

done, and the mixed feed is usually introduced into the column without prior separation for reasons of economy. This will have only a small influence on the number of trays required [6].

Increased Reflux Ratio

As the reflux ratio $R = L_0/D$ is increased, the Δ_D difference point on Fig. 9.21 must be located at higher values of Q' . Since Δ_D , F , and Δ_W are always on the same line, increasing the reflux ratio lowers the location of Δ_W . These changes result in larger values of L_n/G_{n+1} and smaller values of \bar{L}_m/\bar{G}_{m+1} , and the operating curves on the xy diagram move closer to the 45° diagonal. Fewer trays are then required, but Q_C , Q_W , L , \bar{L} , G , and \bar{G} all increase; condenser and reboiler surfaces and tower cross section must be increased to accommodate the larger loads.

Total Reflux

Ultimately, when $R = \infty$, $L_n/G_{n+1} = \bar{L}_m/\bar{G}_{m+1} = 1$, the operating curves both coincide with the 45° line on the xy plot, the Δ points are at infinity on the Hxy plot, and the number of trays required is the minimum value, N_m . This is shown in Fig. 9.23. The condition can be realized practically by returning all the distillate to the top tray as reflux and reboiling all the residue, whereupon the feed to the tower must be stopped.

Constant Relative Volatility

A useful analytical expression for the minimum number of theoretical stages can be obtained for cases where the relative volatility is reasonably constant [13, 63]. Applying Eq. (9.2) to the residue product gives

$$\frac{y_W}{1 - y_W} = \alpha_W \frac{x_W}{1 - x_W} \quad (9.80)$$

where α_W is the relative volatility at the reboiler. At total reflux the operating line coincides with the 45° diagonal so that $y_W = x_{N_m}$. Therefore

$$\frac{x_{N_m}}{1 - x_{N_m}} = \alpha_W \frac{x_W}{1 - x_W} \quad (9.81)$$

Similarly for the last tray of the column, where α_{N_m} pertains,

$$\frac{y_{N_m}}{1 - y_{N_m}} = \alpha_{N_m} \frac{x_{N_m}}{1 - x_{N_m}} = \alpha_{N_m} \alpha_W \frac{x_W}{1 - x_W} \quad (9.82)$$

This procedure can be continued up the column until ultimately

$$\frac{y_1}{1 - y_1} = \frac{x_D}{1 - x_D} = \alpha_1 \alpha_2 \cdots \alpha_{N_m} \alpha_W \frac{x_W}{1 - x_W} \quad (9.83)$$

If some average relative volatility α_{av} can be used,

$$\frac{x_D}{1 - x_D} = \alpha_{av}^{N_m+1} \frac{x_W}{1 - x_W} \quad (9.84)$$

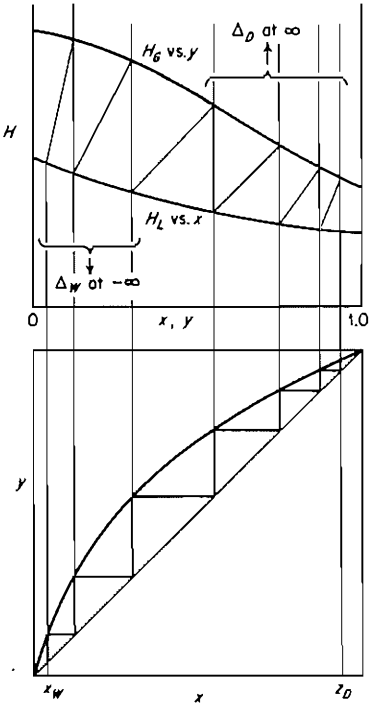


Figure 9.23 Total reflux and minimum stages.

or

$$N_m + 1 = \frac{\log \frac{x_D}{1 - x_D} \frac{1 - x_W}{x_W}}{\log \alpha_{av}} \tag{9.85}$$

which is known as *Fenske's equation*. The total minimum number of theoretical stages to produce products x_D and x_W is $N_m + 1$, which then includes the reboiler. For small variations in α , α_{av} can be taken as the geometric average of the values for the overhead and bottom products, $\sqrt{\alpha_1 \alpha_H}$. The expression can be used only with nearly ideal mixtures, for which α is nearly constant.

Minimum Reflux Ratio

The minimum reflux ratio R_m is the maximum ratio which will require an infinite number of trays for the separation desired, and it corresponds to the minimum reboiler heat load and condenser cooling load for the separation.

Refer to Fig. 9.24a, where the lightly drawn lines are tie lines which have been extended to intersect lines $x = z_D$ and $x = x_W$. It is clear that if Δ_D were located at point K, alternate tie lines and construction lines to Δ_D at the tie line k would coincide, and an infinite number of stages would be required to reach tie line k from the top of the tower. The same is true if Δ_W is located at point J.

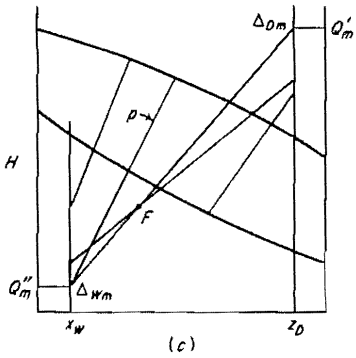
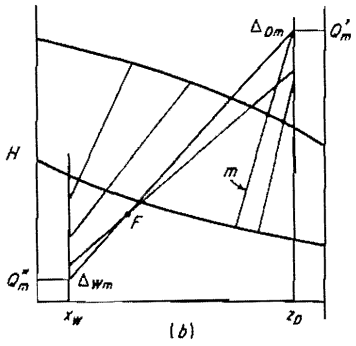
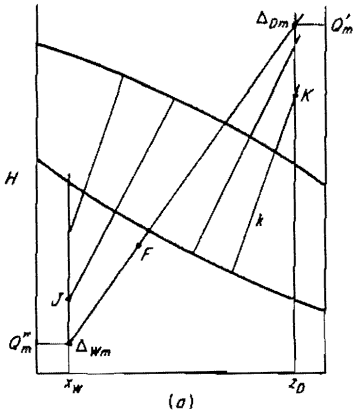


Figure 9.24 Minimum reflux ratio.

Since as Δ_D is moved upward and Δ_W downward the reflux ratio increases, the definition of minimum reflux ratio requires Δ_{D_m} and Δ_{W_m} for the minimum reflux ratio to be located as shown, with Δ_{D_m} at the highest tie-line intersection and Δ_{W_m} at the lowest tie-line intersection. In this case, it is the tie line which, when extended, passes through F , the feed, that determines both, and this is always the case when the xy equilibrium distribution curve is everywhere concave downward.

For some positively deviating mixtures with a tendency to form an azeotrope and for all systems near the critical condition of the more volatile component [66], an enriching-section tie line m in Fig. 9.24*b* gives the highest intersection with $x = z_D$, not that which passes through F . Similarly, as in Fig. 9.24*c* for some negatively deviating mixtures, a stripping-section tie line p gives the lowest intersection with $x = x_W$. These then govern the location of Δ_{D_m} as shown. For the minimum reflux ratio, either Δ_{D_m} is located at the highest intersection of an enriching-section tie line with $x = z_D$, or Δ_{W_m} is at the lowest intersection of a stripping-section tie line with $x = x_W$, consistent with the requirements that Δ_{D_m} , Δ_{W_m} , and F all be on the same straight line and Δ_{D_m} be at the highest position resulting in a pinch. Special considerations are necessary for fractionation with multiple feeds and sidestreams [52].

Once Q_m is determined, the minimum reflux ratio can be computed through Eq. (9.65). Some larger reflux ratio must obviously be used for practical cases, whereupon Δ_D is located above Δ_{D_m} .

Optimum Reflux Ratio

Any reflux ratio between the minimum and infinity will provide the desired separation, with the corresponding number of theoretical trays required varying from infinity to the minimum number, as in Fig. 9.25*a*. Determination of the

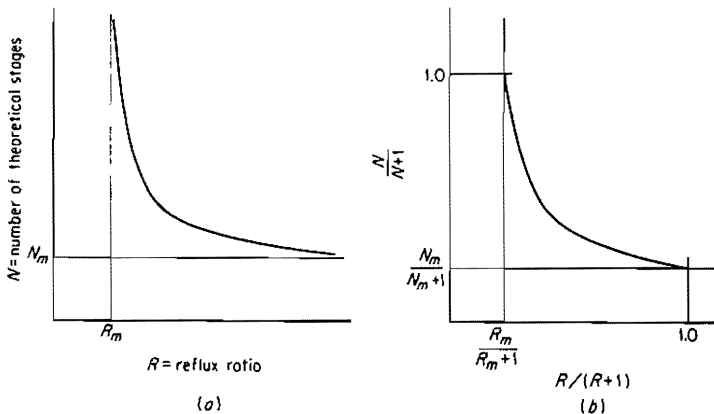


Figure 9.25 Reflux-ratio-stage relation.

number of trays at several values of R , together with the limiting values of N_m and R_m , will usually permit plotting the entire curve with sufficient accuracy for most purposes. The coordinate system of Fig. 9.25*b* [17] will permit locating the ends of the curve readily by avoiding the awkward asymptotes. There have been several attempts at empirically generalizing the curves of Fig. 9.25 [5, 10, 12, 17, 35], but the resulting charts yield only approximate results. An exact relationship for binary distillations, which can also be applied to multicomponent mixtures, is available [59].

The reflux ratio to be used for a new design should be the optimum, or the most economical, reflux ratio, for which the cost will be the least. Refer to Fig. 9.26. At the minimum reflux ratio the column requires an infinite number of trays, and consequently the fixed cost is infinite, but the operating costs (heat for the reboiler, condenser cooling water, power for reflux pump) are least. As R increases, the number of trays rapidly decreases, but the column diameter increases owing to the larger quantities of recycled liquid and vapor per unit quantity of feed. The condenser, reflux pump, and reboiler must also be larger. The fixed costs therefore fall through a minimum and rise to infinity again at total reflux. The heating and cooling requirements increase almost directly with reflux ratio, as shown. The total cost, which is the sum of operating and fixed costs, must therefore pass through a minimum at the optimum reflux ratio. This will frequently but not always occur at a reflux ratio near the minimum value ($1.2R_m$ to $1.5R_m$), on the average probably near the lower limit. A less empirical method for estimating the optimum is available [34].

Illustration 9.8 A methanol (A)–water (B) solution containing 50 wt % methanol at 26.7°C is to be continuously rectified at 1 std atm pressure at a rate of 5000 kg/h to provide a distillate containing 95% methanol and a residue containing 1.0 % methanol (by weight). The feed is to be preheated by heat exchange with the residue, which will leave the system at 37.8°C. The distillate is to be totally condensed to a liquid and the reflux returned at the bubble point. The withdrawn distillate will be separately cooled before storage. A reflux ratio of 1.5 times the minimum will be used. Determine (a) quantity of the products, (b) enthalpy of feed and of

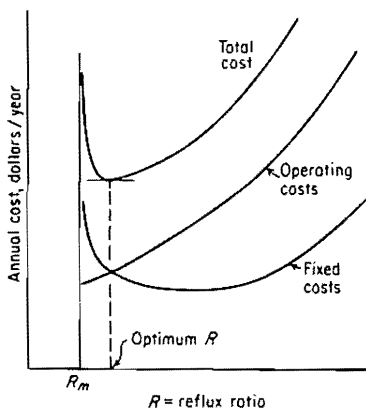


Figure 9.26 Most economical (optimum) reflux ratio.

products, (c) minimum reflux ratio, (d) minimum number of theoretical trays, (e) condenser and reboiler heat loads for specified reflux ratio, (f) number of theoretical trays for specified reflux ratio, and liquid and vapor quantities inside the tower.

SOLUTION (a) Mol wt methanol = 32.04, mol wt water = 18.02. Basis: 1 h. Define quantities in terms of kmol/h.

$$F = \frac{5000(0.50)}{32.04} + \frac{5000(0.50)}{18.02} = 78.0 + 138.8 = 216.8 \text{ kmol/h}$$

$$z_F = \frac{78}{216.8} = 0.360 \text{ mole fraction methanol} \quad M_{av} \text{ for feed} = \frac{5000}{216.8} = 23.1 \text{ kg/kmol}$$

$$x_D = \frac{95/32.04}{95/32.04 + 5/18.02} = \frac{2.94}{3.217} = 0.915 \text{ mole fraction methanol}$$

$$M_{av} \text{ for distillate} = \frac{100}{3.217} = 31.1 \text{ kg/kmol}$$

$$x_W = \frac{1/32.04}{1/32.04 + 99/18.02} = \frac{0.0312}{5.53} = 0.00565 \text{ mole fraction methanol}$$

$$M_{av} \text{ for residue} = \frac{100}{5.53} = 18.08 \text{ kg/kmol}$$

Eq. (9.75):

$$216.8 = D + W$$

Eq. (9.76):

$$216.8(0.360) = D(0.915) + W(0.00565)$$

Solving simultaneously gives

$$D = 84.4 \text{ kmol/h} \quad 84.4(31.1) = 2620 \text{ kg/h}$$

$$W = 132.4 \text{ kmol/h} \quad 132.4(18.08) = 2380 \text{ kg/h}$$

(b) The vapor-liquid equilibrium at 1 std atm pressure is given by Cornell and Montana, *Ind. Eng. Chem.*, 25, 1331 (1933), and by "The Chemical Engineers' Handbook," 4th ed., p. 13-5. Heat capacities of liquid solutions are in the "Handbook," 5th ed., p. 3-136, and latent heats of vaporization of methanol on p. 3-116. Heats of solution are available in "International Critical Tables," vol. V, p. 159, at 19.69°C, which will be used as t_0 , the base temperature for computing enthalpies.

To compute enthalpies of saturated liquids, consider the case of $x = 0.3$ mole fraction methanol, $M_{av} = 22.2$. The bubble point = 78.3°C, heat capacity = 3852 J/kg · K, and the heat of solution = 3055 kJ evolved/kmol methanol.

$$\Delta H_S = -3055(0.3) = -916.5 \text{ kJ/kmol solution. Therefore, Eq. (9.10):}$$

$$H_L = 3852(78.3 - 19.69)22.2 - 916.5 = 4095 \text{ kJ/kmol}$$

To compute the enthalpy of saturated vapors, consider the case of $y = 0.665$ mole fraction methanol. The dew point is 78.3°C. At this temperature the latent heat of methanol is 1046.7 kJ/kg, that of water is 2314 kJ/kg. The heat capacity of methanol is 2583, of water 2323 J/kg · K. Eq. (9.11):

$$\begin{aligned} H_G &= 0.665[2.583(32.04)(78.3 - 19.69) + 1046.7(32.04)] \\ &\quad + (1 - 0.665)[2.323(18.02)(78.3 - 19.69) + 2314(18.02)] \\ &= 40318 \text{ kJ/kmol} \end{aligned}$$

The enthalpy data of Fig. 9.27 were computed in this manner.

From the vapor-liquid equilibria, the bubble point of the residue is 99°C. Heat capacity of the residue is 4179, of the feed 3852 J/kg · K. Enthalpy balance of the feed preheat exchanger:

$$5000(3852)(t_F - 26.7) = 2380(4179)(99 - 37.8)$$

$$t_F = 58.3^\circ\text{C, temp at which feed enters tower}$$

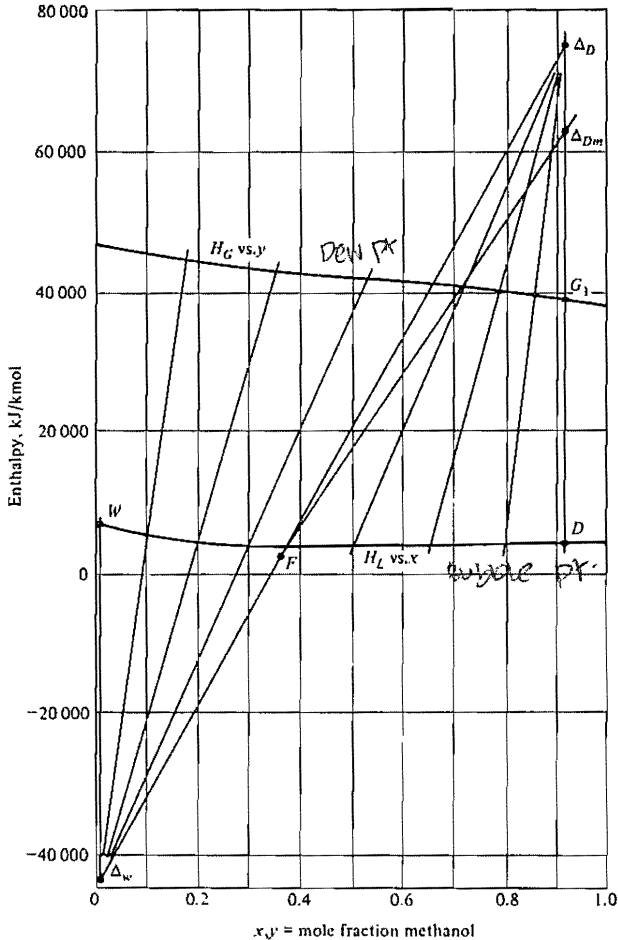


Figure 9.27 Enthalpy-concentration diagram for Illustration 9.8.

(Note: The bubble point of the feed is 76.0°C. Had t_F as computed above exceeded the bubble point, the above enthalpy balance would have been discarded and made in accordance with flash-vaporization methods.) For the feed, $\Delta H_G = -902.5$ kJ/kmol. Enthalpy of feed at 58.3°C is

$$H_F = 3.852(58.3 - 19.69)(23.1) - 902.5 = 2533 \text{ kJ/kmol}$$

From Fig. 9.27, $H_D = H_{L0} = 3640$, $H_W = 6000$ kJ/kmol.

(c) Since the xy diagram (Fig. 9.28) is everywhere concave downward, the minimum reflux ratio is established by the tie line in Fig. 9.27 ($x = 0.37$, $y = 0.71$) which, when extended, passes through F , the feed. At Δ_{Dm} , $Q_m = 62\,570$ kJ/kmol. $H_{G1} = 38\,610$ kJ/kmol. Eq. (9.65):

$$R_m = \frac{62\,570 - 38\,610}{38\,610 - 3640} = 0.685$$

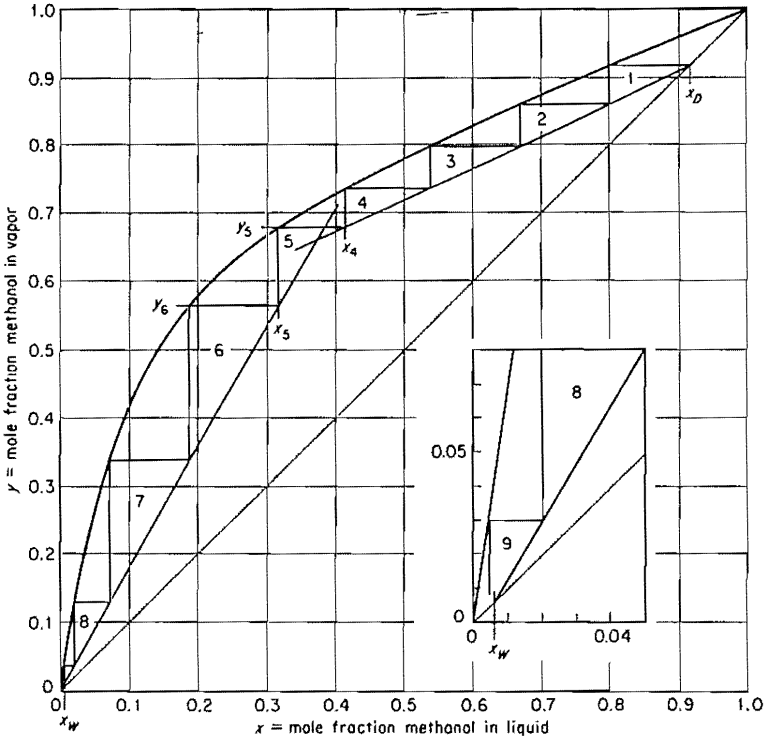


Figure 9.28 xy diagram for Illustration 9.8.

(d) The minimum number of trays was determined on the xy diagram in the manner of the lower part of Fig. 9.23, and 4.9 theoretical stages, including the reboiler, were obtained. $N_m = 4.9 - 1 = 3.9$.

(e) For $R = 1.5(0.685) = 1.029$, Eq. (9.65) becomes

$$1.029 = \frac{Q' - 38\,610}{38\,610 - 3640}$$

$$Q' = 74\,595 = H_D + \frac{Q_C}{D} = 3640 + \frac{Q_C}{84.4} \quad Q_C = 5\,990\,000 \text{ kJ/h} = 1664 \text{ kW}$$

$$\text{Eq. (9.77): } 216.8(2533) = 84.4(74\,595) + 132.4Q''$$

$$Q'' = -43\,403 = H_W - \frac{Q_B}{W} = 6000 - \frac{Q_B}{132.4}$$

$$Q_B = 6\,541\,000 \text{ kJ/h reboiler heat load} = 1817 \text{ kW}$$

(f) In Fig. 9.27, Δ_D at $(x_D = 0.915, Q' = 74\,595)$ and Δ_W at $(x_W = 0.00565, Q'' = -43\,403)$ are plotted. Random lines from the Δ points, as shown, intersect the saturated-vapor and saturated-liquid curves at values of y and x , respectively, corresponding to points on the operating curve (note that for accurate results a large-scale graph and a sharp pencil are needed). These are plotted on Fig. 9.28 to provide the operating curves, which are nearly, but

not exactly, straight. A total of nine theoretical stages including the reboiler, or eight theoretical trays in the tower, are required when the feed tray is the optimum (no. 5) as shown.

At the top of the tower

$$G_1 = D(R + 1) = 84.4(1.029 + 1) = 171.3 \text{ kmol/h}$$

$$L_0 = DR = 84.4(1.029) = 86.7 \text{ kmol/h}$$

At the feed tray, $x_4 = 0.415$, $y_3 = 0.676$, $x_5 = 0.318$, $y_6 = 0.554$ (Fig. 9.28). Eq. (9.64):

$$\frac{L_4}{D} = \frac{L_4}{84.4} = \frac{0.915 - 0.676}{0.676 - 0.415} \quad \text{and} \quad L_4 = 77.2 \text{ kmol/h}$$

Eq. (9.62):

$$\frac{L_4}{G_5} = \frac{77.2}{G_5} = \frac{0.915 - 0.676}{0.915 - 0.415} \quad \text{and} \quad G_5 = 161.5 \text{ kmol/h}$$

Eq. (9.74):

$$\frac{\bar{L}_5}{\bar{W}} = \frac{\bar{L}_5}{132.4} = \frac{0.554 - 0.00565}{0.554 - 0.318} \quad \text{and} \quad \bar{L}_5 = 308 \text{ kmol/h}$$

Eq. (9.72):

$$\frac{\bar{L}_5}{\bar{G}_6} = \frac{308}{\bar{G}_6} = \frac{0.554 - 0.00565}{0.318 - 0.00565} \quad \text{and} \quad \bar{G}_6 = 175.7 \text{ kmol/h}$$

At the bottom of the tower, Eq. (9.66):

$$\bar{L}_{N_r} = \bar{G}_W + W \quad \bar{L}_8 = \bar{G}_W + 132.4$$

Further, $y_W = 0.035$, $x_8 = 0.02$ (Fig. 9.28); Eq. (9.72):

$$\frac{\bar{L}_8}{\bar{G}_W} = \frac{0.035 - 0.00565}{0.02 - 0.00565}$$

Solving simultaneously gives $\bar{G}_W = 127.6$, $\bar{L}_8 = 260 \text{ kmol/h}$.

Reboilers

The heat-exchanger arrangements to provide the necessary heat and vapor return at the bottom of the fractionator may take several forms. Small fractionators used for pilot-plant work may merely require a jacketed kettle, as shown schematically in Fig. 9.29*a*, but the heat-transfer surface and the corresponding vapor capacity will necessarily be small. The tubular heat exchanger built into the bottom of the tower (Fig. 9.29*b*) is a variation which provides larger surface, but cleaning requires a shut-down of the distillation operation. This type can also be built with an internal floating head. Both these provide a vapor entering the bottom tray essentially in equilibrium with the residue product, so that the last stage of the previous computations represents the enrichment due to the reboiler.

External reboilers of several varieties are commonly used for large installations, and they can be arranged with spares for cleaning. The kettle reboiler (Fig. 9.29*c*), with heating medium inside the tubes, provides a vapor to the tower essentially in equilibrium with the residue product and then behaves like a theoretical stage. The vertical thermosiphon reboiler of Fig. 9.29*d*, with the