Dew point The procedure is similar to that for the bubble point. The first estimate is 80°C (176°F), whence $\Sigma y_i/\alpha_{i,\,C_5} = 1.081$ (column 4 = m_{C_5} [Eq. (9.29)]. The corresponding temperature is 83.7°C (183°F). Repetition leads to $m_{C_5} = 1.103$, corresponding to 84.0°C, which is the dew point. The corresponding dew-point-liquid compositions are listed in column 8 ($0.00818/1.103 = 0.0074$, etc.).

SINGLE-STAGE OPERATION—FLASH VAPORIZATION

Flash vaporization, or equilibrium distillation as it is sometimes called, is a single-stage operation wherein a liquid mixture is partially vaporized, the vapor allowed to come to equilibrium with the residual liquid, and the resulting vapor and liquid phases are separated and removed from the apparatus. It may be batchwise or continuous.

A typical flowsheet is shown schematically in Fig. 9.13 for continuous operation. Here the liquid feed is heated in a conventional tubular heat exchanger or by passing it through the heated tubes of a fuel-fired furnace. The pressure is then reduced, vapor forms at the expense of the liquid adiabatically, and the mixture is introduced into a vapor-liquid separating vessel. The separator shown is of the cyclone type, where the feed is introduced tangentially into a covered annular space. The liquid portion of the mixture is thrown by centrifugal force to the outer wall and leaves at the bottom, while the vapor rises through the central chimney and leaves at the top. The vapor may then pass to a condenser, not shown in the figure. Particularly for flash vaporization of a volatile substance from a relatively nonvolatile one, operation in the separator can be carried out under reduced pressure, but not so low that ordinary cooling water will not condense the vapor product.

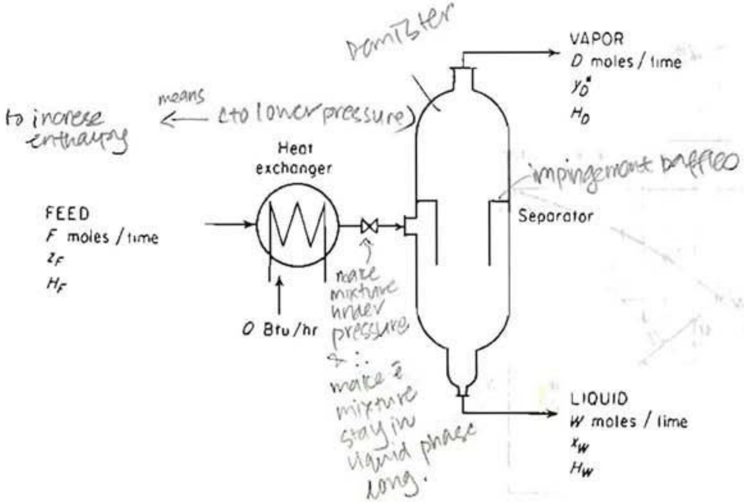


Figure 9.13 Continuous flash vaporization.

The product, D mol/time, richer in the more volatile substance, is in this case entirely a vapor. The material and enthalpy balances are

$$F = D + W \tag{9.31}$$

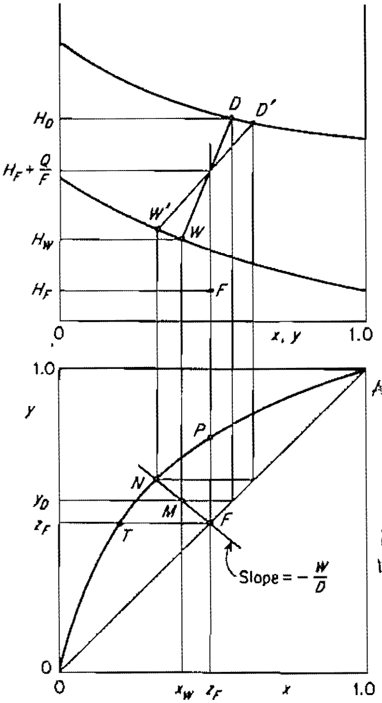
$$Fz_F = Dy_D + Wx_W \tag{9.32}$$

$$FH_F + Q = DH_D + WH_W \tag{9.33}$$

Solved simultaneously, these yield

$$-\frac{W}{D} = \frac{y_D - z_F}{x_W - z_F} = \frac{H_D - (H_F + Q/F)}{H_W - (H_F + Q/F)} \tag{9.34}$$

On the Hxy diagram, this represents a straight line through points of coordinates (H_D, y_D) representing D, (H_W, x_W) representing W, and $(H_F + Q/F, z_F)$ representing the feed mixture after it leaves the heat exchanger of Fig. 9.13. It is shown on the upper part of Fig. 9.14 as the line DW. The two left-hand members of Eq. (9.34) represent the usual single-stage operating line on distribution coordinates, of negative slope as for all single-stage (cocurrent) operations (see Chap. 5), passing through compositions representing the influent and effluent streams, points F and M on the lower figure. If the effluent streams were in equilibrium, the device would be an equilibrium stage and the products



Actual process from F → M

N-M-P represents the flash vaporize process.

Figure 9.14 Flash vaporization.

D' and W' would be on a tie line in the upper figure and on the equilibrium curve at N on the lower figure. The richest vapor, but infinitesimal in amount, is that corresponding to P at the bubble point of the feed; and the leanest liquid, but also infinitesimal in amount, is that corresponding to T at the dew point of the feed. The compositions of the actual products will be between these limits, depending upon the extent of vaporization of the feed and the stage efficiency.

Partial Condensation

All the equations apply equally well to the case where the feed is a vapor and Q, the heat removed in the heat exchanger to produce incomplete condensation, is taken as negative. On the upper part of Fig. 9.14, point F is then either a saturated or superheated vapor.

Illustration 9.4 A liquid mixture containing 50 mol % n-heptane (A), 50 mol % n-octane (B), at 30°C, is to be continuously flash-vaporized at 1 std atm pressure to vaporize 60 mol % of the feed. What will be the composition of the vapor and liquid and the temperature in the separator for an equilibrium stage?

SOLUTION *Basis*: $F = 100$ mol feed, $z_F = 0.50$. $D = 60$ mol, $W = 40$ mol, $-W/D = -40/60 = -0.667$.

The equilibrium data were determined in Illustration 9.1 and are plotted in Fig. 9.15. The point representing the feed composition is plotted at P, and the operating line is drawn with a slope -0.667 to intersect the equilibrium curve at T, where $y_D^* = 0.575$ mole fraction heptane and $x_W = 0.387$ mole fraction heptane. The temperature at T is 113°C.

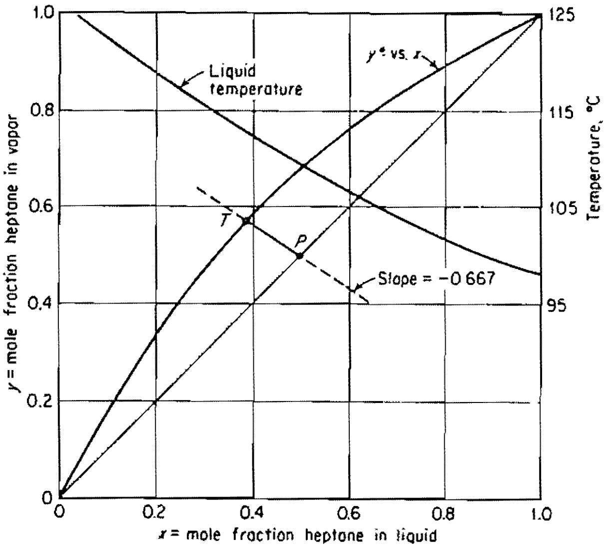


Figure 9.15 Solution to Illustration 9.4.

Multicomponent Systems—Ideal solutions

For mixtures leaving an equilibrium stage containing components A, B, C, etc., the equilibrium relation for any component J can be written

$$y^*_{J,D} = m_J x_{J,W} \tag{9.35}$$

Equation (9.34) also applies for each of the components, and when combined with Eq. (9.35) for any component J, for an equilibrium stage gives

$$\frac{W}{D} = \frac{m_J x_{J,W} - z_{J,F}}{z_{J,F} - x_{J,W}} = \frac{y^*_{J,D} - z_{J,F}}{z_{J,F} - y^*_{J,D}/m_J} \tag{9.36}$$

This provides the following expression, useful for equilibrium vaporization,

$$y^*_{J,D} = \frac{z_{J,F}(W/D + 1)}{1 + W/Dm_J} \tag{9.37}$$

$$\Sigma y^*_D = 1.0 \tag{9.38}$$

and for condensation,

$$x_{J,W} = \frac{z_{J,F}(W/D + 1)}{m_J + W/D} \tag{9.39}$$

$$\Sigma x_W = 1.0 \tag{9.40}$$

Thus Eq. (9.37) can be used for each of the components with appropriate values of m and z_F, and the sum of the y^*_D's so calculated must equal unity if the correct conditions of W/D, temperature, and pressure have been chosen. A similar interpretation is used for Eqs. (9.39) and (9.40). These expressions reduce in the limit to the bubble point ($W/D = \infty$) and dew point ($W/D = 0$), Eqs. (9.22) and (9.30), respectively.

Illustration 9.5 A liquid containing 50 mol % benzene (A), 25 mol % toluene (B), and 25 mol % *o*-xylene (C) is flash-vaporized at 1 std atm pressure and 100°C. Compute the amounts of liquid and vapor products and their composition.

SOLUTION For Raoult's law, $y^* = px/p_t$, so that for each component $m = p/p_t$. $p_t =$ 760 mmHg. In the following table, column 2 lists the vapor pressures p at 100°C for each substance and column 3 the corresponding value of m. The feed composition is listed in column 4. A value of W/D is arbitrarily chosen as 3.0, and Eq. (9.37) used to compute y^*_D's in column 5. Since the sum of the y^*_D's is not unity, a new value of W/D is chosen until finally (column 6) $W/D = 2.08$ is seen to be correct.

Basis: $F = 100$ mol.

$$100 = W + D \qquad \frac{W}{D} = 2.08$$

Therefore $\qquad D = 32.5 \text{ mol} \qquad W = 67.5 \text{ mol}$

The composition of the residual liquid can be found by material balance or by equilibrium relation, as in column 7.

				$\frac{W}{D} = 3.0$	$\frac{W}{D} = 2.08$	$x_W = \frac{Fz_F - Dy^*_D}{W}$
Substance	p = vapor pressure, mmHg	$m = \frac{p}{760}$	z_F	$\frac{z_F(W/D + 1)}{1 + W/D_m} = y^*_D$	y^*_D	$= \frac{y^*_D}{m}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
A	1370	1.803	0.50	$\frac{0.5(3 + 1)}{1 + 3/1.803} = 0.750$	0.715	0.397
B	550	0.724	0.25	0.1940	0.1983	0.274
C	200	0.263	0.25	0.0805	0.0865	0.329
				$\Sigma = 1.0245$	0.9998	1.000

Successive flash vaporizations can be made on the residual liquids in a series of single-stage operations, whereupon the separation will be better than that obtained if the same amount of vapor were formed in a single operation. As the amount of vapor formed in each stage becomes smaller and the total number of vaporizations larger, the operation approaches differential distillation in the limit.

DIFFERENTIAL, OR SIMPLE, DISTILLATION

If during an infinite number of successive flash vaporizations of a liquid only an infinitesimal portion of the liquid were flashed each time, the net result would be equivalent to a differential, or simple, distillation.

In practice this can only be approximated. A batch of liquid is charged to a kettle or still fitted with some sort of heating device such as a steam jacket, as in Fig. 9.16. The charge is boiled slowly, and the vapors are withdrawn as rapidly as they form to a condenser, where they are liquefied, and the condensate (distillate) is collected in the receiver. The apparatus is essentially a large-scale replica of the ordinary laboratory distillation flask and condenser. The first portion of the distillate will be the richest in the more volatile substance, and as distillation proceeds, the vaporized product becomes leaner. The distillate can therefore be collected in several separate batches, called *cuts*, to give a series of distilled products of various purities. Thus, for example, if a ternary mixture contained a small amount of a very volatile substance A, a majority of substance B of intermediate volatility, and a small amount of C of low volatility, the first cut, which would be small, would contain the majority of A. A large second cut would contain the majority of B reasonably pure but nevertheless contaminated with A and C, and the residue left in the kettle would be largely C. While all three cuts would contain all three substances, nevertheless some separation would have been obtained.

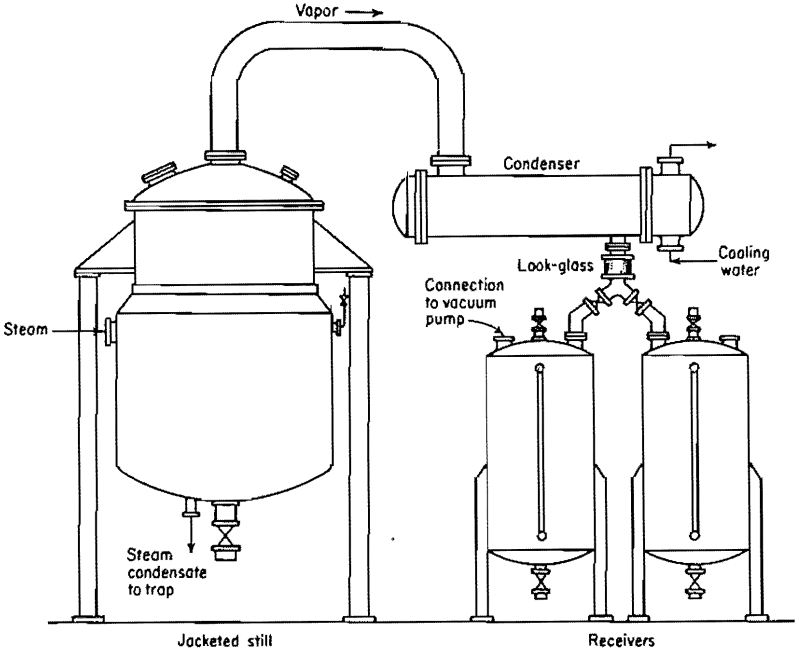


Figure 9.16 Batch still.

For such an operation to approach even approximately the theoretical characteristics of a differential distillation, it would have to proceed infinitely slowly so that the vapor issuing from the liquid would at all times be in equilibrium with the liquid. All entrainment would have to be eliminated, and there could be no cooling and condensation of the vapor before it entered the condenser. Despite the fact that these conditions are substantially impossible to attain, it is nevertheless useful to study the limiting results which a differential distillation could produce as a standard for comparison.

Binary Mixtures

The vapor issuing from a true differential distillation is at any time in equilibrium with the liquid from which it rises but changes continuously in composition. The mathematical approach must therefore be differential. Assume that at any time during the course of the distillation there are L mol of liquid in the still of composition x mole fraction A and that an amount dD mol of distillate is vaporized, of mole fraction y^* in equilibrium with the liquid. Then we have the following material balances:

	Total material	Component A
Moles in	0	0
Moles out	dD	y^*dD
Moles accumulated	dL	$d(Lx) = Ldx + xdL$
In—out = accumulation	$0 - dD = dL$	$0 - y^*dD = Ldx + xdL$

The last two equations become

$$y^*dL = Ldx + xdL \tag{9.41}$$

$$\int_W^F \frac{dL}{L} = \ln\frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{y^* - x} \tag{9.42}$$

where F is the moles of charge of composition x_F and W the moles of residual liquid of composition x_W. This is known as the *Rayleigh equation*, after Lord Rayleigh, who first derived it. It can be used to determine F, W, x_F, or x_W when three of these are known. Integration of the right-hand side of Eq. (9.42), unless an algebraic equilibrium relationship between y^* and x is available, is done graphically by plotting $1/(y^* - x)$ as ordinate against x as abscissa and determining the area under the curve between the indicated limits. The data for this are taken from the vapor-liquid equilibrium relationship. The *composited* distillate composition $y_{D,\,\mathrm{av}}$ can be determined by a simple material balance,

$$Fx_F = Dy_{D,\,\mathrm{av}} + Wx_W \tag{9.43}$$

Differential Condensation

This is a similar operation where a vapor feed is slowly condensed under equilibrium conditions and the condensate withdrawn as rapidly as it forms. As in distillation, the results can only be approximated in practice. A derivation similar to that above leads to

$$\ln\frac{F}{D} = \int_{y_F}^{y_D} \frac{dy}{y - x^*} \tag{9.44}$$

where F is the moles of feed vapor of composition y_F and D the vaporous residue of composition y_D.

Constant Relative Volatility

If Eq. (9.2) can describe the equilibrium relation at constant pressure by use of some average relative volatility α over the concentration range involved, this can be substituted in Eq. (9.42) to yield

$$\ln\frac{F}{W} = \frac{1}{\alpha - 1}\ln\frac{x_F(1 - x_W)}{x_W(1 - x_F)} + \ln\frac{1 - x_W}{1 - x_F} \tag{9.45}$$

and graphical integration can be avoided. This can be rearranged to another useful form

$$\log \frac{Fx_F}{Wx_W} = \alpha \log \frac{F(1 - x_F)}{W(1 - x_W)} \tag{9.46}$$

which relates the number of moles of A remaining in the residue, Wx_W, to that of B remaining, $W(1 - x_W)$. These expressions are most likely to be valid for ideal mixtures, for which α is most nearly constant.

Illustration 9.6 Suppose the liquid of Illustration 9.4 [50 mol % *n*-heptane (A), 50 mol % *n*-octane (B)] were subjected to a differential distillation at atmospheric pressure, with 60 mol % of the liquid distilled. Compute the composition of the composited distillate and the residue.

SOLUTION *Basis*: $F = 100$ mol. $x_F = 0.50$, $D = 60$ mol, $W = 40$ mol. Eq. (9.42):

$$\ln \frac{100}{40} = 0.916 = \int_{x_W}^{0.50} \frac{dx}{y^* - x}$$

The equilibrium data are given in Illustrations 9.1 and 9.4. From these, the following are calculated:

x	0.50	0.46	0.42	0.38	0.34	0.32
y^*	0.689	0.648	0.608	0.567	0.523	0.497
$1/(y^* - x)$	5.29	5.32	5.32	5.35	5.50	5.65

x as abscissa is plotted against $1/(y^* - x)$ as ordinate, and the area under the curve obtained beginning at $x_F = 0.50$. When the area equals 0.916, integration is stopped; this occurs at $x_W = 0.33$ mole fraction heptane in the residue. The composited distillate composition is obtained through Eq. (9.43),

$$100(0.50) = 60y_{D,\text{av}} + 40(0.33)$$

$$y_{D,\text{av}} = 0.614 \text{ mole fraction heptane}$$

Note that, for the same percentage vaporization, the separation in this case is better than that obtained by flash vaporization; i.e., each product is purer in its majority component.

Alternatively, since for this system the average $\alpha = 2.16$ at 1 atm (Illustration 9.1), Eq. (9.46):

$$\log \frac{100(0.5)}{40x_W} = 2.16 \log \frac{100(1 - 0.5)}{40(1 - x_W)}$$

from which by trial and error $x_W = 0.33$.

Multicomponent Systems—Ideal Solutions

For multicomponent systems forming ideal liquid solutions, Eq. (9.46) can be written for any two components. Ordinarily one component is chosen on which to base the relative volatilities, whereupon Eq. (9.46) is written once for each of the others. For example, for substance J, with relative volatility based on substance B,

$$\log \frac{Fx_{J,F}}{Wx_{J,W}} = \alpha_{JB} \log \frac{Fx_{B,F}}{Wx_{B,W}} \tag{9.47}$$

and $$\Sigma x_W = 1.0 \tag{9.48}$$

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,

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

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

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

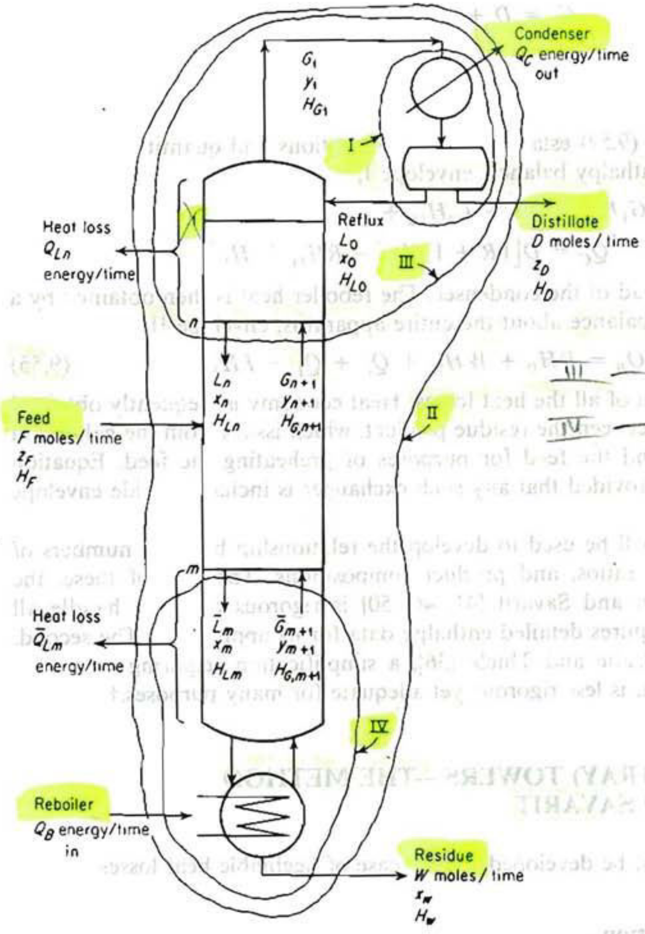
In order to understand how such an operation is carried out, recall the discussion of reboiled absorbers in Chap. 8 and Fig. 8.28. There, because the liquid leaving the bottom of an absorber is at best in equilibrium with the feed and may therefore contain substantial concentrations of volatile component, 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



III — enriching section
IV — stripping section.

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

Equations (9.50) to (9.52) establish the concentrations and quantities at the top of the tower. An enthalpy balance, envelope I,
$$G_1 H_{G1} = Q_C + L_0 H_{L0} + D H_D \tag{9.53}$$
$$Q_C = D\left[(R + 1) H_{G1} - R H_{L0} - H_D\right] \tag{9.54}$$

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,
$Q_L = 0$

$$Q_B = D H_D + W H_W + Q_C + Q_L - F H_F \tag{9.55}$$

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,
$$G_{n+1} y_{n+1} = L_n x_n + D z_D \tag{9.57}$$
$$G_{n+1} y_{n+1} - L_n x_n = D z_D \tag{9.58}$$
[illegible]

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

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† 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 Q'D

$$\text{(III)}\qquad G_{n+1}H_{G_{n+1}} = L_nH_{Ln} + \boxed{Q_C + DH_D}\ \text{heat removed} \tag{9.59}$$

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

$$Q' = \frac{Q_C + DH_D}{D} = \frac{Q_C}{D} + H_D \tag{9.60}$$

and

$$G_{n+1}H_{G_{n+1}} - L_nH_{L_n} = \boxed{DQ'}\ \text{constant} \tag{9.61}$$

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 passing thru'

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

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_{Ln}, 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

$$G_{n+1} - L_n = \Delta_D \tag{9.63}$$

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

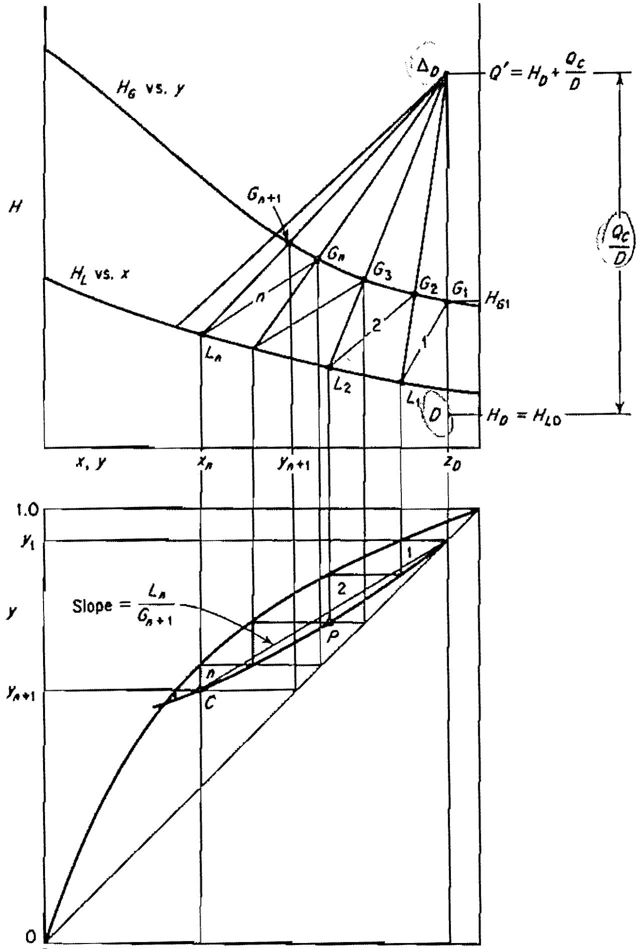


Figure 9.18 Enriching section, total condenser, reflux below the bubble point.

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_Gy and H_Lx 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 $R = L_0/D =$ line $\Delta_D G_1$/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.

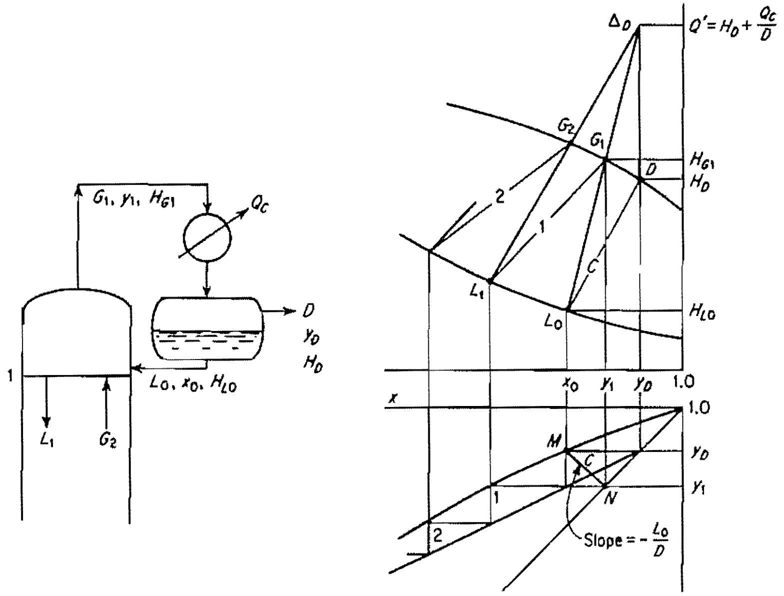


Figure 9.19 Partial condenser.

The Stripping Section

Consider the envelope IV, Fig. 9.17, where tray m is any tray in the stripping section. A balance for total material is

$$\bar{L}_m = \bar{G}_{m+1} + W \tag{9.66}$$

and, for component A,

$$\bar{L}_m x_m = \bar{G}_{m+1} y_{m+1} + W x_W \tag{9.67}$$

$$\bar{L}_m x_m - \bar{G}_{m+1} y_{m+1} = W x_W \tag{9.68}$$

The left-hand side of Eq. (9.68) represents the difference in rate of flow of component A, down − up, or the net flow downward. Since the right-hand side is a constant for a given distillation, the difference is independent of tray number in this section of the tower and equal to the rate of permanent removal of A out the bottom. An enthalpy balance is

$$\bar{L}_m H_{L_m} + Q_B = \bar{G}_{m+1} H_{G_{m+1}} + W H_W \tag{9.69}$$

Define Q'' as the net flow of heat outward at the bottom, per mole of residue

$$Q'' = \frac{WH_W - \overset{Q_B}{\cancel{W_B}}}{W} = H_W - \frac{Q_B}{W} \tag{9.70}$$

whence

$$\bar{L}_m H_{L_m} - \bar{G}_{m+1} H_{G_{m+1}} = WQ'' \tag{9.71}$$

The left-hand side of Eq. (9.71) is the difference in rate of flow of heat, down − up, which then equals the constant net rate of heat flow out the bottom for all trays in this section.

Elimination of W between Eqs. (9.66) and (9.67) and between Eqs. (9.66) and (9.71) provides

goes thru'

$$\frac{\bar{L}_m}{\bar{G}_{m+1}} = \frac{y_{m+1} - x_W}{x_m - x_W} = \frac{H_{G_{m+1}} - Q''}{H_{L_m} - Q''} \tag{9.72}$$

On the Hxy diagram, Eq. (9.72) is a straight line through $(H_{G_{m+1}}, y_{m+1})$ at $\bar{G}_{m+1}$, (H_{L_m}, x_m) at $\bar{L}_m$, and (Q'', x_W) at Δ_W. Δ_W is a *difference* point, whose coordinates mean

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

Thus, Δ_W is a fictitious stream, in amount equal to the net flow outward (in this case W), of properties (Q'', x_W),

$$\bar{L}_m - \bar{G}_{m+1} = \Delta_W \tag{9.73}$$

On the xy diagram, Eq. (9.72) is a straight line of slope $\bar{L}_m / \bar{G}_{m+1}$, through (y_{m+1}, x_m) and $y = x = x_W$. These straight lines are plotted in Fig. 9.20 for both diagrams.

Since Eq. (9.72) applies to all trays of the stripping section, the line on the Hxy plot of Fig. 9.20 from $\bar{G}_{N_p+1}$ (vapor leaving the reboiler and entering the bottom tray N_p of the tower) to Δ_W intersects the saturated-liquid-enthalpy curve at $\bar{L}_{N_p}$, the liquid leaving the bottom tray. Vapor $\bar{G}_{N_p}$ leaving the bottom tray is in equilibrium with liquid $\bar{L}_{N_p}$ and is located on the tie line N_p. Tie lines projected to the xy diagram produce points on the equilibrium curve, and lines through Δ_W provide points such as T on the operating curve. Substitution of Eq. (9.66) into Eq. (9.72) provides

$$\frac{\bar{L}_m}{W} = \frac{H_{G_{m+1}} - Q''}{H_{G_{m+1}} - H_{L_m}} = \frac{y_{m+1} - x_W}{y_{m+1} - x_m} \tag{9.74}$$

The diagrams have been drawn for the type of reboiler shown in Fig. 9.17, where the vapor leaving the reboiler is in equilibrium with the residue, the reboiler thus providing an equilibrium stage of enrichment (tie line B, Fig. 9.20). Other methods of applying heat at the bottom of the still are considered later.

Stripping-section trays can thus be determined entirely on the Hxy diagram by alternating construction lines to Δ_W and tie lines, each tie line accounting for an equilibrium stage. Alternatively, random lines radiating from Δ_W can be drawn, their intersections with curves $H_G y$ and $H_L x$ plotted on the xy diagram

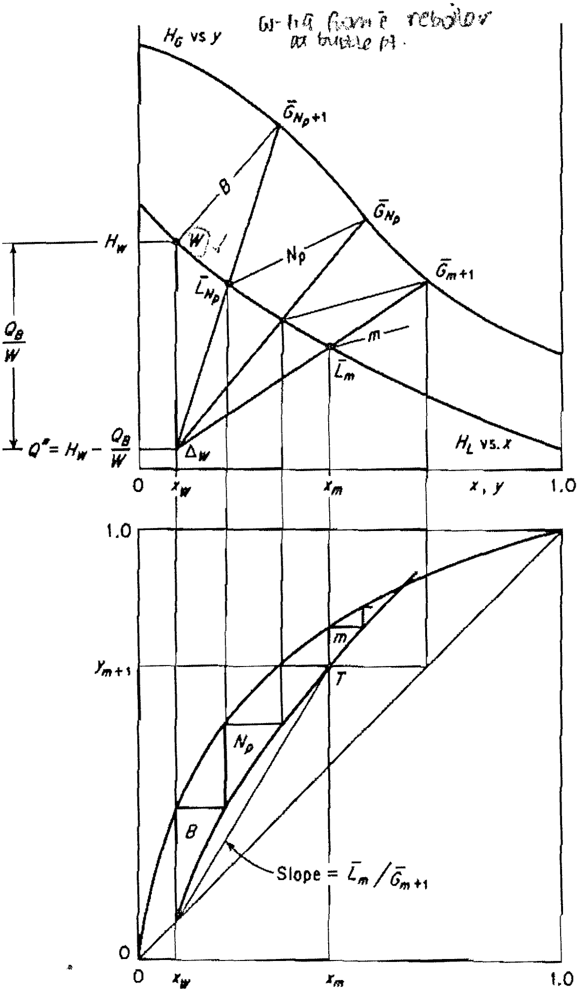


Figure 9.20 Stripping section.

to produce the operating curve, and the stages determined by the usual step construction.

The Complete Fractionator

Envelope II of Fig. 9.17 can be used for material balances over the entire device

$$F = D + W \tag{9.75}$$

$$Fz_F = Dz_D + Wx_W \tag{9.76}$$

Equation (9.55) is a complete enthalpy balance. If, in the absence of heat losses

($Q_L = 0$), the definitions of Q' and Q'' are substituted into Eq. (9.55), it becomes

$$FH_F = DQ' + WQ'' \tag{9.77}$$

If F is eliminated from Eqs. (9.75) to (9.77), there results

$$\frac{D}{W} = \frac{z_F - x_W}{z_D - z_F} = \frac{H_F - Q''}{Q' - H_F} \tag{9.78}$$

This is the equation of a straight line on the Hxy diagram, through (Q', z_D) at Δ_D, (H_F, z_F) at F, and (Q'', x_W) at Δ_W, as plotted in Fig. 9.21. In other words,

$$F = \Delta_D + \Delta_W \tag{9.79}$$

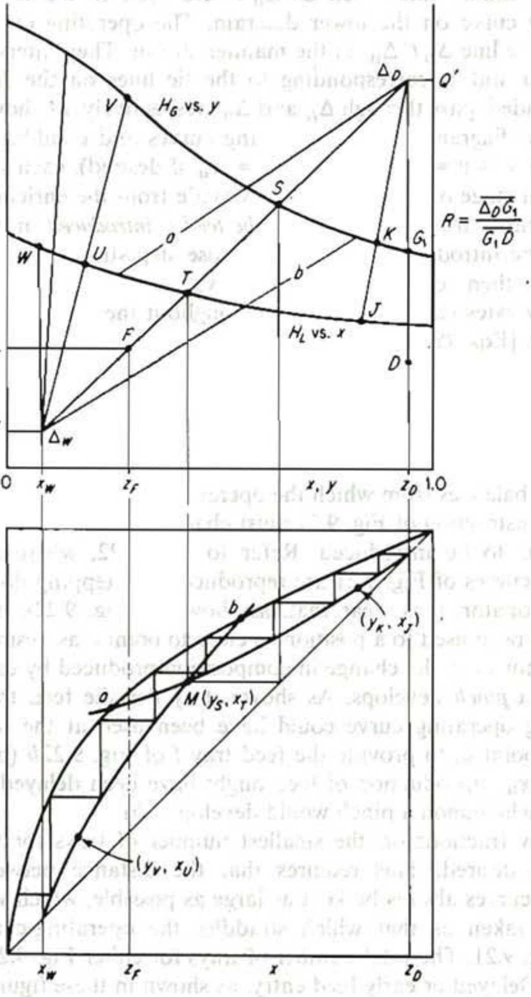


Figure 9.21 The entire fractionator. Feed below the bubble point and a total condenser.

The location of F, representing the feed, on Fig. 9.21 shows the feed in this case to be a liquid below the bubble point. In other situations, F may be on the saturated-liquid or vapor curve, between them, or above the saturated-vapor curve. In any event, the two Δ points and F must lie on a single straight line.

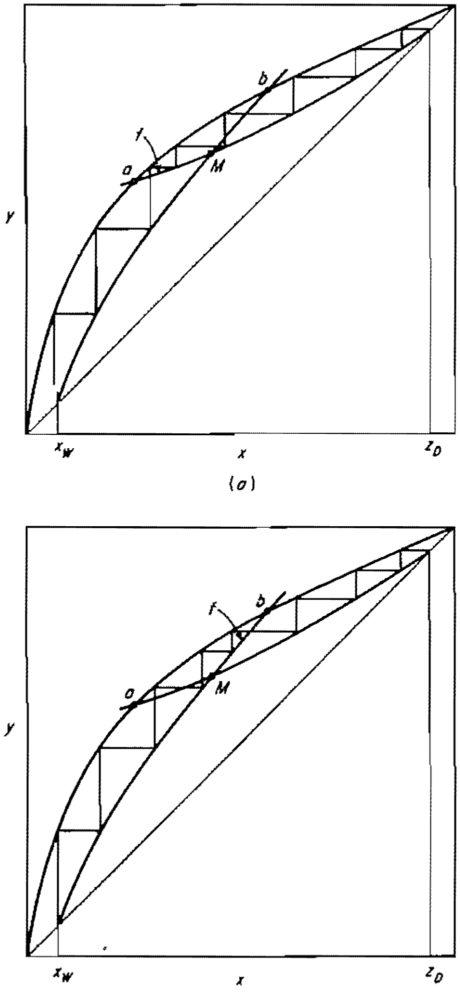
The construction for trays is now clear. After locating F and the concentration abscissas z_D and x_W corresponding to the products on the Hxy diagram, Δ_D is located vertically on line $x = z_D$ by computation of Q' or by the line-length ratio of Eq. (9.65) using the specified reflux ratio R. The line $\Delta_D F$ extended to $x = x_W$ locates Δ_W, whose ordinate can be used to compute Q_B. Random lines such as $\Delta_D J$ are drawn from Δ_D to locate the enriching-section operating curve on the xy diagram, and random lines such as $\Delta_W V$ are used to locate the stripping-section operating curve on the lower diagram. The operating curves intersect at M, related to the line $\Delta_D F \Delta_W$ in the manner shown. They intersect the equilibrium curve at a and b, corresponding to the tie lines on the Hxy diagram which, when extended, pass through Δ_D and Δ_W, respectively, as shown. Steps are drawn on the xy diagram between operating curves and equilibrium curve, beginning usually at $x = y = z_D$ (or at $x = y = x_W$ if desired), each step representing an equilibrium stage or tray. A change is made from the enriching to the stripping operating curve *at the tray on which the feed is introduced*; in the case shown the feed is to be introduced on the tray whose step straddles point M. The step construction is then continued to $x = y = x_W$.

Liquid and vapor flow rates can be computed throughout the fractionator from the line-length ratios [Eqs. (9.62), (9.64), (9.72), and (9.74)] on the Hxy diagram.

Feed-Tray Location

The material and enthalpy balances from which the operating curves are derived dictate that the stepwise construction of Fig. 9.21 must change operating lines at the tray where the feed is to be introduced. Refer to Fig. 9.22, where the equilibrium and operating curves of Fig. 9.21 are reproduced. In stepping down from the top of the fractionator, it is clear that, as shown in Fig. 9.22*a*, the enriching curve could have been used to a position as close to point a as desired. As point a is approached, however, the change in composition produced by each tray diminishes, and at a a *pinch* develops. As shown, tray f is the feed tray. Alternatively, the stripping operating curve could have been used at the first opportunity after passing point b, to provide the feed tray f of Fig. 9.22*b* (had the construction begun at x_W, introduction of feed might have been delayed to as near point b as desired, whereupon a pinch would develop at b).

In the design of a new fractionator, the smallest number of trays for the circumstances at hand is desired. This requires that the distance between operating and equilibrium curves always be kept as large as possible, which will occur if the feed tray is taken as that which straddles the operating-curve intersection at M, as in Fig. 9.21. The total number of trays for either Fig. 9.22*a* or *b* is of necessity larger. Delayed or early feed entry, as shown in these figures,



(a)

(b)

Figure 9.22 Delayed and early feed entries.

is used only where a separation is being adapted to an existing tower equipped with a feed-tray entry nozzle on a particular tray, which must then be used.

Consider again the feed tray of Fig. 9.21. It is understood that if the feed is all liquid, it is introduced above the tray in such a manner that it enters the tray along with the liquid from the tray above. Conversely, if the feed is all vapor, it is introduced underneath the feed tray. Should the feed be mixed liquid and vapor, in principle it should be separated outside the column and the liquid portion introduced above, the vapor portion below, the feed tray. This is rarely 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 $\overline{L}_m/\overline{G}_{m+1}$, 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, $\overline{L}$, G, and $\overline{G}$ all increase; condenser and reboiler surfaces and tower cross section must be increased to accommodate the larger loads.

Total Reflux

Ultimately, when $R = \infty$, $L_n/G_{n+1} = \overline{L}_m/\overline{G}_{m+1} = 1$, 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

$$\frac{y_W}{1 - y_W} = \alpha_W \frac{x_W}{1 - x_W} \tag{9.80}$$

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

$$\frac{x_{N_m}}{1 - x_{N_m}} = \alpha_W \frac{x_W}{1 - x_W} \tag{9.81}$$

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

$$\frac{y_{N_m}}{1 - y_{N_m}} = \alpha_{N_m} \frac{x_{N_m}}{1 - x_{N_m}} = \alpha_{N_m} \alpha_W \frac{x_W}{1 - x_W} \tag{9.82}$$

This procedure can be continued up the column until ultimately

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

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

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

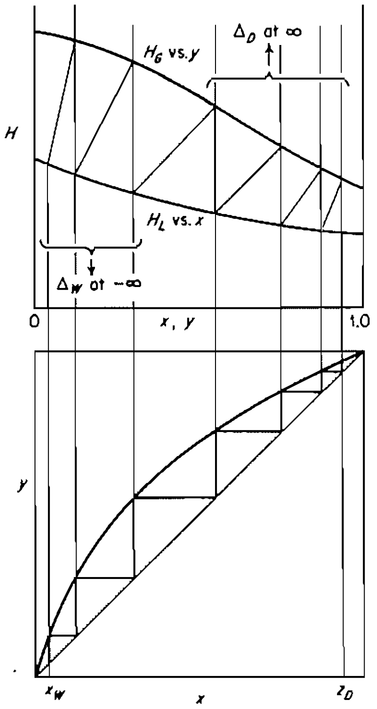


Figure 9.23 Total reflux and minimum stages.

or

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

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, $\sqrt{\alpha_1 \alpha_W}$. 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. 9.24*a*, 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.

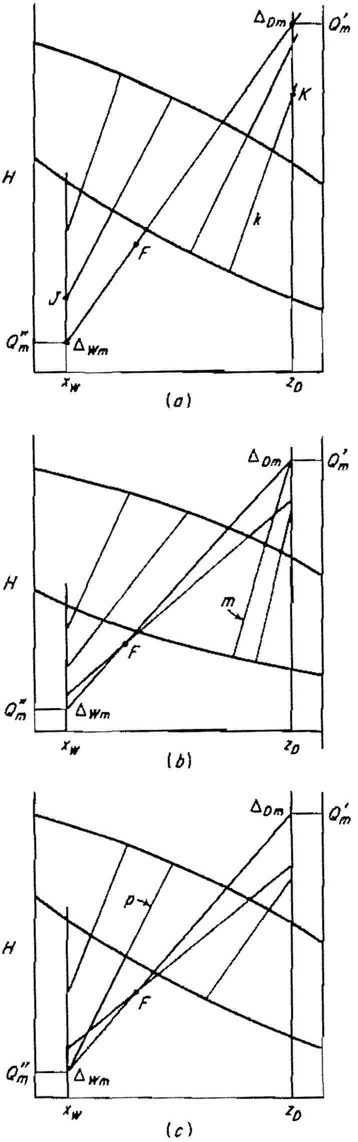


Figure 9.24 Minimum reflux ratio.

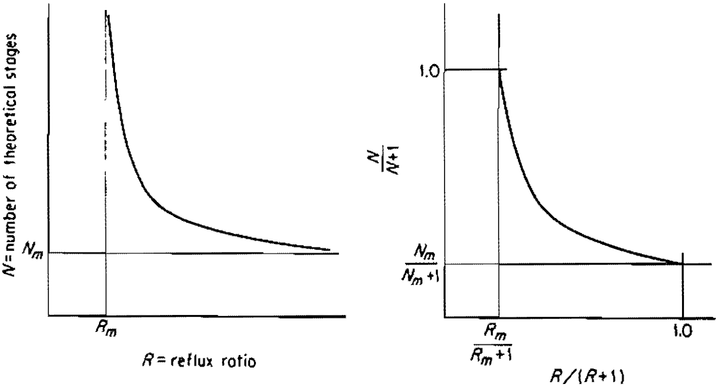
Since as Δ_D is moved upward and Δ_W downward the reflux ratio increases, the definition of minimum reflux ratio requires Δ_{D_m} and Δ_{W_m} for the minimum reflux ratio to be located as shown, with Δ_{D_m} at the highest tie-line intersection and Δ_{W_m} at the lowest tie-line intersection. In this 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



(*a*) (*b*)

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

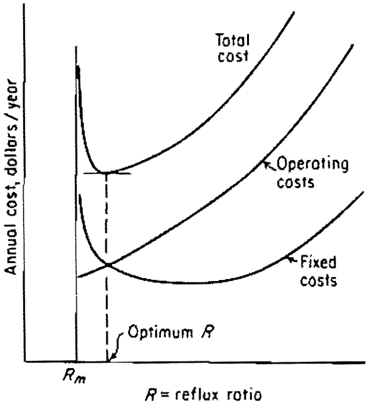


Figure 9.26 Most economical (optimum) reflux ratio.

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.

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

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

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

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

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

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

Eq. (9.75):

$$216.8 = D + W$$

Eq. (9.76):

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

Solving simultaneously gives

$$D = 84.4 \text{ kmol/h} \qquad 84.4(31.1) = 2620 \text{ kg/h}$$
$$W = 132.4 \text{ kmol/h} \qquad 132.4(18.08) = 2380 \text{ kg/h}$$

(*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.

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

$$H_L = 3.852(78.3 - 19.69)22.2 - 916.5 = 4095 \text{ kJ/kmol}$$

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):

$$\begin{aligned} H_G &= 0.665[2.583(32.04)(78.3 - 19.69) + 1046.7(32.04)] \\ &\quad + (1 - 0.665)[2.323(18.02)(78.3 - 19.69) + 2314(18.02)] \\ &= 40\,318 \text{ kJ/kmol} \end{aligned}$$

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:

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

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

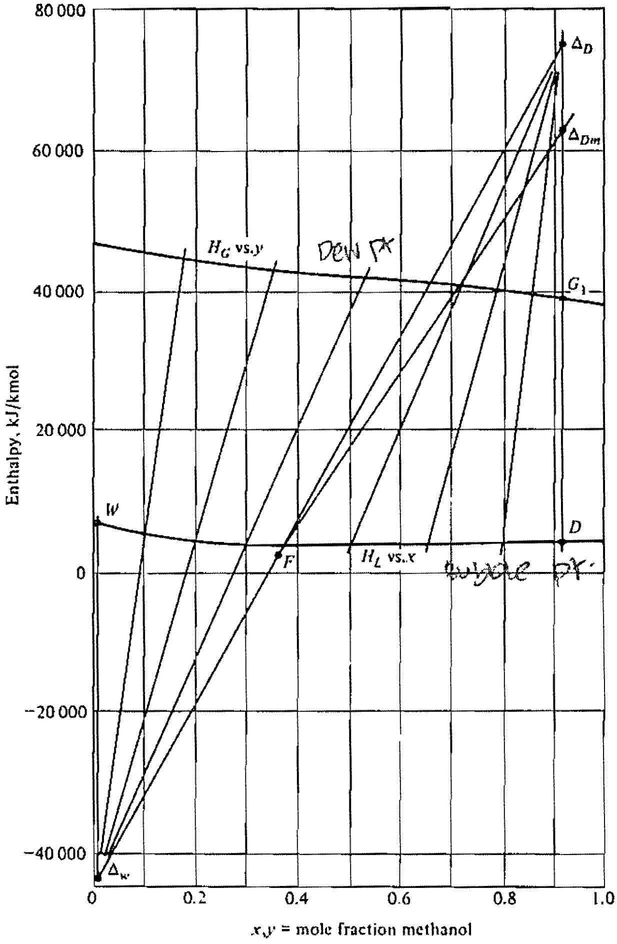


Figure 9.27 Enthalpy-concentration diagram for Illustration 9.8.

(*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, $\Delta H_S = -902.5$ 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_{D_m}, $Q_m = 62\,570$ kJ/kmol. $H_{G1} = 38\,610$ kJ/kmol. Eq. (9.65):

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

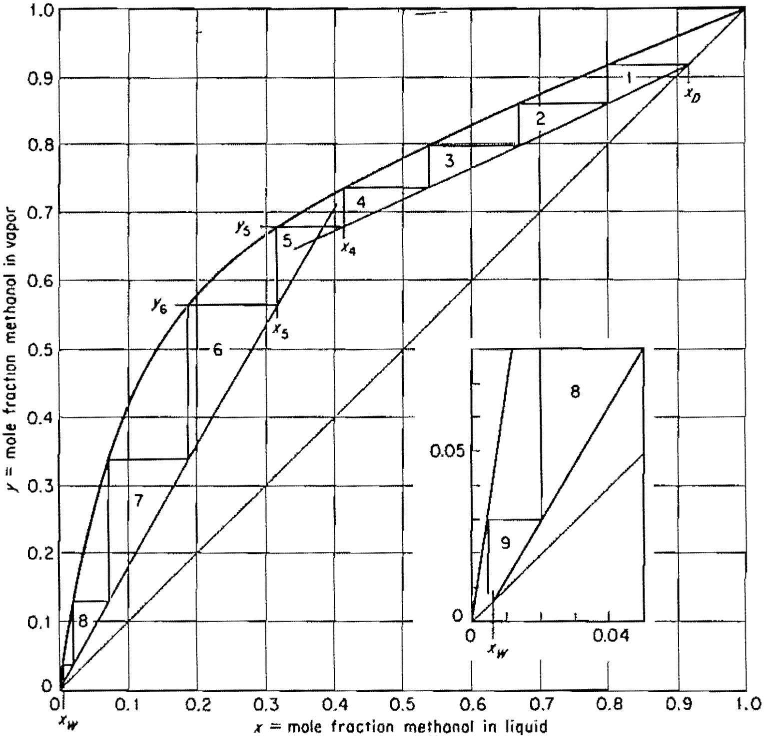


Figure 9.28 *xy* diagram for Illustration 9.8.

(*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

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

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

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

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

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

(*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, $x_4 = 0.415, y_5 = 0.676, x_5 = 0.318, y_6 = 0.554$ (Fig. 9.28). Eq. (9.64):

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

Eq. (9.62):

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

Eq. (9.74):

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

Eq. (9.72):

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

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

$$\bar{L}_{N_p} = \bar{G}_W + W \qquad \bar{L}_8 = \bar{G}_W + 132.4$$

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 $\bar{G}_W = 127.6$, $\bar{L}_8 = 260$ 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

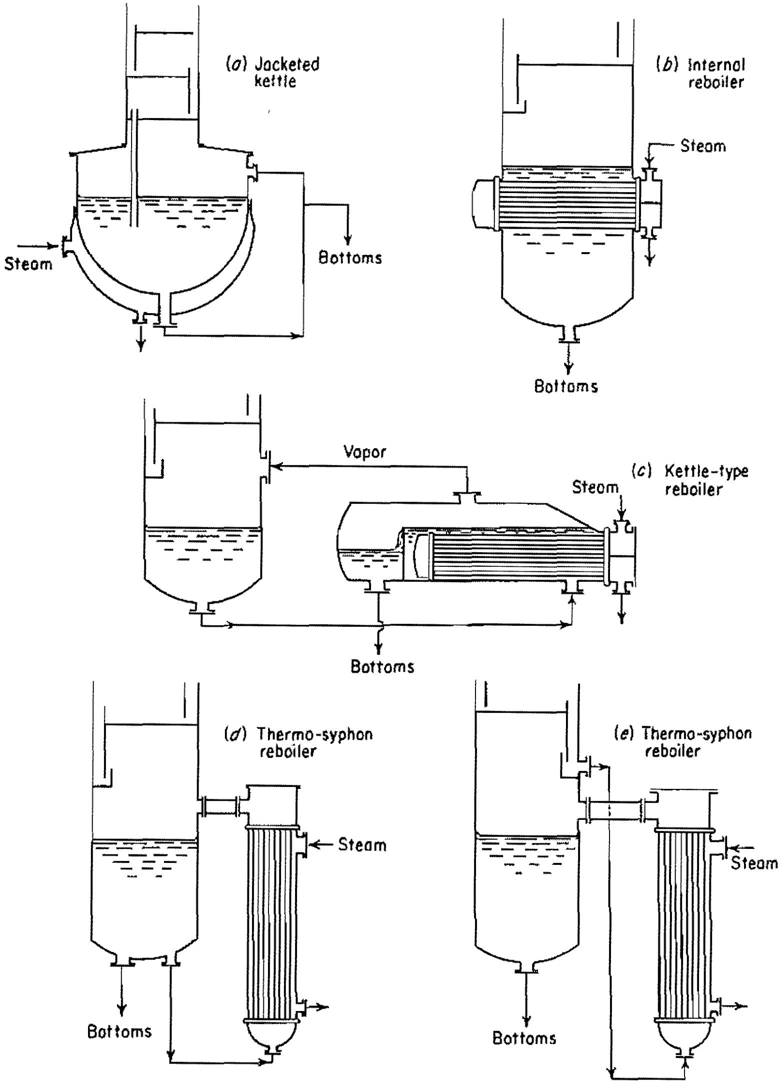


Figure 9.29 Reboiler arrangements (schematic).

heating medium outside the tubes, can be operated so as to vaporize all the liquid entering it to produce a vapor of the same composition as the residue product, in which case no enrichment is provided. However, because of fouling of the tubes, which may occur with this type of operation, it is more customary to provide for only partial vaporization, the mixture issuing from the reboiler comprising both liquid and vapor. The reboiler of Fig. 9.29*e* receives liquid from the trapout of the bottom tray, which it partially vaporizes. Horizontal reboilers are also known [8]. Piping arrangements [27], a review [37], and detailed design methods [14, 49] are available. It is safest not to assume that a theoretical stage's worth of fractionation will occur with thermosiphon reboilers but instead to provide the necessary stages in the tower itself. In Fig. 9.29, the reservoir at the foot of the tower customarily holds a 5- to 10-min flow of liquid to provide for reasonably steady operation of the reboiler.

Reboilers may be heated by steam, heat-transfer oil, or other hot fluids. For some high-boiling liquids, the reboiler may be a fuel-fired furnace.

Use of Open Steam

When a water solution in which the nonaqueous component is the more volatile is fractionated, so that the water is removed as the residue product, the heat required can be provided by admission of steam directly to the bottom of the tower. The reboiler is then dispensed with. For a given reflux ratio and distillate composition, more trays will usually be required in the tower, but they are usually cheaper than the replaced reboiler and its cleaning costs.

Refer to Fig. 9.30. While the enriching section of the tower is unaffected by the use of open steam and is not shown, nevertheless the overall material and enthalpy balances are influenced. Thus, in the absence of important heat loss,

$$F + \overline{G}_{N_p+1} = D + W \tag{9.86}$$

$$Fz_F = Dz_D + Wx_W \tag{9.87}$$

$$FH_F + \overline{G}_{N_p+1}H_{G,\,N_p+1} = WH_W + DH_D + Q_C \tag{9.88}$$

where $\overline{G}_{N_p+1}$ is the molar rate of introducing steam. On the *Hxy* diagram, the Δ_D difference point is located in the usual manner. For the stripping section, Δ_W has its usual meaning, a fictitious stream of size equal to the net flow outward

$$\Delta_W = \overline{L}_m - \overline{G}_{m+1} = W - \overline{G}_{N_p+1} \tag{9.89}$$

of coordinates

$$\Delta_W \begin{cases} x_{\Delta W} = \dfrac{\text{net moles A out}}{\text{net moles out}} = \dfrac{Wx_W}{W - \overline{G}_{N_p+1}} \\[2ex] Q'' = \dfrac{\text{net heat out}}{\text{net moles out}} = \dfrac{WH_W - \overline{G}_{N_p+1}H_{G,\,N_p+1}}{W - \overline{G}_{N_p+1}} \end{cases}$$

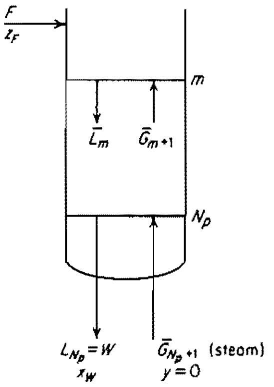


Figure 9.30 Use of open steam.

where H_{G,N_p+1} is the enthalpy of the steam. The point is shown on Fig. 9.31. Thus,

$$\bar{L}_m x_m - \bar{G}_{m+1} y_{m+1} = \Delta_W x_W \tag{9.90}$$

$$\bar{L}_m H_{L_m} - \bar{G}_{m+1} H_{G_{m+1}} = \Delta_W Q'' \tag{9.91}$$

and

$$\frac{\bar{L}_m}{\bar{G}_{m+1}} = \frac{y_{m+1} - x_{\Delta W}}{x_m - x_{\Delta W}} = \frac{H_{G_{m+1}} - Q''}{H_{L_m} - Q''} \tag{9.92}$$

The construction is shown in Fig. 9.31. Equation (9.92) is the slope of a chord (not shown) between points P and T. Here, the steam introduced is shown slightly superheated (H_{G,N_p+1} > saturated enthalpy); had saturated steam been used, $\bar{G}_{N_p+1}$ would be located at point M. Note that the operating curve on the x, y diagram passes through the 45° diagonal at T ($x = x_{\Delta W}$) and through the point ($x_W, y = 0$) corresponding to the fluids passing each other at the bottom of the tower.

Illustration 9.9 Open steam, initially saturated at 69 kN/m^2 (10 lb$_f$/in^2) gauge pressure, will be used for the methanol fractionator of Illustration 9.8, with the same distillate rate and composition and the same reflux ratio. Assuming that the feed enters the tower at the same enthalpy as in Illustration 9.8, determine the steam rate, bottoms composition, and the number of theoretical trays.

SOLUTION From Illustration 9.8, $F = 216.8$ kmol/h, $z_F = 0.360$, $H_F = 2533$ kJ/kmol, $D = 84.4$, $z_D = 0.915$, $H_D = 3640$ and $Q_C = 5\,990\,000$ kJ/h. From the steam tables, the enthalpy of saturated steam at 69 kN/m^2 = 2699 kJ/kg referred to liquid water at 0°C. On expanding adiabatically through a control valve to the tower pressure, it will be superheated at the same enthalpy. The enthalpy of liquid water at 19.7°C (t_0 for Illustration 9.8) = 82.7 kJ/kg referred to 0°C. Therefore $H_{G,N_p+1} = (2699 - 82.7)(18.02) = 47\,146$ kJ/kmol.

Eq. (9.86):

$$216.8 + \bar{G}_{N_p+1} = 84.4 + W$$

Eq. (9.87):

$$216.8(0.360) = 84.4(0.915) + Wx_W$$

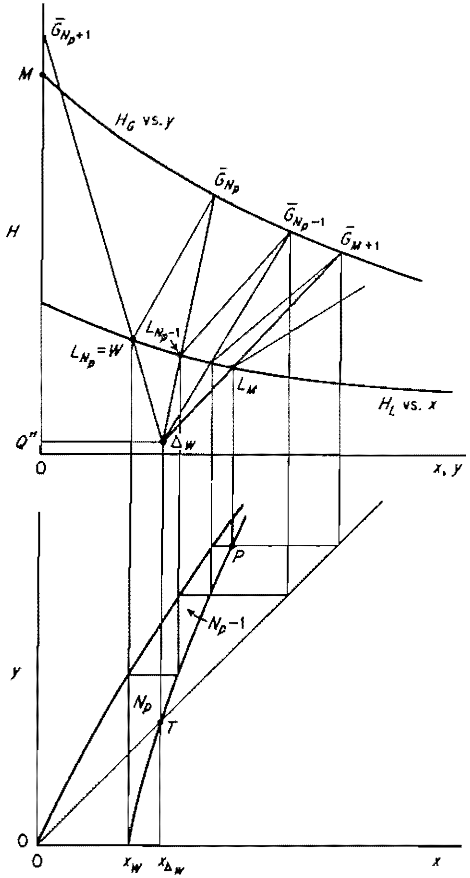


Figure 9.31 Use of open steam.

Eq. (9.88):

$$216.8(2533) + 47\,146\bar{G}_{N_p+1} = WH_W + 84.4(3640) + 5\,990\,000$$

Since the bottoms will be essentially pure water, H_W is tentatively estimated as the enthalpy of saturated water (Fig. 9.27), 6094 kJ/kmol. Solving the equations simultaneously with this value for H_W provides the steam rate as $\bar{G}_{N_p+1} = 159.7$ and $W = 292.1$ kmol/h, with $x_W = 0.00281$. The enthalpy of this solution at its bubble point is 6048, sufficiently close to the 6094 assumed earlier to be acceptable. (Note that had the same interchange of heat between bottoms and feed been used as in Illustration 9.8, with bottoms discharged at 37.8°C, the feed enthalpy would have been changed.) For Δ_W,

$$x_{\Delta W} = \frac{Wx_W}{W - \bar{G}_{N_p+1}} = \frac{292.1(0.00281)}{292.1 - 159.7} = 0.0062$$

$$Q'' = \frac{WH_W - \bar{G}_{N_p+1}H_{G,N_p+1}}{W - \bar{G}_{N_p+1}}$$

$$= \frac{292.1(6048) - 159.7(47\,146)}{292.1 - 159.7} = -43\,520 \text{ kJ/kmol}$$

The *Hxy* and *xy* diagrams for the enriching section are the same as in Illustration 9.8. For the stripping section, they resemble Fig. 9.31. The number of theoretical stages is $N_p = 9.5$, and they must all be included in the tower.

Condensers and Reflux Accumulators

Reflux may flow by gravity to the tower, in which case the condenser and reflux drum (accumulator) must be elevated above the level of top tray of the tower. Alternatively, especially in order to obviate the need for elevated platforms and supports required for withdrawing the condenser tube bundle for cleaning, the assemblage may be placed at ground level and the reflux liquid pumped up to the top tray. Kern [28] describes the arrangements.

Reflux accumulators are ordinarily horizontal drums, length/diameter = 4 to 5, with a liquid holding time of the order of 5 min. From entrainment considerations, the allowable vapor velocity through the vertical cross section of the space above the liquid can be specified as [55]†

$$V = 0.04\left(\frac{\rho_L - \rho_G}{\rho_G}\right)^{0.5} \tag{9.93}$$

Multiple Feeds

There are occasions when two or more feeds composed of the same substances but of different concentrations require distillation to give the same distillate and residue products. A single fractionator will then suffice for all.

Consider the two-feed fractionator of Fig. 9.32. The construction on the *Hxy* diagram for the sections of the column above F_1 and below F_2 is the same as for a single-feed column, with the Δ_D and Δ_W points located in the usual manner. For the middle section between the feeds, the difference point Δ_M can be located by consideration of material and enthalpy balances either toward the top, as indicated by the envelope shown on Fig. 9.32, or toward the bottom; the net result will be the same. Consider the envelope shown in the figure, with Δ_M representing a fictitious stream of quantity equal to the net flow upward and out

$$G'_{r+1} - L'_r = D - F_1 = \Delta_M \tag{9.94}$$

whose coordinates are

$$\Delta_M \begin{cases} x_{\Delta M} = \dfrac{\text{net moles A out}}{\text{net moles out}} = \dfrac{Dz_D - F_1 z_{F1}}{D - F_1} \\[2ex] Q_M = \dfrac{\text{net heat out}}{\text{net moles out}} = \dfrac{Q_C + DH_D - F_1 H_{F_1}}{D - F_1} \end{cases}$$

Δ_M may be either a positive or negative quantity.

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† V in Eq. (9.93) is expressed as m/s. For V in ft/s, the coefficient is 0.13.

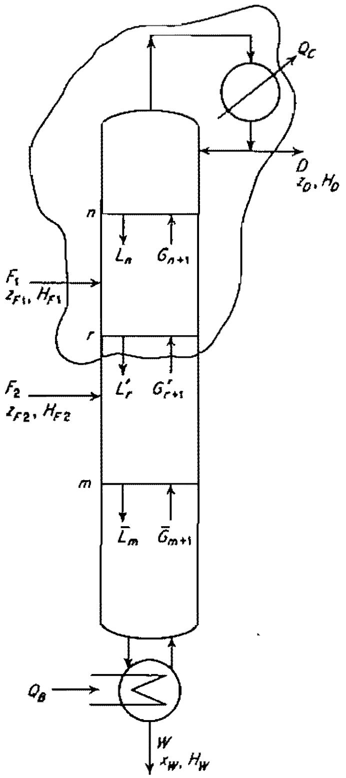

Figure 9.32 Fractionator with two feeds.

Equation (9.94) can be used as a basis for component-A and enthalpy balances

$$G'_{r+1}y_{r+1} - L'_r x_r = \Delta_M x_{\Delta M} \tag{9.95}$$

$$G'_{r+1}H_{G_{r+1}} - L_r H_{L_r} = \Delta_M Q_M \tag{9.96}$$

whence

$$\frac{L'_r}{G'_{r+1}} = \frac{y_{r+1} - x_{\Delta M}}{x_r - x_{\Delta M}} = \frac{H_{G_{r+1}} - Q_M}{H_{L_r} - Q_M} \tag{9.97}$$

Since

$$F_1 + F_2 = D + W = \Delta_D + \Delta_W \tag{9.98}$$

then

$$\Delta_M = F_2 - W \tag{9.99}$$

The construction (both feeds liquid) is shown on Fig. 9.33, where Δ_M lies on the line $\Delta_D F_1$ [Eq. (9.94)] and on the line $\Delta_W F_2$ [Eq. (9.99)]. A solution representing the composited feed, with

$$z_{F,\,\mathrm{av}} = \frac{F_1 z_{F_1} + F_2 z_{F_2}}{F_1 + F_2} \qquad H_{F,\,\mathrm{av}} = \frac{F_1 H_{F_1} + F_2 H_{F_2}}{F_1 + F_2}$$

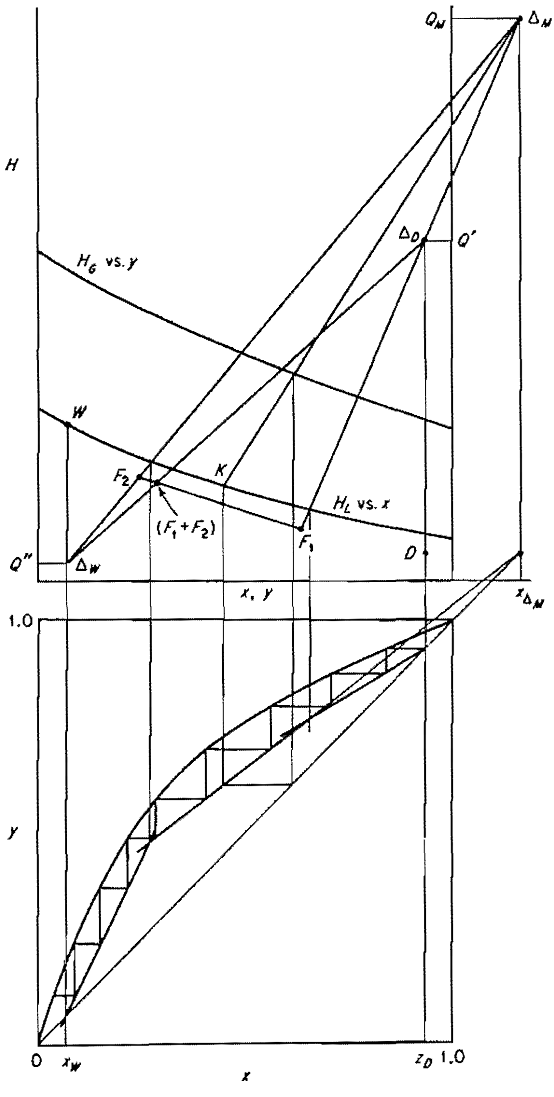

Figure 9.33 Construction for two feeds.

must lie on the line $\Delta_D\Delta_W$ [Eq. (9.98)]. It is also possible for Δ_M to lie below and to the left of Δ_W. The operating curve for the middle section on the xy diagram is located by lines such as $\Delta_M K$, as shown. Trays are best drawn in the usual step fashion on the xy diagram, and for optimum location the feed trays straddle the intersections of the operating curves, as shown.

Side Streams

Side streams are products of intermediate composition withdrawn from the intermediate trays of the column. They are used frequently in the distillation of petroleum products, where intermediate properties not obtainable merely by mixing distillate or bottoms with feed are desired. They are used only infrequently in the case of binary mixtures, and are not treated here (see Prob. 9.17).

Heat Losses

Most fractionators operate above ambient temperature, and heat losses along the column are inevitable since insulating materials have a finite thermal conductivity. The importance of the heat losses and their influence on fractionators will now be considered.

Consider the fractionator of Fig. 9.17. A heat balance for the top n trays of the enriching section (envelope III) which includes the heat loss is [9]

$$G_{n+1}H_{G_{n+1}} = Q_C + DH_D + L_nH_{L_n} + Q_{L_n} \tag{9.100}$$

where Q_{L_n} is the heat loss for trays 1 through n. Defining

$$Q_L' = \frac{Q_C + DH_D + Q_{L_n}}{D} = Q' + \frac{Q_{L_n}}{D} \tag{9.101}$$

we have

$$G_{n+1}H_{G_{n+1}} - L_nH_{L_n} = DQ_L' \tag{9.102}$$

Q_L' is a variable since it depends upon how many trays are included in the heat balance. If only the top tray ($n = 1$) is included, the heat loss is small and Q_L' is nearly equal to Q'. As more trays are included, Q_{L_n} and Q_L' increase, ultimately reaching their largest values when all enriching-section trays are included. Separate difference points are therefore needed for each tray.

For the stripping section up to tray m (envelope IV, Fig. 9.17),

$$\bar{L}_mH_{L_m} + Q_B = WH_W + \bar{G}_{m+1}H_{G_{m+1}} + \bar{Q}_{L_m} \tag{9.103}$$

Letting

$$Q_L'' = \frac{WH_W - Q_B + \bar{Q}_{L_m}}{W} = Q'' + \frac{\bar{Q}_{L_m}}{W} \tag{9.104}$$

results in

$$\bar{L}_mH_{L_m} - \bar{G}_{m+1}H_{G_{m+1}} = WQ_L'' \tag{9.105}$$

If the heat balance includes only the bottom tray, the heat loss is small and Q_L'' nearly equals Q''. As more trays are included, $\bar{Q}_{L_m}$ and therefore Q_L'' increase, reaching their largest values when the balance is made over the entire stripping section. Separate difference points are needed for each tray. An enthalpy balance for the entire tower is

$$FH_F = D\left(H_D + \frac{Q_C}{D} + \frac{Q_L}{D}\right) + W\left(H_W - \frac{Q_B}{W} + \frac{\bar{Q}_L}{W}\right) \tag{9.106}$$

where Q_L and $\bar{Q}_L$ are the total heat losses for the enriching and stripping sections, respectively. When Eq. (9.106) is solved with the material balances, Eqs. (9.75) and (9.76), the result is

$$\frac{D}{W} = \frac{z_F - x_W}{z_D - z_F} = \frac{H_F - \left(H_W - Q_B/W + \bar{Q}_L/W\right)}{\left(H_D + Q_C/D + Q_L/D\right) - H_F} \tag{9.107}$$

This is the equation of the line BFT on Fig. 9.34.

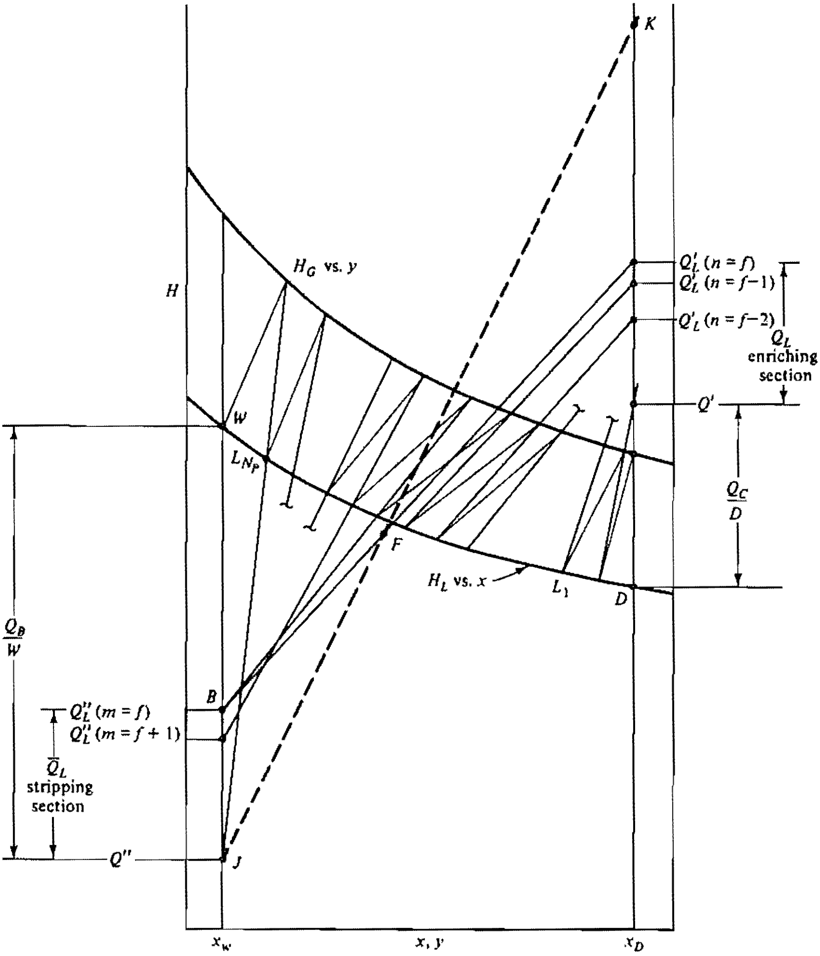

Figure 9.34 Heat losses.