SUBSCRIPTS

    a = assumed value of the variable.

    co = corrected value of the variable.

    k, n = counting integers.

GREEK LETTERS

    γ = thermodynamic activity coefficient.

    $\lambda_j = H_j - h_j$, latent heat of vaporization of the pure solvent at its saturation
        temperature T_j and pressure P_j.

MATHEMATICAL SYMBOLS

$$\sum_{j=1}^{n} x_j = x_1 + x_2 + \cdots + x_n.$$

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Introduction to
the Fundamentals
of Distillation

3

In this chapter, the fundamental principles and relationships involved in making multicomponent distillation calculations are developed from first principles. To enhance the visualization of the fundamental relationships involved in this separation process, the development of the calculational procedures are presented first for the special case of binary mixtures and then for the general case of multicomponent mixtures. All mixtures that contain three or more components are referred to as *multicomponent mixtures.* Proposed calculational procedures are illustrated by numerical examples.

Description of the separation of mixtures by distillation

The general objective of distillation is the separation of substances that have different vapor pressures at any given temperature. The word *distillation* as used here refers to the physical separation of a mixture into two or more fractions that have different boiling points.

If a liquid mixture of two volatile materials is heated, the vapor that comes off will have a higher concentration of the lower boiling material than the liquid from which it was evolved. Conversely, if a warm vapor is cooled,

the higher boiling material has a tendency to condense in a greater proportion than the lower boiling material. The early distillers of alcohol for beverages applied these fundamental ideas. Although distillation was known and practiced in antiquity and a commercial still had been developed by Coffey in 1832, the theory of distillation was not studied until the work of Sorel (19) in 1893. Other early workers were Lord Rayleigh (16) and Lewis (11). Current technology has permitted the large-scale separation by distillation of ethylbenzene and p-xylene, which have only a 3.9°F difference in boiling points (1).

A distillation column consists of a series of plates (or trays). In normal operation, there is a certain amount of liquid on each plate, and some arrangement is made for ascending vapors to pass through the liquid and make contact with it. The descending liquid flows down from the plate above through a downcomer, across the next plate, and then over a *weir* and into another downcomer to the next lower plate as shown in Figure 3-1. For many years, *bubble caps* were used (of which a variety of designs are shown in Figure 3-2) for contacting the vapor with the liquid. These contacting devices promote the production of small bubbles of vapor with relatively large surface areas.

Recent developments of devices for contacting the vapor and liquid streams have tended to displace bubble caps. New columns are usually equipped with either *ballast trays* (see Figure 3-3), sometimes called *valve*
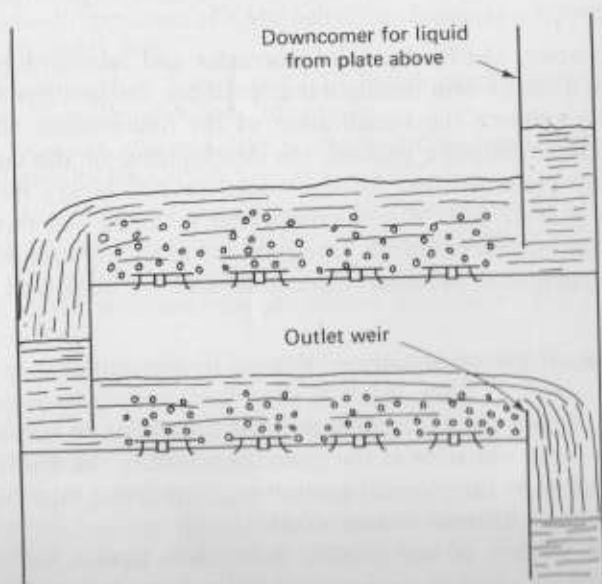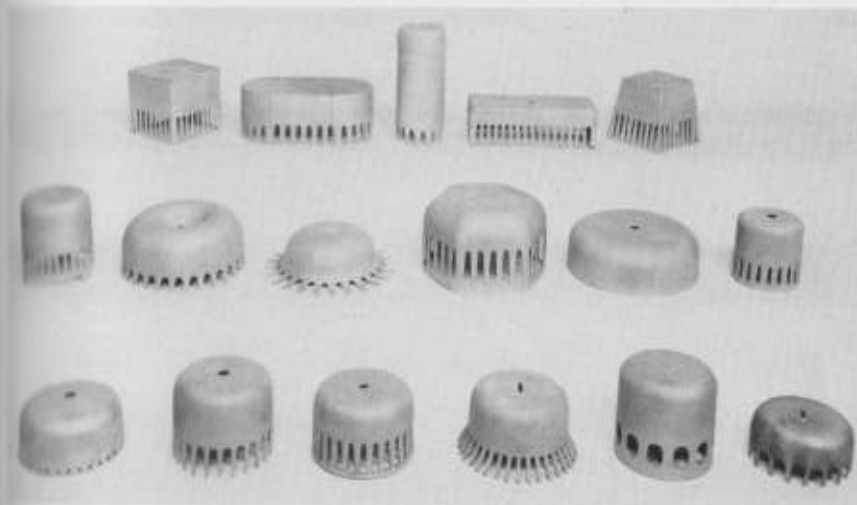

Figure 3-2. Various types of bubble caps used in distillation columns. (*Courtesy of Fritz W. Glitsch & Sons, Inc.*)
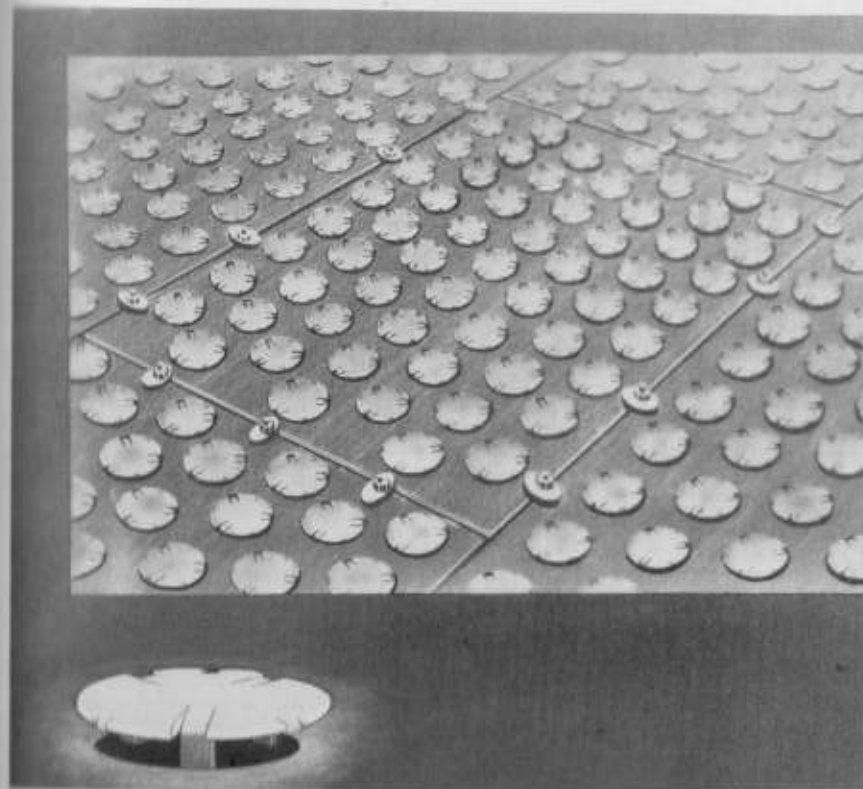
Figure 3-3. Portion of a Glitsch V-1 ballast tray. (*Courtesy of Fritz W. Glitsch & Sons, Inc.*)
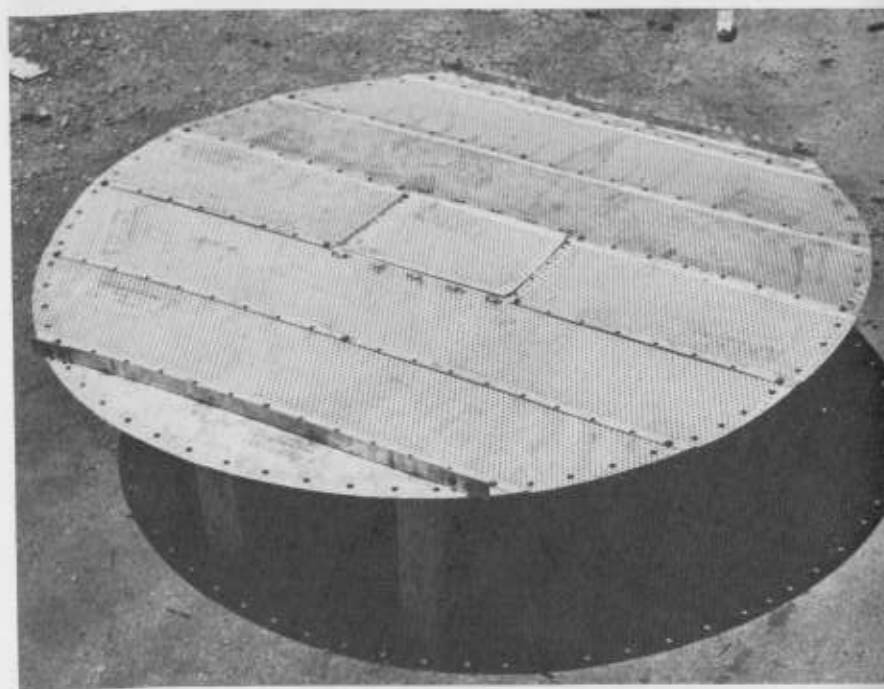

Downcomer for liquid from plate above

Outlet weir

Figure 3-1. The interior of a distillation column. (Taken from Holland and Lindsay, *Encyclopedia Chemical Technology*, Vol. 7, 2nd ed., p. 206.)

Figure 3-4. A perforated or sieve tray, 9 feet in diameter. (*Courtesy of Fritz W. Glitsch & Sons, Inc.*)

trays, or *perforated trays* (see Figure 3-4), sometimes called *sieve trays*. In the valve trays, the valve opens wider as the vapor velocity increases and closes as the vapor velocity decreases. This opening and closing allows the valve to remain immersed in liquid and thereby preserve a liquid seal over wide ranges of liquid and vapor flow rates.

Distillation columns have been built as high as 200 ft. Diameters as large as 44 ft have been used. Construction of a plate for a column with a 40 ft diameter is shown in Figure 3-5. Operating pressures for distillation columns have been reported which range from 15 mm to 500 psia.

As indicated in Figure 3-6, the overhead vapor V_1, upon leaving the top plate enters the condenser where it is either partially or totally condensed. The liquid formed is collected in an accumulator from which the liquid stream L_0 (called *reflux*) and the top product stream D (called the *distillate*) are withdrawn. When the overhead vapor V_1 is totally condensed to the liquid state and the distillate D is withdrawn as a liquid, the condenser is called a *total condenser*. If V_1 is partially condensed to the liquid state to produce the reflux L_0 and the distillate D is withdrawn as a vapor, the condenser is called a *partial condenser*. The amount of liquid reflux is commonly expressed
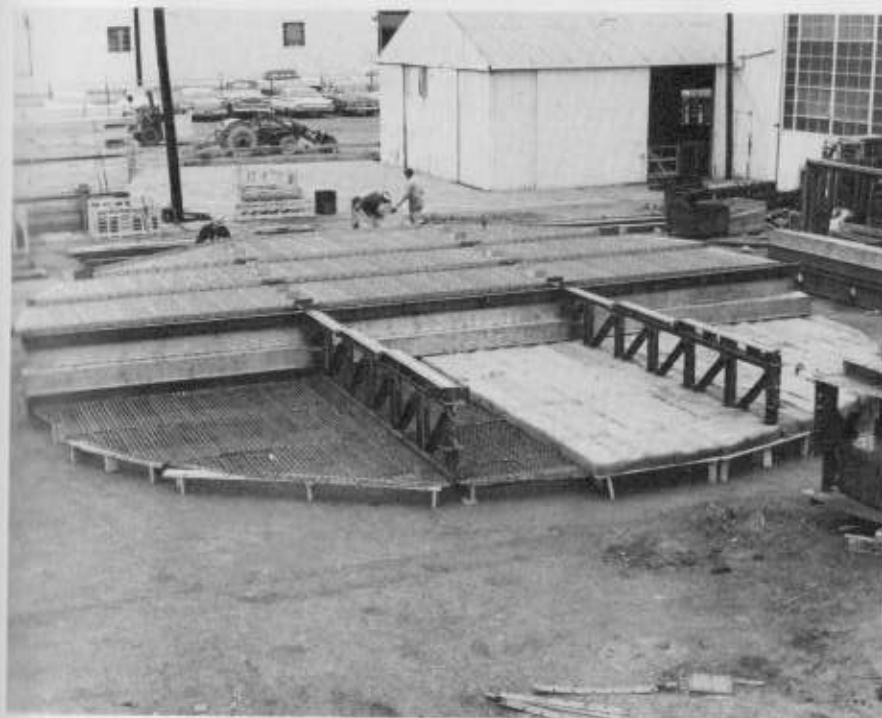
Figure 3-5. A Glitsch A–2 ballast tray with mist eliminator in the process of construction, 40 feet in diameter. (*Courtesy of Fritz W. Glitsch & Sons, Inc.*)

in terms of the *reflux ratio*, L_0/D. Although the internal liquid to vapor ratio, L/V, is sometimes referred to as the internal reflux ratio, the term *reflux ratio* will be reserved herein to mean L_0/D.

The liquid that leaves the bottom plate of the column enters the reboiler, where it is partially vaporized. The vapor produced is allowed to flow back up through the column, and the liquid is withdrawn from the reboiler and called the *bottoms* or *bottom product B*. In practice, the reboiler is generally located externally from the column. A typical commercial installation is shown in Figure 3-7.

Part 1. Fundamental Principles Involved in Distillation

To compute the composition of the top product D and the bottom product B which may be expected by use of a given distillation column operated at a given set of conditions, it is necessary to obtain a solution to the following
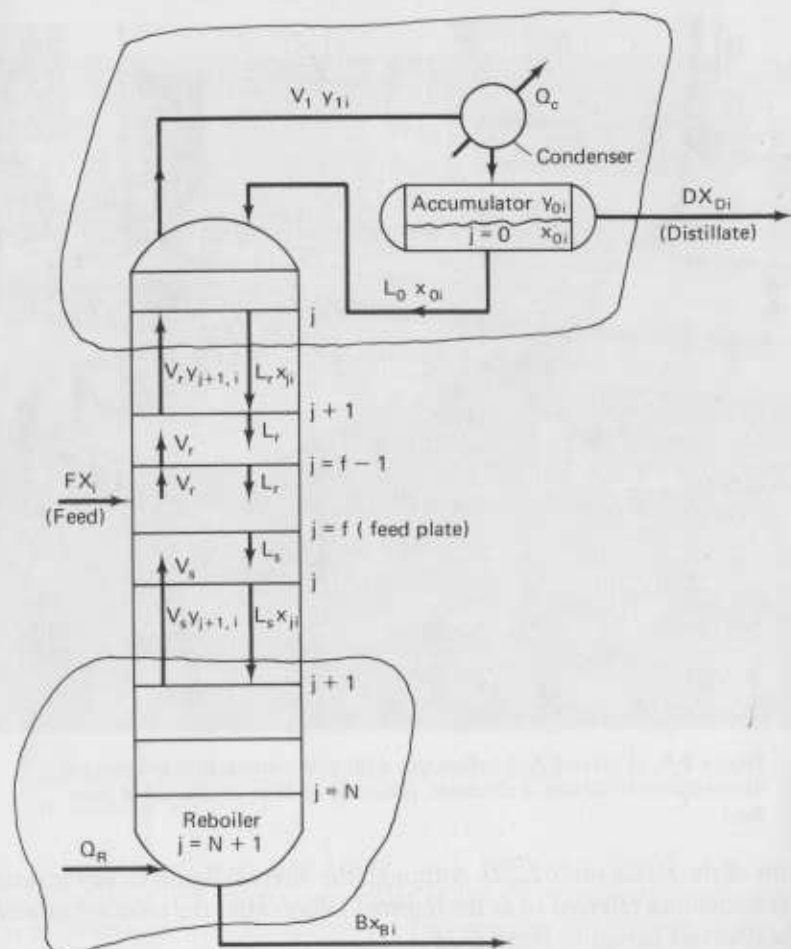
Figure 3-6. Sketch of a conventional column in which the total flow rates are constant within the rectifying and stripping sections.

equations:

1. Equilibrium relationships
2. Component-material balances
3. Total-material balances
4. Energy balances

Consider first equilibrium relationships.

Physical equilibrium

A two-phase multicomponent mixture is said to be in equilibrium if the following necessary conditions are satisfied (5).

Figure 3-7. Typical view of distillation columns at the Mobil Refinery at Beaumont, Texas. (*Courtesy Mobil Oil Corporation.*)

1. The temperature T^V of the vapor phase is equal to the temperature T^L of the liquid phase.
2. The total pressure P^V throughout the vapor phase is equal to the total pressure P^L throughout the liquid phase.   (3-1)
3. The tendency of each component to escape from the liquid phase to the vapor phase is exactly equal to its tendency to escape from the vapor phase to the liquid phase.

In the following analysis it is supposed that a state of equilibrium exists, $T^V = T^L = T$, $P^V = P^L = P$, and the escaping tendencies are equal.

Now consider the special case in which the third condition may be represented by Raoult's law.

$$Py_i = P_i x_i \qquad (3-2)$$

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, and P_i is the vapor pressure of pure component i at the temperature T of the system.

The separation of a binary mixture by distillation may be represented in two-dimensional space, but n-dimensional space is required to represent the separation of a multicomponent mixture. The graphical method proposed by McCabe and Thiele (13) for the solution of problems involving binary mixtures is presented in a subsequent section. The McCabe-Thiele method makes use of an equilibrium curve that may be obtained from the "boiling point diagram."

Construction and interpretation of the boiling point diagram for binary mixtures

When a state of equilibrium exists between a vapor and liquid phase composed of two components A and B, the system is described by the following set of independent equations,

Equilibrium relationships $\begin{cases} Py_A = P_A x_A \\ Py_B = P_B x_B \\ y_A + y_B = 1 \\ x_A + x_B = 1 \end{cases}$ (3-3)

where it is understood that Raoult's law is obeyed. Since the vapor pressures P_A and P_B depend on T alone, Equation (3-3) consists of four equations in six unknowns. Thus, to obtain a solution to this set of equations, two variables must be fixed. (Observe that this result is in agreement with the Gibbs phase rule: $\mathcal{P} + \mathcal{V} = c + 2$. For the above case, the number of phases $\mathcal{P} = 2$, the number of components $c = 2$, and thus the number of degrees of freedom $\mathcal{V} = 2$, that is, the number of variables that must be fixed $= 2$.) In the construction of the boiling point diagram for a binary mixture, the total pressure P is fixed and a solution is obtained for each of several temperatures lying between the temperatures at which the respective vapor pressures P_A and P_B are equal to the total pressure P.

The solution of the expressions given by Equation (3-3) for x_A in terms of P_A, P_B, and P is effected as follows. Addition of the first two expressions followed by the elimination of the sum of the y's by use of the third expression yields

$$P = P_A x_A + P_B x_B \qquad (3-4)$$

Elimination of x_B by use of the fourth expression given by Equation (3-3) followed by rearrangement of the result so obtained yields

$$x_A = \frac{P - P_B}{P_A - P_B} \qquad (3-5)$$

From the definition of a mole fraction ($0 \leq x_A \leq 1$), Equation (3-5) has a meaningful solution at a given P for any T lying between the boiling point temperatures T_A and T_B of pure A and pure B, respectively. (At T_A, $P_A = P$, and at T_B, $P_B = P$.) After x_A has been computed by use of Equation (3-5) at the specified P and T, the corresponding value of y_A which is in equilibrium with the value of x_A so obtained is computed by use of the first expression of Equation (3-3), namely,

$$y_A = \left(\frac{P_A}{P}\right) x_A \qquad (3-6)$$

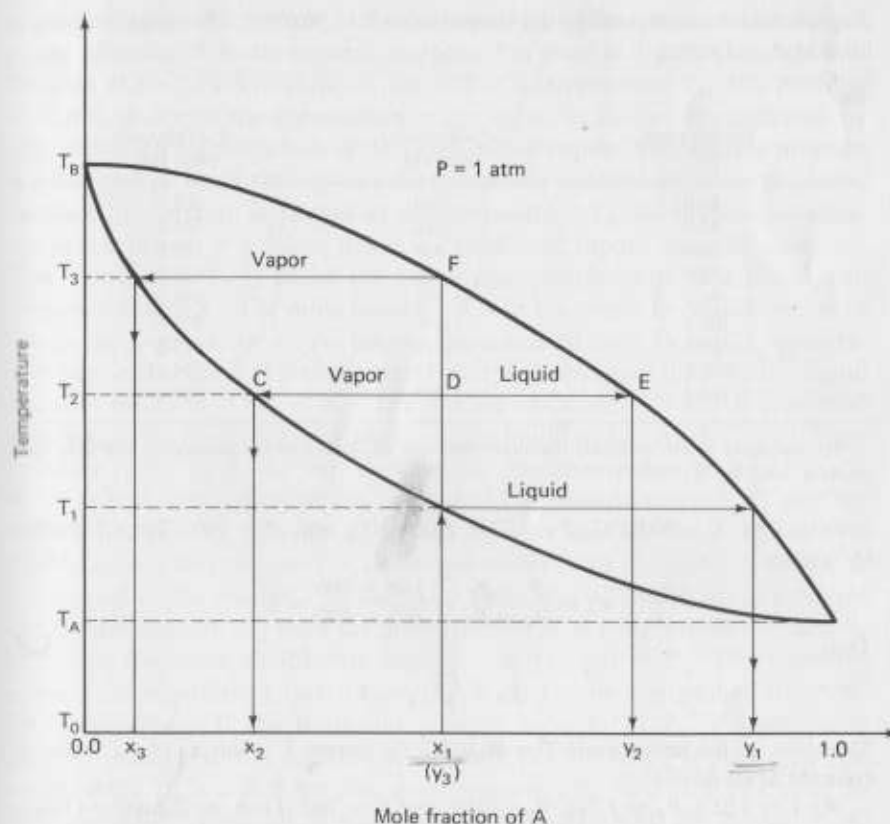By plotting T versus x_A and T versus y_A, the lower and upper curves, respec-

Figure 3-8. The boiling point diagram. (Taken from Holland and Lindsay, *Encyclopedia Chemical Technology*, Vol. 7, 2nd ed., p. 216.)

tively, of Figure 3-8 are typical of those obtained when component A is more volatile than B. Component A is said to be more volatile than component B, if for all T in the closed interval $T_A \leq T \leq T_B$, the vapor pressure of A is greater than the vapor pressure of B, that is, $P_A > P_B$. The parallel lines such as $\overline{CE}$ that join equilibrium pairs (x, y), computed at a given T and P by use of Equations (3-5) and (3-6), are commonly called *Tie lines*.

ILLUSTRATIVE EXAMPLE 3-1*

By use of the following vapor pressures for benzene and toluene (taken from *The Chemical Engineer's Handbook*, 2nd ed., J. H. Perry, editor, McGraw-Hill, New York, 1941), compute the three equilibrium pairs (x, y) on a boiling point

*Taken from C. D. Holland, *Introduction to the Fundamentals of Distillation*. Proceedings to the Fourth Annual Education Symposium of the ISA, April 5–7, 1972, Wilmington, Del. Courtesy Instrument Society of America.

diagram which correspond to the temperature $T = 80.02°C$. The total pressure is fixed at $P = 1$ atm.

Given:

Temperature (°C)	P_A(Benzene) (mm Hg)	P_B(Toluene) (mm Hg)
80.02	760	300.0
84.0	852	333.0
88.0	957	379.5
92.0	1,078	432.0
96.0	1,204	492.5
100.0	1,344	559.0
104.0	1,495	625.5
108.0	1,659	704.5†
110.4	1,748	760.0

†In the more recent editions, the vapor pressure of 704.5 mm for toluene as 108°C is inaccurately listed as 740.5 or 741 mm.

Solution: At $T = 80.02°C$, $P_A = 760$, $P_B = 300$, and $P = 760$. Then Equation (3-5) gives

$$x_A = \frac{P - P_B}{P_A - P_B} = \frac{760 - 300}{760 - 300} = 1$$

Thus,

$$y_A = \frac{P_A}{P} x_A = 1$$

Therefore, at the temperature $T = 80.02°C$, the curves T versus x_A and T versus y_A coincide at (1, 80.02).

At $T = 110.4$, $P_A = 1,748$, $P_B = 760$, and $P = 760$. Then, by Equation (3-5),

$$x_A = \frac{760 - 760}{1,748 - 760} = 0$$

and thus,

$$y_A = \left(\frac{1,748}{760}\right)(0) = 0$$

Hence, the curves T versus x_A and T versus y_A again coincide at the point (0, 110.4).

At any temperature between T_A and T_B, say $T = 100°C$, the calculations are carried out as follows:

$$x_A = \frac{760 - 559}{1,344 - 559} = \frac{201}{785} = 0.256$$

and

$$y_A = \left(\frac{1,344}{760}\right)(0.256) = 0.453$$

These results give the point (0.256, 100) on the T versus x_A curve and the point (0.453, 100) on the T versus y_A curve. Other points on these curves for temperatures lying between T_A and T_B are located in the same manner.

A boiling point diagram is a most convenient aid in the visualization of phase behavior. For definiteness, suppose P is fixed at 1 atm. Consider first the case of the liquid mixture of A and B at a temperature T_0, at a pressure of 1 atm, and with the composition $x_A = x_1$, $x_B = 1 - x_1$. As indicated by Figure 3-8, such a mixture is in the single-phase region. Suppose the pressure is held fixed at 1 atm throughout the course of the following changes. First, suppose the mixture is heated to the temperature T_1. At this temperature, the first evidence of a vapor phase, a "bubble of vapor," may be observed. The temperature T_1 is called the *bubble point* temperature of a liquid with the composition x_1. The mole fraction of A in the vapor in equilibrium with this liquid is seen to be y_1. As the mixture is heated from T_1 to T_2, vaporization continues. Since A has a greater escaping tendency than B, the liquid becomes leaner in A ($x_2 < x_1$). The relative amounts of A and B vaporized also depend on their relative amounts in the liquid phase. As the liquid phase becomes richer in B, the vapor phase also becomes richer in B ($y_2 < y_1$). Point D (the intersection of the horizontal line passing through T_2 and the vertical line passing through x_1) is seen to lie in the two-phase region. It is readily shown that the ratio of the moles of vapor to the moles of liquid at T_2 is equal to the ratio of $\overline{CD}/\overline{DE}$. Also, note that all initial liquid mixtures (at the temperature T_0) with the mole fraction of A lying between x_2 and y_2 will have the same equilibrium composition (x_2, y_2) at T_2. This property permits the equilibrium state (x_2, y_2, T_2, 1 atm) to be approached from different directions. If the particular mixture $x_A = x_1$ at T_0 is heated until point F is reached, the equilibrium mixture (x_3, y_3) at T_3 is obtained. The temperature T_3 is called the *dew point* temperature. At F, the last point in the two-phase region, all of the liquid is vaporized with the exception of, say, one drop. Thus, the dew point temperature is seen to be that temperature at which the first drop of liquid is formed when a vapor with the composition $y_3 = x_1$ is cooled from a temperature greater than its dew point to its dew point temperature, T_3.

Generalized equilibrium relationships

Unfortunately, the phase behavior of many mixtures is not adequately described by Raoult's law. A more precise statement of the third condition of Equation (3-1) is that the partial molar free energies are equal (5) from which the following alternate but equivalent statement may be deduced,

$$\hat{f}_i^V = \hat{f}_i^L \tag{3-7}$$

where $\hat{f}_i^V$ and $\hat{f}_i^L$ are the fugacities of component i in the vapor and liquid phases, evaluated at the P and T of the system. Equation (3-7) may be restated

in the following equivalent form:

$$\gamma_i^v f_i^v y_i = \gamma_i^L f_i^L x_i \tag{3-8}$$

where

f_i^L, f_i^v = fugacities of pure component i in the liquid and vapor states, respectively, evaluated at the total pressure P and temperature T of the system;

x_i, y_i = mole fractions of component i in the liquid and vapor phases, respectively;

γ_i^L, γ_i^v = activity coefficients of component i in the liquid and vapor phases, respectively. $\gamma_i^L = \gamma_i^L(P, T, x_1, \ldots, x_c)$; $\gamma_i^v = \gamma_i^v(P, T, y_1, \ldots, y_c)$.

If, as is usually the case, the vapor may be assumed to form an ideal solution, then $\gamma_i^v = 1$ for each i, and Equation (3-8) may be restated as follows:

$$y_i = \gamma_i^L K_i x_i \tag{3-9}$$

where

$K_i = f_i^L/f_i^v$, the ideal solution K value.

The expression given by Equation (3-9) is recognized as one form of Henry's law. If the liquid phase also forms an ideal solution ($\gamma_i^L = 1$ for all i), then Equation (3-9) reduces to

$$y_i = K_i x_i \tag{3-10}$$

In some of the literature, the activity coefficient γ_i^L is absorbed in K_i, that is, the product $\gamma_i^L K_i$ is called K_i and an equation of the form of Equation (3-10) is obtained which is applicable to systems described by Equation (3-9).

If the effect of total pressure on the liquid fugacity is negligible in the neighborhood of the vapor pressure of pure component i, then

$$f_i^L|_{P,T} \cong f_i^L|_{P_i,T} = f_i^v|_{P_i,T} \tag{3-11}$$

where P_i is the vapor pressure of pure component i. If in addition to the assumptions required to obtain Equations (3-10) and (3-11), one also assumes that the vapor phase obeys the perfect gas law ($PV = RT$), then Equation (3-10) reduces to Raoult's law, Equation (3-2).

Determination of the bubble point and dew point temperatures of multicomponent mixtures

In the interest of simplicity, the equilibrium relationship given by Equation (3-10) is used in the following developments. The state of equilibrium for a two-phase (vapor and liquid) system is described by the following equations in which any number of components c are distributed between the two

phases

$$\text{Equilibrium relationships} \begin{cases} y_i = K_i x_i & (1 \leq i \leq c)^* \\ \sum_{i=1}^{c} y_i = 1 \\ \sum_{i=1}^{c} x_i = 1 \end{cases} \tag{3-12}$$

Since K_i is a function of the total pressure P and the temperature T [$K_i = K_i(P, T)$], it is evident that the expressions represented by Equation (3-12) consist of $c + 2$ equations in $2c + 2$ unknowns. Thus, to obtain a solution to these equations, c variables must be fixed.

When $c - 1$ values of x_i and the total pressure P are fixed, the temperature T required to satisfy these equations is called the *bubble point temperature*. The cth mole fraction may be found by use of the ($c - 1$) fixed values of x_i and the last expression given by Equation (3-12). When the first expression is summed over all components and the sum of the y_i's eliminated by use of the second expression given by Equation (3-12), the following result is obtained,

$$1 = \sum_{i=1}^{c} K_i x_i \tag{3-13}$$

Equation (3-13) consists of one equation in one unknown, the temperature. Since K_i is generally an implicit function of T, the solution of Equation (3-13) for the bubble point temperature becomes a trial-and-error problem. Of the many numerical methods for solving such a problem, only Newton's method (4, 8) is presented. In the application of this method, it is convenient to restate Equation (3-13) in function notation as follows:

$$f(T) = \sum_{i=1}^{c} K_i x_i - 1 \tag{3-14}$$

Thus, the bubble point temperature becomes that T which makes $f(T) = 0$. In the application of Newton's method, the following expression for the first derivative of $f(T)$ is needed.

$$f'(T) = \sum_{i=1}^{c} x_i \frac{dK_i}{dT} \tag{3-15}$$

Newton's method is initiated by the selection of an assumed value for T, say T_n. Then the values of $f(T_n)$ and $f'(T_n)$ are determined. The improved value of T, denoted by T_{n+1}, is found by application of Newton's formula [see Equation (A-9)]

$$T_{n+1} = T_n - \frac{f(T_n)}{f'(T_n)} \tag{3-16}$$

---

*The counting integer i for component number takes on only integral values, and the notation ($1 \leq i \leq c$) is used herein to mean $i = 1, 2, \ldots, c-1, c$.

The value so obtained for T_{n+1} becomes the assumed value for the next trial. This procedure is repeated until $|f(t)|$ is less than some small preassigned positive number ϵ. Observe that when the T has been found that makes $f(T) = 0$, each term $K_i x_i$ of the summation in Equation (3-14) is equal to y_i, the composition of the vapor. In Illustrative Example 3-2, as well as in those that follow, synthetic functions for the K-values and the enthalpies were selected in order to keep the arithmetic simple.

ILLUSTRATIVE EXAMPLE 3-2*

If for a three-component mixture, the following information is available, compute the bubble point temperature at the specified pressure of $P = 1$ atm by use of Newton's method. Take the first assumed value of T_n to be equal to 100°F.

Given:

Component No.	K_i	x_i
1	$K_1 = \dfrac{0.01T\dagger}{P\dagger}$	$\frac{1}{3}$
2	$K_2 = \dfrac{0.02T}{P}$	$\frac{1}{3}$
3	$K_3 = \dfrac{0.03T}{P}$	$\frac{1}{3}$

$\dagger T$ is in °F and P is in atm.

Solution: Assume $T_1 = 100$°F. The total pressure $P = 1$ atm. Then,

Component No.	x_i	K_i @ $P = 1$ atm $T = 100$°F	$K_i x_i$	$\left.\dfrac{dK_i}{dT}\right\|_{T_n=100}$	$x_i \dfrac{dK_i}{dT}$
1	$\frac{1}{3}$	1	$\frac{1}{3}$	0.01	$\frac{0.01}{3}$
2	$\frac{1}{3}$	2	$\frac{2}{3}$	0.02	$\frac{0.02}{3}$
3	$\frac{1}{3}$	3	$\frac{3}{3}$	0.03	$\frac{0.03}{3}$
			$\frac{6}{3} = 2$		$\frac{0.06}{3} = 0.02$

From the above results, it follows that

$$f(100) = \sum_{i=1}^{c} K_i x_i - 1 = 2 - 1 = 1$$

$$f'(100) = \sum_{i=1}^{c} x_i \frac{dK_i}{dT} = 0.02$$

Then

$$T_2 = T_1 - \frac{f(T_1)}{f'(T_1)} = 100 - \frac{1}{0.02} = 50°F$$

*Taken from Holland, *Introduction to the Fundamentals of Distillation.* Courtesy Instrument Society of America.

Assume $T_2 = 50$°F

Component No.	K_i @ $P = 1$ atm $T = 50$°F	$K_i x_i = y_i$
1	$\frac{1}{2}$	$\frac{1}{6}$
2	$\frac{2}{2}$	$\frac{2}{6}$
3	$\frac{3}{2}$	$\frac{3}{6}$
		$\frac{6}{6} = 1$

Therefore, the bubble point temperature is 50°F.

When the y_i's and P are fixed rather than the x_i's and P, the solution temperature of the expressions given by Equation (3-12) is called the *dew point temperature.* By rearranging the first expression of Equation (3-12) to the form $x_i = y_i/K_i$ and carrying out steps analogous to those described above, the dew point function $F(T)$ is obtained.

$$F(T) = \sum_{i=1}^{c} \frac{y_i}{K_i} - 1 \qquad (3\text{-}17)$$

The dew point temperature is that T that makes $F(T) = 0$. In this case

$$F'(T) = -\sum_{i=1}^{c} \frac{y_i}{K_i^2} \frac{dK_i}{dT} \qquad (3\text{-}18)$$

Observe again that when the T is found that makes $F(T) = 0$, each term y_i/K_i of the summation in Equation (3-18) is equal to x_i, the composition of the liquid.

Now observe that if after the bubble point temperature has been determined for a given set of x_i's, the set of y_i's so obtained are used to determine the dew point temperature at the same pressure, it will be found that these two temperatures are equal. For a binary mixture, this result is displayed graphically in Figure 3-8. For example, a bubble point temperature calculation on the basis of the $\{x_{1i}\}$ yields the bubble point temperature T_1 and the composition of the vapor $\{y_{1i}\}$. Then a dew point temperature on the set $\{y_{1i}\}$ yields the dew point temperature T_1 and the original set of x_{1i}'s.

The K_b method for the determination of bubble point and dew point temperature

Robinson and Gilliland (17) pointed out that if the relative values of the K_i's are independent of temperature, the expressions given by Equation (3-12) may be rearranged in a manner such that trial-and-error calculations are avoided in the determination of the bubble point and dew point tempera-

tures. The ratio K_i/K_b is called the relative volatility α_i of component i with respect to component b, that is,

$$\alpha_i = \frac{K_i}{K_b} \qquad (3\text{-}19)$$

where K_i and K_b are evaluated at the same temperature and pressure. Component b may or may not be a member of the given mixture under consideration.

When the x_i's and the pressure P are given and it is desired to determine the bubble point temperature, the formula needed may be developed by first rewriting the first expression of Equation (3-12) as follows:

$$y_i = \left(\frac{K_i}{K_b}\right) K_b x_i = \alpha_i K_b x_i \qquad (3\text{-}20)$$

Summation of the members of Equation (3-20) over all components i, followed by rearrangement yields

$$K_b = \frac{1}{\sum\limits_{i=1}^{c} \alpha_i x_i} \qquad (3\text{-}21)$$

Since the α_i's are independent of temperature, they may be computed by use of the values of K_i and K_b evaluated at any arbitrary value of T and at the specified pressure. After K_b has been evaluated by use of Equation (3-21), the desired bubble point temperature is found from the known relationship between K_b and T.

If the y_i's are known instead of the x_i's, then the desired formula for the determination of the dew point temperature is found by first rearranging Equation (3-20) to the following form

$$K_b x_i = \frac{y_i}{\alpha_i}$$

and then summing over all components to obtain

$$K_b = \sum_{i=1}^{c} \frac{y_i}{\alpha_i} \qquad (3\text{-}22)$$

This equation is used to determine the dew point temperature in a manner analogous to that described for Equation (3-21).

Many families of compounds are characterized by the fact that their vapor pressures may be approximated by the Clausius-Clapeyron equation and by the fact that their latent heats of vaporization are approximately equal. The vapor pressures of the members of such families of compounds fall on parallel lines when plotted against the reciprocal of the absolute temperature. For any two members i and b of such a mixture, it is readily shown that α_i is independent of temperature.

Although there exists many systems whose α_i's are very nearly constant and Equations (3-21) and (3-22) are applicable for the determination of the

bubble point and dew point temperatures, respectively, the greatest use of these relationships lies in their application in the iterative procedures for solving multicomponent distillation problems as described in a subsequent section.

ILLUSTRATIVE EXAMPLE 3-3

Repeat Illustrative Example 3-2 by use of the K_b method.

Solution: Since K_b may be selected arbitrarily, take $K_b = K_1$. Assume $T = 100°$F.

Component No.	x_i	K_i @ $P = 1$ atm $T = 100°$F	$\alpha_i = \frac{K_i}{K_b}$	$\alpha_i x_i$
1	$\frac{1}{3}$	1	1	$\frac{1}{3}$
2	$\frac{1}{3}$	2	2	$\frac{2}{3}$
3	$\frac{1}{3}$	3	3	$\frac{3}{3}$
				$\frac{6}{3} = 2$

Then

$$K_b = \frac{1}{\sum\limits_{i=1}^{c} \alpha_i x_i} = \frac{1}{2} = 0.5$$

and since $K_b = K_1$,

$$0.5 = 0.01T, \quad \text{or} \quad T = 50°F$$

Since the α_i's are independent of temperature, 50°F is the correct value for the bubble point temperature.

Part 2. Separation of Multicomponent Mixtures by Use of a Single Equilibrium Stage

Each of the separation processes considered in this and in Part 3 are special cases of the general separation problem in which a multicomponent mixture is to be separated into two or more parts through the use of any number of equilibrium stages.

Flash calculations

The boiling point diagram (Figure 3-8) is useful for visualizing the necessary conditions required for a flash to occur. Suppose the feed to be flashed has the composition $X_i = x_{1i}(x_{i,A}$ and $x_{1,B})$, and further suppose that this liquid mixture at the temperature T_0 and pressure $P = 1$ atm is to be flashed by raising the temperature to the specified flash temperature $T_F = T_2$ at the

specified flash pressure $P = 1$ atm. First observe that the bubble point temperature of the feed $T_{B.P.}$ at $P = 1$ atm is T_1. The dew point temperature, $T_{D.P.}$, of the feed at the pressure $P = 1$ atm is seen to be T_3. Then it is obvious from Figure 3-8 that a necessary condition for a flash to occur at the specified pressure is that

$$T_{B.P.} < T_F < T_{D.P.} \qquad (3\text{-}23)$$

In practice, the flash process is generally carried out by reducing the pressure on the feed stream rather than heating the feed at constant pressure as described above.

To determine whether or not the feed will flash at a given T_F and P, the above inequality may be tested by determining the bubble point and dew point temperatures of the feed at the specified pressure P. In determination of the bubble point temperature of the feed at the specified P of the flash, the x_i's in Equation (3-14) are replaced by the X_i's of the feed, and in the determination of the dew point temperature at the specified pressure, the y_i's in Equation (3-17) are replaced by the X_i's. Alternately, the inequality given by Equation (3-23) is satisfied if at the specified T_F and P,

$$f(T_F) > 0, \quad \text{and} \quad F(T_F) > 0 \qquad (3\text{-}24)$$

where these functions are defined as follows:

$$f(T_F) = \sum_{i=1}^{c} K_{Fi} X_i - 1, \quad \text{and} \quad F(T_F) = \sum_{i=1}^{c} \frac{X_i}{K_{Fi}} - 1 \qquad (3\text{-}25)$$

The two kinds of flash calculations that are commonly made are generally referred to as *isothermal* and *adiabatic* flashes.

ISOTHERMAL FLASH. In the isothermal flash, the following specifications are made: $T_F, P, \{X_i\}$, and F. It is required to find $V_F, L_F, \{y_{Fi}\}$, and $\{x_{Fi}\}$. In addition to the $c + 2$ equations required to describe the state of equilibrium between the vapor and liquid phases [see Equation (3-12)], "c additional component-material balances are required to describe the isothermal flash process." Thus, the independent equations required to describe this flash process are as follows:

$$\text{Equilibrium relationships} \begin{cases} y_{Fi} = K_{Fi} x_{Fi} & (1 \leq i \leq c) \\ \sum_{i=1}^{c} y_{Fi} = 1 \\ \sum_{i=1}^{c} x_{Fi} = 1 \end{cases} \qquad (3\text{-}26)$$

Material balances $\{FX_i = V_F y_{Fi} + L_F x_{Fi} \qquad (1 \leq i \leq c)$

Equation (3-26) is seen to represent $2c + 2$ equations in $2c + 2$ unknowns $[V_F, L_F, \{y_{Fi}\}, \{x_{Fi}\}]$.

This system of nonlinear equations is readily reduced to one equation in

one unknown (say, V_F) in the following manner. First observe that the total material balance expression (a dependent equation) may be obtained by summing each member of the last expression of Equation (3-26) over all components to give

$$F \sum_{i=1}^{c} X_i = V_F \sum_{i=1}^{c} y_{Fi} + L_F \sum_{i=1}^{c} x_{Fi}, \quad \text{or} \quad F = V_F + L_F \qquad (3\text{-}27)$$

Elimination of the y_{Fi}'s from the last expression given by Equation (3-26) by use of the first expression, followed by rearrangement yields

$$x_{Fi} = \frac{X_i}{\dfrac{L_F}{F} + \dfrac{V_F K_{Fi}}{F}} \qquad (3\text{-}28)$$

Elimination of L_F from Equation (3-28) by use of Equation (3-27) yields

$$x_{Fi} = \frac{X_i}{1 - \Psi(1 - K_{Fi})} \qquad (3\text{-}29)$$

where

$$\Psi = \frac{V_F}{F}$$

When each member of Equation (3-29) is summed over all components i and the result so obtained is restated in functional notation, one obtains

$$P(\Psi) = \sum_{i=1}^{c} \frac{X_i}{[1 - \Psi(1 - K_{Fi})]} - 1 \qquad (3\text{-}30)$$

and

$$P'(\Psi) = \sum_{i=1}^{c} \frac{X_i(1 - K_{Fi})}{[1 - \Psi(1 - K_{Fi})]^2} \qquad (3\text{-}31)$$

From a graph of the branch of the function $P(\Psi)$ (see Figure 3-9) which contains the positive root, it is evident that Newton's method (8) always converges to the desired root when $\Psi = 1$ is taken to be the first assumed value for the root. After this root (the value of $\Psi > 0$ that makes $P(\Psi) = 0$) has been found, both V_F and L_F may be calculated by using the total material balance [Equation (3-27)] and the fact that $\Psi = V_F/F$. Also, it is evident from Equation (3-29) that when the solution value of Ψ has been found, each term in the summation of $P(\Psi) = 0$ is one of the solution values of $\{x_{Fi}\}$. Then the corresponding solution set of y_{Fi}'s is obtained by using the first expression of Equation (3-26), $y_{Fi} = K_{Fi} x_{Fi}$.

ILLUSTRATIVE EXAMPLE 3-4*

It is proposed to flash the following feed at a specified temperature $T_F = 100°F$ and a pressure $P = 1$ atm.

*Taken from Holland, *Introduction to the Fundamentals of Distillation*. Courtesy Instrument Society of America.
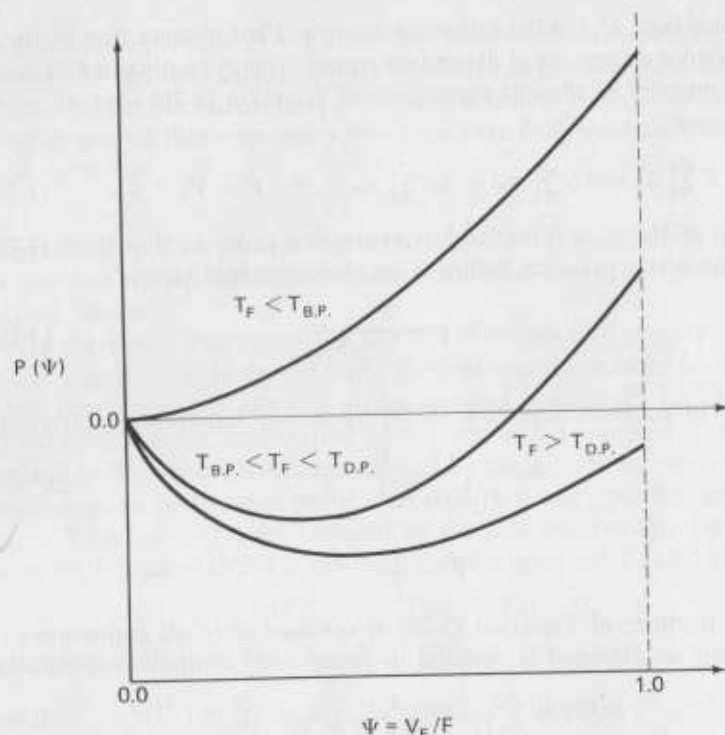
Figure 3-9. Graphical representation of the flash function $P(\Psi)$.

Component No.	K_i	X_i
1	$K_1 = \dfrac{10^{-2}T\dagger}{3P\dagger}$	$\frac{1}{3}$
2	$K_2 = \dfrac{2 \times 10^{-2}T}{P}$	$\frac{1}{3}$
3	$K_3 = \dfrac{7 \times 10^{-2}T}{2P}$	$\frac{1}{3}$

$\dagger T$ is in °F and P is in atm.

If the feed rate to the flash drum is $F = 100$ moles/hr, compute the vapor and liquid rates V_F and L_F leaving the flash as well as the respective mole fractions $\{y_{Fi}\}$ and $\{x_{Fi}\}$ of these streams.

Solution: First, the specified value of T_F will be checked to determine whether or not it lies between the bubble point and dew point temperatures of the feed.

Component No.	$K_{Fi} @ P = 1$ $T = 100°F$	X_i	$K_{Fi}X_i$	$\dfrac{X_i}{K_{Fi}}$
1	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{9}$	1
2	2	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$
3	$\frac{7}{2}$	$\frac{1}{3}$	$\frac{7}{6}$	$\frac{2}{21}$
			1.94	1.2619

Thus,

$$f(T_F) = \sum_{i=1}^{c} K_{Fi}X_i - 1 = 1.94 - 1 = 0.94 > 0$$

$$F(T_F) = \sum_{i=1}^{c} \frac{X_i}{K_{Fi}} - 1 = 1.2619 - 1 = 0.2619 > 0$$

and thus,

$$T_{B.P.} < 100 < T_{D.P.}$$

Trial No. 1: Assume $\Psi = 1$.

Component No.	K_i	$1 - K_{Fi}$	$\Psi(1 - K_{Fi})$	$1 - \Psi(1 - K_{Fi})$
1	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$
2	2	-1	-1	2
3	$\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{5}{2}$	$\frac{7}{2}$

$\dfrac{X_i}{1 - \Psi(1 - K_{Fi})}$	$\dfrac{X_i}{[1 - \Psi(1 - K_{Fi})]^2}$	$\dfrac{X_i(1 - K_i)}{[1 - (1 - K_{Fi})]^2}$
1.0000	3.0000	2.0000
0.1667	0.0833	−0.0833
0.0952	0.0272	−0.0680
1.2619		1.8487

$$P(1) = 1.2619 - 1 = 0.2619$$

$$P'(1) = 1.8487$$

$$\Psi_2 = 1 - \left(\frac{0.2614}{1.8487}\right) = 1 - 0.1417 = 0.8583$$

Trial No. 2: Assume $\Psi = 0.8583$ and repeat the steps shown in the first trial. The results so obtained are as follows:

$$P(0.8583) = 1.0651 - 1 = 0.0651$$

$$P'(0.8583) = 1.0358$$

$$\Psi_3 = 0.8583 - \left(\frac{0.0651}{1.0358}\right) = 0.7955$$

Continuation of this procedure gives the solution value of $\Psi = 0.787$. Thus, $V_F = 78.7$, $L_F = 21.3$, and the solution sets $\{x_{Fi}\}$ and $\{y_{Fi}\}$ are as follows:

Component No.	$1 - K_{Fi}$	$\Psi(1 - K_{Fi})$	$1 - \Psi(1 - K_{Fi})$	$x_{Fi} = \dfrac{X_i}{1 - \Psi(1 - K_{Fi})}$	$y_{Fi} = K_{Fi}x_{Fi}$
1	0.667	0.525	0.475	0.701	0.234
2	−1.000	−0.787	1.787	0.187	0.374
3	−2.500	−1.968	2.968	0.112	0.392

Up to this point no mention has been made of the manner of satisfying the energy requirement of the flash. The specification of T_F implies that the feed either possesses precisely the correct amount of energy for the flash to

occur at T_F at the specified P or that energy is to be added or withdrawn at the flash drum as required. It is common practice to adjust the heat content of the feed before it reaches the flash drum so that the flash occurs adiabatically, that is, the heat added Q at the flash drum is equal to zero.

After the solution $[V_F, L_F, \{y_{Fi}\}, \{x_{Fi}\}]$ has been found for a given isothermal flash problem, the heat content H that the feed must possess in order for the flash to occur adiabatically ($Q = 0$ at the flash drum) may be found by using the enthalpy balance that encloses the entire process

$$FH = V_F H_F + L_F h_F \qquad (3\text{-}32)$$

When the vapor V_F and liquid L_F form ideal solutions, the enthalpies H_F and h_F of the vapor and liquid streams, respectively, may be computed as follows:

$$H_F = \sum_{i=1}^{c} H_{Fi} y_{Fi} \quad \text{and} \quad h_F = \sum_{i=1}^{c} h_{Fi} x_{Fi} \qquad (3\text{-}33)$$

The above procedure may also be used to solve adiabatic flash problems as described below.

ILLUSTRATIVE EXAMPLE 3-5*

On the basis of the solution to Illustrative Example 3-4, compute the enthalpy H which the feed must possess in order for the flash to occur adiabatically.

Given:

Component No.	h_i (Btu/lb mole)	H_i (Btu/lb mole)
1	$h_1 = 10,000 + 30T$†	$H_1 = 17,000 + 30T$†
2	$h_2 = 8,000 + 20T$	$H_2 = 13,000 + 20T$
3	$h_3 = 500 + T$	$H_3 = 800 + T$

†T is in °F.

Solution: Calculation of the enthalpy H of the feed is as follows:

Component No.	x_{Fi}	y_{Fi}	h_{Fi} @ $T_F = 100°F$	$h_{Fi}x_{Fi}$	H_{Fi} @ $T_F = 100°F$	$H_{Fi}y_{Fi}$
1	0.701	0.234	13,000	9,113	20,000	4,680
2	0.187	0.374	10,000	1,870	15,000	5,610
3	0.112	0.392	600	67	900	353
				$h_F = 11,050$		$H_F = 10,643$

Thus,

$$H = \frac{V_F H_F}{F} + \frac{L_F h_F}{F} = (0.787)(10,643) + (0.213)(11,050) = 10,740 \text{ Btu/lb mole}$$

*Taken from Holland, Introduction to the Fundamentals of Distillation. Courtesy Instrument Society of America.

ADIABATIC FLASH. The term adiabatic flash is used to describe the problem wherein the following specifications are made: P, $Q = 0$ (no heat is added at the flash drum), H, $\{X_i\}$, and F. In this case there are $2c + 3$ unknowns $[T_F, V_F, L_F, \{y_{Fi}\}, \{x_{Fi}\}]$. The independent equations are also $2c + 3$ in number, the $2c + 2$ given by Equation (3-26) plus the enthalpy balance given by Equation (3-32), that is,

Equilibrium relationships
$$\begin{cases} y_{Fi} = K_{Fi} x_{Fi} & (1 \leq i \leq c) \\ \sum_{i=1}^{c} y_{Fi} = 1 \\ \sum_{i=1}^{c} x_{Fi} = 1 \end{cases} \qquad (3\text{-}34)$$

Material balances $\{FX_i = V_F y_{Fi} + L_F x_{Fi} \quad (1 \leq i \leq c)$

Enthalpy balance $\{FH = V_F H_F + L_F h_F$

One relatively simple method for solving an adiabatic flash problem consists of the repeated use of the procedure described above whereby an H_n is computed for an assumed T_{Fn}. The problem then reduces to finding a T_{Fn} such that the resulting H_n is equal to the specified value H, that is, it is desired to find the T_{Fn} such that $\delta(T_{Fn}) = 0$, where

$$\delta(T_{Fn}) = \delta_n = H_n - H \qquad (3\text{-}35)$$

One numerical method for solving such a problem is called interpolation regula falsi (4, 8). This method consists of the linear interpolation between the most recent pairs of points, (T_{Fn}, δ_n) and $(T_{F,n+1}, \delta_{n+1})$ by use of the following formula (see Appendix A),

$$T_{F,n+2} = \frac{T_{F,n+1} \delta_n - T_{Fn} \delta_{n+1}}{\delta_n - \delta_{n+1}} \qquad (3\text{-}36)$$

To initiate this interpolation procedure, it is necessary to evaluate δ for each of two assumed temperatures T_{F1} and T_{F2}. Then Equation (3-36) is applied to obtain T_{F3}. After δ_3 has been obtained, the new temperature T_{F4} is found by interpolation between the points (T_{F2}, δ_2) and (T_{F3}, δ_3). When $|\delta|$ has been reduced to a value less than some arbitrary, preassigned positive number, the desired solution is said to have been obtained.

It should be pointed out that the equations required to describe the adiabatic flash are of precisely the same form as those required to describe the separation process that occurs on the plate of a distillation column in the process of separating a multicomponent mixture.

The procedures described above as well as others for solving bubble point, dew point, and flash problems have been described in greater detail elsewhere (8). It is, however, informative to demonstrate briefly the use of the Newton-Raphson method (see Appendix A) for solving an adiabatic flash problem because this method has also been applied in various ways in the solution of problems involving distillation columns.

Solution of the adiabatic flash problem by use of the Newton-Raphson method

To solve a problem by using the Newton-Raphson method, it is, of course, necessary that the number of independent functions be equal to the number of independent variables. To illustrate one application of this procedure to the adiabatic flash problem, consider again the set of equations given by Equation (3-34). The first step in the application of the Newton-Raphson method is the restatement of the independent equations in functional form as follows:

$$f_1 = K_{F1}x_{F1} - y_{F1}$$

Equilibrium relationships

$$f_c = K_c x_{Fc} - y_{Fc}$$

$$f_{c+1} = \sum_{i=1}^{c} y_{Fi} - 1$$

$$f_{c+2} = \sum_{i=1}^{c} x_{Fi} - 1 \qquad (3-37)$$

$$f_{c+3} = V_F y_{F1} + L_F x_{F1} - FX_1$$

Material balances

$$f_{2c+2} = V_F y_{Fc} + L_F x_{Fc} - FX_c$$

Enthalpy balance $\{ f_{2c+3} = V_F H_F + L_F h_F - FH$

As demonstrated in Chapter 2, the application of the Newton-Raphson method to this set of equations may be represented by the following matrix equation.

$$J \Delta X = -f \qquad (3-38)$$

The Jacobian matrix J and the column vectors ΔX and f are defined as follows:

$$J = \begin{bmatrix} \dfrac{\partial f_1}{\partial y_{F1}} & \cdots & \dfrac{\partial f_1}{\partial y_{Fc}} & \dfrac{\partial f_1}{\partial x_{F1}} & \cdots & \dfrac{\partial f_1}{\partial x_{Fc}} & \dfrac{\partial f_1}{\partial V_F} & \dfrac{\partial f_1}{\partial L_F} & \dfrac{\partial f_1}{\partial T_F} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots \\ \dfrac{\partial f_{2c+3}}{\partial y_{F1}} & \cdots & \dfrac{\partial f_{2c+3}}{\partial y_{Fc}} & \dfrac{\partial f_{2c+3}}{\partial x_{F1}} & \cdots & \dfrac{\partial f_{2c+3}}{\partial x_{Fc}} & \dfrac{\partial f_{2c+3}}{\partial V_F} & \dfrac{\partial f_{2c+3}}{\partial L_F} & \dfrac{\partial f_{2c+3}}{\partial T_F} \end{bmatrix}$$

$$\Delta X = [\Delta y_{F1} \ldots \Delta y_{Fc} \, \Delta x_{F1} \ldots \Delta x_{Fc} \, \Delta V_F \, \Delta L_F \, \Delta T_F]^T \qquad (3-39)$$

$$f = [f_1 \ldots f_c f_{c+1} \ldots f_{2c} f_{2c+1} f_{2c+2} f_{2c+3}]^T$$

where each element of ΔX is equal to the new predicted value of the variable minus the assumed value; for example, $\Delta y_{F1} = y_{F1,n+1} - y_{F1,n}$. To initiate the calculational procedure, a complete set of values for the variables must be assumed; say,

$$(y_{F1,n}, \ldots, y_{Fc,n} x_{F1,n}, \ldots, x_{Fc,n}, V_{F,n}, L_{F,n}, T_{F,n})$$

The functions and all of their partial derivatives are evaluated on the basis of this set of assumed values for the variables. Then Equation (3-38) is solved for the elements of ΔX from which the values of the variables to be used for the next trial are computed as described above. [This method for solving the adiabatic flash problem was presented because it is analogous to the method first proposed by Greenstadt et al. (7) for solving problems involving distillation columns.]

In many instances it is possible to reduce the number of equations by the simultaneous elimination of some of the variables before applying the Newton-Raphson method. For example, the expressions given by Equation (3-34) may be reduced to two equations in two unknowns as demonstrated previously (8, 10). As one might expect, the reduction of the number of equations and the number of variables generally results in a set of equations which are of a more complex form than the original set. But, as the number of equations and the number of variables are reduced, it is generally easier to pick an initial set of values of the variables for which the Newton-Raphson method will converge to the desired solution. The convergence of the Newton-Raphson equations is considered in Appendix A.

Part 3. Separation of Binary Mixtures by Use of Multiple Stages

Many of the concepts of distillation may be illustrated by use of the graphical method of design proposed by McCabe and Thiele (13). In the description of this process, the following symbols are used in addition to those explained above (see Figure 3-6). The mole fraction of the most volatile component in the feed is represented by X, in the distillate by X_D, and in the bottoms by x_B. The subscript j is used as the counting integer for the number of the plates. Since the distillate is withdrawn from the accumulator ($j = 0$) and the bottoms is withdrawn from the reboiler ($j = N + 1$), the mole fractions in the distillate and bottoms have double representation, that is, $X_{Di} = x_{0i}$ (for a column having a total condenser) and $x_{Bi} = x_{N+1,i}$. When the column has a partial condenser (D is withdrawn as a vapor), $X_{Di} = y_{0i}$.

The *rectifying section* consists of the partial or total condenser and all plates down to the feed plate. The *stripping section* consists of the feed plate

and all plates below it, including the reboiler. When the total flow rates do not vary from plate to plate within each section of the column, they are denoted by V_r (vapor) and L_r (liquid) in the rectifying section and by V_s and L_s in the stripping section. The feed rate (F), distillate rate (D), bottoms rate (B), and reflux rate (L_0) are all expressed in moles per unit time.

The design method of McCabe and Thiele (13) is best described by solving the following numerical example.

ILLUSTRATIVE EXAMPLE 3-6*

Suppose it is desired to find the minimum number of perfect plates required to effect the separation $(X_D = 0.95$ and $x_B = 0.05)$ of component A from the feed mixture $X_A = X_B = 0.5$ at the following set of operating conditions: (1) The column pressure is 1 atm, and a total condenser is to be used (D is a liquid); (2) the thermal condition of the feed is such that the liquid rate L, leaving the feed plate is given by $L_s = L_r + 0.583F$; and (3) a reflux ratio $L_0/D = 0.52$ is to be employed. The equilibrium sets (x_A, y_A) are given by the equilibrium curve in Figure 3-10.

This set of specifications fixes the system, that is, the number of independent equations that describe the system is equal to the number of unknowns. Before solving this problem, the equations needed are developed. First, the equilibrium pairs (x, y) satisfying the equilibrium relationship $y = Kx$ may be read from a boiling point diagram and plotted in the form of y versus x to give the equilibrium curve (see Figure 3-10). Observe that the equilibrium pairs (x, y) are those mole fractions connected by the tie lines of the boiling point diagram (see Figure 3-8).

A component-material balance enclosing the top of the column and plate j (see Figure 3-6) is given by

$$y_{j+1} = \left(\frac{L_r}{V_r}\right)x_j + \frac{DX_D}{V_r} \qquad (3\text{-}40)$$

Similarly, for the stripping section, the component-material balance (see Figure 3-6) is given by

$$y_{j+1} = \left(\frac{L_s}{V_s}\right)x_j - \frac{Bx_B}{V_s} \qquad (3\text{-}41)$$

The component-material balance enclosing the entire column is given by

$$FX = DX_D + Bx_B \qquad (3\text{-}42)$$

The total flow rates within each section of the column are related by the following defining equation for q, namely,

$$L_s = L_r + qF \qquad (3\text{-}43)$$

By means of a total-material balance enclosing plates $f - 1$ and f, it is readily shown through the use of Equation (3-43) that

$$V_r - V_s = (1 - q)F \qquad (3\text{-}44)$$

By means of energy balances, it can be shown that q is approximately equal to the

*Taken from C. D. Holland and J. D. Lindsay, *Encyclopedia Chemical Technology,* Vol. 7, 2nd ed. (New York: John Wiley & Sons, Inc., 1965), pp. 204–48.

heat required to vaporize one mole of feed divided by the latent heat of vaporization of the feed.

Since Equations (3-40) and (3-41) are straight lines, they intersect at some point (x_i, y_i), provided, of course, they are not parallel. When the point of intersection is substituted into Equations (3-40) and (3-41), and L_r, V_r, L_s, V_s, x_B, and X_D are eliminated by use of Equations (3-42) through (3-44), the following equation for the *q-line* is obtained.

$$y_i = -\left(\frac{q}{1-q}\right)x_i + \left(\frac{1}{1-q}\right)X \qquad (3\text{-}45)$$

Solution: With the aid of the above equations, the number of plates required to effect the specified separation may be determined. To plot the operating line (Equation 3-40) for the rectifying section, the y intercept (DX_D/V_r) is computed in the following manner: Since $V_r = L_r + D$ and $L_0 = L_r$, it follows that

$$\frac{DX_D}{V_r} = \frac{X_D}{\dfrac{L_r}{D}+1} = \frac{0.95}{1.52} = 0.63$$

Since $y_i = X_D$ (for a total condenser), the point (y_1, X_D) lies on the 45° diagonal. The y intercept and the point (y_1, X_D) locate the operating line for the rectifying section as shown in Figure 3-10.

When $x_i = X$ is substituted in Equation (3-45), the result $y_i = X$ is obtained, and hence the q-line passes through the point (X, X) which in this case is the point $(0.5, 0.5)$. Since $q = 0.583$, the y intercept of the q-line [Equation (3-45)] is computed as follows:

$$\frac{X}{1-q} = \frac{0.5}{(1-0.583)} = 1.2$$

Since the operating line for the stripping section [Equation (3-41)] passes through the point $(x_B, x_B) = (0.05, 0.05)$ and the intersection of the q-line with the operating line for the rectifying section, it may be constructed simply by connecting these two points as shown in Figure 3-10.

The number of perfect plates required to effect the specified separation may be determined graphically as indicated in Figure 3-10. It is readily confirmed that the construction shown in Figure 3-10 gives the desired solution. Since $y_1 = X_D = x_0$ (for a total condenser) and since y_1 is in equilibrium with x_1, the desired value of x_1 is determined by the point of intersection of line 1 and the equilibrium curve as shown in Figure 3-10. Line 1 also represents plate 1. When x_1 is substituted into Equation (3-40), the value of y_2 is obtained. Since (x_1, y_2) lies on the operating line for the rectifying section, this point is located by passing a vertical line through (x_1, y_1). The ordinate y_2 obtained is displayed graphically in Figure 3-10. When the first opportunity to change operating lines is taken, the minimum number of total plates needed to effect the specified separation at the specified operating conditions is obtained. As seen in Figure 3-10, a total of five equilibrium stages is required, four plates plus the reboiler, when the feed enters on the third plate from the top of the column.
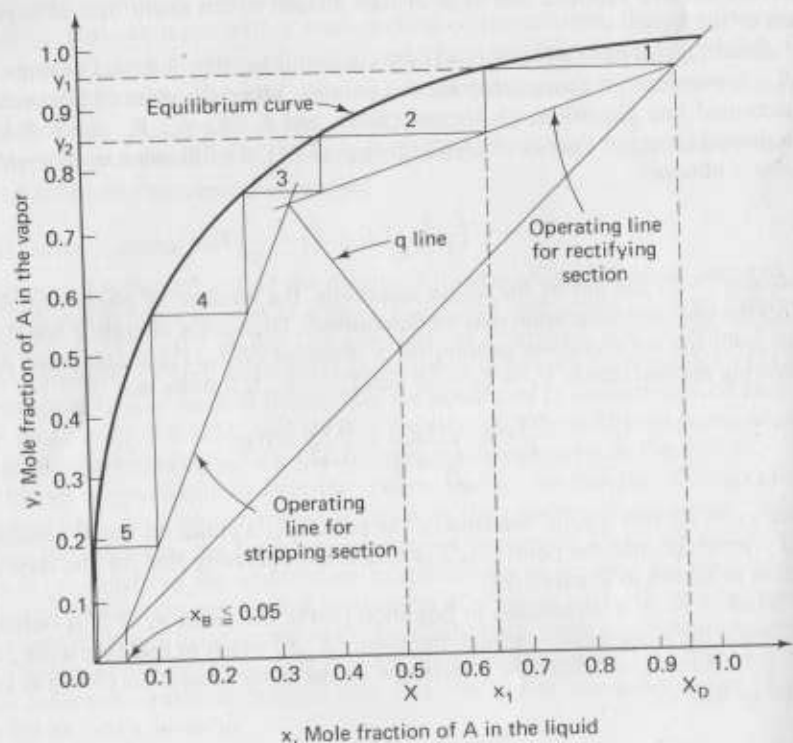
Figure 3-10. Graphical solution of Illustrative Example 3-6 by the McCabe-Thiele method. (Taken from Holland and Lindsay, *Encyclopedia Chemical Technology*, Vol. 7, 2nd ed., p. 217.)

It should be noted that if the operating line for the rectifying section is used indefinitely instead of changing to the operating line for the stripping section, the specified value of $x_B = 0.05$ can never be attained even though infinitely many plates are employed.

If the specified value of the reflux ratio (L_0/D) is decreased, the intersection of the two operating lines would be closer to the equilibrium line and the minimum number of plates required to effect the specified separation $(x_B = 0.05, X_D = 0.95)$ increases. But, as L_0/D is decreased, the condenser and reboiler duties decrease. The *minimum reflux ratio* is the smallest one that can be used to effect the specified separation. This reflux ratio requires infinitely many plates in each section as demonstrated in Figure 3-11. It should be noted that here the plates at and adjacent to the feed plate have the same composition.

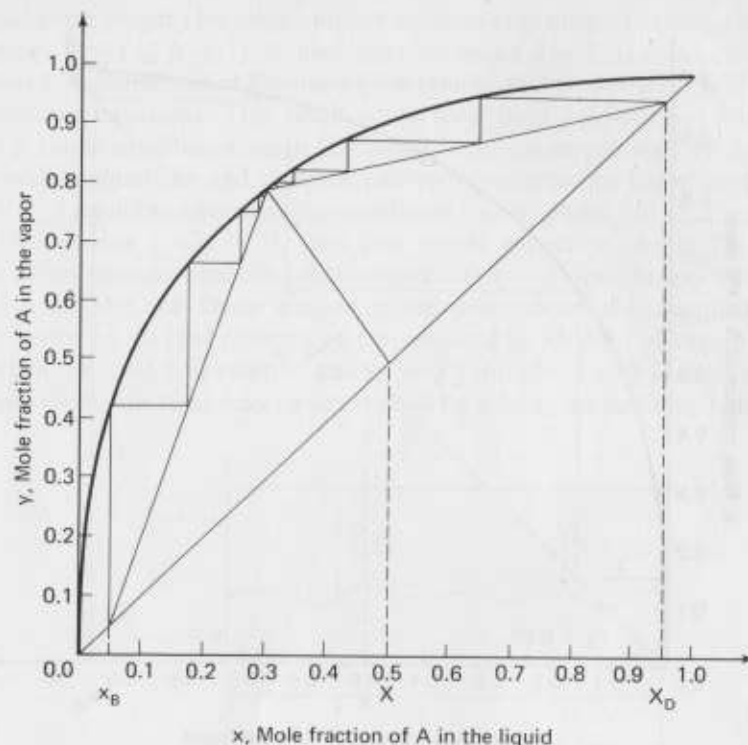At total reflux, the operating lines approach indefinitely closer to the

Figure 3-11. At the minimum reflux ratio (L_0/D), it is seen that infinitely many plates are required to effect the specified separation (X_D, x_B). (Taken from Holland and Lindsay, *Encyclopedia Chemical Technology*, p. 219.)

45° line. This gives the smallest number of plates needed to effect the separation. As pointed out by Robinson and Gilliland (17), two physical interpretations of total reflux are possible. From a laboratory or operational point of view, total reflux is attained by introducing an appropriate quantity of feed to the column and then operating so that $F = D = B = 0$. From the standpoint of design, total reflux can be thought of as a column of infinite diameter operating at infinite vapor and liquid rates, and with a feed that enters at a finite rate F and with distillate and bottoms that leave at the rates D and B, where $F = D + B$. At total reflux, two plates and the reboiler are required to effect the specified separation, as shown in Figure 3-12.

In order to demonstrate that the set of equations required to describe a distillation column in the process of separating a binary mixture is merely an extension of the sets stated previously for the boiling point diagram [Equation (3-3)], bubble point and dew point temperatures [Equation (3-12)], and the flash process [Equation (3-26)], the complete set of equations solved
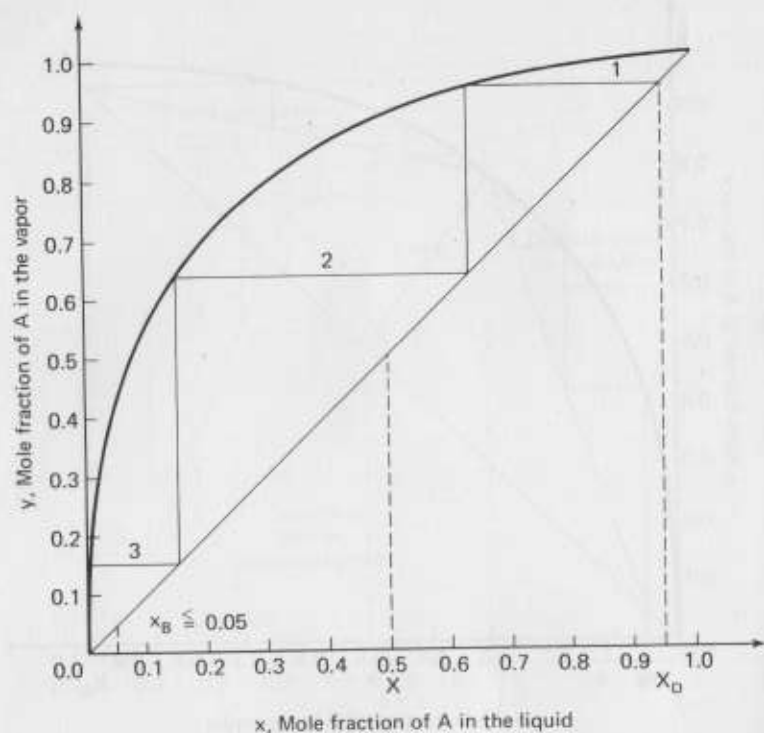
Figure 3-12. Determination of the total number of plates required to effect the specified separation at total reflux. At this reflux the minimum number of plates is required. (Taken from Holland and Lindsay, *Encyclopedia Chemical Technology*, p. 220.)

above by the McCabe-Thiele method are summarized as follows for purposes of comparison.

Equilibrium relationships
$$\begin{cases} y_{ji} = K_{ji}x_{ji} & \begin{pmatrix} i=1,2 \\ 0 \le j \le N+1 \end{pmatrix} \\ \sum_{i=1}^{2} y_{ji} = 1 & (0 \le j \le N+1) \\ \sum_{i=1}^{2} x_{ji} = 1 & (0 \le j \le N+1) \end{cases}$$

Material balances
$$\begin{cases} V_r y_{j+1,i} = L_r x_{ji} + DX_{Di} & \begin{pmatrix} i=1,2 \\ 0 \le j \le f-1 \end{pmatrix} \\ V_s y_{j+1,i} = L_s x_{ji} - Bx_{Bi} & \begin{pmatrix} i=1,2 \\ f \le j \le N \end{pmatrix} \\ FX_i = DX_{Di} + Bx_{Bi} & (i=1,2) \end{cases}$$

(3-46)

The counting integer j for stage number takes on only integral values, and the notation $(0 \le j \le N+1)$ is used here to mean $j = 0, 1, 2, \ldots, N-1, N, N+1$. Examination of Equation (3-46) shows that it consists of $6(N+2)$ independent equations. This result could have been predicted as follows: Since a single equilibrium stage [Equation (3-26)] is represented by $2c+2$ independent equations and since the column represented by Equation (3-46) has $N+2$ equilibrium stages [the condenser $j=0$, plates $j=1, 2, \ldots, N$, and the reboiler $j=N+1$], then one would expect to obtain $(2c+2)(N+2)$ independent equations that reduce to $6(N+2)$ for a binary mixture. Also, in the McCabe-Thiele method as presented above, it is assumed that the behavior on the feed plate may be represented by Model 1 of Figure 3-13.

When the total flow rates V_j and L_j vary throughout each section of the column, these flow rates may be determined by solving the enthalpy balances
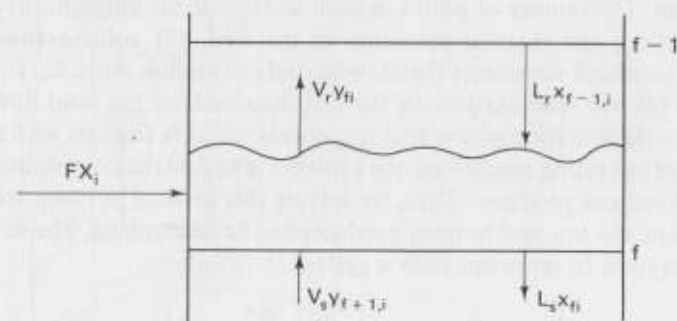
Model 1.   Assumed in the McCabe-Thiele method
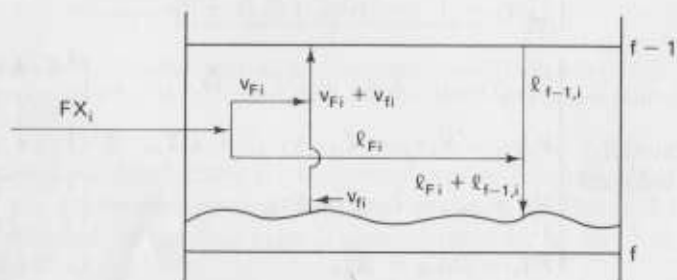
Model 2.   Behavior assumed on the feed plate.

Figure 3-13. Models for the behavior of the feed plate. (Taken from Holland, *Introduction to the Fundamentals of Distillation*, Proceedings of the Fourth Annual Education Symposium of the Instrument Society of America, April 5-7, 1972, Wilmington, Delaware.)

simultaneously with the above set of equations. For binary mixtures, the desired solution may be found by using either graphical methods (15, 18) or the numerical methods proposed below for multicomponent systems.

Part 4. Separation of Multicomponent Mixtures by Use of Conventional Distillation Columns with Multiple Stages

A conventional distillation column is defined as one that has one feed and two product streams, the distillate D and the bottoms B. This column has the same configuration as the one shown in Figure 3-14. First consider the case in which the following specifications are made for a column at steady-state operation: (1) number of plates in each section of the column, (2) quantity, composition, and thermal condition of the feed, (3) column pressure, (4) type of overhead condenser (total or partial), (5) reflux ratio, L_0/D, or V_1 or L_0, and (6) one specification on the distillate such as the total flow rate D. Steady-state operation means that no process variable changes with time. For this set of operating conditions, the problem is to find the compositions of the top and bottom products. Thus, by solving this kind of problem the characteristics of the top and bottom products can be determined. The set of equations required to represent such a system is as follows:

Equilibrium relationships
$$\begin{cases} y_{ji} = K_{ji}x_{ji} & \left(\begin{matrix}1 \le i \le c \\ 0 \le j \le N+1\end{matrix}\right) \\ \sum_{i=1}^{c} y_{ji} = 1 & (0 \le j \le N+1) \\ \sum_{i=1}^{c} x_{ji} = 1 & (0 \le j \le N+1) \end{cases}$$

Material balances
$$\begin{cases} V_{j+1}y_{j+1,i} = L_j x_{ji} + DX_{Di} & \left(\begin{matrix}1 \le i \le c \\ 0 \le j \le f-2\end{matrix}\right) \\ V_f y_{fi} + V_F y_{Fi} = L_{f-1}x_{f-1,i} + DX_{Di} & (1 \le i \le c) \\ V_{j+1}y_{j+1,i} = L_j x_{ji} - Bx_{Bi} & \left(\begin{matrix}1 \le i \le c \\ f \le j \le N\end{matrix}\right) \\ FX_i = DX_{Di} + Bx_{Bi} & (1 \le i \le c) \end{cases}$$

Enthalpy balances
$$\begin{cases} V_{j+1}H_{j+1} = L_j h_j + DH_D + Q_c & (0 \le j \le f-2) \\ V_f H_f + V_F H_F = L_{f-1}h_{f-1} + DH_D + Q_c \\ V_{j+1}H_{j+1} = L_j h_j - Bh_B + Q_R & (f \le j \le N) \\ FH = Bh_B + DH_D + Q_c - Q_R \end{cases}$$

$$(3\text{-}47)$$

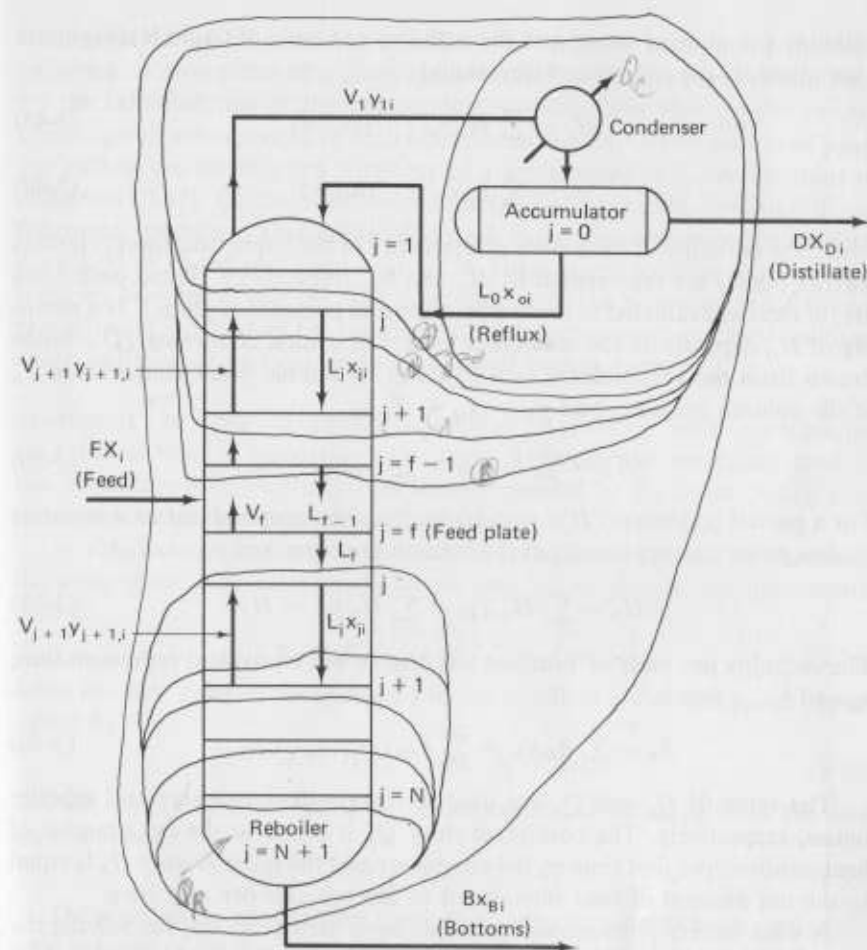Inspection of this set of equations shows that the equations are a logical

Figure 3-14. Representation of the component-material balances given by Equation (3-47). (Taken from Holland, *Introduction to the Fundamentals of Distillation.*)

extension of those stated above for the binary system. A schematic representation of the component-material balances is shown in Figure 3-14. The behavior assumed on the feed plate is demonstrated by Model 2 of Figure 3-13.

The above enthalpy balances may be represented by the same enclosures shown in Figure 3-14. As in the case of the material balances for any one component, the number of independent energy balances is equal to the number of stages ($j = 0, 1, 2, \ldots, N, N+1$). In this case the total number of independent equations is equal to $(2c+3)(N+2)$, as might be expected from the fact that an adiabatic flash is represented by $2c+3$ equations. When it is supposed that the vapor and liquid streams form ideal solutions, the

enthalpy per mole of vapor and the enthalpy per mole of liquid leaving plate j are given by the following expressions:

$$H_j = \sum_{i=1}^{c} H_{ji} y_{ji} \quad \text{(vapor)} \tag{3-48}$$

$$h_j = \sum_{i=1}^{c} h_{ji} x_{ji} \quad \text{(liquid)} \tag{3-49}$$

where the enthalpy of each pure component i in the vapor and liquid streams leaving plate j are represented by H_{ji} and h_{ji}, respectively. These enthalpies are, of course, evaluated at the temperature and pressure of plate j. The meaning of H_D depends on the condenser used. For a total condenser (D is withdrawn from the accumulator as a liquid at its bubble point temperature T_0 at the column pressure, and $y_{1i} = x_{0i} = X_{Di}$),

$$H_D = \sum_{i=1}^{c} h_{0i} X_{Di} = \sum_{i=1}^{c} h_{0i} x_{0i} = h_0 \tag{3-50}$$

For a partial condenser (D is withdrawn from the accumulator as a vapor at its dew point temperature T_0 at the column pressure, and $y_{0i} = X_{Di}$),

$$H_D = \sum_{i=1}^{c} H_{0i} X_{Di} = \sum_{i=1}^{c} H_{0i} y_{0i} = H_0 \tag{3-51}$$

The enthalpy per mole of bottoms has double but equivalent representation, h_B and h_{N+1}, that is,

$$h_B = \sum_{i=1}^{c} h_{Bi} x_{Bi} = \sum_{i=1}^{c} h_{N+1,i} x_{N+1,i} = h_{N+1} \tag{3-52}$$

The symbols Q_c and Q_R are used to denote the condenser and reboiler duties, respectively. The condenser duty Q_c is equal to the net amount of heat removed per unit time by the condenser and the reboiler duty Q_R is equal to the net amount of heat introduced to the reboiler per unit time.

A wide variety of numerical methods have been proposed for solving the set of equations represented by Equation (3-47). The calculational procedure described below consists of an iterative technique which employs the θ method of convergence (12), the tridiagonal formulation of the component-material balances and equilibrium relationships, the K_b method for the determination of temperatures, and the constant-composition method for the determination of the total flow rates. Following Thiele and Geddes (21), the temperatures are taken to be the independent variables. This choice of independent variables has come to be known as the Thiele and Geddes method.

The Thiele and Geddes method plus the θ method, K_b method, and constant-composition method

Merely the statement that the Thiele and Geddes choice of independent variables (or the Thiele and Geddes method) has been employed to solve a problem does not sufficiently describe the calculational procedure. In the

solution of a set of nonlinear equations by iterative techniques, the convergence or divergence of a given calculational procedure depends not only on the initial choice of the independent variables but also on the precise ordering and arrangement of each equation of the set. Over a period of years the author has investigated a variety of arrangements and combinations of Equation (3-47). Of these the most successful combination consisted of the following procedure that contains certain improvements over the original θ method as stated by Lyster et al. (12). These improvements were summarized by Nartker et al. (14). The development of the proposed calculational procedure is initiated by the restatement of the component-material balances and equilibrium relationships in tridiagonal matrix form.

STATEMENT OF THE COMPONENT-MATERIAL BALANCES AND EQUILIBRIUM RELATIONSHIPS AS A TRIDIAGONAL MATRIX. Although the equations used in this procedure differ in form from those presented by Equation (3-47), they are an equivalent independent set.

In the case of the component-material balances, a new set of variables, the component flow rates in the vapor and liquid phases, are introduced, namely,

$$v_{ji} = V_j y_{ji} \quad \text{and} \quad l_{ji} = L_j x_{ji} \tag{3-53}$$

Also, the flow rates of component i in the distillate and bottoms are represented by

$$d_i = DX_{Di} \quad \text{and} \quad b_i = Bx_{Bi} \tag{3-54}$$

and the flow rates of component i in the vapor and liquid parts of the feed are represented by

$$v_{Fi} = V_F y_{Fi} \quad \text{and} \quad l_{Fi} = L_F x_{Fi} \tag{3-55}$$

The equilibrium relationship $y_{ji} = K_{ji} x_{ji}$ may be restated in an equivalent form in terms of the component flow rates v_{ji} and l_{ji} as follows. First, observe that the expression $y_{ji} = K_{ji} x_{ji}$ may be restated in the form:

$$V_j y_{ji} = \left(\frac{V_j K_{ji}}{L_j}\right) L_j x_{ji} \tag{3-56}$$

and from Equation (3-53), it follows that

$$v_{ji} = S_{ji} l_{ji} \quad \text{and} \quad l_{ji} = A_{ji} v_{ji} \tag{3-57}$$

where

$$A_{ji} = \frac{1}{S_{ji}} = \frac{L_j}{K_{ji} V_j}$$

Instead of enclosing the end of the column and the respective plates in each section of the column as demonstrated by Equation (3-47) and Figure 3-14, an equivalent set of component-material balances is obtained by enclosing each plate ($j = 0, 1, 2, \ldots, N, N+1$) by a component-material balance as demonstrated in Figure 3-15. The corresponding set of material
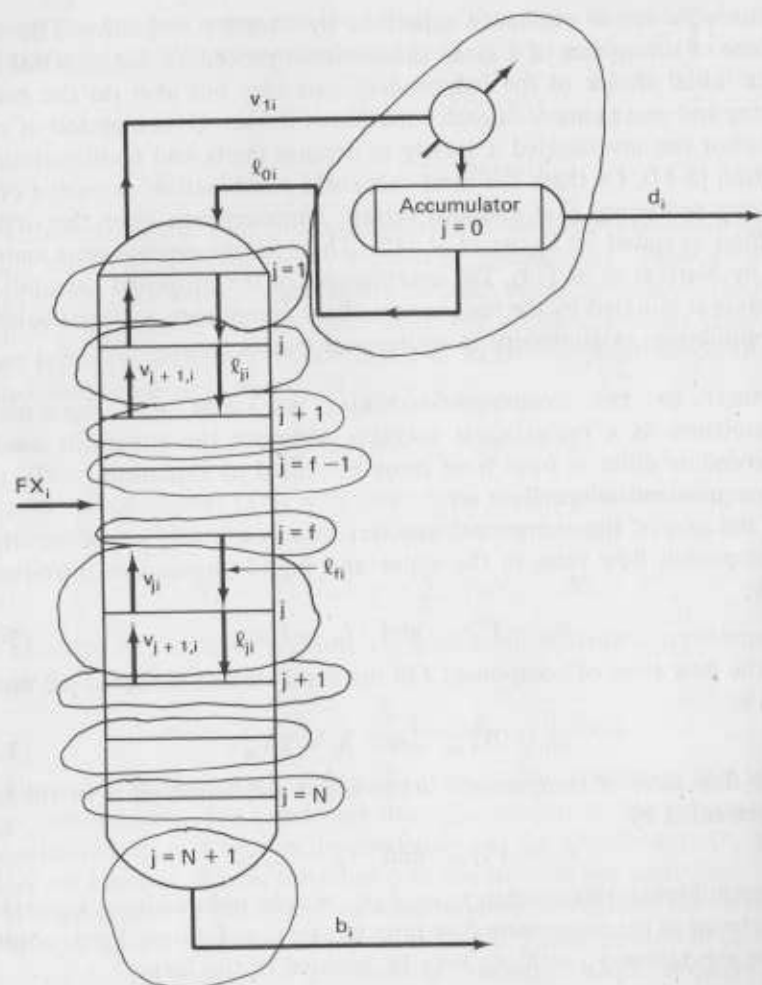
Figure 3-15. Representation of the component-material balances given by Equation (3-58). (Taken from Holland, *An Introduction to the Fundamentals of Distillation.*)

balances for each component i are as follows:

$$
\text{Material balances}
\begin{cases}
-l_{0i} - d_i + v_{1i} = 0 \\
l_{j-1,i} - v_{ji} - l_{ji} + v_{j+1,i} = 0 & (1 \leq j \leq f-2) \\
l_{f-2,i} - v_{f-1,i} - l_{f-1,i} + v_{fi} = -v_{Fi} \\
l_{f-1,i} - v_{fi} - l_{fi} + v_{f+1,i} = -l_{Fi} \\
l_{j-1,i} - v_{ji} - l_{ji} + v_{j+1,i} = 0 & (f+1 \leq j \leq N) \\
l_{Ni} - v_{N+1,i} - b_i = 0
\end{cases}
\tag{3-58}
$$

Except for the first expression of Equation (3-58), the l_{ji}'s may be eliminated from Equation (3-58) by use of the equilibrium relationship, Equation (3-57). For the case of a total condenser, l_{0i} and d_i have the same composition, and thus,

$$
l_{0i} = \left(\frac{L_0}{D}\right) d_i \tag{3-59}
$$

For a partial condenser, $y_{0i} = X_{Di}$, and hence

$$
DX_{Di} = \left(\frac{DK_{0i}}{L_0}\right) L_0 x_{0i} \tag{3-60}
$$

Thus,

$$
l_{0i} = A_{0i} d_i \tag{3-61}
$$

where

$$
A_{0i} = \frac{L_0}{K_{0i} D}
$$

The expression given by Equation (3-61) may be used to represent both a partial condenser and a total condenser, provided A_{0i} is set equal to L_0/D for a total condenser.* Also, the form of $A_{N+1,i}$ differs slightly from that for A_{ji} because of the double representation of the reboiler by the subscripts "$N+1$" and "B," that is,

$$
V_{N+1}y_{N+1,i} = \left(\frac{V_{N+1}K_{N+1,i}}{B}\right) Bx_{Bi} \quad \text{or} \quad b_i = A_{N+1,i}v_{N+1,i} \tag{3-62}
$$

where

$$
A_{N+1,i} = \frac{B}{K_{N+1,i}V_{N+1}}
$$

When the l_{ji}'s and b_i are eliminated from Equation (3-58) by use of Equations (3-57), (3-59), (3-61), and (3-62), the following result is obtained.

$$
\begin{aligned}
&\text{Material} \\
&\text{balances} \\
&\text{and} \\
&\text{equilibrium} \\
&\text{relationships}
\end{aligned}
\begin{cases}
-(A_{0i} + 1)d_i + v_{1i} = 0 \\
A_{j-1,i}v_{j-1,i} - (A_{ji} + 1)v_{ji} + v_{j+1,i} = 0 & (1 \leq j \leq f-2) \\
A_{f-2,i}v_{f-2,i} - (A_{f-1,i} + 1)v_{f-1,i} + v_{fi} = -v_{Fi} \\
A_{f-1,i}v_{f-1,i} - (A_{fi} + 1)v_{fi} + v_{f+1,i} = -l_{Fi} \\
A_{j-1,i}v_{j-1,i} - (A_{ji} + 1)v_{ji} + v_{j+1,i} = 0 & (f+1 \leq j \leq N) \\
A_{Ni}v_{Ni} - (A_{N+1,i} + 1)v_{N+1,i} = 0
\end{cases}
$$

$$\tag{3-63}$$

*This symbolic operation of convenience should not be taken to mean that $K_{0i} = 1$ for a total condenser, for the boiling point temperature T_0 of the distillate leaving a total condenser is computed by use of the equation:

$$
\sum_{i=1}^{c} y_{0i} = 1 = \sum_{i=1}^{c} K_{0i} X_{Di}
$$

This set of equations may be stated in the matrix form

$$A_i v_i = -\mathcal{L}_i \qquad (3\text{-}64)$$

where

$$A_i = \begin{bmatrix} -\rho_{0i} & 1 & 0 & 0 & \cdots\cdots\cdots\cdots\cdots\cdots & 0 \\ A_{0i} & -\rho_{1i} & 1 & 0 & \cdots\cdots\cdots\cdots\cdots\cdots & 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ 0 \cdots 0 & A_{f-2,i} & -\rho_{f-1,i} & 1 & 0 & 0 \cdots 0 \\ 0 \cdots 0 & 0 & A_{f-1,i} & -\rho_{fi} & 1 & 0 \cdots 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ 0 & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & 0 & A_{N-1,i} & -\rho_{Ni} & 1 \\ 0 & \cdots\cdots\cdots\cdots\cdots\cdots\cdots & 0 & 0 & A_{Ni} & -\rho_{N+1,i} \end{bmatrix}$$

$$v_i = [d_i v_{1i} v_{2i} \ldots v_{f-1,i} v_{fi} \ldots v_{Ni} v_{N+1,i}]^T$$

$$\mathcal{L}_i = [0\ 0\ 0 \ldots v_{Fi} l_{Fi} \ldots 0\ 0]^T$$

$$\rho_{ji} = A_{ji} + 1$$

The remainder of the development of the calculational procedure is ordered in the same sequence in which the calculations are carried out. The calculational procedure is initiated by the assumption of a set of temperatures $\{T_j\}$ and a set of vapor rates $\{V_j\}$ from which the corresponding set of liquid rates $\{L_j\}$ is found by using the total-material balances enumerated below. This particular choice of independent variables was first proposed by Thiele and Geddes (21). On the basis of the assumed temperatures and total flow rates, the absorption factors $\{A_{ji}\}$ appearing in Equation (3-64) may be evaluated for component i on each plate j. Since matrix A_i in Equation (3-64) is of tridiagonal form, this matrix equation may be solved for the calculated values of the vapor rates for component i [denoted by $(v_{ji})_{ca}$] by use of the Thomas algorithm (4, 8) that follows. Consider the following set of linear equations in the variables $x_0, x_1, \ldots, x_N, x_{N+1}$ whose coefficients form a tridiagonal matrix.

$$B_0 x_0 + C_0 x_1 = D_0$$
$$A_1 x_0 + B_1 x_1 + C_1 x_2 = D_1$$
$$A_2 x_1 + B_2 x_2 + C_2 x_3 = D_2$$
$$\cdots$$
$$A_N x_{N-1} + B_N x_N + C_N x_{N+1} = D_N$$
$$A_{N+1} x_N + B_{N+1} x_{N+1} = D_{N+1}$$

The following recurrence formulas are applied in the order stated:

$$f_0 = \frac{C_0}{B_0}, \quad g_0 = \frac{D_0}{B_0}$$

$$f_k = \frac{C_k}{B_k - A_k f_{k-1}} \qquad (k = 1, 2, \ldots, N)$$

$$g_k = \frac{D_k - A_k g_{k-1}}{B_k - A_k f_{k-1}} \qquad (k = 1, 2, \ldots, N+1)$$

After the f's and g's have been computed, the values of $x_{N+1}, x_N, \ldots, x_1, x_0$ are computed as follows:

$$v_{N+1} = g_{N+1}$$

$$x_k = g_k - f_k x_{k+1} \qquad (k = N, N-1, \ldots, 2, 1, 0)$$

The development of the recurrence formulas is outlined in Problem 3-14. As pointed out by Boston and Sullivan (2), the above recurrence formulas are subject to round-off error for columns which have both a large number of plates and components whose respective absorption factors are less than unity in one section of the column and greater than unity in another section. The modified version of the above recurrence formulas suggested by Boston and Sullivan (2) was shown to reduce the round-off errors to insignificant levels.

After these recurrence formulas have been applied for each component i and the complete set of vapor rates $\{(v_{ji})_{ca}\}$ has been found, the corresponding set of liquid rates $\{(l_{ji})_{ca}\}$ is then found by use of Equation (3-57). These sets of calculated flow rates are used in conjunction with the θ method of convergence and the K_b method in the determination of an improved set of temperatures.

FORMULATION OF THE θ METHOD OF CONVERGENCE. In this application of the θ method of convergence, it is used to weight the mole fractions that are employed in the K_b method for computing a new temperature profile. The corrected set of product rates is used as weight factors in the calculation of improved sets of mole fractions. The corrected terminal rates are selected so that they are both in overall component-material balance and in agreement with the specified value of D, that is,

$$FX_i = (d_i)_{ca} + (b_i)_{ca} \qquad (3\text{-}65)$$

and

$$\sum_{i=1}^{c} (d_i)_{co} = D \qquad (3\text{-}66)$$

These two conditions may be satisfied simultaneously by suitably choosing the multiplier θ, which is defined by

$$\left(\frac{b_i}{d_i}\right)_{co} = \theta\left(\frac{b_i}{d_i}\right)_{ca} \qquad (3\text{-}67)$$

(The subscripts "co" and "ca" are used throughout this discussion to distin-

guish between the corrected and calculated values of a variable, respectively.) Elimination of $(b_i/d_i)_{co}$ from Equation (3-65) and (3-67) yields the formula for $(d_i)_{co}$, namely,

$$(d_i)_{co} = \frac{FX_i}{1 + \theta\left(\frac{b_i}{d_i}\right)_{ca}} \tag{3-68}$$

Since the specified values of $(d_i)_{co}$ are to have a sum equal to the specified value of D, the desired value of θ is that $\theta > 0$ that makes $g(\theta) = 0$, where

$$g(\theta) = \sum_{i=1}^{c} (d_i)_{co} - D \tag{3-69}$$

A graph of this function is shown in Figure 3-16.

In the determination of θ by Newton's method, the following formula for the first derivative, $g'(\theta)$, is needed.

$$g'(\theta) = \sum_{i=1}^{c} \frac{d(d_i)_{co}}{d\theta} = -\sum_{i=1}^{c} \frac{\left(\frac{b_i}{d_i}\right)_{ca} FX_i}{\left[1 + \theta\left(\frac{b_i}{d_i}\right)_{ca}\right]^2} \tag{3-70}$$
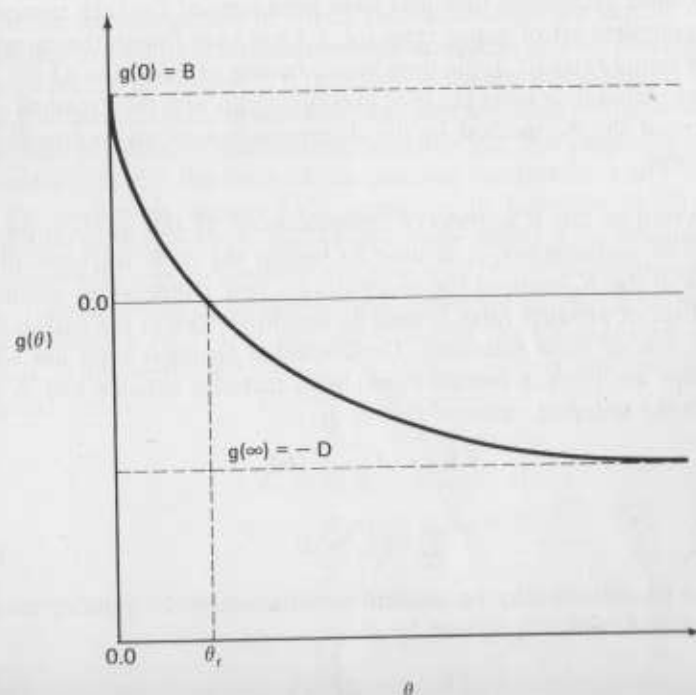

Figure 3-16. Geometrical representation of the function $g(\theta)$ in the neighborhood of the positive root θ_r. [Taken from Holland, *Multicomponent Distillation* (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1963), p. 84.]

After the desired value of θ has been obtained, $(b_i)_{co}$ may be computed by using Equation (3-67). [Note that Newton's method converges to the positive root of $g(\theta)$, provided that $\theta = 0$ is taken to be the first trial value (see Problem 3-15)].

The corrected mole fractions for the liquid and vapor phases are computed as follows:

$$x_{ji} = \frac{\left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{co}}{\sum_{i=1}^{c}\left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{co}} \tag{3-71}$$

$$y_{ji} = \frac{\left(\frac{v_{ji}}{d_i}\right)_{ca} (d_i)_{co}}{\sum_{i=1}^{c}\left(\frac{v_{ji}}{d_i}\right)_{ca} (d_i)_{co}} \tag{3-72}$$

These expressions are consistent with the definition of θ given by Equation (3-67); see Problem 3-21.

DETERMINATION OF AN IMPROVED SET OF TEMPERATURES BY USE OF THE K_b METHOD. On the basis of the mole fractions given by Equations (3-71) and (3-72) and the last temperature profile (the one assumed to make the nth trial), the new temperature profile is found using the K_b method (8, 14) in the following manner: For any plate j, Equations (3-21) or (3-22) may be applied as follows:

$$K_{jb}|_{T_{j,n+1}} = \frac{1}{\sum_{i=1}^{c} \alpha_{ji}|_{T_{jn}} x_{ji}} \quad \text{or} \quad K_{jb}|_{T_{j,n+1}} = \sum_{i=1}^{c} \frac{y_{ji}}{\alpha_{ji}|_{T_{jn}}} \tag{3-73}$$

where

$\alpha_{ji} = K_{ji}/K_{jb}$, the relative volatility of component i at the temperature of plate j. The rate of convergence of the entire calculational procedure is dependent upon the precise choice of K_{jb}.

It can be shown that the x_{ji}'s and y_{ji}'s defined by Equations (3-71) and (3-72), respectively, form a consistent set in that they give the same value of K_{jb} (8) (see also Problem 3-16). Component b represents a hypothetical base component whose K value is given by

$$\log_e K_{jb} = \frac{a}{T_j} + b \tag{3-74}$$

where the constants a and b are evaluated on the basis of the values of K at the upper and lower limits of the curve fits of the mid-boiling component of the mixture or one just lighter. Thus, after K_{jb} has been computed by use of Equation (3-73), the temperature $T_{j,n+1}$ to be assumed for the next trial is calculated directly by use of Equation (3-74) or an improved variation of it (3).

The corrected compositions and the new temperatures are used in the enthalpy balances to determine the total flow rates to be used for the next trial through the column.

DETERMINATION OF AN IMPROVED SET OF TOTAL FLOW RATES BY USE OF THE CONSTANT-COMPOSITION METHOD. In the constant-composition method (8), one total flow rate (V_j or L_j) is eliminated from each of the enthalpy balances given by Equation (3-47) by use of one set of the component-material balances given by Equation (3-47). To illustrate the development of these equations, consider the enthalpy balance enclosing any plate j of the rectifying section, namely,

$$V_{j+1}H_{j+1} = L_j h_j + DH_D + Q_c \qquad (1 \leq j \leq f-2) \qquad (3-75)$$

The total flow rate V_{j+1} is eliminated from Equation (3-75) by use of component-material balance enclosing plate j

$$v_{j+1,i} = l_{ji} + d_i \qquad (1 \leq j \leq f-2)$$

as follows:

$$V_{j+1}H_{j+1} = \sum_{i=1}^{c} H_{j+1,i} v_{j+1,i} = \sum_{i=1}^{c} H_{j+1,i}(l_{ji} + d_i)$$

$$= L_j \sum_{i=1}^{c} H_{j+1,i} x_{ji} + D \sum_{i=1}^{c} H_{j+1,i} X_{Di}$$

$$= L_j H(x_j)_{j+1} + DH(X_D)_{j+1} \qquad (3-76)$$

where

$$H(x_j)_{j+1} = \sum_{i=1}^{c} H_{j+1,i} x_{ji}; \quad H(X_D)_{j+1} = \sum_{i=1}^{c} H_{j+1,i} X_{Di}$$

Elimination of $V_{j+1}H_{j+1}$ from Equations (3-75) and (3-76) yields

$$L_j = \frac{D[H_D - H(X_D)_{j+1}] + Q_c}{[H(x_j)_{j+1} - h_j]} \qquad (1 \leq j \leq f-2) \qquad (3-77)$$

Similarly,

$$L_{f-1} = \frac{D[H_D - H(X_D)_f] + V_F[H(y_F)_f - H_F] + Q_c}{[H(x_{f-1})_f - h_{f-1}]} \qquad (3-78)$$

and

$$Q_c = L_0[H(x_0)_1 - h_0] + D[H(X_D)_1 - H_D] \qquad (3-79)$$

where the enthalpy expressions appearing in these equations are defined in a manner analogous to those stated below Equation (3-76).

The flow rates in the stripping section may be determined by using enthalpy balances that enclose either the top or the bottom of the column. When the reboiler is enclosed, the following formula for the computation of the vapor rates is developed in a manner analogous to that demonstrated above:

$$V_{j+1} = \frac{B[h(x_B)_j - h_j] + Q_R}{[H_{j+1} - h(y_{j+1})_j]} \qquad (f \leq j \leq N) \qquad (3-80)$$

where

$$h(x_B)_j = \sum_{i=1}^{c} h_{ji} x_{Bi}; \quad h(y_{j+1})_j = \sum_{i=1}^{c} h_{ji} y_{j+1,i}$$

The reboiler duty Q_R is found by use of the overall enthalpy balance [the last expression given by Equation (3-47)]. When the vapor and liquid phases do not form ideal solutions, the pure component enthalpies h_{ji} and H_{ji} in the above expressions should be replaced by the corresponding partial molar enthalpies. Formulas for the calculation of suitable values for the partial molar enthalpies are developed in Appendix D.

The total flow rates of the vapor and liquid streams are related by the following total-material balances, which are readily obtained by use of the enclosures shown in Figure 3-14.

$$V_{j+1} = L_j + D \qquad (0 \leq j \leq f-2)$$
$$V_f + V_F = L_{f-1} + D$$
$$L_j = V_{j+1} + B \qquad (f \leq j \leq N) \qquad (3-81)$$
$$F = D + B$$

After the L_j's for the rectifying section and the V_j's for the stripping section have been determined by use of the enthalpy balances, the remaining total flow rates are found by use of Equation (3-81). These most recent sets of values of the variables $\{T_{j,n+1}\}$, $\{V_{j,n+1}\}$, and $\{L_{j,n+1}\}$ are used to make the next trial through the column. The procedure described is repeated until values of the desired accuracy have been obtained. A summary of the steps of the proposed calculational procedure follow:

1. Assume a set of temperatures $\{T_j\}$ and a set of vapor rates $\{V_j\}$. [The set of liquid rates corresponding to the set of assumed vapor rates are found by use of the total-material balances as in Equation (3-81).]
2. On the basis of the temperatures and flow rates assumed in Step 1, compute the component-flow rates by use of Equation (3-64) for each component i.
3. Find the $\theta > 0$ that makes $g(\theta) = 0$ [see Equations (3-68) through (3-70)]. [Newton's method (8) always converges to the desired θ, provided that the first assumed value of θ is taken to be equal to zero.]
4. Use Equation (3-71) to compute the set of corrected x_{ji}'s for each component i and plate j.
5. Use the results of Step 4 to compute the K_{jb} for each j by use of the first expression of Equation (3-73). Use the K_{jb}'s so obtained to compute a new set of temperatures $\{T_{j,n+1}\}$ by use of Equation (3-74).
6. Use the results of Steps 4 and 5 to compute new sets of total flow rates, $\{V_{j,n+1}\}$ and $\{L_{j,n+1}\}$, by use of Equations (3-77) through (3-81).
7. If θ, the T_j's and V_j's are within the prescribed tolerances, convergence

has been achieved; otherwise, repeat Steps 2 through 6 on the basis of the most recent set of T_j's and V_j's.

The solution of the component-material balances and equilibrium relationships by using the above recurrence formulas is demonstrated by the following numerical example.

ILLUSTRATIVE EXAMPLE 3-7

On the basis of the initial set of temperatures ($T_0 = T_1 = T_2 = T_3 = T_4 = 100°F$) and the total flow rates displayed in Figure 3-17, solve Equation (3-64) for the component flow rates by use of the above recurrence formulas for tridiagonal matrices.
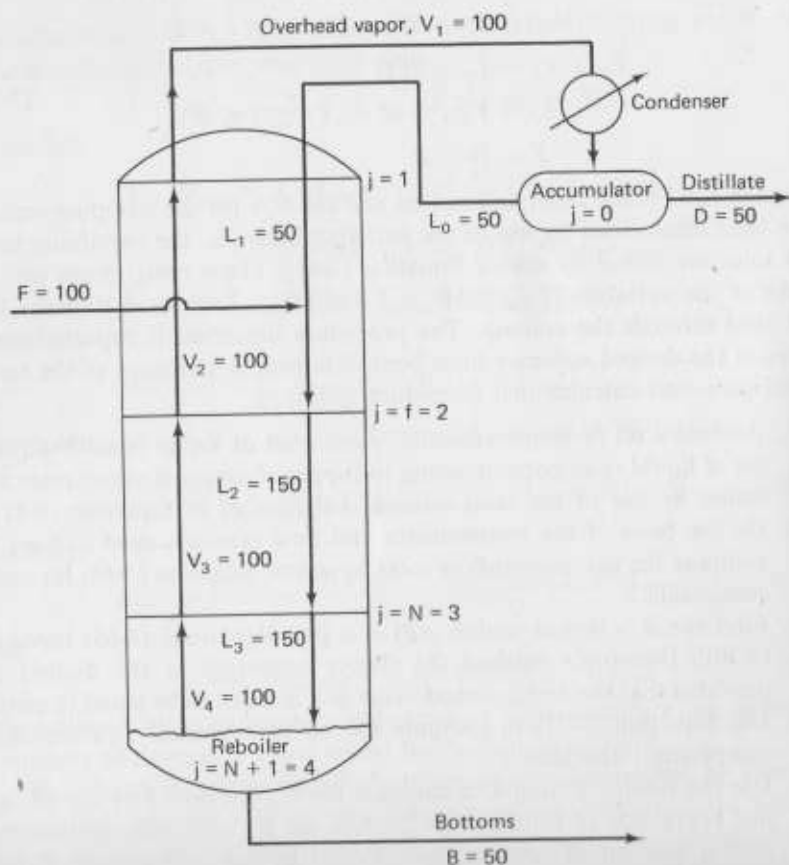

Figure 3-17. Flow diagram for Illustrative Example 3-7. (Taken from Holland, *Multicomponent Distillation*, p. 55.)

Labels in figure:
Overhead vapor, $V_1 = 100$
Condenser
$j = 1$
Accumulator $j = 0$
$L_0 = 50$
Distillate
$D = 50$
$L_1 = 50$
$F = 100$
$V_2 = 100$
$j = f = 2$
$L_2 = 150$
$V_3 = 100$
$j = N = 3$
$L_3 = 150$
$V_4 = 100$
Reboiler $j = N + 1 = 4$
Bottoms
$B = 50$

Given:

Component No.	FX_i	K_i	SPECIFICATIONS
1	33.3	$0.01T/P*$	Total condenser, $P = 1$ atm, boiling point
2	33.3	$0.027T/P$	liquid feed ($l_{Fi} = FX_i$), $N = 3$, $f = 2$,
3	33.4	$0.03T/P$	$F = 100$ moles/hr, $D = L_0 = L_1 = 50$
			moles/hr, $V_1 = V_2 = V_3 = V_4 = 100$
			moles/hr, $L_2 = L_3 = 150$ moles/hr.

*T is in °F and P is in atm.

Solution: Correspondence of the symbols in the recurrence formulas and the elements of A_i and $\mathscr{f}_i$ for the above example is as follows:

$$B_0 = -(A_{0i} + 1), \quad C_0 = 1, \quad D_0 = 0, \quad A_1 = A_{0i}$$
$$B_1 = -(A_{1i} + 1), \quad C_1 = 1, \quad D_1 = 0, \quad A_2 = A_{1i}$$
$$B_2 = -(A_{2i} + 1), \quad C_2 = 1, \quad D_2 = -FX_i, \quad A_3 = A_{2i}$$
$$B_3 = -(A_{3i} + 1), \quad C_3 = 1, \quad D_3 = 0, \quad A_4 = A_{3i}$$
$$B_4 = -(A_{4i} + 1), \quad D_4 = 0$$

Calculation of the A_{ji}'s is as follows:

Component No.	$A_{0i} = \dfrac{L_0}{D}$	K_{1i}, K_{2i}, K_{3i} K_{4i} @ 100°F and 1 atm	$A_{1i} = \dfrac{L_1}{K_{1i}V_1} = \dfrac{1}{2K_{1i}}$	$A_{2i} = \dfrac{L_2}{K_{2i}V_2} = \dfrac{3}{2K_{2i}}$
1	1	1	$\frac{1}{2}$	$\frac{3}{2}$
2	1	2	$\frac{1}{4}$	$\frac{3}{4}$
3	1	3	$\frac{1}{6}$	$\frac{1}{2}$

Component No.	$A_{3i} = \dfrac{L_3}{K_{3i}V_3} = \dfrac{3}{2K_{3i}}$	$A_{4i} = \dfrac{B}{K_{4i}V_4} = \dfrac{1}{2K_{4i}}$
1	$\frac{3}{2}$	$\frac{1}{2}$
2	$\frac{3}{4}$	$\frac{1}{4}$
3	$\frac{1}{2}$	$\frac{1}{6}$

Application of the recurrence formulas for tridiagonal matrix equations is as follows:

Comp. No.	B_0	C_0	D_0	A_1	B_1	C_1	D_1	A_2	B_2	C_2	D_2
1	-2	1	0	1	-1.50000	1	0	0.50000	-2.5	1	33.3
2	-2	1	0	1	-1.25000	1	0	0.25000	-1.75	1	33.3
3	-2	1	0	1	-1.16667	1	0	0.16667	-1.5	1	33.4

Component No.	A_3	B_3	C_3	D_3	A_4	B_4	D_4
1	1.50	-2.50	1	0	1.50	-1.50000	0
2	0.75	-1.75	1	0	0.75	-1.25000	0
3	0.50	-1.50	1	0	0.50	-1.16667	0

Comp. No.	$f_0 = \dfrac{C_0}{B_0}$	g_0	$A_1 f_0$
1	-0.5	0	-0.5
2	-0.5	0	-0.5
3	-0.5	0	-0.5

Comp. No.	$B_1 - A_1 f_0$	$f_1 = \dfrac{C_1}{B_1 - A_1 f_0}$	$D_1 - A_1 g_0$	$g_1 = \dfrac{D_1 - A_1 g_0}{B_1 - A_1 f_0}$	$A_2 f_1$	$B_2 - A_2 f_1$	$A_2 g_1$
1	-1.00000	-1.00000	0	0	-0.50000	-2.00000	0
2	-0.75000	-1.33333	0	0	-0.33333	-1.41667	0
3	-0.66667	-1.50000	0	0	-0.25000	-1.25000	0

Comp. No.	$D_2 - A_2 g_1$	$f_2 = \dfrac{C_2}{B_2 - A_2 f_1}$	$g_2 = \dfrac{D_2 - A_2 g_1}{B_2 - A_2 f_1}$	$A_3 f_2$	$B_3 - A_3 f_2$
1	-33.3	-0.50000	16.65000	-0.75000	-1.75000
2	-33.3	-0.70588	23.50583	-0.52941	-1.22059
3	-33.4	-0.80000	26.72000	-0.40000	-1.10000

Comp. No.	$A_3 g_2$	$D_3 - A_3 g_2$	$f_3 = \dfrac{C_3}{B_3 - A_3 f_2}$	$g_3 = \dfrac{D_3 - A_3 g_2}{B_3 - A_3 f_2}$
1	24.97500	-24.97500	-0.57143	14.27142
2	17.62937	-17.62937	-0.81928	14.44331
3	13.36000	-13.36000	-0.90909	12.14547

Comp. No.	$A_4 f_3$	$B_4 - A_4 f_3$	$A_4 g_3$	$v_{4i} = x_4 = g_4 = \dfrac{D_4 - A_4 g_3}{B_4 - A_4 f_3}$
1	-0.85714	-0.64286	21.40714	33.29985
2	-0.61446	-0.63554	10.83248	17.04453
3	-0.45454	-0.71212	6.07274	8.52768

Comp. No.	$f_3 x_4$	$v_{3i} = x_3 = g_3 - f_3 x_4$	$f_2 x_3$	$v_{2i} = x_2 = g_2 - f_2 x_3$
1	-19.02853	33.29995	-16.64998	33.29998
2	-13.96424	28.40759	-20.05247	43.55830
3	-7.75244	19.89790	-15.91833	42.63833

Comp. No.	$v_{1i} = x_1 = g_1 - f_1 x_2$	$d_i = x_0 = g_0 - f_0 x_1$	$b_i = A_4 v_{4i}$
1	33.29998	16.64999	16.64993
2	58.07759	29.03880	4.26113
3	63.95750	31.97875	1.42128

The student may confirm his ability to apply the proposed calculational procedure in its entirety (the recurrence formulas, the θ method, the K_b method, and the constant-composition method) by solving Problems 3-11 through 3-13.

The tridiagonal formulation of the component-material balances and equilibrium relationships is generally preferred in computer applications because the method is readily applied to other kinds of columns such as absorbers and strippers as demonstrated in Chapter 4. For making calculations for conventional distillation columns by hand, however, the use of nesting equations as originally suggested by Thiele and Geddes (21) is perhaps the more convenient of the two methods.

SOLUTION OF THE COMPONENT-MATERIAL BALANCES AND EQUILIBRIUM RELATIONSHIPS BY USE OF NESTING EQUATIONS. Nesting equations are obtained by first restating those given by Equation (3-47) in terms of the component flow rates as follows:

$$
\begin{cases}
v_{j+1,i} = l_{ji} + d_i & (0 \le j \le f - 2) \\
v_{fi} + v_{Fi} = l_{f-1,i} + d_i & \\
v_{j+1,i} = l_{ji} - b_i & (f \le j \le N) \\
FX_i = d_i + b_i &
\end{cases}
\tag{3-82}
$$

Elimination of l_{ji} from the first expression of Equation (3-82) by means of the equilibrium relationship $l_{ji} = A_{ji} v_{ji}$ [Equation (3-57)] yields the following expression upon rearrangement:

$$
\frac{v_{j+1,i}}{d_i} = A_{ji}\left(\frac{v_{ji}}{d_i}\right) + 1
\tag{3-83}
$$

for $j = 1, 2, \ldots, f - 1$. For $j = 0$ (the condenser-accumulator section) and for a total condenser, the first expression of Equation (3-82) becomes

$$
\frac{v_{1i}}{d_i} = \frac{l_{0i}}{d_i} + 1 = \frac{L_0 x_{0i}}{D X_{Di}} + 1 = \frac{L_0}{D} + 1
\tag{3-84}
$$

since $x_{0i} = X_{Di}$.

For a partial condenser, $y_{0i} = X_{Di}$, $y_{0i} = K_{0i} x_{0i}$ or $l_{0i} = A_{0i} d_i$, and the first expression of Equation (3-82) reduces to

$$
\frac{v_{1i}}{d_i} = A_{0i} + 1
\tag{3-85}
$$

where $A_{0i} = L_0/K_{0i} D$. By use of Equation (3-84) or (3-85) and Equation (3-83), the nesting calculations are initiated at the top of the column and continued down toward the feed plate. For the case of boiling point liquid and subcooled feed, the nesting calculations are discontinued as soon as v_{fi}/d_i has been obtained. For the case of dew point vapor and superheated

feeds, the nesting calculations are ceased as soon as $v_{f-1,i}/d_i$ has been determined, as discussed below.

The nesting equations for the stripping section are initiated at the reboiler. Since $y_{N+1,i} = K_{N+1,i}x_{N+1,i} = K_{N+1,i}x_{Bi}$ or $v_{N+1,i} = S_{N+1,i}b_i$, the component-material balance enclosing the reboiler [given by Equation (3-82) for $j = N$] reduces to

$$\frac{l_{Ni}}{b_i} = \left(\frac{S_{N+1,i}}{b_i}\right)b_i + 1 = S_{N+1,i} + 1 \tag{3-86}$$

where $S_{N+1,i} = B/(V_{N+1}K_{N+1,i})$. After a number value has been obtained for l_{Ni}/b_i, it is used to compute $l_{N-1,i}/b_i$ by use of the following equation which is obtained by eliminating $v_{j+1,i}/b_i$ from the expressions $(f \leq j \leq N)$ of Equation (3-84) by use of the equilibrium relationship $v_{ji} = S_{ji}l_{ji}$, that is,

$$\frac{l_{ji}}{b_i} = S_{j+1,i}\left(\frac{l_{j+1,i}}{b_i}\right) + 1 \tag{3-87}$$

which holds for $j = f, f+1, \ldots, N-1$. After l_{fi}/b_i has been computed, the nesting calculations are ceased and the quantity v_{fi}/b_i is computed by use of the equilibrium relationship, namely,

$$\frac{v_{fi}}{b_i} = S_{fi}\left(\frac{l_{fi}}{b_i}\right)$$

For the case of a boiling point liquid or subcooled feed, $v_{Fi} = 0$, $l_{Fi} = FX_i$, and hence the moles of vapor entering plate $f-1$ is equal to the moles of vapor leaving plate j. Thus, b_i/d_i may be computed from the number values found for v_{Fi}/d_i and v_{fi}/b_i by the nesting calculations as follows:

$$\frac{b_i}{d_i} = \frac{\dfrac{v_{fi}}{d_i}}{\dfrac{v_{fi}}{b_i}} \tag{3-88}$$

Next, the overall component-material balance of Equation (3-82) may be solved for d_i in terms of b_i/d_i in the following manner:

$$FX_i = d_i\left(1 + \frac{b_i}{d_i}\right) \quad \text{and} \quad d_i = \frac{FX_i}{1 + \dfrac{b_i}{d_i}} \tag{3-89}$$

After d_i has been obtained, the complete set of component flow rates $\{b_i, v_{ji}, l_{ji}\}$ may be obtained from previously calculated results in an obvious manner.

For the general case of a partially vaporized feed, the expression for computing b_i/d_i is obtained by commencing with the second expression of Equation (3-82) and rearranging it to give

$$\left(\frac{v_{fi}}{b_i}\right)\left(\frac{b_i}{d_i}\right) + \left(\frac{v_{Fi}}{FX_i}\right)\left(\frac{FX_i}{d_i}\right) = \frac{l_{f-1,i}}{d_i} + 1 \tag{3-90}$$

Since

$$\frac{v_{Fi}}{FX_i} = 1 - \frac{l_{Fi}}{FX_i} \quad \text{and} \quad \frac{FX_i}{d_i} = 1 + \frac{b_i}{d_i}$$

Equation (3-90) may be solved for b_i/d_i to give

$$\frac{b_i}{d_i} = \frac{\dfrac{l_{f-1,i}}{d_i} + \dfrac{l_{Fi}}{FX_i}}{\dfrac{v_{Fi}}{b_i} + \dfrac{v_{Fi}}{FX_i}} \tag{3-91}$$

When the appropriate values for l_{Fi} and v_{Fi} are employed, Equation (3-91) may be used to calculate b_i/d_i for a feed of any thermal condition. For bubble point liquid and subcooled feeds, $l_{Fi} = FX_i$ and $v_{Fi} = 0$. For feeds that enter the column as dew point and superheated vapors, $v_{Fi} = FX_i$ and $l_{Fi} = 0$.

The use of the nesting equations for solving the component-material balances and equilibrium relationships is demonstrated by the following example.

ILLUSTRATIVE EXAMPLE 3-8

Use the nesting equations developed above to solve Illustrative Example 3-7.

Solution: Below are calculations for the rectifying section.

Comp. No.	$\dfrac{L_0}{D}$	$\dfrac{v_{1i}}{d_i} = \dfrac{L_0}{D} + 1$	K_{1i} @ 100°F and 1 atm	$\dfrac{A_{1i}}{=\dfrac{L_1}{K_{1i}V_1}}$	$\dfrac{l_{1i}}{d_i} = A_{1i}\left(\dfrac{v_{1i}}{d_i}\right)$	$\dfrac{v_{2i}}{d_i} = \dfrac{l_{1i}}{d_i} + 1$
1	1.0	2.0	1.0	0.5	1.0	2.0
2	1.0	2.0	2.0	0.25	0.5	1.5
3	1.0	2.0	3.0	0.1666667	0.33333334	1.33333333

Below are calculations for the stripping section and for the d_i's.

Comp. No.	K_{4i} @ 100°F and 1 atm	$S_{4i} = \dfrac{K_{4i}V_4}{B}$	$\dfrac{l_{3i}}{b_i} = S_{4i} + 1$	K_{3i} @ 100°F and 1 atm	$S_{3i} = \dfrac{K_{3i}V_3}{L_3}$	$\dfrac{v_{3i}}{b_i} = S_{3i}\left(\dfrac{l_{3i}}{b_i}\right)$
1	1.0	2.0	3.0	1.0	0.66666666	1.9999998
2	2.0	4.0	5.0	2.0	1.3333333	6.6666660
3	3.0	6.0	7.0	3.0	1.9999999	13.999999

Product distribution

Comp. No.	$\dfrac{l_{2i}}{b_i} = \dfrac{v_{3i}}{b_i} + 1$	K_{2i} @ 100°F and 1 atm	$S_{2i} = \dfrac{K_{2i}V_2}{L_2}$	$\dfrac{v_{2i}}{b_i} = S_{2i}\dfrac{l_{2i}}{b_i}$	$\dfrac{b_i}{d_i} = \dfrac{\dfrac{v_{2i}}{d_i}}{\dfrac{v_{2i}}{b_i}}$	$d_i = \dfrac{FX_i}{1 + \dfrac{b_i}{d_i}}$
1	2.9999999	1	0.66666666	1.9999999	1.0000000	16.649999
2	7.6666666	2	1.3333333	10.222222	0.14673913	29.038862
3	14.999999	3	1.9999999	29.999995	0.04444444	31.978724

$$D_{is} = 77.667585.$$

Convergence characteristics of the θ method

The θ method and the associated calculational procedure described above is one of the fastest known methods for solving problems involving distillation columns (3), and it converges for almost all problems of this type.

Some of the convergence characteristics of the θ method may be demonstrated by comparing it with the method of direct iteration. The method of direct iteration differs from the θ method only by the procedure used to compute the compositions. Instead of Equations (3-71) and (3-72), the following expressions are used in the method of direct iteration:

$$x_{ji} = \frac{\left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{ca}}{\sum_{i=1}^{c} \left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{ca}} \tag{3-92}$$

$$y_{ji} = \frac{\left(\frac{v_{ji}}{d_i}\right)_{ca} (d_i)_{ca}}{\sum_{i=1}^{c} \left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{ca}} \tag{3-93}$$

By comparison of these expressions with Equations (3-71), (3-72), and (3-68), it is evident that the method of direct iteration amounts to setting $\theta = 1$ in Equation (3-68) for all trials. The results obtained for Illustrative Example 3-7 by the θ method are presented in Table 3-1. When the method of direct iteration was used, a calculated value of 52.14 was obtained for D at the end of the third trial, and eleven trials were required to obtain temperatures that did not change in the eighth digit (8). The outstanding convergence characteristics of the θ method result in part, perhaps, from the fact that the θ method constitutes an exact solution to certain problems at total reflux. In order to demonstrate this important result, it is necessary to develop the well-known Fenske equation (6) for a conventional distillation column at total reflux.

SEPARATION OF MULTICOMPONENT MIXTURES IN CONVENTIONAL DISTILLATION COLUMNS AT TOTAL REFLUX. In the following developments, the concept of total reflux from the design point of view is utilized, that is, the total flow rates $[L_j\ (0 \leq j \leq N),\ V_j\ (1 \leq j \leq N+1)]$ are unbounded while the feed and product rates are finite. More precisely,

$$\lim_{V_{j+1} \to \infty} \left(\frac{L_j}{V_{j+1}}\right) = 1 - \lim_{V_{j+1} \to \infty} \left(\frac{D}{V_{j+1}}\right) = 1$$

and

$$F = D + B$$

where F, D, and B are all nonzero, finite, and positive. The corresponding component-material balances are given by

$$y_{j+1,i} = x_{ji} \left[\lim_{V_{j+1} \to \infty} \left(\frac{L_j}{V_{j+1}}\right)\right] + X_{Di} \left[\lim_{V_{j+1} \to \infty} \left(\frac{D}{V_{j+1}}\right)\right] = x_{ji} \tag{3-94}$$

TABLE 3-1

SOLUTION OF ILLUSTRATIVE EXAMPLE 3-7 BY USE OF THE THIELE AND GEDDES METHOD, THE θ METHOD, AND THE K_b METHOD[*]

Calculated Values of the Temperatures, °F

Plate No.	1	2	3	4	5	6	7
0	41.086575	41.362833	41.372024	41.372407	41.372426	41.372427	41.372427
1	46.121292	46.719933	46.738321	46.739097	46.739133	46.739136	46.739136
2	48.755212	51.157089	51.154290	51.154505	51.154520	51.154523	51.154522
3	55.069408	55.398386	55.401216	55.401135	55.401126	55.401126	55.401126
4	63.770834	63.11654	63.095157	63.094266	63.094222	63.094220	63.094220
D	77.667585	49.006364	49.999530	49.999902	49.999993	49.999998	49.999999
(Calculated)	5.6215101	0.94749173	0.99997452	0.99999469	0.99999961	0.99999987	0.99999998

Final Flow Rates

Comp. No.	b	d
1	27.764577	5.535423
2	15.224283	18.075717
3	7.011140	26.388860

[*]Taken from C.D. Holland, *Multicomponent Distillation* (Englewood Cliffs, N.J.: Prentice Hall, Inc., 1963), p. 87.

The final equality follows from the limits stated above. By the alternate application of Equation (3-94) and the equilibrium relationship $y_{ji} = K_{ji}x_{ji}$, the Fenske equation (6),

$$\frac{b_i}{d_i} = \frac{\frac{B}{D}}{\prod_{j=1}^{N+1} K_{ji}} \tag{3-95}$$

is obtained (for a column having a total condenser). An abbreviated development of this equation follows. The component-material balance enclosing the condenser-accumulator section is given by $y_{1i} = x_{0i}$, and for a total condenser $y_{1i} = x_{0i} = X_{Di}$. Elimination of y_{1i} from the second expression by use of the equilibrium relationship for plate 1 $(y_{1i} = K_{1i}x_{1i})$ gives

$$x_{1i} = \frac{X_{Di}}{K_{1i}} \tag{3-96}$$

For plate 2, the component-material balance and equilibrium relationship for component i are as follows:

$$y_{2i} = x_{1i} \quad \text{and} \quad y_{2i} = K_{2i}x_{2i}$$

Elimination of x_{1i} and y_{2i} from these expressions and Equation (3-96) yields

$$x_{2i} = \frac{X_{Di}}{K_{1i}K_{2i}} \tag{3-97}$$

Continuation of this procedure for plates $j = 3$ through $j = N + 1$ (the reboiler) yields

$$x_{N+1,i} = \frac{X_{Di}}{K_{1i}K_{2i}\ldots K_{Ni}K_{N+1,i}} \tag{3-98}$$

Since $x_{N+1,i} = x_{Bi}$, it is evident that Equation (3-95) is obtained by multiplying both sides of Equation (3-98) by B/D. [It should be noted that the alternate use of material balances and equilibrium relationships in the above derivation is the same procedure used to obtain the graphical solution for a binary mixture (see Figure 3-12).]

An alternate form of Equation (3-95) which reduces to an exact solution when the relative volatilities are constant is obtained as follows. First, state Equation (3-95) for the base component b, and then divide the members of Equation (3-95) by the corresponding members for component b and rearrange the result so obtained to give

$$\frac{b_i}{d_i} = \frac{\frac{b_b}{d_b}}{\alpha_{1i}\alpha_{2i}\ldots\alpha_{Ni}\alpha_{N+1,i}} \tag{3-99}$$

If the α_{ij}'s are independent of temperature, Equation (3-99) reduces to

$$\frac{b_i}{d_i} = \frac{b_b}{d_b}\alpha_i^{-(N+1)} \tag{3-100}$$

For the case of a partial condenser $(y_{0i} = X_{Di})$, the appropriate expressions for b_i/d_i are obtained by replacing the exponent $(N + 1)$ in the above expressions by the exponent $(N + 2)$, that is, the partial condenser counts as an additional equilibrium stage.

At a fixed number of plates N, the set of b_i/d_i's relative to b_b/d_b may be computed for a given system by use of Equation (3-100). Then for any specified value of b_b/d_b, the corresponding set d_i's and D may be computed by use of Equation (3-89) and the following formula for D, which is obtained by summing each member of Equation (3-89) over all components

$$D = \sum_{i=1}^{c} \frac{FX_i}{1 + \frac{b_i}{d_i}} \tag{3-101}$$

In summary, Equations (3-89), (3-100), and (3-101) may be used to compute the best possible separation (the lightest possible distillate and heaviest bottoms) which may be achieved with a fixed number of plates at the limiting condition of total reflux, provided, of course, that the α_i's are constant throughout the column. At this limiting condition of total reflux, the column diameter as well as the reboiler and condenser duties become infinite. Problem 3-19 requires the use of Equation (3-100) for the computation of the b_i/d_i's for different specified values of b_b/d_b.

A plot of Equation (3-100) for an example such as the one described in Problem 3-19 where two different distillate rates are employed is plotted in Figure 3-18. The distance between these two lines has been denoted by $|\log_e \theta|$. The equation of the upper line is

$$\log_e \left(\frac{b_i}{d_i}\right)_2 = \log_e \left(\frac{b_b}{d_b}\right)_2 - (N + 1)\log_e \alpha_i \tag{3-102}$$

and for the lower line

$$\log_e \left(\frac{b_i}{d_i}\right)_1 = \log_e \left(\frac{b_b}{d_b}\right)_1 - (N + 1)\log_e \alpha_i \tag{3-103}$$

where the subscripts "1" and "2" refer to problems analogous to those posed by Parts (a) and (b), respectively, of Problem 3-19. When the members of Equation (3-103) are subtracted from the corresponding members of Equation (3-102), one obtains the following result upon rearrangement

$$\log_e \left(\frac{b_i}{d_i}\right)_2 = \log_e \left(\frac{b_i}{d_i}\right)_1 + \log_e \theta \tag{3-104}$$

where

$$\log_e \theta = \log_e \frac{\left(\frac{b_b}{d_b}\right)_2}{\left(\frac{b_b}{d_b}\right)_1}$$
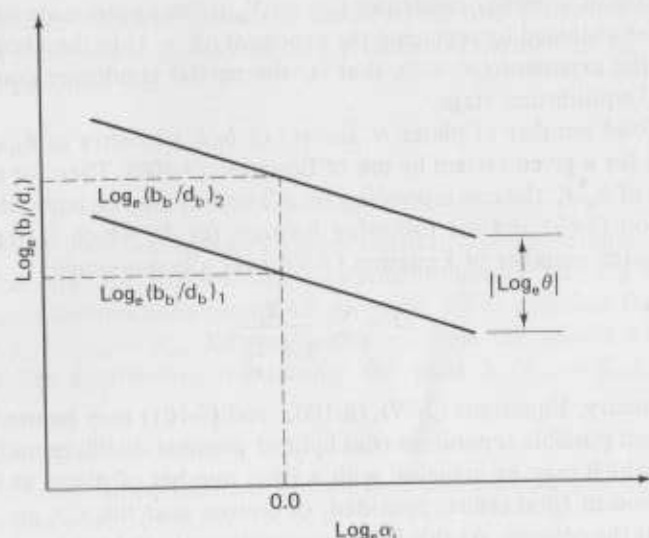
Figure 3-18. A graphical representation of θ is obtained by considering two arbitrarily specified values for a base component, b, in a column at total reflux.

Restatement of Equation (3-104) in product form yields

$$\left(\frac{b_i}{d_i}\right)_2 = \theta\left(\frac{b_i}{d_i}\right)_1 \tag{3-105}$$

Thus, if the b_i/d_i's are known at one condition (a given distillate rate), they may be determined at any other specified distillate rate by use of the θ method. Once θ has been determined, the b_i/d_i's at the new distillate rate will have been determined; thus, the θ method constitutes an exact solution. Since the component flow rates at condition 2 must be in material balance and in agreement with the specified value of D, the g function is obtained by replacing the subscripts "ca" and "co" in Equations (3-65) through (3-69) by "1" and "2," respectively. That the θ method constitutes an exact solution to problems of the type mentioned is illustrated by solving Problem 3-20.

Since many of the methods proposed for solving problems involving conventional distillation columns are analogous to those presented in the next chapter for absorbers and strippers, further discussion of these methods is delayed until after absorbers and strippers have been considered.

PROBLEMS

3-1(a). Complete the construction of the boiling point diagram initiated in Illustrative Example 3-1.

3-1(b). From the plot obtained in Problem 3-1 (a), construct the equilibrium curve.

3-2. Find the minimum reflux ratio (L_0/D) required to effect the following separation of a mixture of 50 mole % A and 50 mole % B. The feed is 55% vaporized at the column pressure of 1 atm.

$$X_{D,A} = 0.95$$
$$X_{B,A} = 0.05$$

Given the following equilibrium data for component A.

x	y
0.1	0.57
0.2	0.7
0.3	0.8
0.5	0.905
0.9	0.995

Ans. $\left(\dfrac{L_0}{D}\right)_{min} = 0.435$

3-3. Find the minimum total number of plates required to effect the separation of Problem 3-2 for the following conditions:
   1. Column pressure $= 1$ atm
   2. Total condenser
   3. Use an operating reflux ratio L_0/D equal to two times the minimum reflux ratio found in Problem 3-2.

Ans. Three plates plus the reboiler. The feed plate is the second plate from the top of the column.

3-4. For the case in which the distillate is withdrawn as a vapor, the partial condenser represents an additional separation stage. In this case

$$X_D = y_0 = K_0 x_0$$

where y_0 is the vapor in equilibrium with the liquid reflux x_0 in the accumulator. The material balance enclosing the condenser-accumulator section is represented by

$$y_1 = \frac{L_r}{V_r} x_0 + \frac{D X_D}{V_r}$$

Repeat Problem 3-3 for the case in which a partial condenser instead of a total condenser is used and the distillate is withdrawn as a vapor with the vapor composition $X_D = 0.95$ rather than as a liquid with this same composition.

Ans. Two plates plus the reboiler plus the partial condenser. The feed plate is the top plate in the column.

3-5(a). Repeat Illustrative Example 3-2 for the case in which the first assumed value of T is taken to be equal to 40°F.
Ans. 50°F.

3-5(b). Repeat Illustrative Example 3-3 for the case in which the assumed value of T is taken to be equal to 60°F.
Ans. 50°F.

3-5(c). After the bubble point temperature has been determined by each of the above methods, compute the corresponding values of y_i's which are in equilibrium with the x_i's.

Ans. $y_1 = \frac{1}{6}$, $y_2 = \frac{1}{3}$, $y_3 = \frac{1}{2}$.

3-6. Repeat Problem 3-5 where the following vapor compositions are known instead of the liquid compositions. In this case determine the dew point temperature at a specified total pressure of $P = 1$ atm. (If Newton's method should fail for $T_1 = 100°F$, try taking $T_1 = 80°F$.) After the dew point temperature has been determined by each of the methods, compute the corresponding x_i's that are in equilibrium with the y_i's.

Component No.	K_i	y_i
1	$K_1 = \dfrac{0.01T^*}{P^*}$	$\dfrac{1}{6}$
2	$K_2 = \dfrac{0.02T}{P}$	$\dfrac{1}{3}$
3	$K_3 = \dfrac{0.03T}{P}$	$\dfrac{1}{2}$

*T is in °F and P is in atm.

Ans. $T_{D.P.} = 50°F$, $x_1 = \frac{1}{3}$, $x_2 = \frac{1}{3}$, $x_3 = \frac{1}{3}$.

3-7. Repeat Problem 3-5 for the case in which the K_i's vary with temperature in the following manner:

$$K_i = C_i e^{-E_i/T}$$

where T is in °R.

Component No.	C_i	E_i
1	$2.35 \times \dfrac{10^3}{P^*}$	4.6×10^3
2	$4.7 \times \dfrac{10^3}{P}$	4.6×10^3
3	$9.4 \times \dfrac{10^3}{P}$	4.6×10^3

*P is in atm.

Ans. 74.3°F.

3-8. If the α_i's are not independent of temperature, then the temperature found at the end of the first trial by use of the K_b method depends on the component selected as the base component as well as on the temperature assumed to evaluate the α_i's. These facts are illustrated by solving the following problems:

Component No.	K_i at $P = 1$ atm	x_i
1	$0.01T^*$	$\dfrac{1}{3}$
2	$0.0002T^2$	$\dfrac{1}{3}$
3	$0.03T$	$\dfrac{1}{3}$

*T is in °F.

(a). Find the correct bubble point temperature at a specified total pressure of 1 atm.

Ans. 58.1°F.

(b). Make one trial by use of the K_b method. Evaluate the α_i's at an assumed temperature of 100°F. Take component 1 as the base component.

Ans. 50°F.

(c). Repeat Part (b) for the case in which component 2 is selected as the base component.

Ans. 70.7°F.

(d). Repeat Part (b) for the case in which the α_i's are evaluated at an assumed temperature of 50°F rather than 100°F.

Ans. 60°F.

3-9(a). On the basis of the solutions obtained for Illustrative Example 3-4 and 3-5, determine the temperature that the feed must have in order for it to possess the enthalpy H found in Illustrative Example 3-5. Assume the feed is at a pressure such that it is all liquid.

Ans. 269°F.

3-9(b). Find the smallest pressure the feed can be under at the temperature found in Problem 3-9 (a) and be in the liquid state.

Ans. 5.23 atm.

3-10. Use the results found in Problem 3-9 to restate this problem as an adiabatic flash problem. Initiate the calculational procedure outlined in the text by making two complete trials on the basis of

$$T_{F1} = T_{B.P.} \text{ of the feed}$$
$$T_{F2} = T_{D.P.} \text{ of the feed}$$

Use the corresponding values $\delta(T_{F1})$ and $\delta(T_{F2})$ to predict the improved value of T_F, namely, T_{F3}.

Ans. $T_{F3} = 103°F$.

3-11. This problem and Problems 3-12 and 3-13 are formulated in such a way that their solutions require that one complete trial be made by use of the calculational procedure proposed in the text for distillation columns.

On the basis of the set of assumed temperatures,

$$T_0 = T_1 = T_2 = T_3 = 100°F$$

and the set of assumed flow rates

$$V_1 = V_2 = V_3 = 100 \text{ lb-moles/hr}$$
$$L_1 = 50, \text{ and } L_2 = 150 \text{ lb-moles/hr}$$

solve the component-material balances and equilibrium relationships by use of the recurrence formulas given below Equation (3-64), and show that

Comp. No.	$\left(\dfrac{b_i}{d_i}\right)_{ca}$
1	1.000000
2	0.225000
3	0.095218

The feed, K values, and column specifications are as follows:

Comp. No.	X_i	K_i	Specifications
1	$\frac{1}{3}$	$\frac{T^*}{P^*}$	The feed $\{X_i\}$ enters the column as a liquid at its bubble point at the column pressure of $P = 100$ psia. $F = 100$ lb-moles/hr, $D = L_0 = 50$ lb-moles/hr, $N = 2$, $f = 2$, and a total condenser is used.
2	$\frac{1}{3}$	$\frac{2T}{P}$	
3	$\frac{1}{3}$	$\frac{3T}{P}$	

*P is the total pressure in psia and T is the temperature in °F.

3-12(a). Find the θ that makes $g(\theta) = 0$ for the set of calculated b_i/d_i's found in Problem 3-11.
Ans. $\theta = 3.69$.

3-12(b). On the basis of the θ that makes $g(\theta) = 0$, calculate the corrected sets of the x_{ji}'s and y_{ji}'s [see Equations (3-71) and (3-72)]. Use these x_{ji}'s or y_{ji}'s to compute K_{jb} for plate $j = 0, 1, 2$, and 3. Base the α_{ji}'s on the K-value for component No. 1, that is, $K_{jb} = K_{j1}$.
Ans. $K_{0b} = 0.425$, $K_{1b} = 0.489$, $K_{2b} = 0.522$, $K_{3b} = 0.606$.

3-12(c). From the results of Problem 3-12 (b), find the new set of temperatures, T_0, T_1, T_2, and T_3.
Ans. $T_0 = 42.5°F$, $T_1 = 48.9°F$, $T_2 = 52.2°F$, and $T_3 = 60.6°F$.

3-13. On the basis of the new sets of compositions and temperatures found in Problem 3-12, find the new set of total flow rates to be used for the next trial through the column. Use the relationships given by Equations (3-77) through (3-81) and the enthalpy data given in Illustrative Example 3-5.
Ans. $V_2 = 87$, $V_3 = 70$, $L_1 = 37$, $L_2 = 120$ mole/hr.

3-14. The recurrence formulas given below Equation (3-64) for solving equations that are tridiagonal in form may be developed as outlined below by use of the Gaussian elimination. Consider the system of linear equations represented by the following matrix equation.

$$\begin{bmatrix} B_0 & C_0 & 0 & 0 & 0 & \cdots & 0 \\ A_1 & B_1 & C_1 & 0 & 0 & \cdots & 0 \\ 0 & A_2 & B_2 & C_2 & 0 & \cdots & 0 \\ \multicolumn{7}{c}{\cdots\cdots\cdots\cdots\cdots\cdots} \\ 0 & \cdots & 0 & A_N & B_N & C_N \\ 0 & \cdots & 0 & 0 & A_{N+1} & B_{N+1} \end{bmatrix} \begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \cdots \\ x_N \\ x_{N+1} \end{bmatrix} = \begin{bmatrix} D_0 \\ D_1 \\ D_2 \\ \cdots \\ D_N \\ D_{N+1} \end{bmatrix} \quad (A)$$

(a). By using the following definitions of f_0, g_0, f_k, and g_k given in the text, show that Equation (A) may be transformed to the following form.

$$\begin{bmatrix} 1 & f_0 & 0 & 0 & 0 & \cdots & 0 \\ 0 & 1 & f_1 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 1 & f_2 & 0 & \cdots & 0 \\ \multicolumn{7}{c}{\cdots\cdots\cdots\cdots\cdots\cdots} \\ 0 & \cdots & 0 & 1 & f_N \\ 0 & \cdots & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ \cdots \\ x_N \\ x_{N+1} \end{bmatrix} = \begin{bmatrix} g_0 \\ g_1 \\ g_2 \\ \cdots \\ g_N \\ g_{N+1} \end{bmatrix} \quad (B)$$

(b). Commencing with the bottom row of Equation (B), show that the matrix multiplication rule may be applied to give

$$x_{N+1} = g_{N+1}, \qquad x_k = g_k - f_k x_{k+1},$$
$$(k = N, N-1, N-2, \ldots, 0) \quad (C)$$

3-15(a). Show that the branch of $g(\theta)$ that contains the positive root is as depicted in Figure 3-16.

3-15(b). Show that if $\theta = 0$ is selected as the first assumed value of θ, then Newton's method always converges to the positive root of $g(\theta)$.

3-16. To prove that the same value for K_{jb} is obtained by use of either the x_{ji}'s or y_{ji}'s, begin with one of the expressions of Equation (3-73) for K_{jb} and Equations (3-71), (3-72), (3-57) and produce the other expression given for K_{jb} in Equation (3-73).

3-17. A variety of forms for the flash function have been proposed. Alternate but equivalent forms such as the one presented in the next chapter are obtained by different choices of independent variables and function formulations. For example, if in the development of $P(\Psi)$, the x_{Fi}'s are eliminated from the component-material balances instead of the y_{Fi}'s by use of $y_{Fi} = K_{Fi}x_{Fi}$, show that the following form of the flash function is obtained.

$$p(\psi) = \sum_{i=1}^{c} \frac{X_i}{1 - \psi\left(1 - \frac{1}{K_{Fi}}\right)} - 1$$

where

$$y_{Fi} = \frac{X_i}{1 - \psi\left(1 - \frac{1}{K_{Fi}}\right)}; \qquad \psi = \frac{L_F}{F}$$

3-18. If 100 moles/hr of the following mixture are to be flashed at 150°F and 50 psia, find the moles of vapor and the moles of liquid formed per hour.

Component	X_i	K_i^* @ 150°F and 50 psia
C_2H_6	0.0079	16.2
C_3H_8	0.1321	5.2
$i\text{-}C_4H_{10}$	0.0849	2.6
$n\text{-}C_4H_{10}$	0.2690	1.98
$i\text{-}C_5H_{12}$	0.0589	0.91
$n\text{-}CH_{12}$	0.1321	0.72
$n\text{-}C_6H_{14}$	0.3151	0.28

*The values of the K's were taken from the fifth edition of the *Technical Manual* (1946) prepared by the Natural Gasoline Supply Men's Association, 422 Kennedy Bldg., Tulsa 3, Oklahoma.

Ans. $L_F = 45.11$ and $V_F = 55.89$ moles/hr.

3-19. Given a column which has two plates, a reboiler, a total condenser, a reboiler, and a feed F of 100 moles per hour. The composition of the feed and the relative volatilities (which are independent of temperature) are as

follows:

Component	X_i	α_i
1	$\frac{1}{3}$	1
2	$\frac{1}{3}$	2
3	$\frac{1}{3}$	3

Find the distillate rates D that must be employed for the above column in order to achieve the following separations of the base component (component 1)

(a). $\dfrac{b_b}{d_b} = 8$

(b). $\dfrac{b_b}{d_b} = 16$

at total reflux.

Ans. (a) $D = 56.2634$; (b) $D = 46.4632$.

3-20. Given a column that has two plates, a reboiler, a total condenser, and a feed F of 100 moles per hour. The composition of the feed and the relative volatilities are the same as those stated in Problem 3-19. Initially, the column is operating at total reflux at a distillate rate $D_1 = 56.2634$ and with the following set of b_i/d_i's

Component No.	$\left(\dfrac{b_i}{d_i}\right)_1$
1	8.0000
2	0.5000
3	0.09875

If the distillate rate is changed to $D_2 = 46.4632$ while the column remains at total reflux operation, find the corresponding steady state values of b_i/d_i at D_2 by use of the θ method of convergence.

3-21. Let the corrected component flow rates be defined in terms of the undetermined multipliers η_j and σ_j.

$$(l_{ji})_{co} = \eta_j \left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{co}$$

$$(v_{ji})_{co} = \sigma_j \left(\frac{v_{ji}}{d_i}\right)_{ca} (d_i)_{co}$$

(a). If the multipliers η_j and σ_j are picked such that

$$\sum_{i=1}^{c} (l_{ji})_{co} = (L_j)_{co}$$

$$\sum_{i=1}^{c} (v_{ji})_{co} = (V_j)_{co}$$

show that the expressions given by Equations (3-71) and (3-72) follow from the above expressions and the definition of a mole fraction.

(b). Show that if the undetermined multiplier η_{N+1} for the reboiler is called θ, then the defining equation for θ [Equation (3-67)] follows from the definition of $(l_{ji})_{co}$ for $j = N + 1$ (the reboiler).

NOTATION

A_{ji} = absorption factor; defined by Equation (3-57).

b_i = flow rate of component i in the bottoms lb-mole/hr.

B = total flow rate of bottoms, lb-mole/hr.

c = total number of components.

d_i = flow rate of component i in the distillate, lb-mole/hr.

D = total flow rate of the distillate, lb-mole/hr.

$\hat{f}_i^L, \hat{f}_i^V$ = fugacities of components i in the liquid and vapor phases (composed of any number of components), respectively; evaluated at the total pressure and temperature of the two-phase system, atm.

f_i^L, f_i^V = fugacities of pure component i in the liquid and vapor phases, respectively; evaluated at the total pressure and temperature of the two-phase system, atm.

$f(T)$ = bubble point function; defined by Equation (3-14).

$\mathcal{f}_i$ = feed vector.

$F(T)$ = dew point function; defined by Equation (3-17).

F = total flow rate of the feed, lb-mole/hr.

$g(\theta)$ = a function of θ; defined by Equation (3-69).

h_{Fi}, H_{Fi} = enthalpies of pure component i; evaluated at the temperature T_F and pressure P of the flash, Btu/lb-mole.

$h_j = \sum_{i=1}^{c} h_{ji} x_{ji}$, for an ideal solution; evaluated at the temperature T_j, pressure and composition of the liquid leaving the jth plate, Btu/lb-mole.

$H_j = \sum_{i=1}^{c} H_{ji} y_{ji}$, for an ideal solution; evaluated at the temperature T_j, pressure, and composition of the vapor leaving the jth plate, Btu/lb-mole.

H = enthalpy per mole of feed, regardless of state, Btu/lb-mole.

$H(x_j)_k = \sum_{i=1}^{c} H_{ki} x_{ji}$, for an ideal solution; evaluated at the temperature and pressure of the vapor leaving the kth stage and at the composition of the liquid leaving the jth stage.

$h(y_j)_k = \sum_{i=1}^{c} h_{ki} y_{ji}$, for an ideal solution; evaluated at the temperature and pressure of the liquid leaving the kth stage and at the composition of the vapor leaving the jth stage.

K_{ji} = equilibrium vaporization constant; evaluated at the temperature and pressure of the liquid leaving the jth stage.

l_{ji} = flow rate at which component i in the liquid phase leaves the jth mass transfer section, lb-mole/hr.

l_{0i} = flow rate of component i in the liquid reflux, lb-mole/hr.

l_{Fi}, v_{Fi} = flow rates of component i in the liquid and vapor parts, respectively, of a partially vaporized feed, lb-mole/hr. For bubble point liquid and subcooled feeds, $l_{Fi} = FX_i$ and $v_{Fi} = 0$. For dewpoint vapor and superheated feeds; $v_{Fi} = FX_i$ and $l_{Fi} = 0$.

L_j = total flow rate at which liquid leaves the jth stage, lb-mole/hr.

N = total number of plates.

P_i = vapor pressure of component i, atm.

P = total pressure, atm.

$P(\Psi)$ = flash function; defined by Equation (3-30).

q = a factor related to the thermal condition of the feed; defined by Equation (3-43).

Q_c = condenser duty, Btu/hr.

Q_R = reboiler duty, Btu/hr.

$S_{ji} = K_{ji}V_j/L_j$, stripping factor for component i; evaluated at the conditions of the liquid leaving the jth stage.

T = temperature. $T_{B.P.}$ = bubble point temperature; and $T_{D.P.}$ = dewpoint temperature.

T_F = flash temperature.

v_{ji} = flow rate at which component i in the vapor phase leaves the jth stage, lb-mole/hr.

V_j = total flow rate of vapor leaving the jth stage, lb-mole/hr.

x_{Fi} = mole fraction of component i in the liquid leaving a flash process.

x_{ji} = mole fraction of component i in the liquid leaving the jth stage.

x_{Bi} = mole fraction of component i in the bottoms.

x_i = abscissa of the point of intersection of the operating lines for a binary mixture.

X_i = total mole fraction of component i in the feed (regardless of state).

X_{Di} = total mole fraction of component i in the distillate (regardless of state).

y_{ji} = mole fraction of component i in the vapor leaving plate j.

y_i = ordinate of the point of intersection of the operating lines for a binary mixture.

GREEK LETTERS

α_{ji} = relative volatility, $\alpha_{ji} = K_{ji}/K_{jb}$.

δ = function of T_F; defined by Equation (3-35).

γ_i^L, γ_i^v = activity coefficients for component i in the liquid and vapor, respectively.

Ψ = fraction of the feed converted to vapor by a flash process, $\Psi = V_F/F$.

θ = a multiplier defined by Equation (3-67).

SUBSCRIPTS

ca = calculated value.

co = corrected value.

f = feed plate.

F = variables associated with a partially vaporized feed.

i = component number, $i = 1, 2, \ldots, c$ or $(1 \leq i \leq c)$.

j = plate number; $j = 0$ for the accumulator; for the top plate $j = 1$, for the feed plate $j = f$, for the bottom plate $j = N$, and for the reboiler $j = N + 1$, that is, $j = 0, 1, 2, \ldots, f, \ldots, N, N + 1$, or $(0 \leq j \leq N + 1)$.

n = trial number.

N = total number of plates.

r = rectifying section.

s = stripping section.

SUPERSCRIPTS

L = liquid phase.

V = vapor phase.

MATHEMATICAL SYMBOLS

$\sum_{i=1}^{c} x_i$ = sum over all values x_i, $i = 1, 2, \ldots, c$, or $(1 \leq i \leq c)$.

$\{x_j\}$ = set of all values x_j belonging to the particular set under consideration.

$\prod_{j=1}^{c} x_j = x_1 x_2 \ldots x_{c-1} x_c$, product of the x_j's from $j = 1$ through $j = c$.

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Absorbers and Strippers **4**

From a light gas stream such as natural gas that contains primarily methane plus small quantities of say ethane through n-pentane, the desired quantities of the components heavier than methane may be removed by contacting the natural gas stream with a heavy oil stream (say n-octane or heavier) in a countercurrent, multiple stage column such as the one shown in Figure 4-1. Since absorption is a heat liberating process, the lean oil is customarily introduced at a temperature below the average temperature at which the column is expected to operate. The flow rate of the lean oil is denoted by L_0, and the lean oil enters at the top of the column as implied by Figure 4-1. The *rich gas* (which is sometimes called the *wet gas*) enters at the bottom of the column at a temperature equal to or above its dew point temperature at the column pressure but generally below the average operating temperature of the column. The total flow rate of the rich gas is denoted by V_{N+1}. The absorber oil plus the material that it has absorbed leave at the bottom of the column; this stream is called the *rich oil*. The treated gas leaving the top of the column is called the *lean gas* (or the *stripped gas*).

Strippers are used to remove relatively light gases from a heavy oil stream by contacting it with a relatively light gas stream such as steam. The sketch of a typical stripper is shown in Figure 4-1.

In Part 1 of this chapter, a relatively simple model is presented for approximating the behavior of absorbers and strippers. In Part 2, calculational procedures are developed for more exact models for absorbers and strippers. A brief description of the application of certain of the methods developed

FUNDAMENTALS AND MODELING OF SEPARATION PROCESSES

Absorption, Distillation, Evaporation, and Extraction

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To

Nancy
Charlotte
and Thomas