and $$\Sigma x_W = 1.0 \qquad (9.48)$$

where $x_{J,F}$ is the mole fraction of J in the feed and $x_{J,W}$ that in the residue.

Illustration 9.7 A liquid containing 50 mol % benzene (A), 25 mol % toluene (B), and 25 mol % o-xylene (C) is differentially distilled at 1 atm, with vaporization of 32.5 mol % of the charge. Raoult's law applies. Compute the distillate and residue compositions. Note that this is the same degree of vaporization as in Illustration 9.5.

SOLUTION The average temperature will be somewhat higher than the bubble point of the feed (95°C, see Illustration 9.3) but is unknown. It will be taken as 100°C. Corrections can later be made by computing the bubble point of the residue and repeating the work at the average temperature, but α's vary little with moderate changes in temperature. The vapor pressures at 100°C are tabulated and α's calculated relative to toluene, as follows:

Substance	p = vapor pressure, 100°C, mmHg	α	x_F
A	1370	1370/550 = 2.49	0.50
B	550	1.0	0.25
C	200	0.364	0.25

Basis: $F = 100$ mol, $D = 32.5$ mol, $W = 67.5$ mol. Eq. (9.47):

For A: $$\log\frac{100(0.50)}{67.5x_{A,W}} = 2.49 \log\frac{100(0.25)}{67.5x_{B,W}}$$

For C: $$\log\frac{100(0.25)}{67.5x_{C,W}} = 0.364 \log\frac{100(0.25)}{67.5x_{B,W}}$$

Eq. (9.48):

$$x_{A,W} + x_{B,W} + x_{C,W} = 1.0$$

Solving simultaneously by assuming values of $x_{B,W}$, computing $x_{A,W}$ and $x_{C,W}$, and checking their sum until it equals unity gives $x_{A,W} = 0.385$, $x_{B,W} = 0.285$, $x_{C,W} = 0.335$. The sum is 1.005, which is taken as satisfactory.

The composited distillate composition is computed by material balances. For A,

$$100(0.50) = 32.5y_{A,D,\text{av}} + 67.5(0.385) \qquad y_{A,D,\text{av}} = 0.742$$

Similarly, $y_{B,D,\text{av}} = 0.178$ and $y_{C,D,\text{av}} = 0.075$

Note the improved separation over that obtained by flash vaporization (Illustration 9.5).

CONTINUOUS RECTIFICATION—BINARY SYSTEMS

Continuous rectification, or fractionation, is a multistage countercurrent distillation operation. For a binary solution, with certain exceptions it is ordinarily possible by this method to separate the solution into its components, recovering each in any state of purity desired.

Rectification is probably the most frequently used separation method we have, although it is relatively new. While simple distillation was known in the first century, and perhaps earlier, it was not until about 1830 that Aeneas Coffey

of Dublin invented the multistage, countercurrent rectifier for distilling ethanol from fermented grain mash [56]. His still was fitted with trays and down-spouts, and produced a distillate containing up to 95 percent ethanol, the azeotrope composition. We cannot do better today except by special techniques.

The Fractionation Operation

In order to understand how such an operation is carried out, recall the discussion of reboiled absorbers in Chap. 8 and Fig. 8.28. There, because the liquid leaving the bottom of an absorber is at best in equilibrium with the feed and may therefore contain substantial concentrations of volatile component, trays installed below the feed point were provided with vapor generated by a reboiler to strip out the volatile component from the liquid. This component then entered the vapor and left the tower at the top. The upper section of the tower served to wash the gas free of less volatile component, which entered the liquid to leave at the bottom.

So, too, with distillation. Refer to Fig. 9.17. Here the feed is introduced more or less centrally into a vertical cascade of stages. Vapor rising in the section above the feed (called the *absorption*, *enriching*, or *rectifying* section) is washed with liquid to remove or absorb the less volatile component. Since no extraneous material is added, as in the case of absorption, the washing liquid in this case is provided by condensing the vapor issuing from the top, which is rich in more volatile component. The liquid returned to the top of the tower is called *reflux*, and the material permanently removed is the *distillate*, which may be a vapor or a liquid, rich in more volatile component. In the section below the feed (*stripping* or *exhausting* section), the liquid is stripped of volatile component by vapor produced at the bottom by partial vaporization of the bottom liquid in the reboiler. The liquid removed, rich in less volatile component, is the *residue*, or *bottoms*. Inside the tower, the liquids and vapors are always at their bubble points and dew points, respectively, so that the highest temperatures are at the bottom, the lowest at the top. The entire device is called a *fractionator*.

The purities obtained for the two withdrawn products will depend upon the liquid/gas ratios used and the number of ideal stages provided in the two sections of the tower, and the interrelation of these must now be established. The cross-sectional area of the tower, however, is governed entirely by the quantities of materials handled, in accordance with the principles of Chap. 6.

Overall Enthalpy Balances

In Fig. 9.17, the theoretical trays are numbered from the top down, and subscripts generally indicate the tray from which a stream originates: for example, L_n is mol liquid/time falling from the nth tray. A bar over the quantity indicates that it applies to the section of the column below the point of introduction of the feed. The distillate product may be liquid, vapor, or a mixture. The reflux, however, must be liquid. The molar ratio of reflux to
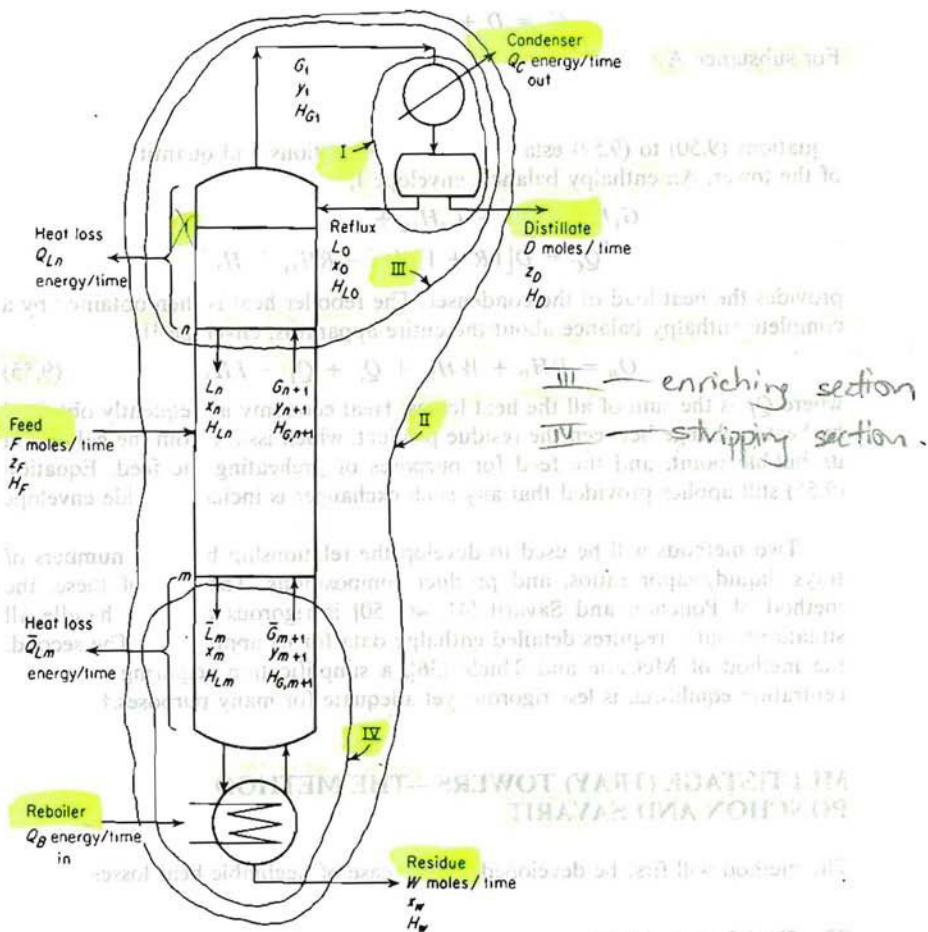
Figure 9.17 Material and enthalpy balances of a fractionator.

withdrawn distillate is the *reflux ratio*, sometimes called the *external reflux ratio*,

$$R = \frac{L_0}{D} \tag{9.49}$$

which is specified in accordance with principles to be established later.†

Consider the condenser, envelope I (Fig. 9.17). A total material balance is

$$G_1 = D + L_0 \tag{9.50}$$

† The ratio L/G is sometimes called the *internal reflux ratio*; L/F is also used for certain reflux correlations.

or
$$G_1 = D + RD = D(R + 1) \tag{9.51}$$

For substance A

$$G_1 y_1 = Dz_D + L_0 x_0 \tag{9.52}$$

Equations (9.50) to (9.52) establish the concentrations and quantities at the top of the tower. An enthalpy balance, envelope I,

$$G_1 H_{G1} = Q_C + L_0 H_{L0} + DH_D \tag{9.53}$$

$$Q_C = D[(R + 1)H_{G1} - RH_{L0} - H_D] \tag{9.54}$$

provides the heat load of the condenser. The reboiler heat is then obtained by a complete enthalpy balance about the entire apparatus, envelope II,

If Q_L negligible,
$Q_L = 0$

$$Q_B = DH_D + WH_W + Q_C + Q_L - FH_F \tag{9.55}$$

where Q_L is the sum of all the heat losses. Heat economy is frequently obtained by heat exchange between the residue product, which issues from the column at its bubble point, and the feed for purposes of preheating the feed. Equation (9.55) still applies provided that any such exchanger is included inside envelope II.

Two methods will be used to develop the relationship between numbers of trays, liquid/vapor ratios, and product compositions. The first of these, the method of Ponchon and Savarit [41, 46, 50] is rigorous and can handle all situations, but it requires detailed enthalpy data for its application. The second, the method of McCabe and Thiele [36], a simplification requiring only concentration equilibria, is less rigorous yet adequate for many purposes.†

MULTISTAGE (TRAY) TOWERS—THE METHOD OF PONCHON AND SAVARIT

The method will first be developed for the case of negligible heat losses.

The Enriching Section III

Consider the enriching section through tray n, envelope III, Fig. 9.17. Tray n is any tray in this section. Material balances for the section are, for total material,

$$G_{n+1} = L_n + D \tag{9.56}$$

and for component A,

$$G_{n+1} y_{n+1} = L_n x_n + Dz_D \tag{9.57}$$

$$G_{n+1} y_{n+1} - L_n x_n = Dz_D \quad \text{constant} \tag{9.58}$$

The left-hand side of Eq. (9.58) represents the difference in rate of flow of

---

† The treatment of each method is complete in itself, independent of the other. For instructional purposes, they may be considered in either order, or one may be omitted entirely.

component A, up − down, or the net flow upward. Since for a given distillation the right-hand side is constant, it follows that the difference, or net rate of flow of A upward, is constant, independent of tray number in this section of the tower, and equal to that permanently withdrawn at the top.

An enthalpy balance, envelope III, with *heat loss negligible*, is

$$G_{n+1}H_{G_{n+1}} = L_n H_{L_n} + Q_C + DH_D \quad (9.59)$$

Let Q' be the heat removed in the condenser and the permanently removed distillate, per mole of distillate. Then

$$Q' = \frac{Q_C + DH_D}{D} = \frac{Q_C}{D} + H_D \quad (9.60)$$

and

$$G_{n+1}H_{G_{n+1}} - L_n H_{L_n} = DQ' \quad (9.61)$$

The left-hand side of Eq. (9.61) represents the difference in rate of flow of heat, up − down, or the net flow upward. Since for a given set of circumstances the right-hand side is constant, the difference, or net rate of flow upward, is constant, independent of tray number in this section of the tower, and equal to that permanently taken out at the top with the distillate and at the condenser.

Elimination of D between Eqs. (9.56) and (9.57) and between Eqs. (9.56) and (9.61) yields

$$\frac{L_n}{G_{n+1}} = \frac{z_D - y_{n+1}}{z_D - x_n} = \frac{Q' - H_{G_{n+1}}}{Q' - H_{L_n}} \quad (9.62)$$

L_n/G_{n+1} is called the *internal reflux ratio*.

On the Hxy diagram, Eq. (9.62) is the equation of a straight line through $(H_{G_{n+1}}, y_{n+1})$ at G_{n+1}, (H_{L_n}, x_n) at L_n, and (Q', z_D) at Δ_D. The last is called a *difference point*, since its coordinates represent differences in rates of flow:

$$\Delta_D \begin{cases} Q' = \dfrac{\text{difference in heat flow, up} - \text{down}}{\text{net moles total substance out}} = \dfrac{\text{net heat out}}{\text{net moles out}} \\[2ex] z_D = \dfrac{\text{difference in flow of component A, up} - \text{down}}{\text{net moles total substance out}} = \dfrac{\text{net moles A out}}{\text{net moles out}} \end{cases}$$

Δ_D then represents a fictitious stream, in amount equal to the net flow outward (in this case D) and of properties (Q', z_D) such that

$$G_{n+1} - L_n = \Delta_D \quad (9.63)$$

On the xy diagram, Eq. (9.62) is the equation of a straight line of slope L_n/G_{n+1}, through (y_{n+1}, x_n) and $y = x = z_D$. These are plotted on Fig. 9.18, where both diagrams are shown.

Figure 9.18 is drawn for a total condenser. The distillate D and reflux L_0 then have identical coordinates and are plotted at point D. The location shown indicates that they are below the bubble point. If they were at the bubble point, D would be on the saturated-liquid curve. The saturated vapor G_1 from the top tray, when totally condensed, has the same composition as D and L_0. Liquid L_1

Figure 9.18 Enriching section, total condenser, reflux below the bubble point.

leaving ideal tray 1 is in equilibrium with G_1 and is located at the end of tie line 1. Since Eq. (9.62) applies to all trays in this section, G_2 can be located on the saturated-vapor curve by a line drawn from L_1 to Δ_D; tie line 2 through G_2 locates L_2, etc. Thus, alternate tie lines (each representing the effluents from an ideal tray) and construction lines through Δ_D provide the stepwise changes in concentration occurring in the enriching section. Intersections of the lines radiating from Δ_D with the saturated-enthalpy curves, such as points G_3 and L_2,

when projected to the lower diagram, produce points such as P. These in turn produce the operating curve CP, which passes through $y = x = z_D$. The tie lines, when projected downward, produce the equilibrium-distribution curve, and the stepwise nature of the concentration changes with tray number then becomes obvious. The difference point Δ_D is used in this manner for all trays in the enriching section, working downward until the feed tray is reached.

Enriching trays can thus be located on the Hxy diagram alone by alternating construction lines to Δ_D and tie lines, each tie line representing an ideal tray. As an alternative, random lines radiating from Δ_D can be drawn, their intersections with the $H_G y$ and $H_L x$ curves plotted on the xy diagram to produce the operating curve, and the trays determined by the step construction typical of such diagrams.

At any tray n (compare Fig. 9.12) the L_n/G_{n+1} ratio is given by the ratio of line lengths $\Delta_D G_{n+1}/\Delta_D L_n$ on the upper diagram of Fig. 9.18 or by the slope of the chord as shown on the lower diagram. Elimination of G_{n+1} between Eqs. (9.56) and (9.62) provides

$$\frac{L_n}{D} = \frac{Q' - H_{G_{n+1}}}{H_{G_{n+1}} - H_{L_n}} = \frac{z_D - y_{n+1}}{y_{n+1} - x_n} \tag{9.64}$$

Applying this to the top tray provides the external reflux ratio, which is usually the one specified:

$$R = \frac{L_0}{D} = \frac{Q' - H_{G1}}{H_{G1} - H_{L0}} = \frac{\text{line } \Delta_D G_1}{\text{line } G_1 L_0} = \frac{\text{line } \Delta_D G_1}{\text{line } G_1 D} \tag{9.65}$$

For a given reflux ratio, the line-length ratio of Eq. (9.65) can be used to locate Δ_D vertically on Fig. 9.18, and the ordinate Q' can then be used to compute the condenser heat load.

In some cases a *partial condenser* is used, as in Fig. 9.19. Here a saturated vapor distillate D is withdrawn, and the condensate provides the reflux. This is frequently done when the pressure required for complete condensation of the vapor G_1, at reasonable condenser temperatures, would be too large. The Δ_D is plotted at an abscissa y_D corresponding to the composition of the withdrawn distillate. Assuming that an equilibrium condensation is realized, reflux L_0 is at the end of the tie line C. G_1 is located by the construction line $L_0 \Delta_D$, etc. In the lower diagram, the line MN solves the equilibrium-condensation problem (compare Fig. 9.14). The reflux ratio $R = L_0/D = \text{line } \Delta_D G_1/\text{line } G_1 L_0$, by application of Eq. (9.65). It is seen that the equilibrium partial condenser provides one equilibrium tray's worth of rectification. However, it is safest not to rely on such complete enrichment by the condenser but instead to provide trays in the tower equivalent to all the stages required.