)x + \left( \frac{1}{R + 1} \right)x_D \quad (7-9)$$

If values of  $R$  and  $x_D$  are specified, (7-9) plots as a straight line with an intersection at  $y = x_D$  on the 45° line, a slope of  $L/V = R/(R + 1)$ , and an intersection at  $y = x_D/(R + 1)$  for  $x = 0$ , as shown in Figure 7.5b, which also contains a 45° line and an equilibrium curve. The equilibrium stages are stepped off in the manner described in Section 6.3 for absorption. Starting from the point ( $y_1 = x_D$ ,  $x_0 = x_D$ ) on the operating line and the 45° line, a horizontal line is drawn to the left until it intersects the equilibrium curve at ( $y_1$ ,  $x_1$ ), that is, the compositions of the *equilibrium phases* leaving the top equilibrium stage. A vertical line is now dropped until it intersects the operating line at the point ( $y_2$ ,  $x_1$ ), the compositions of the two *phases passing* each other between stages 1 and 2. The horizontal- and vertical-line constructions are

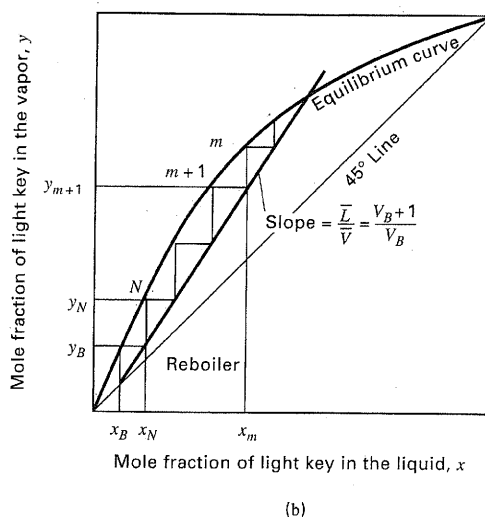
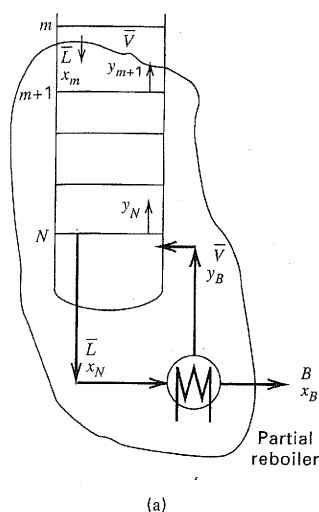


Figure 7.6 McCabe-Thiele operating line for the stripping section.

continued down the rectifying section in the manner shown in Figure 7.5b to give the staircase construction shown, which is arbitrarily terminated at stage 5. The optimal stage for termination is considered later.

### Stripping Section

As shown in Figure 7.2, the stripping section of equilibrium stages extends from the feed to the bottom stage. In Figure 7.6a, consider a bottom portion of the stripping stages, including the partial reboiler and extending up from stage  $N$  to stage  $m+1$ , located somewhere below the feed. A material balance for the light key over the envelope shown in Figure 7.6a results in

$$\bar{L}x_m = \bar{V}y_{m+1} + Bx_B \quad (7-10)$$

Solving for  $y_{m+1}$ :

$$y_{m+1} = \frac{\bar{L}}{\bar{V}}x_m - \frac{B}{\bar{V}}x_B$$

$$\text{or} \quad y = \frac{\bar{L}}{\bar{V}}x - \frac{B}{\bar{V}}x_B \quad (7-11)$$

where  $\bar{L}$  and  $\bar{V}$  are the total molar flows, which by the constant-molar-overflow assumption remain constant from stage to stage. The slope of this operating line for the compositions of passing streams in the stripping section is seen to be  $\bar{L}/\bar{V}$ . Because  $\bar{L} > \bar{V}$ ,  $\bar{L}/\bar{V} > 1$ , as seen in Figure 7.6b. This is the inverse of conditions in the rectifying section.

The vapor leaving the partial reboiler is assumed to be in equilibrium with the liquid bottoms product. Thus, the partial reboiler acts as an additional equilibrium stage. The vapor rate leaving it is called the *boilup*,  $\bar{V}_{N+1}$ , and its ratio to the bottoms product rate,  $V_B = \bar{V}_{N+1}/B$ , is the *boilup ratio*. Because of the constant-molar-overflow assumption,  $V_B$  is constant in the stripping section. Since  $\bar{L} = \bar{V} + B$ ,

$$\frac{\bar{L}}{\bar{V}} = \frac{\bar{V} + B}{\bar{V}} = \frac{V_B + 1}{V_B} \quad (7-12)$$

Similarly,

$$\frac{B}{\bar{V}} = \frac{1}{V_B} \quad (7-13)$$

Combining (7-11), (7-12), and (7-13), the operating-line equation for the stripping section becomes

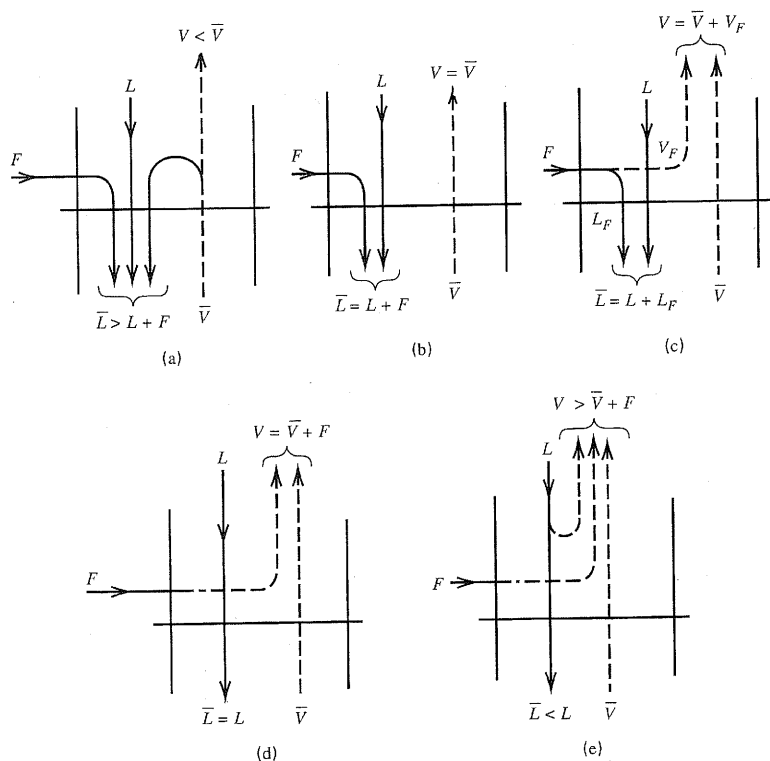
$$y = \left( \frac{V_B + 1}{V_B} \right) x - \left( \frac{1}{V_B} \right) x_B \quad (7-14)$$

If values of  $V_B$  and  $x_B$  are known, (7-14) can be plotted, together with the equilibrium curve and a 45° line, as a straight line with an intersection at  $y = x_B$  on the 45° line and a slope of  $\bar{L}/\bar{V} = (V_B + 1)/V_B$ , as shown in Figure 7.6b. The equilibrium stages are stepped off, in a manner similar to that described for the rectifying section, starting from the point ( $y = x_B$ ,  $x = x_B$ ) on the operating and 45° lines and moving upward on a vertical line until the equilibrium curve is intersected at ( $y = y_B$ ,  $x = x_B$ ), which represents the equilibrium mole fractions in the vapor and liquid leaving the partial reboiler. From that point, the staircase is constructed by drawing horizontal and then vertical lines, moving back and forth between the operating line and equilibrium curve, as observed in Figure 7.6b, where the staircase is arbitrarily terminated at stage  $m$ . Next, we determine where to terminate the two operating lines.

### Feed-Stage Considerations

Thus far, the McCabe-Thiele construction has not considered the feed to the column. In determining the operating lines for the rectifying and stripping sections, it is very important to note that although  $x_D$  and  $x_B$  can be selected independently,  $R$  and  $V_B$  are related by the feed phase condition.

Consider the five possible feed conditions shown in Figure 7.7, which assumes that the feed has been flashed adiabatically to the feed-stage pressure. If the feed is a bubble-point liquid, it adds to the reflux,  $L$ , coming from the stage above to give  $\bar{L} = L + F$ . If the feed is a dew-point



**Figure 7.7** Possible feed conditions: (a) subcooled-liquid feed; (b) bubble-point liquid feed; (c) partially vaporized feed; (d) dew-point vapor feed; (e) superheated-vapor feed.

[Adapted from W.L. McCabe, J.C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering*, 5th ed., McGraw-Hill, New York (1993).]

vapor, it adds to the boilup vapor,  $\bar{V}$ , coming from the stage below to give  $V = \bar{V} + F$ . For a partially vaporized feed, as shown in Figure 7.7c,  $F = L_F + V_F$  and  $\bar{L} = L + L_F$  and  $V = \bar{V} + V_F$ . If the feed is a subcooled liquid, it will cause a portion of the boilup,  $\bar{V}$ , to condense, giving  $\bar{L} > L + F$  and  $V < \bar{V}$ . If the feed is a superheated vapor, it will cause a portion of the reflux,  $L$ , to vaporize, giving  $\bar{L} < L$  and  $V > \bar{V} + F$ .

For cases (b), (c), and (d) of Figure 7.7, covering a range of feed conditions from a saturated liquid to a saturated vapor, the boilup  $\bar{V}$  is related to the reflux  $L$  by the material balance:

$$\bar{V} = L + D - V_F \quad (7-15)$$

and the boilup ratio,  $V_B = \bar{V}/B$ , is

$$V_B = \frac{L + D - V_F}{B} \quad (7-16)$$

Alternatively, the reflux can be determined from the boilup by

$$L = \bar{V} + B - L_F \quad (7-17)$$

Although distillation operations can be specified by either the reflux ratio  $R$  or the boilup ratio  $V_B$ , by tradition  $R$  or  $R/R_{\min}$  is used because the distillate product is most often the more important product.

For the other two cases, (a) and (e) of Figure 7.7,  $V_B$  and  $R$  cannot be related by simple material balances alone. It is necessary to consider an energy balance to convert sensible enthalpy into latent enthalpy of phase change. This is most

conveniently done by defining a parameter,  $q$ , as the ratio of the increase in molar reflux rate across the feed stage to the molar feed rate,

$$q = \frac{\bar{L} - L}{F} \quad (7-18)$$

or by material balance around the feed stage,

$$q = 1 + \frac{\bar{V} - V}{F} \quad (7-19)$$

Values of  $q$  for the five feed conditions are

Feed condition	$q$
Subcooled liquid	$> 1$
Bubble-point liquid	1
Partially vaporized	$L_F/F = 1 - \text{molar fraction vaporized}$
Dew-point vapor	0
Superheated vapor	$< 0$

To determine values of  $q$  for subcooled liquid and superheated vapor, a more general definition of  $q$  is applied:

$q$  = enthalpy change to bring the feed to a dew-point vapor divided by enthalpy of vaporization of the feed (dew-point vapor minus bubble-point liquid), that is,

$$q = \frac{(h_F)_{\text{sat'd vapor temperature}} - (h_F)_{\text{feed temperature}}}{(h_F)_{\text{sat'd vapor temperature}} - (h_F)_{\text{sat'd liquid temperature}}} \quad (7-20)$$

For a subcooled liquid feed, (7-20) becomes

$$q = \frac{\Delta H^{\text{vap}} + C_{P_L}(T_b - T_F)}{\Delta H^{\text{vap}}} \quad (7-21)$$

For a superheated vapor, (7-20) becomes

$$q = \frac{C_{P_V}(T_d - T_F)}{\Delta H^{\text{vap}}} \quad (7-22)$$

where  $C_{P_L}$  and  $C_{P_V}$  are the liquid and vapor molar heat capacities, respectively,  $\Delta H^{\text{vap}}$  is the molar enthalpy change from the bubble point to the dew point, and  $T_F$ ,  $T_d$ , and  $T_b$  are the feed, dew-point, and bubble-point temperatures, respectively, of the feed at the column operating pressure.

Instead of using (7-14) to locate the stripping operating line on the McCabe-Thiele diagram, it is more common to use an alternative method that involves a  $q$ -line (feed line), which is included in Figure 7.4. The  $q$ -line, one point of which is the intersection of the rectifying and stripping operating lines, is derived in the following manner. Combining (7-11) with (7-6) gives

$$y(V - \bar{V}) = (L - \bar{L})x + Dx_D + Bx_B \quad (7-23)$$

But

$$Dx_D + Bx_B = Fz_F \quad (7-24)$$

and a material balance around the feed stage gives

$$F + \bar{V} + L = V + \bar{L} \quad (7-25)$$

Combining (7-23) to (7-25) with (7-18) gives

$$y = \left( \frac{q}{q-1} \right) x - \left( \frac{z_F}{q-1} \right) \quad (7-26)$$

which is the equation for the  $q$ -line. This line is located on the McCabe-Thiele diagram by noting that when  $x = z_F$ , (7-26) reduces to the point  $y = z_F = x$ , which lies on the 45° line. From (7-26), the slope of the line is  $q/(q-1)$ . This construction is shown in Figure 7.4 for a partially vaporized feed, for which  $0 < q < 1$  and  $-\infty < [q/(q-1)] < 0$ . Following the placement of the rectifying-section operating line and the  $q$ -line, the stripping-section operating line is located by drawing a straight line from the point ( $y = x_B$ ,  $x = x_B$ ) on the 45° line to and through the point of intersection of the  $q$ -line and the rectifying-section operating line as shown in Figure 7.4. The point of intersection must lie somewhere between the equilibrium curve and the 45° line.

As  $q$  changes from a value greater than 1 (subcooled liquid) to a value less than 0 (superheated vapor), the slope of the  $q$ -line,  $q/(q-1)$ , changes from a positive value to a negative value and back to a positive value, as shown in Figure 7.8. For a saturated liquid feed, the  $q$ -line is vertical; for a saturated vapor, the  $q$ -line is horizontal.

### Determination of Number of Equilibrium Stages and Feed-Stage Location

Following the construction of the five lines shown in Figure 7.4, the number of equilibrium stages required for the entire column, as well as the location of the feed stage, are determined by stepping off stages by any of several ways. The stages can be stepped off first from the top down and

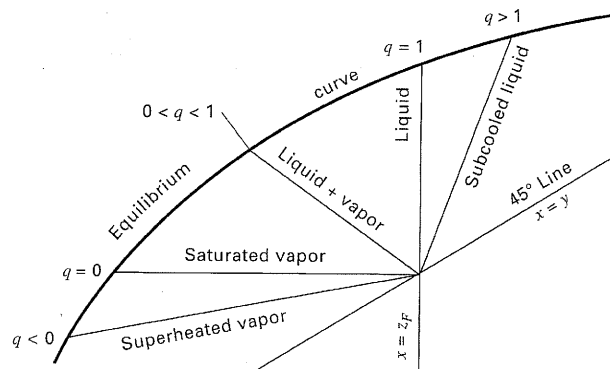
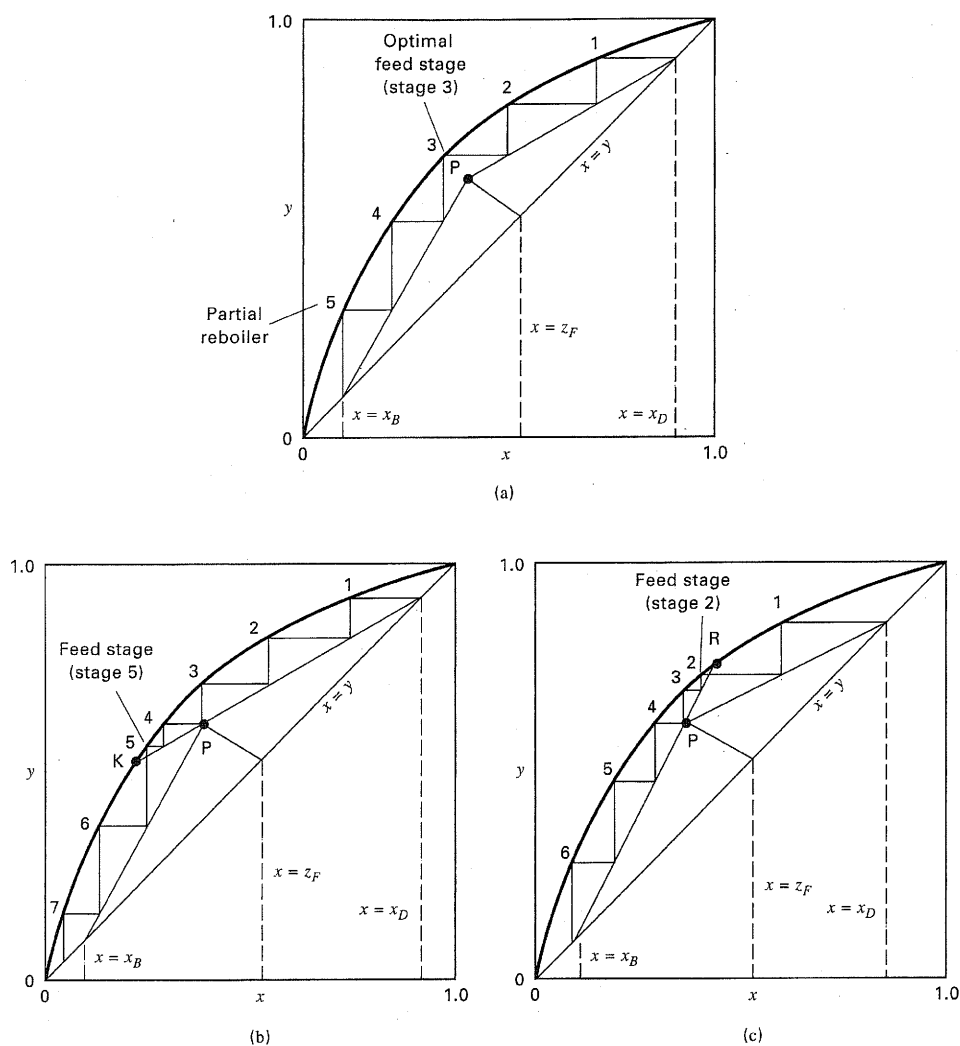


Figure 7.8 Effect of thermal condition of feed on slope of  $q$ -line.

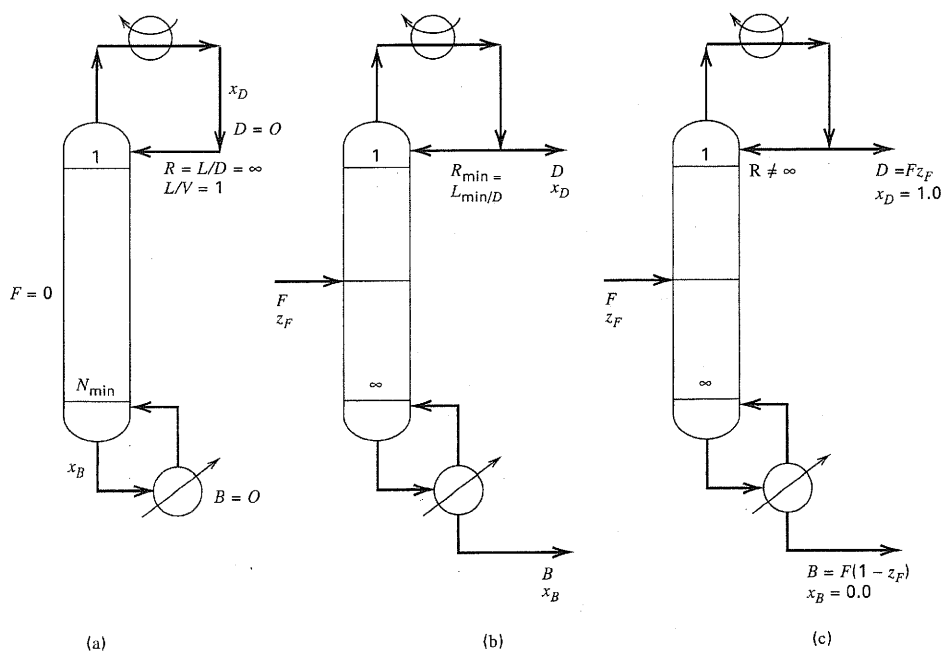
then from the bottom up, as described above, until a point of merger is found for the feed stage. Alternatively, the stages can be stepped off from the bottom all the way to the top, or vice versa. Hardly ever will an integer number of stages result, but rather a fractional stage will appear near the middle, at the top, or at the bottom. Usually the staircase is stepped off from the top and continued all the way to the bottom, starting from the point ( $y = x_D$ ,  $x = x_D$ ) on the 45° line, as shown in Figure 7.9 for the case of a partially vaporized feed. In that figure, point P is the intersection of the  $q$ -line with the two operating lines. The transfer point for stepping off stages between the rectifying-section operating line and the equilibrium curve to stepping off stages between the stripping-section operating line and the equilibrium curve occurs at the feed stage. In Figure 7.9a, the feed stage is stage 3 from the top and a fortuitous total of exactly five stages is required, where the last stage is the partial reboiler. In Figure 7.9b the feed stage is stage 5 and a total of about 6.4 stages is required. In Figure 7.9c, the feed stage is stage 2 and a total of about 5.9 stages is required. In Figure 7.9b, the stepping off of stages in the rectifying section can be continued indefinitely, finally approaching, but never reaching, point K. In Figure 7.9c, if the stepping off of stages had started from the partial reboiler at the point ( $y = x_B$ ,  $x = x_B$ ) and proceeded upward, the staircase in the stripping section could have been continued indefinitely, finally approaching, but never reaching, point R. In Figure 7.9, it is seen that the smallest number of total stages occurs when the transfer is made at the first opportunity after a horizontal line of the staircase passes over point P, as in Figure 7.9a. This feed-stage location is optimal.

### Limiting Conditions

For a given specification (Table 7.2), a reflux ratio can be selected anywhere from the minimum,  $R_{\min}$ , to an infinite value (total reflux) where all of the overhead vapor is condensed and returned to the top stage (thus, no distillate is withdrawn). As shown in Figure 7.10b, the minimum reflux corresponds to the need for an infinite number of stages, while in Figure 7.10a the infinite reflux ratio corresponds to



**Figure 7.9** Optimal and nonoptimal locations of feed stage: (a) optimal feed-stage location; (b) feed-stage location below optimal stage; (c) feed-stage location above optimal stage.



**Figure 7.10** Limiting conditions for distillation: (a) total reflux, minimum stages; (b) minimum reflux, infinite stages; (c) perfect separation for nonazeotropic system.



the minimum number of equilibrium stages. The McCabe-Thiele graphical method can quickly determine the two limits,  $N_{\min}$  and  $R_{\min}$ . Then, for a practical operation,  $N_{\min} < N < \infty$  and  $R_{\min} < R < \infty$ .

### Minimum Number of Equilibrium Stages

As the reflux ratio is increased, the slope of the rectifying-section operating line, given by (7-7), increases from  $L/V < 1$  to a limiting value of  $L/V = 1$ . Correspondingly, the boilup ratio increases and the slope of the stripping section operating line, given by (7-12), decreases from  $\bar{L}/\bar{V} > 1$  to a limiting value of  $\bar{L}/\bar{V} = 1$ . Thus, at this limiting condition, both the rectifying and stripping operating lines coincide with the 45° line and neither the feed composition,  $z_F$ , nor the  $q$ -line influences the staircase construction. This is total reflux because when  $L = V$ ,  $D = B = 0$ , and the total condensed overhead is returned to the column as reflux. Furthermore, all liquid leaving the bottom stage is vaporized and returned as boilup to the column. If both distillate and bottoms flow rates are zero, the feed to the column is also zero, which is consistent with the lack of influence of the feed condition. It is possible to operate a column at total reflux, and such an operation is convenient for the experimental measurement of tray efficiency because a steady-state operating condition is readily achieved.

A simple example of the McCabe-Thiele construction for this limiting condition is shown in Figure 7.11 for two equilibrium stages. Because the operating lines are located as far away as possible from the equilibrium curve, a minimum number of stages is required.

### Minimum Reflux Ratio

As the reflux ratio decreases from the limiting case of infinity (i.e., total reflux), the intersection of the two operating lines and the  $q$ -line moves away from the 45° line toward the equilibrium curve. The number of equilibrium stages required increases because the operating lines move closer and closer to the equilibrium curve, thus requiring more and

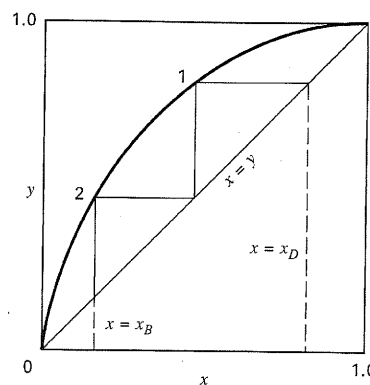


Figure 7.11 Construction for minimum stages at total reflux.

more stairs to move from the top of the column to the bottom. Finally a limiting condition is reached when the point of intersection is on the equilibrium curve, as shown in Figure 7.12. For binary mixtures that are not highly nonideal, the typical case is shown in Figure 7.12a, where the intersection, P, is at the feed stage. To reach that stage from either the rectifying section or the stripping section, an infinite number of stages is required. The point P is called a *pinch point* because the two operating lines each pinch the equilibrium curve.

For a highly nonideal binary system, the pinch point may occur at a stage above or below the feed stage. The former case is illustrated in Figure 7.12b, where the operating line for the rectifying section intersects the equilibrium curve before the feed stage is reached. The slope of this operating line cannot be reduced further because it would then cross over the equilibrium curve and thereby violate the second law of thermodynamics because of a reversal in the direction of mass transfer. This would require spontaneous mass transfer from a region of low concentration to a region of high concentration. This is similar to a second-law violation by a temperature crossover in a heat exchanger. Now, the pinch point occurs entirely in the rectifying section, where an infinite number of stages exists; the stripping section contains a finite number of stages.

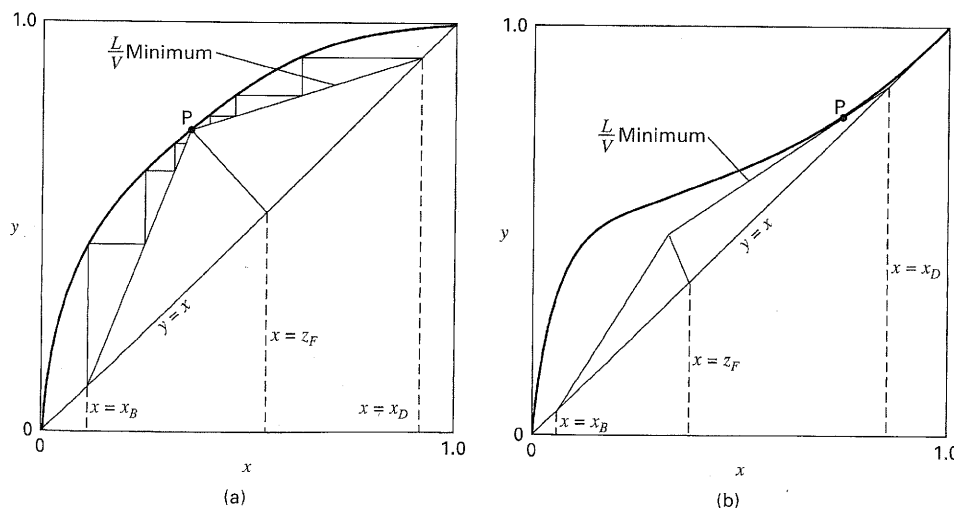


Figure 7.12 Construction for minimum reflux at infinite stages: (a) typical ideal or near-ideal system, pinch point at the feed stage; (b) typical nonideal system, pinch point above the feed stage.

From the slope of the limiting operating line for the rectifying section, the minimum reflux ratio can be determined. From (7-7), the minimum feasible slope is

$$(L/V)_{\min} = R_{\min}/(R_{\min} + 1)$$

or

$$R_{\min} = (L/V)_{\min}/[1 - (L/V)_{\min}] \quad (7-27)$$

Alternatively, the limiting condition of infinite stages corresponds to a minimum boilup ratio for  $(\bar{L}/\bar{V})_{\max}$ . From (7-12),

$$(V_B)_{\min} = 1/[(\bar{L}/\bar{V})_{\max} - 1] \quad (7-28)$$

### Perfect Separation

A third limiting condition of interest involves the degree of separation. As a perfect split ( $x_D = 1$ ,  $x_B = 0$ ) is approached, for a reflux ratio at or greater than the minimum value, the number of stages required near the top and near the bottom

of the column increases rapidly and without limit until pinches are encountered at  $x_D = 1$  and  $x_B = 0$ . Thus, a perfect separation of a binary mixture that does not form an azeotrope requires an infinite number of stages in both sections of the column. However, this is not the case for the reflux ratio. In Figure 7.12a, as  $x_D$  is moved from, say, 0.90 toward 1.0, the slope of the operating line at first increases, but in the range of  $x_D$  from 0.99 to 1.0 the slope changes only slightly. Furthermore, the value of the slope, and therefore the value of  $R$ , is finite for a perfect separation. For example, if the feed is a saturated liquid, application of (7-4) and (7-7) gives the following equation for the minimum reflux of a perfect binary separation:

$$R_{\min} = \frac{1}{z_F(\alpha - 1)} \quad (7-29)$$

where the relative volatility,  $\alpha$ , is evaluated at the feed condition.

### EXAMPLE 7.1

A trayed tower is to be designed to continuously distill 450 lbmol/h (204 kmol/h) of a binary mixture of 60 mol% benzene and 40 mol% toluene. A liquid distillate and a liquid bottoms product of 95 mol% and 5 mol% benzene, respectively, are to be produced. The feed is preheated so that it enters the column with a molar percent vaporization equal to the distillate-to-feed ratio. Use the McCabe–Thiele method to compute the following, assuming a uniform pressure of 1 atm (101.3 kPa) throughout the column: (a) Minimum number of theoretical stages,  $N_{\min}$ ; (b) Minimum reflux ratio,  $R_{\min}$ ; and (c) Number of equilibrium stages  $N$ , for a reflux-to-minimum reflux ratio,  $R/R_{\min}$ , of 1.3 and the optimal location of the feed stage.

### SOLUTION

Calculate  $D$  and  $B$ . An overall material balance on benzene gives

$$0.60(450) = 0.95D + 0.05B \quad (1)$$

$$\text{A total balance gives } 450 = D + B \quad (2)$$

Combining (1) and (2) to eliminate  $B$ , followed by solving the resulting equation for  $D$  and (2) for  $B$  gives  $D = 275$  lbmol/h,  $B = 175$  lbmol/h, and  $D/F = 0.611$

Calculate the slope of the  $q$ -line:

$V_F/F = D/F$  for this example = 0.611 and  $q$  for a partially vaporized feed is

$$\frac{L_F}{F} = \frac{(F - V_F)}{F} = 1 - \frac{V_F}{F} = 0.389$$

From (7-26),

$$\text{the slope of the } q\text{-line is } \frac{q}{q - 1} = \frac{0.389}{0.389 - 1} = -0.637$$

- In Figure 7.13, where  $y$  and  $x$  refer to benzene, the more-volatile component, with  $x_D = 0.95$  and  $x_B = 0.05$ , the number of minimum equilibrium stages is stepped off from the top between the equilibrium curve and the 45° line, giving  $N_{\min} = 6.7$ .
- In Figure 7.14, a  $q$ -line is drawn that has a slope of  $-0.637$  and passes through the feed composition ( $z_F = 0.60$ ) on the 45° line. For the minimum-reflux condition, an operating line for the rectifying section passes through the point  $x = x_D = 0.95$  on

the 45° line and through the point of intersection of the  $q$ -line and the equilibrium curve ( $y = 0.684$ ,  $x = 0.465$ ). The slope of this operating line is 0.55, which from (7-9) equals  $R/(R + 1)$ . Therefore,  $R_{\min} = 1.22$ .

- The operating reflux ratio is  $1.3R_{\min} = 1.3(1.22) = 1.59$

From (7-9), the slope of the operating line for the rectifying section is

$$\frac{R}{R + 1} = \frac{1.59}{1.59 + 1} = 0.614$$

The construction for the resulting two operating lines, together with the  $q$ -line, is shown in Figure 7.15, where the operating line for the stripping section is drawn to pass through the point  $x = x_B = 0.05$  on the 45° line and the point of intersection of the  $q$ -line and the operating line for the stripping section. The number of equilibrium stages is stepped off between, first, the rectifying-section operating line and the equilibrium curve and then the stripping-section operating line and the equilibrium curve, starting from point A

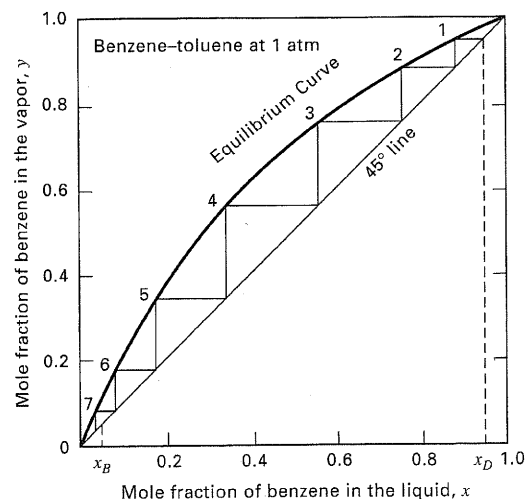


Figure 7.13 Determination of minimum stages for Example 7.1.

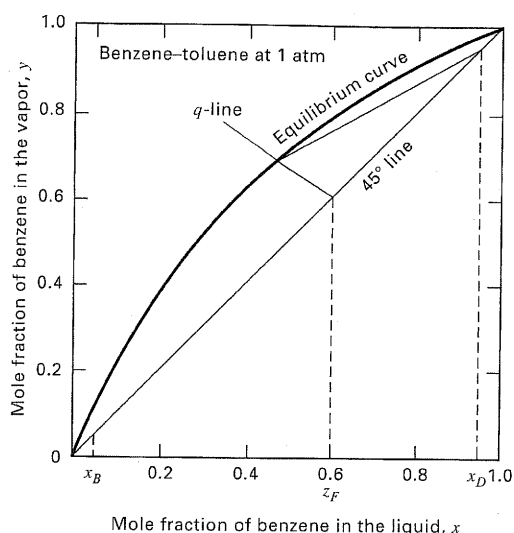


Figure 7.14 Determination of minimum reflux for Example 7.1.

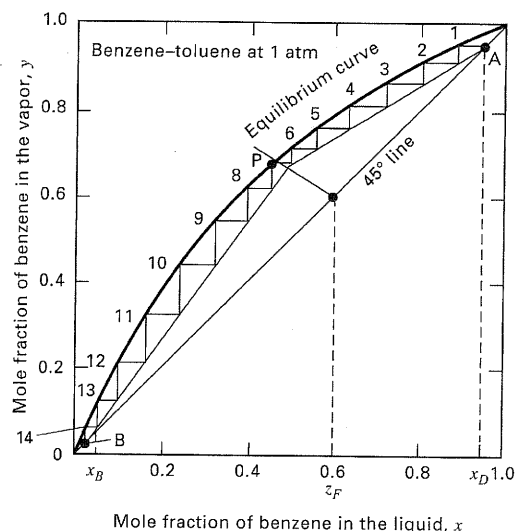


Figure 7.15 Determination of number of equilibrium stages and feed-stage location for Example 7.1.

(at  $x = x_D = 0.95$ ) and finishing at point B (to the left of  $x = x_B = 0.05$ ). For the optimal feed-stage location, the transfer from the rectifying-section operating line to the stripping-section operating line takes place at point P. The result is  $N = 13.2$  equilibrium

stages, with stage 7 from the top being the feed stage. Thus, for this example,  $N/N_{\min} = 13.2/6.7 = 1.97$ . The bottom stage is the partial reboiler, leaving 12.2 equilibrium stages contained in the column. If the plate efficiency were 0.8, 16 trays would be needed.

### Column Operating Pressure and Condenser Type

For preliminary design, column operating pressure and condenser type are established by the procedure shown in Figure 7.16, which is formulated to achieve, if possible, a reflux-drum pressure,  $P_D$ , between 0 and 415 psia (2.86 MPa) at a minimum temperature of 120°F (49°C) (corresponding to the use of water as the coolant in the condenser). The pressure and temperature limits are representative only and depend on economic factors. Columns can operate at pressures higher than 415 psia if the critical or convergence

pressure of the mixture is not approached. A condenser pressure drop of 0 to 2 psi (0 to 14 kPa) and an overall, column pressure drop of 5 psi (35 kPa) may be assumed. However, when column tray requirements are known, more refined computations should result in approximately 0.1 psi/tray (0.7 kPa/tray) pressure drop for atmospheric and superatmospheric pressure operation and 0.05 psi/tray (0.35 kPa/tray) pressure drop for vacuum-column operation. Column bottom temperature must not result in bottoms decomposition or correspond to a near-critical condition. Therefore, after

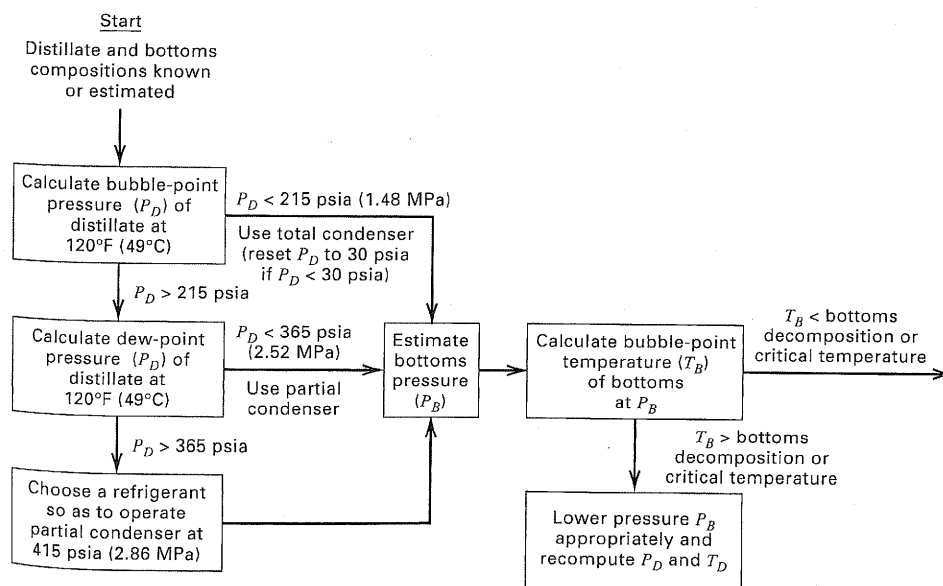
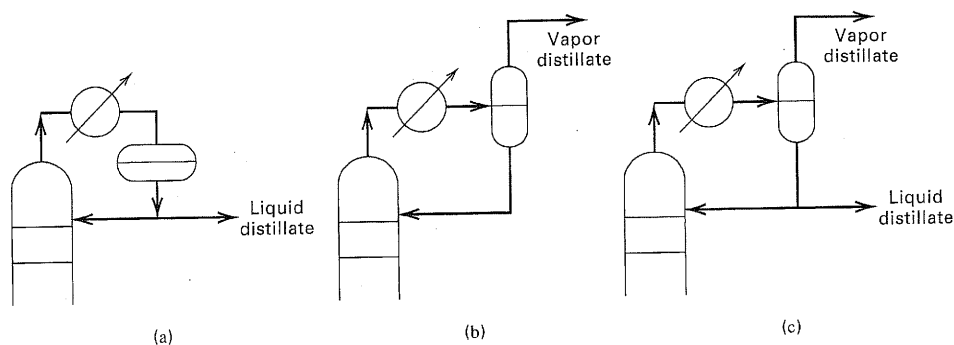


Figure 7.16 Algorithm for establishing distillation-column pressure and condenser type.



**Figure 7.17** Condenser types: (a) total condenser; (b) partial condenser; (c) mixed condenser.

the bottoms pressure is estimated from the pressure in the reflux drum, a bubble-point temperature of the bottoms is computed at the bottoms pressure. If that temperature exceeds the bottoms decomposition or critical temperature, then the bottoms pressure is recomputed at or below the bubble-point decomposition or critical temperature. The pressure in the reflux drum will then be lower and must be recomputed, together with the distillate temperature, from the assumed column and condenser pressure drops. This will result often in vacuum operation. If the recomputed distillate temperature is less than 120°F (49°C), a refrigerant, rather than cooling water, is used for the condenser.

A total condenser is recommended for reflux drum pressures to 215 psia (1.48 MPa). A partial condenser is appropriate from 215 psia to 365 psia (2.52 MPa). However, a partial condenser can be used below 215 psia when a vapor distillate is desired. A mixed condenser can provide both vapor and liquid distillates. The three types of condenser configurations are shown in Figure 7.17. A refrigerant is often used as condenser coolant if pressure tends to exceed 365 psia.

When a partial condenser is specified, the McCabe–Thiele staircase construction for the case of a total condenser must be modified, as will be illustrated in Example 7.2, to account for the fact that the first equilibrium stage, counted down from the top, is now the partial condenser. This is based on the assumption that the liquid reflux leaving the reflux drum is in equilibrium with the vapor distillate.

### Subcooled Reflux

Although most distillation columns are designed so that the reflux is a saturated (bubble-point) liquid, such is not always the case for operating columns. If the condenser type is partial or mixed, the reflux is a saturated liquid unless heat losses cause its temperature to decrease. For a total condenser, however, the operating reflux is often a subcooled liquid at column pressure, and the distillate bubble-point temperature is significantly higher than the inlet cooling-water temperature. If the condenser outlet pressure is lower than the top-tray pressure of the column, the reflux is subcooled for any of the three types of condensers.

When subcooled reflux enters the top tray, its temperature rises and causes vapor entering the tray to condense. The

latent enthalpy of condensation of the vapor provides the sensible enthalpy to heat the subcooled reflux to the bubble point. In that event, the internal reflux ratio within the rectifying section of the column is higher than the external reflux ratio from the reflux drum. The McCabe–Thiele construction should be based on the internal reflux ratio, which can be estimated by the following equation derived from an approximate energy balance around the top tray:

$$R_{\text{internal}} = R \left( 1 + \frac{C_{P_L} \Delta T_{\text{subcooling}}}{\Delta H^{\text{vap}}} \right) \quad (7-30)$$

where  $C_{P_L}$  and  $\Delta H^{\text{vap}}$  are per mole and  $\Delta T_{\text{subcooling}}$  is the degrees of subcooling. The internal reflux ratio replaces  $R$ , the external reflux ratio, in (7-9). If a correction is not made for subcooled reflux, the calculated number of equilibrium stages is somewhat more than required.

### EXAMPLE 7.2

One thousand kmol/h of a feed containing 30 mol% *n*-hexane and 70% *n*-octane is to be distilled in a column consisting of a partial reboiler, one equilibrium (theoretical) plate, and a partial condenser, all operating at 1 atm (101.3 kPa). Thus, hexane is the light key and octane is the heavy key. The feed, a bubble-point liquid, is fed to the reboiler, from which a liquid bottoms product is continuously withdrawn. Bubble-point reflux is returned from the partial condenser to the plate. The vapor distillate, in equilibrium with the reflux, contains 80 mol% hexane, and the reflux ratio,  $L/D$ , is 2. Assume that the partial reboiler, plate, and partial condenser each function as equilibrium stages.

- Using the McCabe–Thiele method, calculate the bottoms composition and kmol/h of distillate produced.
- If the relative volatility  $\alpha$  is assumed constant at a value of 5 over the composition range (the relative volatility actually varies from approximately 4.3 at the reboiler to 6.0 at the condenser), calculate the bottoms composition analytically.

### SOLUTION

First determine whether the problem is completely specified. From Table 5.4c, we have  $N_D = C + 2N + 6$  degrees of freedom, where  $N$  includes the partial reboiler and the stages in the column, but not the partial condenser. With  $N = 2$  and  $C = 2$ ,  $N_D = 12$ . Specified in

Mole fraction of hexane in the vapor,  $y$

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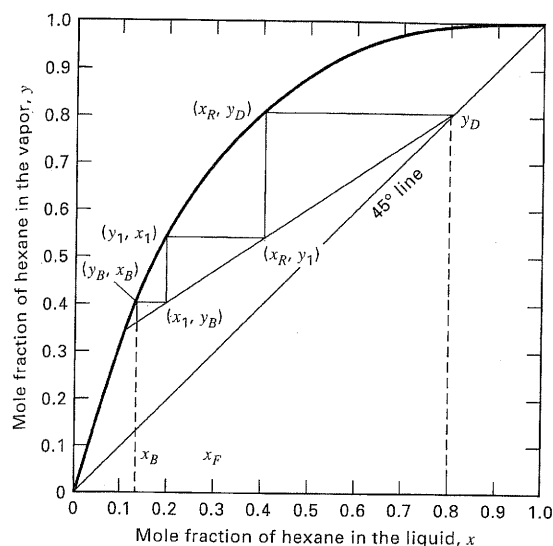


Figure 7.18 Solution to Example 7.2.

this problem are

Feed-stream variables	4
Plate and reboiler pressures	2
Condenser pressure	1
$Q (=0)$ for plate	1
Number of stages	1
Feed-stage location	1
Reflux ratio, $L/D$	1
Distillate composition	1
Total	12

Thus, the problem is fully specified and can be solved.

(a) *Graphical solution.* A diagram of the separator is given in Figure 7.18 as is the McCabe–Thiele graphical solution, which is constructed in the following manner.

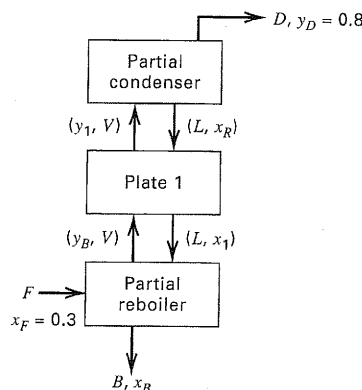
1. The point  $y_D = 0.8$  at the partial condenser is located on the  $x = y$  line.
2. Conditions in the condenser are fixed because  $x_R$  (reflux composition) is in equilibrium with  $y_D$ . Hence, the point  $(x_R, y_D)$  is located on the equilibrium curve.
3. Noting that  $(L/V) = 1 - 1/[1 + (L/D)] = 2/3$ , the operating line with slope  $L/V = 2/3$  is drawn through the point  $y_D = 0.8$  on the 45° line until it intersects the equilibrium curve. Because the feed is introduced into the partial reboiler, there is no stripping section.
4. Three theoretical stages (partial condenser, plate 1, and partial reboiler) are stepped off and the bottoms composition  $x_B = 0.135$  is read.

The amount of distillate is determined from overall material balances. For hexane,  $z_F F = y_D D + x_B B$ . Therefore,  $(0.3)(1,000) = (0.8)D + (0.135)B$ . For the total flow,  $B = 1,000 - D$ . Solving these two equations simultaneously,  $D = 248$  kmol/h.

(b) *Analytical solution.* For constant  $\alpha$ , equilibrium liquid compositions for the light key, in terms of  $\alpha$  and  $y$  are given by a rearrangement of (7-3):

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

where  $\alpha$  is assumed constant at a value of 5.



The steps in the solution are as follows:

1. The liquid leaving the partial condenser at  $x_R$  is calculated from (1), for  $y = y_D = 0.8$ :

$$x_R = \frac{0.8}{0.8 + 5(1 - 0.8)} = 0.44$$

2. Then  $y_1$  is determined by a material balance about the partial condenser:

$$Vy_1 = Dy_D + Lx_R \quad \text{with} \quad D/V = 1/3 \quad \text{and} \quad L/V = 2/3$$

$$y_1 = (1/3)(0.8) + (2/3)(0.44) = 0.56$$

3. From (1), for plate 1,  $x_1 = \frac{0.56}{0.56 + 5(1 - 0.56)} = 0.203$

4. By material balance around plate 1 and the partial condenser,

$$Vy_B = Dy_D + Lx_1$$

$$\text{and} \quad y_B = (1/3)(0.8) + (2/3)(0.203) = 0.402$$

5. From (1), for the partial reboiler,

$$x_B = \frac{0.402}{0.402 + 5(1 - 0.402)} = 0.119.$$

By approximating the equilibrium curve with  $\alpha = 5$ , an answer of 0.119 is obtained rather than 0.135 for  $x_B$  obtained in part (a). Note that for a larger number of theoretical plates, part (b) can be readily computed with a spreadsheet program.

### EXAMPLE 7.3

Consider Example 7.2. (a) Solve it graphically, assuming that the feed is introduced on plate 1, rather than into the reboiler. (b) Determine the minimum number of stages required to carry out the separation. (c) Determine the minimum reflux ratio.

### SOLUTION

(a) The flowsheet and solution given in Figure 7.19 are obtained as follows.

1. The point  $x_R, y_D$  is located on the equilibrium line.
2. The operating line for the enriching section is drawn through the point  $y = x = 0.8$ , with a slope of  $L/V = 2/3$ .

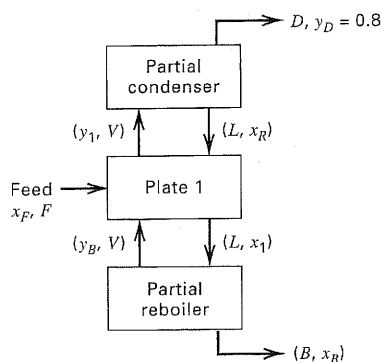
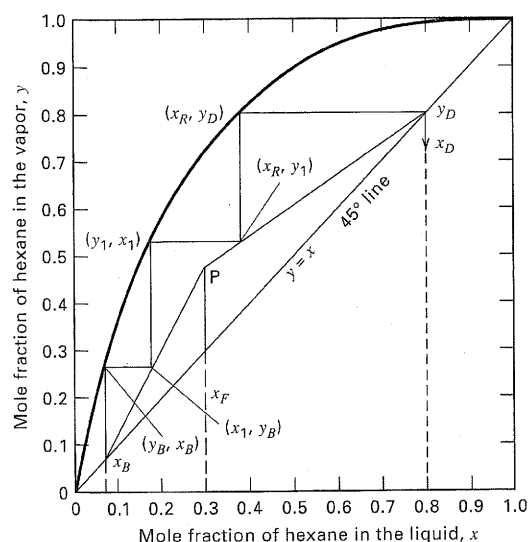


Figure 7.19 Solution to Example 7.3.

- The intersection of the  $q$ -line,  $x_F = 0.3$  (which, for a saturated liquid, is a vertical line), with the enriching-section operating line is located at point P. The stripping-section operating line must also pass through this point, but its slope and the point  $x_B$  are not known initially.
- The slope of the stripping-section operating line is found by trial and error to give three equilibrium contacts in the column, with the middle stage involved in the switch from one operating line to the other. If the middle stage is the optimal feed-stage location, the result is  $x_B = 0.07$ , as shown in Figure 7.19. The amount of distillate is obtained from the combined total and hexane overall material balances to give  $(0.3)(1,000) = (0.8D) + 0.07(1,000 - D)$ . Solving,  $D = 315$  kmol/h.

Comparing this result to that obtained in Example 7.2, we find that the bottoms purity and distillate yield are improved by introduction of the feed to plate 1, rather than to the reboiler. This improvement could have been anticipated if the  $q$ -line had been constructed in Figure 7.18. That is, the partial reboiler is not the optimal feed-stage location.

- The construction corresponding to total reflux ( $L/V = 1$ , no products, no feed, minimum equilibrium stages) is shown

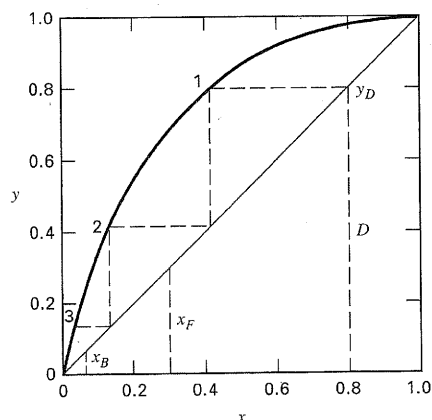


Figure 7.20 Solution for total reflux in Example 7.3.

in Figure 7.20. Slightly more than two stages are required for an  $x_B$  of 0.07, compared to the three stages previously required.

- To determine the minimum-reflux ratio, the vertical  $q$ -line in Figure 7.19 is extended from point P until the equilibrium curve is intersected, which is determined to be the point (0.71, 0.3). The slope,  $(L/V)_{\min}$  of the operating line for the rectifying section, which connects this point to the point (0.8, 0.8) on the 45° line is 0.18. Thus  $(L/D)_{\min} = (L/V_{\min})/[1 - (L/V_{\min})] = 0.22$ . This is considerably less than the  $L/D = 2$  specified.

## Reboiler Type

Different types of reboilers are used to provide boilup vapor to the stripping section of a distillation column. For small laboratory and pilot-plant-size columns, the reboiler consists of a reservoir of liquid located just below the bottom plate to which heat is supplied from (1) a jacket or mantle that is heated by an electrical current or by condensing steam, or (2) tubes that pass through the liquid reservoir carrying condensing steam. Both of these types of reboilers have limited heat-transfer surface and are not suitable for industrial applications.

For plant-size distillation columns, the reboiler is usually an external heat exchanger, as shown in Figure 7.21, of either the kettle or vertical thermosyphon type. Both can provide the amount of heat-transfer surface required for large installations. In the former case, liquid leaving the sump (reservoir) at the bottom of the column enters the kettle, where it is partially vaporized by the transfer of heat from tubes carrying condensing steam or some other heating medium. The bottoms product liquid leaving the reboiler is assumed to be in equilibrium with the vapor returning to the bottom tray of the column. Thus the kettle reboiler is a partial reboiler equivalent to one equilibrium stage. The kettle