DISTILLATION AND GAS ABSORPTION

The feasibility of separation of mixtures by distillation, absorption, or stripping depends on the fact that the compositions of vapor and liquid phases are different from each other at equilibrium. The vapor or gas phase is said to be richer in the more volatile or lighter or less soluble components of the mixture. Distillation employs heat to generate vapors and cooling to effect partial or total condensation as needed. Gas absorption employs a liquid of which the major components are essentially nonvolatile and which exerts a differential solvent effect on the components of the gas. In a complete plant, gas absorption is followed by a stripping operation for regeneration and recycle of the absorbent and for recovering the preferentially absorbed substances. In reboiled absorbers, partial stripping of the lighter components is performed in the lower part of the equipment. In distillation, absorption, or rectification and stripping are performed in the same equipment. Figures 13.1 and 13.2 show the basic types of equipment.

13.1. VAPOR–LIQUID EQUILIBRIA

This topic is concerned with the relations between vapor and liquid compositions over a range of temperature and pressure. Functionally, the dependence of the mol fraction \( y_i \) of component \( i \) in the vapor phase depends on other variables as

\[
y_i = f(T, P, x_1, x_2, \ldots, x_n). \tag{13.1}
\]

The dependence on composition alone often is approximated by

\[
y_i = K_i x_i \tag{13.2}
\]

where \( K_i \), the vaporization equilibrium ratio (VER) is assumed to depend primarily on the temperature and pressure and the nature of the substance, and only secondarily on the composition. Equation (13.2) can be viewed as suggested by Raoult's law,

\[
y_i = (P_i^{\text{sat}} / P) x_i \tag{13.3}
\]

with

\[
(K_i)_{\text{ideal}} = P_i^{\text{sat}} / P \tag{13.4}
\]

These distinctions between the two operations are partly traditional. The equipment is similar, and the mathematical treatment, which consists of material and energy balances and phase equilibrium relations, also is the same for both. The fact, however, that the bulk of the liquid phase in absorption-stripping plants is nonvolatile permits some simplifications in design and operation.

Equipment types are of two kinds, tray-type or packed, stagewise or continuous. The trays function as individual stages and produce stepwise changes in concentration. In packed towers concentration changes occur gradually. Until recently packed towers were used only in small equipment and where their construction was an advantage under corrosive conditions or when low pressure drop was mandatory. The picture now has changed somewhat and both types often are competitive over a wide range of sizes.
where \( P_i^{m} \) is the vapor pressure of component \( i \) and \( P \) is the system pressure. Several correlations have been developed for VERs, chiefly for hydrocarbon systems, for example, the one in Figure 13.3. The effect of composition is expressed in terms of a convergence pressure, which is explained for instance in the API Data Book (1969–date). The correction is small for system pressures under 10 atm or so and is neglected in this book.

A more nearly complete expression of \( K \) is derived upon noting that at equilibrium partial fugacities of each component are the same in each phase, that is

\[
\hat{f}_i^* = \hat{f}_i^\prime
\]

or in terms of fugacity and activity coefficients,

\[
\chi_i \hat{f}_i^* P = x_i \hat{f}_i^\prime P \text{ atm}.
\]

(13.5)

(13.6)

Figure 13.3. Vaporization equilibrium ratios (Hadden and Grayson, 1961; Courtesy Mobil Oil Corp., New York).
The relation between mol fractions becomes

\[ y_i = \gamma_i \phi_i^{\text{sat}} \frac{\phi_i^{\text{sat}}}{P} x_i, \quad (13.7) \]

which makes the vaporization equilibrium ratio

\[ K_i = \gamma_i \frac{\phi_i^{\text{sat}}}{\phi_i^{\text{sat}}} P. \quad (13.8) \]

Additionally, usually small corrections for pressure, called Poynting factors, also belong in Eq. (13.6) and following but are omitted here. The new terms are

\[ \gamma_i = \text{activity coefficient in the liquid phase}, \]
\[ \phi_i^{\text{sat}} = \text{fugacity coefficient of the pure component at its vapor pressure}, \]
\[ \phi_i = \text{partial fugacity coefficient in the vapor phase}. \]

Equations for fugacity coefficients are derived from equations of state. Table 13.1 has them for the popular Soave equation of state. At pressures below 5–6 atm, the ratio of fugacity coefficients in Eq. (13.8) often is near unity. Then the VER may be written

\[ K_i = \gamma_i \frac{P}{P} \quad (13.9) \]

and is independent of the nature of the vapor phase.

Values of the activity coefficients are deduced from experimental data of vapor–liquid equilibria and correlated or extended by any one of several available equations. Values also may be calculated approximately from structural group contributions by methods called UNIFAC and ASOG. For more than two components, the correlating equations favored nowadays are the Wilson, the NRTL, and UNIQUAC, and for some applications a solubility parameter method. The first and last of these are given in Table 13.2. Calculations from measured equilibrium compositions are made with the rearranged equation

\[ \gamma_i = \frac{\phi_i^{\text{sat}}}{\phi_i} \frac{y_i}{x_i} = \frac{P}{P} \frac{y_i}{x_i}. \quad (13.10) \]

The last approximation usually may be made at pressures below 5–6 atm. Then the activity coefficient is determined by the vapor pressure, the system pressure, and the measured equilibrium compositions.

Since the fugacity and activity coefficients are mathematically complex functions of the compositions, finding corresponding compositions of the two phases at equilibrium when the equations are known requires solutions by trial. Suitable procedures for making flash calculations are presented in the next section, and in greater detail in some books on thermodynamics, for instance, the one by Walas (1985). In making such calculations, it is usual to start by assuming ideal behavior, that is,

\[ \frac{\phi_i^{\text{sat}}}{\phi_i} = \gamma_i = 1. \quad (13.12) \]

After the ideal equilibrium compositions have been found, they are used to find improved values of the fugacity and activity coefficients. The process is continued to convergence.
TABLE 13.2. Activity Coefficients from Solubility Parameters and from the Wilson Equation

### Binary Mixtures

<table>
<thead>
<tr>
<th>Name</th>
<th>Parameters</th>
<th>In γ₁ and In γ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scatchard–Hildebrand</td>
<td>δ₁, δ₂</td>
<td>( \frac{V_1}{RT} (1 - \phi_1)^2 (\delta_1 - \delta_2)^2 )</td>
</tr>
<tr>
<td>Wilson</td>
<td>( \lambda_{12}, \lambda_{21} )</td>
<td>( -\ln(x_1 + \lambda_{12} x_2) + x_2 \left( \frac{\lambda_{12}}{x_1 + \lambda_{12} x_2} - \frac{\lambda_{21}}{x_2 + \lambda_{21} x_1 + x_2} \right) )</td>
</tr>
</tbody>
</table>

\[ \phi_1 = \frac{V_1}{V} \frac{x_1}{x_1 + x_2} \]

\[ \lambda_{12} = \frac{V_3}{V_i} \exp \left( -\frac{\lambda_{12}}{RT} \right) \]

\[ \lambda_{21} = \frac{V_4}{V_i} \exp \left( -\frac{\lambda_{21}}{RT} \right) \]

\( V_i \): molar volume of pure liquid component \( i \).

### Ternary Mixtures

\[ \ln γ_1 = 1 - \ln(x_1 \lambda_{12} + x_2 \lambda_{12} + x_3 \lambda_{13}) - \frac{x_1 \lambda_{12}}{x_1 + x_2 \lambda_{12} + x_3 \lambda_{13}} \]

\[ \lambda_{12} = \frac{x_1 \lambda_{12}}{x_1 + x_2 \lambda_{12} + x_3 \lambda_{13}} \]

\[ \lambda_{13} = \lambda_{12} \exp \left( -\frac{\lambda_{12}}{RT} \right) \]

\[ \lambda_{21} = \lambda_{23} \exp \left( -\frac{\lambda_{21}}{RT} \right) \]

\( \lambda_{ij} = 1 \)

### Multicomponent Mixtures

<table>
<thead>
<tr>
<th>Equation</th>
<th>Parameters</th>
<th>In γ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scatchard–Hildebrand</td>
<td>δ₁</td>
<td>( \frac{V_1}{RT} \left[ \delta_1 - \frac{\sum x_j \phi_j}{\sum x_j V_j} \right]^2 )</td>
</tr>
<tr>
<td>Wilson</td>
<td>( \lambda_{ij} )</td>
<td>( -\ln \left( \sum x_j \lambda_{ij} \right) + 1 - \frac{\sum x_j \lambda_{ij}}{\sum_j x_j \lambda_{ij}} )</td>
</tr>
</tbody>
</table>

\[ \lambda_{ij} = 1 \]

### RELATIVE VOLATILITY

The compositions of vapor and liquid phases of two components at equilibrium sometimes can be related by a constant relative volatility which is defined as

\[ \alpha_{12} = \frac{y_1}{x_1} / \frac{x_2}{y_2} = \left( \frac{y_1}{1 - y_1} \right) / \left( \frac{x_1}{1 - x_1} \right) \]

(13.13)

Then

\[ \frac{y_1}{1 - y_1} = \alpha_{12} \frac{x_1}{1 - x_1} \]

(13.14)

In terms of vaporization equilibrium ratios,

\[ \alpha_{12} = K_1 / K_2 = \gamma_1 P_1^\text{sat} / \gamma_2 P_2^\text{sat} \]

(13.15)

and when Raoult's law applies the relative volatility is the ideal value,

\[ \alpha_{\text{ideal}} = \frac{P_1^\text{sat}}{P_2^\text{sat}}. \]

(13.16)

Usually the relative volatility is not truly constant but is found to depend on the composition, for example,

\[ \alpha_{12} = k_1 + k_2 x_1 \]

(13.17)

Other relations that have been proposed are

\[ \frac{y_1}{1 - y_1} = k_1 \left( \frac{x_1}{1 - x_1} \right) \]

(13.18)

and

\[ \frac{y_1}{1 - y_1} = k_1 \left( \frac{x_1}{1 - x_1} \right)^{k_2} \]

(13.19)

A variety of such relations is discussed by Hala (Vapor–Liquid
EXAMPLE 13.1
Correlation of Relative Volatility

Data for the system ethanol + butanol at 1 atm are taken from the collection of Kogan et al. (1966, #1038). The values of $x/(100 - x)$, $y/(100 - y)$, and $\alpha$ are calculated and plotted. The plot on linear coordinates shows that relative volatility does not plot linearly with $x$, but from the linear log-log plot it appears that

$$\frac{y}{100 - y} = 4.364 \left(\frac{x}{100 - x}\right)^{0.045} \text{ or } \alpha = 4.364 \left(\frac{x}{100 - x}\right)^{0.045}$$

The definition of relative volatility, Eq. (13.14), is rearranged into this form:

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

Representative $x$-$y$ diagrams appear in Figure 13.4. Generally they are plots of direct experimental data, but they can be calculated from fundamental data of vapor pressure and activity coefficients. The basis is the bubblepoint condition:

$$y_1 + y_2 = \frac{Y_1 P_{vap}}{P} x_1 + \frac{Y_2 P_{vap}}{P} (1 - x_1) = 1.$$  

In order to relate $y_1$ and $x_1$, the bubblepoint temperatures are found over a series of values of $x_1$. Since the activity coefficients depend on the composition of the liquid and both activity coefficients and vapor pressures depend on the temperature, the calculation requires a respectable effort. Moreover, some vapor-liquid measurements must have been made for evaluation of a correlation of activity coefficients. The method does permit calculation of equilibria at several pressures since activity coefficients are substantially independent of pressure. A useful application is to determine the effect of pressure on azeotropic composition (Walas, 1985, p. 227).
Figure 13.4. Some vapor-liquid composition diagrams at essentially atmospheric pressure. This is one of four such diagrams in the original reference (Kirschbaum, Destillier und Rektifizietechnik, Springer, Berlin, 1969). Compositions are in weight fractions of the first-named.

dewpoint; and the compositions and the relative amounts of vapor and liquid phases at equilibrium under specified conditions of temperature and pressure or enthalpy and pressure. The first cases examined will take the $K_i$ to be independent of composition. These problems usually must be solved by iteration, for which the Newton–Raphson method is suitable. The dependence of $K$ on temperature may be represented adequately by

$$K_i = \exp[A_i - B_i/(T + C_i)].$$

(13.25)

An approximate relation for the third constant is

$$C_i = 18 - 0.19T_b,$$

(13.26)

where $T_b$ is the normal boiling point in °K. The dependence of $K$ on pressure may be written simply as

$$K_i = a_i P^b.$$ (13.27)

Linear expressions for the enthalpies of the two phases are

$$h_i = a_i + b_i T,$$ (13.28)  

$$H_i = c_i + d_i T,$$ (13.29)

assuming negligible heats of mixing. The coefficients are evaluated by readings off Figure 13.3, for example, and tabulations of pure component enthalpies. First derivatives are needed for application of the Newton–Raphson method:

$$\partial K_i / \partial T = B_i K_i/(T + C_i)^2,$$ (13.30)  

$$\partial K_i / \partial P = b_i K_i / P.$$ (13.31)

**Bubblepoint Temperature and Pressure**

The temperature at which a liquid of known composition first begins to boil is found from the equation

$$f(T) = \sum K_i x_i - 1 = 0,$$ (13.32)
where the $K_i$ are known functions of the temperature. In terms of Eq. (13.25), the Newton–Raphson algorithm is

$$T = T - \frac{-1 + \sum K_i x_i}{\sum [B_i K_i x_i/(T + C_i)]^2}. \quad (13.33)$$

Similarly, when Eq. (13.27) represents the effect of pressure, the bubblepoint pressure is found with the N–R algorithm:

$$f(P) = \sum K_i x_i - 1 = 0, \quad (13.34)$$
$$P = P - \frac{-1 + \sum a_i P^b x_i}{\sum a_i b_i P^{b_i-1} x_i}. \quad (13.35)$$

**DEWPOINT TEMPERATURE AND PRESSURE**

The temperature or pressure at which a vapor of known composition first begins to condense is given by solution of the appropriate equation,

$$f(T) = \sum y_i / K_i - 1 = 0, \quad (13.36)$$
$$f(P) = \sum y_i / K_i - 1 = 0. \quad (13.37)$$

In terms of Eqs. (13.25) and (13.27) the N–R algorithms are

$$T = T + \frac{-1 + \sum y_i / K_i}{\sum [(y_i / K_i^2) \partial K_i / \partial T]} = T + \frac{-1 + \sum y_i / K_i}{\sum [B_i y_i / K_i (T + C_i)^2]}, \quad (13.38)$$
$$P = P + \frac{-1 + \sum y_i / K_i}{\sum [(y_i / K_i^2) \partial K_i / \partial P]} = P + \frac{-1 + \sum y_i / K_i P}{\sum (b_i y_i / K_i)}. \quad (13.39)$$

**FLASH AT FIXED TEMPERATURE AND PRESSURE**

At temperatures and pressures between those of the bubblepoint and dewpoint, a mixture of two phases exists whose amounts and compositions depend on the conditions that are imposed on the system. The most common sets of such conditions are fixed $T$ and $P$, or fixed $H$ and $P$, or fixed $S$ and $P$. Fixed $T$ and $P$ will be considered first.

For each component the material balances and equilibria are:

$$F_{z_i} = L x_i + V y_i, \quad (13.40)$$
$$y_i = K_i x_i. \quad (13.41)$$

On combining these equations and introducing $\beta = V/F$, the fraction vaporized, the flash condition becomes

$$f(\beta) = -1 + \sum x_i = -1 + \sum \frac{y_i}{1 + \beta(K_i - 1)} = 0, \quad (13.42)$$

and the corresponding N-R algorithm is

$$\beta = \beta + \frac{-1 + \sum [z_i/(1 + \beta(K_i - 1))] - \sum ((K_i - 1) z_i/[1 + \beta(K_i - 1)]^2)}{\sum (z_i / [1 + \beta(K_i - 1)]^2)}. \quad (13.43)$$

After $\beta$ has been found by successive approximation, the phase compositions are obtained with

$$x_i = \frac{z_i}{1 + \beta(K_i - 1)}, \quad (13.44)$$
$$y_i = K_i x_i. \quad (13.45)$$

A starting value of $\beta = 1$ always leads to a converged solution by this method.

**FLASH AT FIXED ENTHALPY AND PRESSURE**

The problem will be formulated for a specified final pressure and enthalpy, and under the assumption that the enthalpies are additive (that is, with zero enthalpy of mixing) and are known functions of temperature at the given pressure. The enthalpy balance is

$$H_f = (1 - \beta) \sum x_i H_i + \beta \sum y_i H_i, \quad (13.46)$$
$$= (1 - \beta) \sum \frac{z_i H_i}{1 + \beta(K_i - 1)} + \beta \sum \frac{K_i y_i H_f}{1 + \beta(K_i - 1)}. \quad (13.47)$$

This equation and the flash Eq. (13.42) constitute a set:

$$f(\beta, T) = -1 + \sum \frac{z_i}{1 + \beta(K_i - 1)} = 0, \quad (13.48)$$
$$g(\beta, T) = H_f - (1 - \beta) \sum \frac{z_i H_i}{1 + \beta(K_i - 1)} - \beta \sum \frac{K_i y_i H_f}{1 + \beta(K_i - 1)} = 0, \quad (13.49)$$

from which the phase split $\beta$ and temperature can be found when the enthalpies and the vaporization equilibrium ratios are known functions of temperature. The N–R method applied to Eqs. (13.48) and (13.49) finds corrections to initial estimates of $\beta$ and $T$ by solving the linear equations

$$h \frac{\partial f}{\partial \beta} + k \frac{\partial f}{\partial T} + f = 0, \quad (13.50)$$
$$h \frac{\partial g}{\partial \beta} + k \frac{\partial g}{\partial T} + g = 0, \quad (13.51)$$

where all terms are evaluated at the assumed values $(\beta_0, T_0)$ of the two unknowns. The corrected values, suitable for the next trial if that is necessary, are

$$\beta = \beta_0 + h, \quad (13.52)$$
$$T = T_0 + K. \quad (13.53)$$

Example 13.2 applies these equations for dewpoint, bubblepoint, and flashes.

**EQUILIBRIA WITH $K_s$ DEPENDENT ON COMPOSITION**

The procedure will be described only for the case of bubblepoint temperature for which the calculation sequence is represented on Figure 13.5. Equations (13.8) and (13.32) are combined as

$$f(T) = \sum \frac{y_i \phi_i \rho_{vap} F_{z_i}}{\phi_i P} - x_i - 1 = 0. \quad (13.54)$$

The liquid composition is known for a bubblepoint determination, but the temperature is not at the start, so that starting estimates must be made for both activity and fugacity coefficients. In the flow diagram, the starting values are proposed to be unity for all the variables. After a trial value of the temperature is chosen, subsequent calculations on the diagram can be made directly. The correct value of $T$ has been chosen when $\sum y_i = 1$.

Since the equations for fugacity and activity coefficients are complex, solution of this kind of problem is feasible only by computer. Reference is made in Example 13.3 to such programs. There also are given the results of such a calculation which reveals the magnitude of deviations from ideality of a common organic system at moderate pressure.
**Example 13.2**

**Vaporization and Condensation of a Ternary Mixture**

For a mixture of ethane, n-butane, and n-pentane, the bubblepoint and dewpoint temperatures at 100 psia, a flash at 100°F and 100 psia, and an adiabatic flash at 100 psia of a mixture initially liquid at 100°F will be determined. The overall composition \( z_r \), the coefficients \( A, B, \) and \( C \) of Eq. (13.22) and the coefficients \( a, b, c, \) and \( d \) of Eqs. (13.28) and (13.29) are tabulated:

<table>
<thead>
<tr>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z_a )</td>
</tr>
<tr>
<td>0.3</td>
</tr>
<tr>
<td>0.3</td>
</tr>
<tr>
<td>0.4</td>
</tr>
</tbody>
</table>

The bubblepoint temperature algorithm is

\[
T = T_0 - \left( \frac{1 + \sum K_i x_i}{\sum (K_i - 1) z_i/(1 + \beta (K_i - 1))^2} \right) \quad (13.33)
\]

and the dewpoint temperature algorithm is

\[
T = T_0 + \left( \frac{1 + \sum y_i/K_i}{\sum (B_i y_i/K_i (T + C_i)^2} \right) \quad (13.38)
\]

Results of successive iterations are:

<table>
<thead>
<tr>
<th>Bubblepoint</th>
<th>Dewpoint</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000.0000</td>
<td>700.0000</td>
</tr>
<tr>
<td>696.1614</td>
<td>597.8363</td>
</tr>
<tr>
<td>560.1387</td>
<td>625.9790</td>
</tr>
<tr>
<td>506.5023</td>
<td>635.3072</td>
</tr>
<tr>
<td>496.1742</td>
<td>636.0697</td>
</tr>
<tr>
<td>495.7966</td>
<td>636.0743</td>
</tr>
<tr>
<td>495.7963</td>
<td></td>
</tr>
</tbody>
</table>

The algorithm for the fraction vapor at specified \( T \) and \( P \) is

\[
\beta = \frac{V}{L} = \frac{1 + \sum x_i/(1 + \beta (K_i - 1))}{\sum (K_i - 1) z_i/(1 + \beta (K_i - 1))^2} \quad (13.43)
\]

and the equations for the vapor and liquid compositions are

\[
x_i = \frac{z_i}{1 + \beta (K_i - 1)} \quad (13.44)
\]

\[
y_i = \frac{K_i x_i}{1 + \beta (K_i - 1)} \quad (13.45)
\]

Results for successive iterations for \( \beta \) and the final phase compositions are

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>( x_0 )</th>
<th>( x_1 )</th>
<th>( y_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0000</td>
<td>0.3</td>
<td>0.1339</td>
<td>0.7231</td>
</tr>
<tr>
<td>0.8257</td>
<td>0.3</td>
<td>0.3458</td>
<td>0.1833</td>
</tr>
<tr>
<td>0.5964</td>
<td>0.4</td>
<td>0.5203</td>
<td>0.0936</td>
</tr>
<tr>
<td>0.3986</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2830</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2819</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adiabatic flash calculation: Liquid and vapor enthalpies off charts in the API data book are fitted with linear equations

\[
h = a + bT \quad (\text{°F}),
\]

\[
H = c + dT \quad (\text{°F}).
\]

The inlet material to the flash drum is liquid at 100°F, with \( H_0 = 8,575.8 \text{ Btu}/\text{lb mol} \). The flash Eq. (13.43) applies to this part of the example. The enthalpy balance is

\[
H_0 = 8575.8 = (1 - \beta) \sum M_i x_i h_i + \beta \sum M_i y_i H_i
\]

\[
= (1 - \beta) \sum M_i x_i h_i + \beta \sum M_i y_i H_i
\]

The procedure consists of the steps.

1. Assume \( T \).
2. Find the \( K_i, h_i, \) and \( H_i \).
3. Find \( \beta \) from the flash equation (13.43).
4. Evaluate the enthalpy of the mixture and compare with \( H_0, \) Eq. (13.47).

The results of several trials are shown:

\[
T(\text{°R}) \quad \beta \quad h
\]

| 530.00 | 0.1601 | 8475.70 |
| 532.00 | 0.1681 | 8585.46 |
| 531.82 | 0.1674 | 8575.68--8575.8, check. |

The final VERs and the liquid and vapor compositions are:

\[
K \quad x \quad y
\]

| C_2 | 4.2897 | 0.1935 | 0.8299 |
| nC_4 | 0.3534 | 0.3364 | 0.1189 |
| nC_6 | 0.1089 | 0.4701 | 0.0512 |

The numerical results were obtained with short computer programs which are given in Walas (1985, p. 317).

**13.3. Evaporation or Simple Distillation**

As a mixture of substances is evaporated, the residue becomes relatively depleted in the more volatile constituents. A relation for binary mixtures due to Rayleigh is developed as follows: The differential material balance for a change \( dL \) in the amount of liquid remaining is

\[
-\gamma dL = d(LX) = L \, dx + X \, dL \quad (13.55)
\]

Upon rearrangement and integration, the result is

\[
\ln \left( \frac{L}{L_0} \right) = \int_{x_0}^{x} \frac{dx}{x - y} \quad (13.56)
\]

In terms of a constant relative volatility

\[
y = \frac{\alpha x}{1 - (\alpha - 1)x} \quad (13.57)
\]
KEY CONCEPTS OF THE CALCULATION OF DISTILLATION ARE WELL ILLUSTRATED BY ANALYSIS OF THE DISTILLATION OF BINARY MIXTURES. MOREOVER, MANY REAL SYSTEMS ARE ESSENTIALLY BINARY OR CAN BE TREATED AS BINARY MASSES MADE UP OF TWO PSEUDO COMPONENTS, FOR WHICH IT IS POSSIBLE TO CALCULATE UPPER AND LOWER LIMITS TO THE EQUIPMENT SIZE FOR A DESIRED SEPARATION.

THE CALCULATIONAL BASE CONSISTS OF EQUILIBRIUM RELATIONS AND MATERIAL AND ENERGY BALANCES. EQUILIBRIUM DATA FOR MANY BINARY SYSTEMS ARE AVAILABLE AS TABULATIONS OF x VS. y AT CONSTANT TEMPERATURE OR PRESSURE OR IN GRAPHICAL FORM AS ON FIGURE 13.4. OFTEN THEY CAN BE EXTENDED TO OTHER PRESSURES OR TEMPERATURES OR EXPRESSED IN MATHEMATICAL FORM AS EXPLAINED IN SECTION 13.1. SOURCES OF EQUILIBRIUM DATA ARE LISTED IN THE REFERENCES.

GRAPHICAL CALCULATION OF DISTILLATION PROBLEMS OFTEN IS THE MOST CONVENIENT.

### Example 13.3
**Bubblepoint Temperature with the Virial and Wilson Equations**

A mixture of acetone (1) + butanone (2) + ethylacetate (3) with the composition \( x_1 = x_2 = 0.3 \) and \( x_3 = 0.4 \) is at 20 atm. Data for the system such as vapor pressures, critical properties, and Wilson coefficients are given with a computer program in Walas (1985, p. 325). The bubblepoint temperature was found to be 468.7 K. Here only the properties at this temperature will be quoted to show deviations from ideality of a common system. The ideal and real \( K_i \) differ substantially.

<table>
<thead>
<tr>
<th>Component</th>
<th>( \phi^{11} )</th>
<th>( \phi^{12} )</th>
<th>( \phi^{13} )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.84363</td>
<td>0.84353</td>
<td>1.00111</td>
<td>1.00320</td>
</tr>
<tr>
<td>2</td>
<td>0.79219</td>
<td>0.79071</td>
<td>1.00186</td>
<td>1.35567</td>
</tr>
<tr>
<td>3</td>
<td>0.79152</td>
<td>0.78356</td>
<td>1.00785</td>
<td>1.04995</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>( K_{ideal} )</th>
<th>( K_{real} )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.26576</td>
<td>1.25591</td>
<td>0.3779</td>
</tr>
<tr>
<td>2</td>
<td>0.72462</td>
<td>0.98405</td>
<td>0.2961</td>
</tr>
<tr>
<td>3</td>
<td>0.77266</td>
<td>0.81762</td>
<td>0.3270</td>
</tr>
</tbody>
</table>
method, but numerical procedures may be needed for highest accuracy.

**MATERIAL AND ENERGY BALANCES**

In terms of the nomenclature of Figure 13.6, the balances between stage \( n \) and the top of the column are

\[
\begin{align*}
V_{n+1}y_{n+1} &= L_n x_n + D x_D, \\
V_{n+1}h_{n+1} &= L_n h_n + D h_D + Q_e \\
&= L_n h_n + D Q',
\end{align*}
\]

where

\[
Q' = h_D + Q_e / D
\]

is the enthalpy removed at the top of the column per unit of overhead product. These balances may be solved for the liquid/vapor ratio as

\[
\frac{L_n}{V_{n+1}} = \frac{y_{n+1} - x_D}{x_n - x_D} = \frac{Q' - h_{n+1}}{Q' - h_n}
\]

and rearranged as a combined material and energy balance as

\[
\frac{L_n}{V_{n+1}} = \frac{y_{n+1} - x_D}{x_n - x_D} = \frac{Q' - h_{n+1}}{Q' - h_n}
\]

Similarly the balance between plate \( m \) below the feed and the bottom of the column can be put in the form

\[
y_m = \frac{Q^* - H_{m-1}}{Q^* - h_{m+1}} x_{m+1} + \frac{h_{m+1} - H_m}{h_{m+1} - O'} x_B,
\]

where

\[
Q^* = h_B - Q_e / D
\]

is the enthalpy removed at the bottom of the column per unit of bottoms product.

For the problem to be tractable, the enthalpies of the two phases must be known as functions of the respective phase compositions. When heats of mixing and heat capacity effects are small, the enthalpies of mixtures may be compounded of those of the pure components; thus

\[
H = yH_v + (1 - y)H_b,
\]

\[
h = xh_v + (1 - x)h_b,
\]

where \( H_v \) and \( H_b \) are vapor enthalpies of the pure components at their dewpoints and \( h_v \) and \( h_b \) are corresponding liquid enthalpies at their bubblepoints.

Overall balances are

\[
\begin{align*}
F &= D + B, \\
F x_D &= D x_D + B x_B, \\
F h_D &= D h_D + B h_B.
\end{align*}
\]

In the usual distillation problem, the operating pressure, the feed composition and thermal condition, and the desired product compositions are specified. Then the relations between the reflux rates and the number of trays above and below the feed can be found by solution of the material and energy balance equations together with a vapor-liquid equilibrium relation, which may be written in the general form

\[
f(x_n, y_n) = 0.
\]

The procedure starts with the specified terminal compositions and applies the material and energy balances such as Eqs. (13.64) and (13.65) and equilibrium relations alternately stage by stage. When the compositions from the top and from the bottom agree closely, the correct numbers of stages have been found. Such procedures will be illustrated first with a graphical method based on constant molal overflow.

**CONSTANT MOLAL OVERFLOW**

When the molal heats of vaporization of the two components are equal and the tower is essentially isothermal throughout, the molal flow rates \( L_m \) and \( V_m \) remain constant above the feed tray, and \( L_m \) and \( V_m \) likewise below the feed. The material balances in the two sections are

\[
\begin{align*}
\frac{L_m}{V_m} &= \frac{L_{m+1} x_n + D}{V_{m+1} x_D}, \\
\frac{y_m}{V_m} &= \frac{L_{m+1} x_{m+1} - B}{V_{m+1} x_B}.
\end{align*}
\]

The flow rates above and below the feed stage are related by the liquid–vapor proportions of the feed stream, or more generally by the thermal condition of the feed, \( q \), which is the ratio of the heat
required to convert the feed to saturated vapor and the heat of vaporization, that is,

$$q = \frac{(H_F^{\text{sat}} - H_V)}{(\Delta H)_{\text{vap}}}.$$  
(13.79)

For instance, for subcooled feed $q > 1$, for saturated liquid $q = 1$, and for saturated vapor $q = 0$. Upon introducing also the reflux ratio

$$R = \frac{L_n}{D},$$  
(13.80)

the relations between the flow rates become

$$L_m = L_n + qF = RD + qF,$$
(13.81)

$$V_m = L_m - B = RD + qF - B.$$  
(13.82)

Accordingly, the material balances may be written

$$y = \frac{R}{R + 1} x_n + \frac{1}{R + 1} x_D,$$  
(13.83)

$$y_m = \frac{RD + qF}{RD + qF - B} x_{m+1} - \frac{B}{RD + qF - B} x_B.$$  
(13.84)

The coordinates of the point of intersection of the material balance lines, Eqs. (13.83) and (13.84), are located on a "q-line" whose equation is

$$y = \frac{q - 1}{q} x + \frac{1}{q - 1} x_F.$$  
(13.85)

Figure 13.7(b) shows these relations.

---

**Figure 13.7.** Features of McCabe–Thiele diagrams for constant molal overflow. (a) Operating line equations and construction and minimum reflux construction. (b) Orientations of q-lines, with slope $q/(q - 1)$, for various thermal conditions of the feed. (c) Minimum trays, total reflux. (d) Operating trays and reflux. (e) Minimum reflux determined by point of contact nearest $x_D$. 
BASIC DISTILLATION PROBLEM

The basic problem of separation by distillation is to find the numbers of stages below and above the feed stage when the quantities \( x_F, x_D, x_B, F, D, R \) and \( R \) are known together with the phase equilibrium relations. This means that all the terms in Eqs. (13.83) and (13.84) are to be known except the running \( x \)'s and \( y \)'s. The problem is solved by starting with the known compositions, \( x_D \) and \( x_B \), at each end and working one stage at a time towards the feed stage until close agreement is reached between the pairs \((x_m, y_m)\) and \((x_n, y_n)\). The procedure is readily implemented on a programmable calculator; a suitable program for the enriching section is included in the solution of Example 13.4. A graphical solution is convenient and rapid when the number of stages is not excessive, which depends on the scale of the graph attempted.

Figure 13.7 illustrates various aspects of the graphical method. A minimum number of trays is needed at total reflux, that is, with no product takeoff. Minimum reflux corresponds to a separation requiring an infinite number of stages, which is the case when the equilibrium curve and the operating lines touch somewhere. Often this can occur on the \( q \)-line, but another possibility is shown on Figure 13.7(a). The upper operating line passes through point \((x_D, y_D)\) and \(x_D/(R + 1)\) on the lower ordinate. The lower operating line passes through the intersection of the upper with the \( q \)-line and point \((x_B, y_B)\). The feed tray is the one that crosses the intersection of the operating lines on the \( q \)-line. The construction is shown with Example 13.5. Constructions for cases with two feeds and with two products above the feed plate are shown in Figure 13.8.

**Optimum Reflux Ratio.** The reflux ratio affects the cost of the tower, both in the number of trays and the diameter, as well as the cost of operation which consists of costs of heat and cooling supply and power for the reflux pump. Accordingly, the proper basis for choice of an optimum reflux ratio is an economic balance. The sizing and economic factors are considered in a later section, but reference may be made now to the results of such balances summarized in Table 13.3. The general conclusion may be drawn that the optimum reflux ratio is about 1.2 times the minimum, and also that the number of trays is about 2.0 times the minimum. Although these conclusions are based on studies of systems with nearly ideal vapor-liquid equilibria near atmospheric pressure, they are often applied more generally, sometimes as a starting basis for more detailed analysis of reflux and tray requirements.

**Azeotropic and Partially Miscible Systems.** Azeotropic mixtures are those whose vapor and liquid equilibrium compositions are identical. Their \( x-y \) lines cross or touch the diagonal. Partially miscible substances form a vapor phase of constant composition over the entire range of two-phase liquid compositions; usually the horizontal portion of the \( x-y \) plot intersects the diagonal, but those of a few mixtures do not, notably those of mixtures of methylcyclohexane and phenol with water. Separation of azeotropic mixtures sometimes can be effected in several towers at different pressures, as illustrated by Example 13.6 for ethanol-water mixtures. Partially miscible constant boiling mixtures usually can be separated with two towers and a condensate phase separator, as done in Example 13.7 for \( n \)-butanol and water.

**UNEQUAL MOLAL HEATS OF VAPORIZATION**

Molal heats of vaporization often differ substantially, as the few data of Table 13.4 suggest. When sensible heat effects are small, however, the condition of constant molal overflow still can be preserved by adjusting the molecular weight of one of the components, thus making it a pseudocomponent with the same molal heat of vaporization as the other substance. The \( x-y \) diagram and all of the compositions also must be converted to the adjusted molecular weight. Example 13.5 compares tray requirements on the basis of true and adjusted molecular weights for the separation of ethanol and acetic acid whose molal heats of vaporization are in the ratio 1.63. In this case, the assumption of constant molal overflow with the true molecular weight overestimates the tray requirements. A more satisfactory, but also more laborious, solution of the problem takes the enthalpy balance into account, as in the next section.

**MATERIAL AND ENERGY BALANCE BASIS**

The enthalpies of mixtures depend on their compositions as well as the temperature. Enthalpy-concentration diagrams of binary mixtures, have been prepared in general form for a few important systems. The most comprehensive collection is in Landolt-Börnstein [1V4b, 188, (1972)] and a few diagrams are in Chemical Engineers Handbook (1984), for instance, of ammonia and water, of ethanol and water, of oxygen and nitrogen, and some others. Such diagrams are named after Merkel.

For purposes of distillation calculations, a rough diagram of saturated vapor and liquid enthalpy concentration lines can be drawn on the basis of pure component enthalpies. Even with such a rough diagram, the accuracy of distillation calculation can be much superior to those neglecting enthalpy balances entirely. Example 13.8 deals with preparing such a Merkel diagram.

A schematic Merkel diagram and its application to distillation calculations is shown in Figure 13.9. Equilibrium compositions of vapor and liquid can be indicated on these diagrams by tie-lines, but are more conveniently used with associated \( x-y \) diagrams as shown with this figure. Lines passing through point \( P \) with coordinates \((x_P, Q')\) are represented by Eq. (13.69) and those through point \( Q \) with coordinates \((x_Q, Q')\) by Eq. (13.70). Accordingly, any line through \( P \) to the right of \( PQ \) intersects the vapor and liquid enthalpy lines in corresponding \((x_m, y_m)\) and similarly the intersections of random lines through \( Q \) determine corresponding \((x_m+1, y_m+1)\). When these coordinates are transferred to the \( x-y \) diagram, they determine usually curved operating lines. Figure 13.9(b) illustrates the stepping off process for finding the number of stages. Points \( P, F, \) and \( Q \) are collinear.

The construction for the minimum number of trays is independent of the heat balance. The minimum reflux corresponds to a minimum condenser load \( Q \) and hence to a minimum value of \( Q' = h_P + Q/D \). It can be found by trial location of point \( P \) until an operating curve is found that touches the equilibrium curve.

**ALGEBRAIC METHOD**

Binary systems of course can be handled by the computer programs devised for multicomponent mixtures that are mentioned later. Constant molal overflow cases are handled by binary computer programs such as the one used in Example 13.4 for the enriching section which employ repeated alternate application of material balance and equilibrium stage-by-stage. Methods also are available that employ closed form equations that can give desired results quickly for the special case of constant or suitable average relative volatility.

**Minimum Trays.** This is found with the Fenske–Underwood equation,

\[
N_m = \frac{\ln [x_D/(1-x_D)/x_B(1-x_B)]}{\ln a}
\]

(13.86)
13.4. BINARY DISTILLATION

Batch Distillation of Chlorinated Phenols

A mixture of chlorinated phenols can be represented as an equivalent binary with 90% 2,4-dichlorophenol (DCP) and the balance 2,4,6-trichlorophenol with a relative volatility of 3.268. Product purity is required to be 97.5% of the lighter material, and the residue must be below 20% of 2,4-DCP. It is proposed to use a batch distillation with 10 theoretical stages. Vaporization rate will be maintained constant.

a. For operation at constant overhead composition, the variations of reflux ratio and distillate yield with time will be found.

The bottom compositions at a particular value of $R$ are found by successive applications of the equations

$$y_n = \frac{a x_n}{1 + (a - 1)x_n}$$

$$R_n/(R_n + 1) = 0.975 - 0.9671$$

$$x_{n+1} = \frac{y_n}{R + 1}$$

With $q = 1$ and $x_n = 0.9$,

$$y_n = \frac{3.268(0.9)}{1 + 2.268(0.9)} = 0.9671$$

$$x_{n+1} = \frac{0.975 - 0.9671}{0.975 - 0.9} = 0.1051$$

$$R_n = 0.1174$$

The bottom compositions at a particular value of $R$ are found by successive applications of the equations

$$x_n = \frac{y_n}{a - (a - 1) y_n}$$

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

Start with $y_1 = y_D = 0.975$. The calculations are performed with the given computer program and the results are tabulated. The values of $L/L_0$ are found by material balance:

$$L/L_0 = (0.975 - 0.900)/(0.975 - x_L)$$

The values of $V/L_0$ are found with Eq. (13.111).

$$V/L_0 = (y_D - x_L)\int_{x_L}^{x_D} \frac{R + 1}{R} \, dx_L = (0.975 - 0.900) \int_{x_L}^{x_D} \frac{R + 1}{0.9(0.975 - x_L)} \, dx_L$$

From the tabulation, the cumulative vaporization is

$$V/L_0 = 1.2566$$

The average reflux ratio is

$$\bar{R} = \frac{V - D}{D} = \frac{V}{L_0} - 1 = \frac{V/L_0 - 1}{1/L_0} = 1.2566$$

$$1 - 0.0968 - 1 = 0.3913.$$
**Example 13.4** (continued)

This is less than the constant reflux, \( R = 0.647 \), to be found in part b.

At constant vaporization rate, the time is proportional to the cumulative vapor amount:

\[
\frac{t}{\tau} = \frac{V}{V_{\text{final}}} = \frac{V/L_0}{1.2566}. 
\]

Also

\[
D/L_0 = 1 - L/L_0. 
\]

From these relations and the tabulated data, \( D/L_0 \) and \( R \) are plotted against reduced time \( t/\tau \).

b. At constant reflux: A reflux ratio is found by trial to give an average overhead composition \( y_0 = 0.975 \) and a residue composition \( x_L = 0.2 \). The average overhead composition is found with material balance

\[
y_D = \frac{[x_L - (L/L_0)x_L]}{(1 - L/L_0)} = \frac{x_L}{y_0 - x_L}. 
\]

The value of \( L/L_0 \) is calculated as a function of \( y_D \) from

\[
\ln \frac{L}{L_0} = \frac{x_L}{y_0 - x_L} \cdot \frac{1}{\ln y_0 - x_L}. 
\]

At a trial value of \( R \), values of \( x_{\text{cap}} \) are found for a series of assumed \( y_0 \)'s until \( x_{\text{cap}} \) equals or is less than 0.20. The given computer program is based on Eqs. (1) and (2). The results of two trials and interpolation to the desired bottoms composition, \( x_L = 0.200 \), are

\[
R \quad 0.6 \quad 0.7 \quad 0.647 \\
x_L \quad 0.2305 \quad 0.1662 \quad 0.200 \\

<table>
<thead>
<tr>
<th>Reflux ratio ( R )</th>
<th>( y_0 )</th>
<th>( x_L )</th>
<th>1/(( y_0 - x_L ))</th>
<th>( L/L_0 )</th>
<th>( y_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R = 0.6 )</td>
<td>0.9900</td>
<td>0.9000</td>
<td>10.2035</td>
<td>0.9900</td>
<td>0.9000</td>
</tr>
<tr>
<td>( R = 0.7 )</td>
<td>0.9995</td>
<td>0.9000</td>
<td>10.1051</td>
<td>0.9995</td>
<td>0.9000</td>
</tr>
</tbody>
</table>

10 ! Example 13.9. Distillation at constant reflux

A=3.268

30 OPTION BASE 1

40 DIM X(10), Y(11)

50 INPUT R ! reflux ratio

60 INPUT Y(1)

70 FOR N=1 TO 10

80 X(N)=1/(A+Y(N)-A+1)

90 Y(N+1)=1/(R+1)*X(R)*X(N)+Y(1))

100 NEXT N

110 I=1/(Y(1)-X(10))

120 DISP USING 130 ; Y(1), X(10), I

130 IMAGE .DDDD, 2X, .DDDD, 2X, DD.

140 GOTO 60

150 END
EXAMPLE 13.5.
Distillation of Substances with Widely Different Molal Heats of Vaporization

The molal heats of vaporization of ethanol and acetic acid are 9225 and 5663 cal/g mol. A mixture with ethanol content of $x_F = 0.50$ is to be separated into products with $x_B = 0.05$ and $x_D = 0.95$. Pressure is 1 atm, feed is liquid at the boiling point, and the reflux ratio is to be 1.3 times the minimum. The calculation of tray requirements is to be made with the true molecular weight, 60.05, of acetic acid and with adjustment to make the apparent molal heat of vaporization the same as that of ethanol, which becomes

$$60.05\frac{9225}{5663} = 98.14.$$ 

The adjusted mol fractions, $x'$ and $y'$, are related to the true ones by

$$x' = \frac{x}{x + 0.6119(1 - x)}, \quad y' = \frac{y}{y + 0.6119(1 - y)}.$$

The experimental and converted data are tabulated following and plotted on McCabe–Thiele diagrams. The corresponding compositions involved in this distillation are:

| $x_B$ | 0.05 | $x_B'$ | 0.0792 |
| $x_F$ | 0.50 | $x_F'$ | 0.6204 |
| $x_D$ | 0.95 | $x_D'$ | 0.9688 |

In terms of the true molecular weight, minimum reflux is given by

$$x_D'/(R_{min} + 1) = 0.58,$$

whence

$$R_m = 0.6379, \quad R = 1.3(0.6379) = 0.8293,$$

$$x_D/(R + 1) = 0.5193, \quad x_D'/R + 1 = 0.5296.$$

Taking straight operating lines in each case, the numbers of trays are

$$N = 11.0 \quad \text{with true molecular weight of acetic acid}, \quad N' = 9.8 \quad \text{with adjusted molecular weight}.$$ 

In this case it appears that assuming straight operating lines, even though the molal heats of vaporization are markedly different, results in overestimation of the number of trays needed for the separation.
Figure 13.8. Operating and q-line construction with several feeds and top products. (a) One feed and one overhead product. (b) Two feeds and one overhead product. (c) One feed and two products from above the feed point.
TABLE 13.3. Economic Optimum Reflux Ratio for Typical Petroleum Fraction Distillation near 1 atm*

<table>
<thead>
<tr>
<th>Factor for optimum reflux</th>
<th>Factor for optimum trays</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f = \left( \frac{R_m}{R_{opt}} \right) - 1 )</td>
<td>( \frac{N_m}{N_{opt}} )</td>
</tr>
<tr>
<td>( R_m = \left( 1 + f \right) R_{opt} )</td>
<td>( R_m = \left( 1 + \frac{N_m}{N_{opt}} \right) R_{opt} )</td>
</tr>
</tbody>
</table>

| \( N_m = 10 \) | \( N_m = 20 \) | \( N_m = 50 \) |
| \( R_m \) | \( R_m \) | \( R_m \) |
| \( R_m \) | \( R_m \) | \( R_m \) |

<table>
<thead>
<tr>
<th>Base case</th>
<th>1</th>
<th>3</th>
<th>10</th>
<th>1</th>
<th>3</th>
<th>10</th>
<th>1</th>
<th>3</th>
<th>10</th>
<th>1</th>
<th>3</th>
<th>10</th>
<th>1</th>
<th>3</th>
<th>10</th>
<th>1</th>
<th>3</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Payout time 1 yr</td>
<td>0.20</td>
<td>0.12</td>
<td>0.10</td>
<td>0.24</td>
<td>0.17</td>
<td>0.16</td>
<td>0.31</td>
<td>0.21</td>
<td>2.4</td>
<td>2.3</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Payout time 5 yr</td>
<td>0.24</td>
<td>0.14</td>
<td>0.12</td>
<td>0.28</td>
<td>0.20</td>
<td>0.17</td>
<td>0.37</td>
<td>0.24</td>
<td>2.2</td>
<td>2.1</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam cost $0.30/M lb</td>
<td>0.13</td>
<td>0.09</td>
<td>0.07</td>
<td>0.17</td>
<td>0.13</td>
<td>0.10</td>
<td>0.22</td>
<td>0.15</td>
<td>2.7</td>
<td>2.5</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam cost $0.75/M lb</td>
<td>0.22</td>
<td>0.13</td>
<td>0.11</td>
<td>0.27</td>
<td>0.16</td>
<td>0.14</td>
<td>0.35</td>
<td>0.22</td>
<td>2.3</td>
<td>2.1</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( G_0 = 50 ) lb mole/(hr)(sqft)</td>
<td>0.18</td>
<td>0.11</td>
<td>0.09</td>
<td>0.21</td>
<td>0.13</td>
<td>0.11</td>
<td>0.29</td>
<td>0.19</td>
<td>2.5</td>
<td>2.3</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The "base case" is for payout time of 2 yr, steam cost of $0.50/1000 lb, vapor flow rate \( G_0 = 15 \) lb mol/(hr)(sqft).

Minimum Reflux. Underwood's method employs two relations. First an auxiliary parameter \( \theta \) is found in the range \( 1 < \theta < \alpha \) by solving

\[
\frac{\alpha x_F}{\alpha - \theta} + \frac{1 - x_F}{1 - \theta} = 1 - q
\]

or

\[
(1 - q) \theta^2 + [(\alpha - 1)x_F + q(\alpha + 1) - \alpha] \theta - \alpha q = 0,
\]

or in two important special cases:

when \( q = 0, \quad \theta = \alpha - (\alpha - 1)x_F, \quad (13.89) \)

when \( q = 1, \quad \theta = \frac{\alpha}{(\alpha - 1)x_F + 1}. \quad (13.90) \)

Then \( R_m \) is found by substitution into

\[
R_m = 1 + \frac{\alpha x_F}{\alpha - \theta} + \frac{1 - x_F}{1 - \theta}, \quad (13.91)
\]

Formulas for the numbers of trays in the enriching and stripping sections at operating reflux also are due to Underwood (Trans. Inst. Chem. Eng. 10, 112-152, 1932). For above the feed, these groups of terms are defined:

\[
K_1 = L_m/V_m = R_1(R + 1). \quad (13.92)
\]

Then the relation between the compositions of the liquid on tray 1

EXAMPLE 13.6

Separation of an Azeotropic Mixture by Operation at Two Pressure Levels

At atmospheric pressure, ethanol and water form an azetrope with composition \( x = 0.846 \), whereas at 95 Torr the composition is about \( x = 0.94 \). As the diagram shows, even at the lower pressure the equilibrium curve hugs the \( x = y \) line. Accordingly, a possibly feasible separation scheme may require three columns, two operating at 760 Torr and the middle one at 95 Torr, as shown on the sketch. The basis for the material balance used is that 99% of the ethanol fed to any column is recovered, and that the ethanol-rich products from the columns have \( x = 0.8, 0.9, \) and 0.995, resp.

Although these specifications lead to only moderate tray and reflux requirements, in practice distillation with only two towers and the assistance of an azeotropic separating agent such as benzene is found more economical. Calculation of such a process is made by Robinson and Gilliland (1950, p. 313).
EXAMPLE 13.6—(continued)

Ethanol-water vapor-liquid equilibria at 95 and 760 Torr.

EXAMPLE 13.7
Separation of a Partially Miscible Mixture

Water and n-butanol in the concentration range of about 50–98.1 mol % water form two liquid phases that boil at 92.7°C at one atm. On cooling to 40°C, the hetero-azeotrope separates into phases containing 53 and 98 mol % water.

A mixture containing 12 mol % water is to be separated by distillation into products with 99.5 and 0.5 mol % butanol. The accompanying flowsketch of a suitable process utilizes two columns with condensing-subcooling to 40°C. The 53% saturated solution is refluxed to the first column, and the 98% is fed to the second column. The overhead of the second column contains a small amount of butanol that is recycled to the condenser for recovery. The recycle material balance is shown with the sketch.

The three sets of vapor–liquid equilibrium data appearing on the x–y diagram show some disagreement, so that great accuracy cannot be expected from determination of tray requirements, particularly at the low water concentrations. The upper operating line in the first column is determined by the overall material balance so it passes through point (0.995, 0.995), but the initial point on the operating line is at \( x = 0.53 \), which is the composition of the reflux. The construction is shown for 50% vaporized feed. That result and those for other feed conditions are summarized:

<table>
<thead>
<tr>
<th>( q )</th>
<th>( R_m )</th>
<th>( R_m = 1.3R_m )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.02</td>
<td>2.62</td>
<td>12</td>
</tr>
<tr>
<td>0.5</td>
<td>5.72</td>
<td>7.44</td>
<td>8</td>
</tr>
<tr>
<td>0</td>
<td>9.70</td>
<td>12.81</td>
<td>6</td>
</tr>
</tbody>
</table>

| Water | 12 | 0.44 | 18.4139 | 0.7862 | 19.1801 | 6.8539 | 12.3262 | 11.56 |
| Butanol | 88 | 87.94 | 6.1379 | 0.1916 | 6.3295 | 6.0779 | 0.2516 | 0.06 |
| % Water | 12 | 0.5 | 75 | 80 | 75.19 | 53 | 98 | 99.5 |
EXAMPLE 13.7—(continued)

In the second column, two theoretical trays are provided and are able to make a 99.6 mol % water waste, slightly better than the 99.5 specified. The required \( L/V \) is calculated from compositions read off the diagram:

\[
L/V = (0.966 - 0.790)/(0.996 - 0.981) = 13.67.
\]

If live steam were used instead of indirect heat, the bottoms concentration would be higher in water. This distillation is studied by Billet (1979, p. 216). Stream compositions are given below the flowsketch.

The number of trays above the feed plus the feed tray is obtained after substituting the feed composition \( x_F \) for \( x_a \).

Below the feed,

\[
K_2 = V_m/L_m = (RD + qF - B)/(RD + qF),
\]

\[
\phi_2 = (\alpha - 1)/(K_2\alpha - 1).
\]

The relation between the compositions at the bottom and at tray \( m \) is

\[
(K_2\alpha)^n = 1/x_m - \phi_2 / 1/x_m - \phi_2
\]

The number of trays below the feed plus the feed tray is found after replacing \( x_m \) by \( x_F \). The number of trays in the whole column then is

\[
N = m + n - 1.
\]

Example 13.9 applies these formulas.
TABLE 13.4. Molal Heats of Vaporization at Their Normal Boiling Points of Some Organic Compounds That May Need To Be Separated from Water

<table>
<thead>
<tr>
<th>Compound</th>
<th>NBP (°C)</th>
<th>cal/g mol</th>
<th>Molecular Weight</th>
<th>True Adjusted*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
<td>5717</td>
<td>18.02</td>
<td>18.02</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>118.3</td>
<td>5663</td>
<td>60.05</td>
<td>103.04</td>
</tr>
<tr>
<td>Acetone</td>
<td>56.5</td>
<td>6952</td>
<td>58.08</td>
<td>81.18</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>197</td>
<td>11860</td>
<td>62.07</td>
<td>50.85</td>
</tr>
<tr>
<td>Phenol</td>
<td>181.4</td>
<td>9730</td>
<td>94.11</td>
<td>94.0</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>97.8</td>
<td>9982</td>
<td>60.09</td>
<td>58.49</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.4</td>
<td>9295</td>
<td>46.07</td>
<td>48.37</td>
</tr>
</tbody>
</table>

*The adjustment of molecular weight is to make the molal heat of vaporization the same as that of water.

13.5. BATCH DISTILLATION

A batch distillation plant consists of a still or reboiler, a column with several trays, and provisions for reflux and for product collection. Figure 13.10(c) is a typical equipment arrangement with controls. The process is applied most often to the separation of mixtures of several components at production rates that are too small for a continuous plant of several columns equipped with individual reboilers, condensers, pumps, and control equipment.

The number of continuous columns required is one less than the number of components or fractions to be separated. Operating conditions of a typical batch distillation making five cuts on an 8-hr cycle are in Figure 13.11.

Operation of a batch distillation is an unsteady state process whose mathematical formulation is in terms of differential equations since the compositions in the still and of the holdups on individual trays change with time. This problem and methods of solution are treated at length in the literature, for instance, by Holland and Liapis (Computer Methods for Solving Dynamic Separation Problems, 1983, pp. 177–213). In the present section, a simplified analysis will be made of batch distillation of binary mixtures in columns with negligible holdup on the trays. Two principal modes of operating batch distillation columns may be employed:

1. With constant overhead composition. The reflux ratio is adjusted continuously and the process is discontinued when the concentration in the still falls to a desired value.

2. With constant reflux. A reflux ratio is chosen that will eventually produce an overhead of desired average composition and a still residue also of desired composition.

Both modes usually are conducted with constant vaporization rate at an optimum value for the particular type of column construction. Figure 13.10 represents these modes on McCabe–Thiele diagrams. Small scale distillations often are controlled

**EXAMPLE 13.8**

Enthalpy-Concentration Lines of Saturated Vapor and Liquid of Mixtures of Methanol and Water at a Pressure of 2 atm

A basis of 0°C is taken. Enthalpy data for methanol are in Chemical Engineers’ Handbook (McGraw-Hill, New York, 1984, p. 3.204) and for water in Keenan et al. (Steam Tables: SI Units, Wiley, New York, 1978).

Methanol: \( T = 82.8°C \)
\[ H_v = 10,010 \text{ cal/g mol}, \]
\[ h_v = 1882 \text{ cal/g mol}, \]
\[ \Delta H_v = 8128 \text{ cal/g mol}, \]
\[ C_p = 22.7 \text{ cal/g mol °C}. \]

Water: \( T = 120.6°C \)
\[ H_v = 11,652 \text{ cal/g mol}, \]
\[ h_v = 2180 \text{ cal/g mol}, \]
\[ \Delta H_v = 9472 \text{ cal/g mol}, \]

Experimental \( x–y \) data are available at 1 and 3 atm (Hirata, 1976, #517, #519). Values at 2 atm can be interpolated by eye. The lines show some overlap. Straight lines are drawn connecting enthalpies of pure vapors and enthalpies of pure liquids. Shown is the tie line for \( x = 0.5, y = 0.77 \).
13.5. BATCH DISTILLATION

Random lines to locate points on the operating lines

Figure 13.9. Combined McCabe-Thiele and Merkel enthalpy-concentration diagrams for binary distillation with heat balances. (a) Showing key lines and location of representative points on the operating lines. (b) Completed construction showing determination of the number of trays by stepping off between the equilibrium and operating lines.

Manually, but an automatic control scheme is shown in Figure 13.10(c). Constant overhead composition can be assured by control of temperature or directly of composition at the top of the column. Constant reflux is assured by flow control on that stream. Sometimes there is an advantage in operating at several different reflux rates at different times during the process, particularly with multicomponent mixtures as on Figure 13.11.

MATERIAL BALANCES

Assuming negligible holdup on the trays, the differential balance between the amount of overhead, \(dD\), and the amount \(L\) remaining in the still is

\[
y_D \, dD = -y_L \, dL = -d(Lx_L) = -L \, dx_L - x_L \, dL,
\]

which is integrated as

\[
\ln(L/L_0) = \int_{x_L}^{x_{L_0}} \frac{1}{y_D - x_L} \, dx_L.
\]

The differences \(y_D - x_L\) depend on the number of trays in the column, the reflux ratio, and the vapor-liquid equilibrium relationship. For constant molal overflow these relations may be taken as

\[
y_{n+1} = \frac{R}{R+1} x_n + \frac{1}{R+1} y_D,
\]

\[
y_n = f(x_n).
\]

When the overhead composition is constant, Eq. 13.103 is integrable directly, but the same result is obtained by material balance,

\[
\frac{L}{L_0} = \frac{y_D - x_{L_0}}{y_D - x_L}.
\]

With variable overhead composition, the average value is represented by the same overall balance,

\[
\bar{y}_D = \frac{x_{L_0} - \frac{L}{L_0}x_L}{1 - \frac{L}{L_0}},
\]
**EXAMPLE 13.9**

**Algebraic Method for Binary Distillation Calculation**

An equimol binary mixture which is half vaporized is to be separated with an overhead product of 99% purity and 95% recovery. The relative volatility is 1.3. The reflux is to be selected and the number of trays above and below the feed are to be found with the equations of Section 13.4.6.

The material balance is

<table>
<thead>
<tr>
<th>Component</th>
<th>F</th>
<th>D</th>
<th>x₀</th>
<th>B</th>
<th>xₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>49.50</td>
<td>0.99</td>
<td>0.50</td>
<td>0.0100</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.48</td>
<td>0.01</td>
<td>49.52</td>
<td>0.9900</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>49.98</td>
<td>50.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Minimum no. of trays,

\[ N_m = \frac{\ln(0.99/0.01)(0.99/0.01)}{\ln 1.3} = 35.03. \]

For minimum reflux, by Eqs. (13.88) and (13.91),

\[ \theta^2 = 1.3, \]

\[ \theta = 1.1402, \]

but it is also necessary to know what reflux will result in the desired overhead and residue compositions.

For constant overhead composition at continuously varied reflux ratios, the total vaporization is found as follows. The differential balance is

\[ dD = dV - dL = (1 - dL/dV) dV \]  
(13.108)

The derivative \( dL/dV \) is the slope of the operating line so that

\[ 1 - \frac{dL}{dV} = 1 - \frac{R}{R + 1} = \frac{1}{R + 1}. \]  
(13.109)

Substitution from Eqs. (13.103), (13.106), and (13.109) into Eq. (13.108) converts this into

\[ dV = \frac{L_0(x_L - \bar{y}_D)}{(x_L - \bar{y}_D)^2} \frac{R + 1}{x_L - \bar{y}_D} dx_L, \]  
(13.110)

from which the total amount of vapor generated up to the time the residue composition becomes \( x_L \) is

\[ V = \frac{L_0(x_L - \bar{y}_D)}{(x_L - \bar{y}_D)^2} \int_{x_L}^{\bar{y}_D} \frac{R + 1}{x_L - \bar{y}_D} dx_L. \]  
(13.111)

**Figure 13.10.** Batch distillation: McCabe–Thiele constructions and control modes. (a) Construction for constant overhead composition with continuously adjusted reflux rate. (b) Construction at constant reflux at a series of overhead compositions with an objective of specified average overhead composition. (c) Instrumentation for constant vaporization rate and constant overhead composition. For constant reflux rate, the temperature or composition controller is replaced by a flow controller.
At constant vaporization rate the time is proportional to the amount of vapor generated, or

\[ t = \frac{V}{V_{\text{total}}} \]  \hspace{1cm} (13.112)

Hence the reflux ratio, the amount of distillate, and the bottoms composition can be related to the fractional distillation time. This is done in Example 13.4, which studies batch distillations at constant overhead composition and also finds the suitable constant reflux ratio that enables meeting required overhead and residue specifications. Although the variable reflux operation is slightly more difficult to control, this example shows that it is substantially more efficient thermally—the average reflux ratio is much lower—than the other type of operation.

Equation (13.97) can be used to find the still composition—\( x_n \) in that equation—at a particular reflux ratio in a column-reboiler combination with \( n \) stages. Example 13.4 employs instead a computer program with Equations (13.104) and (13.105). That procedure is more general in that a constant relative volatility need not be assumed, although that is done in this particular example.

13.6 MULTICOMPONENT SEPARATION: GENERAL CONSIDERATIONS

A tower comprised of rectifying (above the feed) and stripping (below the feed) sections is capable of making a more or less sharp separation between two products or pure components of the mixture, that is, between the light and heavy key components. The light key is the most volatile component whose concentration is to be controlled in the bottom product and the heavy key is the least volatile component whose concentration is to be controlled in the overhead product. Components of intermediate volatilities whose distribution between top and bottom products is not critical are called distributed keys. When more than two sharply separated products are needed, say \( n \) top and bottom products, the number of columns required will be \( n - 1 \).

In some cases it is desirable to withdraw sidestreams of intermediate compositions from a particular column. For instance, in petroleum fractionation, such streams may be mixtures of suitable boiling ranges or which can be made of suitable boiling range by stripping in small auxiliary columns. Other cases where intermediate streams may be withdrawn are those with minor but critical impurities that develop peak concentrations at these locations in the column because of inversion of volatility as a result of concentration gradient. Thus, pentyne-1 in the presence of \( n \)-pentane in an isoprene-rich \( C_5 \) cracked mixture exhibits this kind of behavior and can be drawn off as a relative concentrate at an intermediate point. In the rectification of fermentation alcohol, whose column profile is shown in Figure 13.12(a), undesirable esters and higher alcohols concentrate at certain positions because their solubilities are markedly different in high and low concentrations of ethanol in water, and are consequently withdrawn at these points.

Most distillations, however, do not develop substantial concentration peaks at intermediate positions. Figure 13.12(b) is of normal behavior.

SEQUENCING OF COLUMNS

The number \( n \) of top and bottom products from a battery of \( n - 1 \) columns can be made in several different ways. In a direct method, the most volatile components are removed one-by-one as overheads in successive columns with the heaviest product as the bottoms of the last column. The number of possible ways of separating components goes up sharply with the number of products, from two arrangements with three products to more than 100 with seven products. Table 13.5 identifies the five possible arrangements for

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Figure 13.10—(continued)

Figure 13.11. Operation of a batch distillation with five cuts.
Figure 13.12. Concentration profiles in two kinds of distillations. (a) Purifying column for fermentation alcohol; small streams with high concentrations of impurities are withdrawn as sidestreams (Robinson and Gilliland, Elements of Fractional Distillation, McGraw-Hill, New York, 1939 edition). (b) Typical concentration profiles in separation of light hydrocarbon mixtures when no substantial inversions of relative volatilities occur (Van Winkle, Distillation, McGraw-Hill, New York, 1967).

separating four components with three columns. Such arrangements may differ markedly in their overall thermal and capital cost demands, so in large installations particularly a careful economic balance may be needed to find the best system.

TABLE 13.5. The Five Possible Sequences for the Separation of Four Components ABCD by Three Columns

<table>
<thead>
<tr>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ovhd</td>
<td>Btms</td>
<td>Ovhd</td>
</tr>
<tr>
<td>A</td>
<td>BCD</td>
<td>B</td>
</tr>
<tr>
<td>A</td>
<td>BCD</td>
<td>BC</td>
</tr>
<tr>
<td>AB</td>
<td>CD</td>
<td>A</td>
</tr>
<tr>
<td>ABC</td>
<td>D</td>
<td>A</td>
</tr>
<tr>
<td>ABC</td>
<td>D</td>
<td>AB</td>
</tr>
</tbody>
</table>

The literature of optimum sequencing of columns is referenced by King (1980, pp. 711-720) and Henley and Seader (1981, pp. 527-555). For preliminary selection of near optimal sequences, several rules can be stated as guides, although some conflicts may arise between recommendations based on the individual rules. Any recommended cases then may need economic evaluations.

1. Perform the easiest separation first, that is, the one least demanding of trays and reflux, and leave the most difficult to the last.
2. When neither relative volatility nor concentration in the feed varies widely, remove the components one-by-one as overhead products.
3. When the adjacent ordered components in the process feed vary widely in relative volatility, sequence the splits in the order of decreasing relative volatility.
4. When the concentrations in the feed vary widely but the relative
volatilities do not, sequence the splits to remove components in the order of decreasing concentration in the feed.

**NUMER OF FREE VARIABLES**

The performance of a given column or the equipment requirements for a given separation are established by solution of certain mathematical relations. These relations comprise, at every tray, heat and material balances, vapor–liquid equilibrium relations, and mol fraction constraints. In a later section, these equations will be stated in detail. For now, it can be said that for a separation of \( C \) components in a column of \( n \) trays, there still remain a number, \( C + 6 \), of variables besides those involved in the cited equations. These must be fixed in order to define the separation problem completely. Several different combinations of these \( C + 6 \) variables may be feasible, but the ones commonly fixed in column operation are the following:

<table>
<thead>
<tr>
<th>Item</th>
<th>Name</th>
<th>Number of Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>feed rate</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>feed composition</td>
<td>( C - 1 )</td>
</tr>
<tr>
<td>3</td>
<td>feed enthalpy</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>ratio of overhead and feed rates</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>reflux enthalpy</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>reflux ratio, L/D or L/V</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>number of trays</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>column pressure</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( C + 6 )</td>
<td></td>
</tr>
</tbody>
</table>

A common alternate specification is of the overhead and bottoms compositions expressed through distribution of the keys (two variables) as a replacement of items 4 and 7.

**13.7. ESTIMATION OF REFLUX AND NUMBER OF TRAYS** *(FENSKE–UNDERWOOD–GILLILAND METHOD)*

The first step in the design of distillation equipment is specification of the required distribution of light and heavy key components. Then the specific operating conditions and equipment size are established, ultimately on the basis of an economic balance or simply by exercise of judgment derived from experience. The design parameters that need to be determined include intermediate ones such as limiting reflux and trays that are needed for establishing a working design. These design parameters are the following:

1. Minimum number of theoretical trays,
2. Distribution of nonkeys between the overhead and bottoms products,
3. Minimum reflux,
4. Operating reflux,
5. Number of theoretical trays,
6. Location of the feed tray,
7. Tray efficiencies.

In packed towers, the variation of conditions from top to bottom is continuous and not interrupted as at trays. Nevertheless, it is convenient to speak of packing heights equivalent to a theoretical tray (HETU), so that tray tower theory can be applied to the design of packed towers.

All of the values of this list can be established at least approximately by rapid shortcut methods. In some instances such values may be useful as final ones, but ordinarily they are for exploratory purposes or as a starting basis for a computer design. Computer design of fractionation is an iterative process which depends for rapid convergence on good starting estimates of the principal quantities.

The background of shortcut methods is well treated in the books of King (1980) and Henley and Seader (1981). Here attention will be directed to application of the techniques. These shortcut methods assume constant molal overflow in the rectifying and stripping zones and constant relative volatilities, which may be taken at the conditions of the feed tray or as a geometric mean of the values at the top and bottom of the column. Since the top conditions are not known completely in advance, evaluation of a mean relative volatility is an iterative process that can be started with the value at the feed tray or at the feed condition. Particular modes of variation of \( \alpha \) sometimes are assumed. The method of Winn assumes that the vaporization equilibrium ratios vary as

\[
K_{1k} = \beta K^0_{hk}
\]

or

\[
\alpha = K_{1k}/K_{hk} = \beta K^{0-1}_{hk}
\]

The constants \( \beta \) and \( \delta \) for the conditions of the tower are deduced from log–log plots of \( K \)'s, which usually are available for hydrocarbons and natural gas constituents but can be evaluated from

\[
K = \gamma^{p_{max}}/P,
\]

with activity coefficient \( \gamma \) of unity if no better information is known.

**MINIMUM TRAYS**

This is found from the relative volatility and the distribution of the keys between the overhead and bottoms by the Underwood–Fenske equation

\[
N_m = \frac{\ln[(x_P/x_P)_1k/(x_P/x_P)_ak]}{\ln(\alpha_{1k}/\alpha_{ak})} = \frac{\ln[(d/b)_{1k}/(d/b)_{ak}]}{\ln(\alpha_{1k}/\alpha_{ak})}.
\]

In terms of the variation of VERs according to Eq. (13.113),

\[
N_m = \frac{\ln[(d/b)_{1k}/(d/b)_{ak}^{\pm \gamma}]}{\ln \beta}
\]

**DISTRIBUTION OF NONKEYS**

A convenient approximation is that the distributions of nonkeys require the minimum number of trays as given by Eq. (13.116). Designating the nonkey by subscript \( nk \), that equation becomes

\[
\ln(d/b)_{nk} = \ln(d/b)_{1k} + N_m \ln(\alpha_{nk}/\alpha_{1k})
\]

or

\[
(d/b)_{nk} = (d/b)_{1k}(\alpha_{nk}/\alpha_{1k})^{N_m}.
\]

The distribution of nonkeys actually depends somewhat on the reflux ratio. For instance, in the case of Example 13.10, the distributions at minimum trays (total reflux) and minimum reflux are substantially different. Often it turns out, however, that the distributions predicted by Eq. (13.119) are close to those at finite reflux whenever \( R \) is near 1.2\( R_m \), which is often near the economic value for the reflux ratio. Further discussion of this topic is by Hengstebeck (Distillation, 1961) and Stupin and Lockhart (1968) whose work is summarized by King (1980, p. 434). Knowledge of the complete distribution is needed for estimation of top and bottom temperatures and for determination of the minimum reflux by the method to be cited.
Example 13.10
Shortcut Design of Multicomponent Fractionation

A mixture of the given composition and relative volatilities has a thermal condition \( q = 0.8 \) and a pressure of 10 atm. It is to be fractionated so that 98% of component C and 1% of component E will appear in the overhead. The tray and reflux requirements are to be found. In the following table, the quantities in brackets are calculated in the course of the solution. \( f_i, d_i, \) and \( b_i \) are the mols of component \( i \) per mol of total feed.

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( f )</th>
<th>( d )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.1</td>
<td>0.03</td>
<td>[0.030] [0.0002]</td>
</tr>
<tr>
<td>B</td>
<td>2.6</td>
<td>0.07</td>
<td>[0.0098]</td>
</tr>
<tr>
<td>C ( A_k )</td>
<td>2.2</td>
<td>0.15</td>
<td>0.147</td>
</tr>
<tr>
<td>D ( A_k )</td>
<td>1.3</td>
<td>0.33</td>
<td>[0.0481] [0.2819]</td>
</tr>
<tr>
<td>D ( A_k )</td>
<td>1.0</td>
<td>0.30</td>
<td>0.003</td>
</tr>
<tr>
<td>F</td>
<td>0.8</td>
<td>0.12</td>
<td>[0.0000] [0.1200]</td>
</tr>
</tbody>
</table>

*The corrected distribution of component D will be found along with the minimum reflux.

The minimum number of trays is

\[
N_m = \frac{\ln \left( \frac{0.147}{0.003} \right)}{\ln 2.2} = 10.76
\]

The distribution of component A is found as

\[
\begin{align*}
\left( \frac{d}{d_i} \right) &= \left( \frac{f - b}{b_i} \right) \frac{d}{d_i} \left( \frac{a_i}{a_i} \right)^{N_m} \\
&= 0.147 \left( \frac{3.1}{2.2} \right)^{10.76} = 0.003 \\
b_i &= \frac{d_i}{1 + (d/b_i)} = \frac{0.03}{1 + 1.5(E - 5)} = 0.03 \\
d_i &= f_i - b_i = 0.03 - 1.5(E - 5) = 0.300.
\end{align*}
\]

Distributions of the other components are found in the same way. Since component D is distributed, two values of \( \theta \) are found from Eq. (13.120):

\[
\begin{align*}
\frac{3.1(0.03)}{3.1 - \theta} + \frac{2.6(0.7)}{2.6 - \theta} + \frac{2.2(0.15)}{2.2 - \theta} + \frac{1.3(0.33)}{1.3 - \theta} \\
&+ \frac{1.3d_D + 0.003}{1.3 - \theta_1} = 3.1(0.03) + \frac{2.6(0.07)}{2.6 - \theta_1} + \frac{2.2(0.147)}{2.2 - \theta_1} + \frac{1.3d_D + 0.003}{1.3 - \theta_1}
\end{align*}
\]

Upon substituting \( \theta_1 = 1.8817 \), \( \theta_2 = 1.12403 \),

\[
\begin{align*}
d_{D_{\text{b}}} &= 0.09311, \\
D &= 0.2498 + 0.09311 = 0.3429, \\
(R_m + 1)D &= 1.1342, \\
R_m &= 2.3077.
\end{align*}
\]

Let \( R = 1.2 \), \( R_m = 1.2(2.3077) = 2.7692. \) Apply Eq. (13.124):

\[
\begin{align*}
X &= \frac{R - R_m}{R + 1} = \frac{0.2(2.3077) - 0.1225}{3.7692} \\
Y &= 0.5313 \\
N &= \frac{N_m + Y}{1 - Y} = \frac{10.76 + 0.5313}{1 - 0.5313} = 24.1.
\end{align*}
\]

Feed plate location:

\[
\begin{align*}
N_{\text{above}} &= \frac{\ln \left( \frac{0.147}{0.003} \right)}{\ln 0.15 / 0.3} = 1.75. \\
N_{\text{below}} &= \frac{\ln \left( 0.003 / 0.297 \right)}{\ln 0.15 / 0.3} = 1.175.
\end{align*}
\]

Since \( N_{\text{above}} + N_{\text{below}} = 24.1 \),

feed tray = 24.1 = 13 from the top.

For comparison, apply Eqs. (13.129) and (13.130):

\[
\begin{align*}
N^*_m &= \frac{0.6572}{0.3428} \left[ \frac{0.30}{0.15} \right] \left[ \frac{0.003/0.6572}{0.003/0.3428} \right]^{2.0.206} \\
&= 1.0088, \\
N^*_m &= 12.05, \\
N &= 12.05 - 0.5 \log 24 = 10.46 from the top.
\end{align*}
\]

Presumably 10.46 from the top is more accurate than 13.0, but it also may be in error because of the approximate fashion in which the distributions of nonkeys were found.

Note that the predicted distributions of component D do not agree closely.
MINIMUM REFLUX

The method of Underwood employs auxiliary parameters \( \theta \) derived from the equation

\[
\sum_{i=1}^{c} \frac{q_{\theta_i}}{\alpha_i - \theta} = 1 - q,
\]

(13.120)

where \( q \) is the thermal condition of the feed and the summation extends over all the components in the feed. The only roots required are those in numerical value between the relative volatilities of the light and heavy keys. For instance, if there is one distributed component, subscript \( d \), the required roots \( \alpha_1 \) and \( \alpha_2 \) are in the ranges

\[
\alpha_{1d} > \alpha_1 > \alpha_{d},
\]

\[
\alpha_{2d} > \alpha_2 > \alpha_{d}.
\]

Then the minimum reflux and the distribution of the intermediate component are found from the two equations that result from substitution of the two values of \( \theta \) into Underwood's second equation

\[
R_m + 1 = \frac{1}{D} \sum \frac{q_{\theta_i} x_{df}}{\alpha_i - \theta},
\]

(13.121)

The number of values of \( \theta \) and the number of Eqs. (13.121) is equal to 1 plus the number of components with relative volatilities between those of the light and heavy keys. When there is no distributed component, Eq. (13.121) may be used in terms of mol fractions and only a single form is needed for finding the minimum reflux,

\[
R_m + 1 = \sum \frac{q_{\theta_i} x_{df}}{\alpha_i - \theta},
\]

(13.122)

Occasionally the minimum reflux calculated by this method comes out a negative number. That, of course, is a signal that some other method should be tried, or it may mean that the separation between feed and overhead can be accomplished in less than one equilibrium stage.

OPERATING REFLUX

As discussed briefly in Section 13.4, the operating reflux is an amount in excess of the minimum that ultimately should be established by an economic balance between operating and capital costs for the operation. In many cases, however, as stated there the assumptions \( R = 1.2 R_m \) often is close to the optimum and is used without further study unless the installation is quite a large one.

ACTUAL NUMBER OF THEORETICAL TRAYS

An early observation by Underwood ([Trans. Inst. Chem. Eng. 10, pp. 112–152, 1932]) of the plate–reflux relation was

\[
(R - R_m)(N - N_m) = \text{const},
\]

(13.123)

but no general value for the constant was possible. Several correlations of calculated data between these same variables have since been made. A graphical correlation made by Gilliland ([Ind. Eng. Chem. 32, 1101, 1940]) has found wide acceptance because of its fair accuracy and simplicity of use. Of the several representations of the plot by equations, that of Molokanov et al. ([Int. Chem. Eng. 12, 209–212 (1972)]) is accurate and easy to use:

\[
Y = \frac{N - N_{\text{min}}}{N + 1} = 1 - \exp \left[ \frac{1 + 54.4 X}{11 + 117.2 X} \left( \frac{X - 1}{X^{0.5}} \right) \right],
\]

(13.124)

where

\[
X = \frac{R - R_{\text{min}}}{R + 1},
\]

(13.125)

from which the number of theoretical trays is

\[
N = \frac{N_m + Y}{1 - Y}.
\]

(13.126)

The Gilliland correlation appears to be conservative for feeds with low values of \( q \) (the thermal condition of the feed), and can be in error when there is a large difference in tray requirements above and below the feed. The principal value of the correlation appears to be for preliminary exploration of design variables which can be refined by computer calculations. Although it is often used for final design, that should be done with caution. Other possibly superior but more difficult to use correlations have been proposed and are described in standard textbooks; for example, Hines and Maddox (1985).

FEED TRAY LOCATION

Particularly when the number of trays is small, the location of the feed tray has a marked effect on the separation in the column. An estimate of the optimum location can be made with the Underwood–Fenske equation (13.116), by applying it twice, between the overhead and the feed and between the feed and the bottoms. The ratio of the numbers of rectifying \( N_r \) and stripping \( N_s \) trays is

\[
\frac{N_r}{N_s} = \ln \left[ \frac{([df]_{ik})([df]_{ab})}{([df]_{ia})([df]_{ab})} \right]
\]

(13.127)

\[
\frac{N_r}{N_s} = \ln \left[ \frac{([f/b]_{ia})([f/b]_{ab})}{([f/b]_{ia})([f/b]_{ab})} \right]
\]

(13.128)

An improved relation that, however, requires more information is due to Akashah, Erbar, and Maddox [Chem. Eng. Commun. 3, 461 (1979)]. It is

\[
N_r = N^*_s - 0.5 \log(N_i),
\]

(13.129)

where \( N_i \) is the total number of trays in the column and \( N^*_s \) is given by the empirical Kirkbride ([Petrol. Refiner 23 (9), 321, 1944]) equation,

\[
N^*_s = \frac{N^*_r}{\alpha_{df} x_{df} x_{DAk}} \left( \frac{[f/b]_{ia} ([f/b]_{ab})}{([f/b]_{ia})([f/b]_{ab})} \right)^{0.2\alpha_X}.
\]

(13.130)

TRAY EFFICIENCIES

The calculations made thus far are of theoretical trays, that is, trays on which vapor–liquid equilibrium is attained for all components. Actual tray efficiencies vary widely with the kind of system, the flow rates, and the tray construction. The range can be from less than 10% to more than 100% and constitutes perhaps the greatest uncertainty in the design of distillation equipment. For hydrocarbon fractionation a commonly used efficiency is about 60%. Section 13.14 discusses this topic more fully.