

vapour to be obtained that is substantially richer in the more volatile component than is the liquid left in the still. This is achieved by an arrangement known as a fractionating column which enables successive vaporisation and condensation to be accomplished in one unit. Detailed consideration of this process is given in Section 11.4.

### 11.3.4. Batch distillation

In batch distillation, which is considered in detail in Section 11.6, the more volatile component is evaporated from the still which therefore becomes progressively richer in the less volatile constituent. Distillation is continued, either until the residue of the still contains a material with an acceptably low content of the volatile material, or until the distillate is no longer sufficiently pure in respect of the volatile content.

## 11.4. THE FRACTIONATING COLUMN

### 11.4.1. The fractionating process

The operation of a typical fractionating column may be followed by reference to Figure 11.11. The column consists of a cylindrical structure divided into sections by

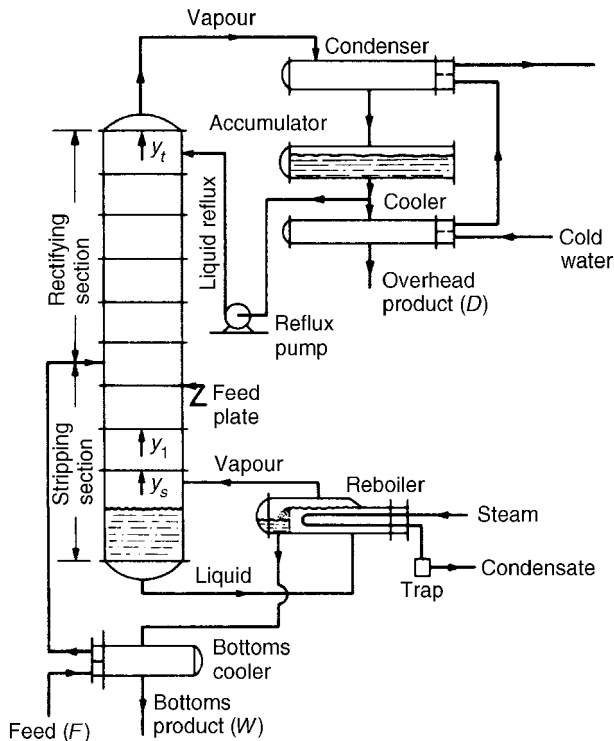


Figure 11.11. Continuous fractionating column with rectifying and stripping sections

a series of perforated trays which permit the upward flow of vapour. The liquid reflux flows across each tray, over a weir and down a downcomer to the tray below. The vapour rising from the top tray passes to a condenser and then through an accumulator or reflux drum and a reflux divider, where part is withdrawn as the overhead product D, and the remainder is returned to the top tray as reflux R.

The liquid in the base of the column is frequently heated, either by condensing steam or by a hot oil stream, and the vapour rises through the perforations to the bottom tray. A more commonly used arrangement with an external reboiler is shown in Figure 11.11 where the liquid from the still passes into the reboiler where it flows over the tubes and weir and leaves as the bottom product by way of a bottoms cooler, which preheats the incoming feed. The vapour generated in the reboiler is returned to the bottom of the column with a composition  $y_s$ , and enters the bottom tray where it is partially condensed and then revaporised to give vapour of composition  $y_1$ . This operation of partial condensation of the rising vapour and partial vaporisation of the reflux liquid is repeated on each tray. Vapour of composition  $y_t$  from the top tray is condensed to give the top product D and the reflux R, both of the same composition  $y_t$ . The feed stream is introduced on some intermediate tray where the liquid has approximately the same composition as the feed. The part of the column above the feed point is known as the rectifying section and the lower portion is known as the stripping section. The vapour rising from an ideal tray will be in equilibrium with the liquid leaving, although in practice a smaller degree of enrichment will occur.

In analysing the operation on each tray it is important to note that the vapour rising to it, and the reflux flowing down to it, are not in equilibrium, and adequate rates of mass and heat transfer are essential for the proper functioning of the tray.

The tray as described is known as a sieve tray and it has perforations of up to about 12 mm diameter, although there are several alternative arrangements for promoting mass transfer on the tray, such as valve units, bubble caps and other devices described in Section 11.10.1. In all cases the aim is to promote good mixing of vapour and liquid with a low drop in pressure across the tray.

On each tray the system tends to reach equilibrium because:

- (a) Some of the less volatile component condenses from the rising vapour into the liquid thus increasing the concentration of the more volatile component (MVC) in the vapour.
- (b) Some of the MVC is vaporised from the liquid on the tray thus decreasing the concentration of the MVC in the liquid.

The number of molecules passing in each direction from vapour to liquid and in reverse is approximately the same since the heat given out by one mole of the vapour on condensing is approximately equal to the heat required to vaporise one mole of the liquid. The problem is thus one of equimolecular counterdiffusion, described in Volume 1, Chapter 10. If the molar heats of vaporisation are approximately constant, the flows of liquid and vapour in each part of the column will not vary from tray to tray. This is the concept of constant molar overflow which is discussed under the heat balance heading in Section 11.4.2. Conditions of varying molar overflow, arising from unequal molar latent heats of the components, are discussed in Section 11.5.

In the arrangement discussed, the feed is introduced continuously to the column and two product streams are obtained, one at the top much richer than the feed in the MVC and the second from the base of the column weaker in the MVC. For the separation of small quantities of mixtures, a batch still may be used. Here the column rises directly from a large drum which acts as the still and reboiler and holds the charge of feed. The trays in the column form a rectifying column and distillation is continued until it is no longer possible to obtain the desired product quality from the column. The concentration of the MVC steadily falls in the liquid remaining in the still so that enrichment to the desired level of the MVC is not possible. This problem is discussed in more detail in Section 11.6.

A complete unit will normally consist of a feed tank, a feed heater, a column with boiler, a condenser, an arrangement for returning part of the condensed liquid as reflux, and coolers to cool the two products before passing them to storage. The reflux liquor may be allowed to flow back by gravity to the top plate of the column or, as in larger units, it is run back to a drum from which it is pumped to the top of the column. The control of the reflux on very small units is conveniently effected by hand-operated valves, and with the larger units by adjusting the delivery from a pump. In many cases the reflux is divided by means of an electromagnetically operated device which diverts the top product either to the product line or to the reflux line for controlled time intervals.

#### 11.4.2. Number of plates required in a distillation column

In order to develop a method for the design of distillation units to give the desired fractionation, it is necessary, in the first instance, to develop an analytical approach which enables the necessary number of trays to be calculated. First the heat and material flows over the trays, the condenser, and the reboiler must be established. Thermodynamic data are required to establish how much mass transfer is needed to establish equilibrium between the streams leaving each tray. The required diameter of the column will be dictated by the necessity to accommodate the desired flowrates, to operate within the available drop in pressure, while at the same time effecting the desired degree of mixing of the streams on each tray.

Four streams are involved in the transfer of heat and material across a plate, as shown in Figure 11.12 in which plate  $n$  receives liquid  $L_{n+1}$  from plate  $n + 1$  above, and vapour  $V_{n-1}$  from plate  $n - 1$  below. Plate  $n$  supplies liquid  $L_n$  to plate  $n - 1$ , and vapour  $V_n$  to plate  $n + 1$ .

The action of the plate is to bring about mixing so that the vapour  $V_n$ , of composition  $y_n$ , approaches equilibrium with the liquid  $L_n$ , of composition  $x_n$ . The streams  $L_{n+1}$  and  $V_{n-1}$  cannot be in equilibrium and, during the interchange process on the plate, some of the more volatile component is vaporised from the liquid  $L_{n+1}$ , decreasing its concentration to  $x_n$ , and some of the less volatile component is condensed from  $V_{n-1}$ , increasing the vapour concentration to  $y_n$ . The heat required to vaporise the more volatile component from the liquid is supplied by partial condensation of the vapour  $V_{n-1}$ . Thus the resulting effect is that the more volatile component is passed from the liquid running down the column to the vapour rising up, whilst the less volatile component is transferred in the opposite direction.

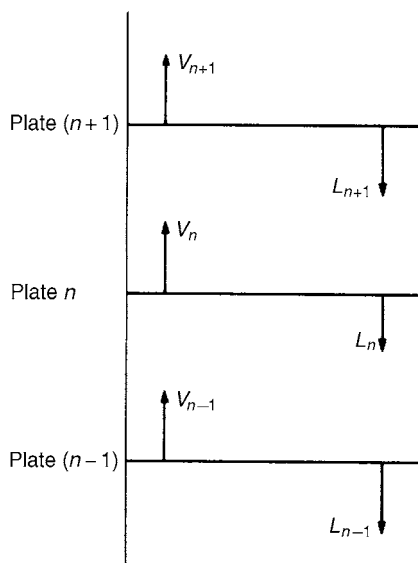


Figure 11.12. Material balance over a plate

### Heat balance over a plate

A heat balance across plate  $n$  may be written as:

$$L_{n+1}H_{n+1}^L + V_{n-1}H_{n-1}^V = V_nH_n^V + L_nH_n^L + \text{losses} + \text{heat of mixing} \quad (11.32)$$

where:  $H_n^L$  is the enthalpy per mole of the liquid on plate  $n$ , and

$H_n^V$  is the enthalpy per mole of the vapour rising from plate  $n$ .

This equation is difficult to handle for the majority of mixtures, and some simplifying assumptions are usually made. Thus, with good lagging, the heat losses will be small and may be neglected, and for an ideal system the heat of mixing is zero. For such mixtures, the molar heat of vaporisation may be taken as constant and independent of the composition. Thus, one mole of vapour  $V_{n-1}$  on condensing releases sufficient heat to liberate one mole of vapour  $V_n$ . It follows that  $V_n = V_{n-1}$ , so that the molar vapour flow is constant up the column unless material enters or is withdrawn from the section. The temperature change from one plate to the next will be small, and  $H_n^L$  may be taken as equal to  $H_{n+1}^L$ . Applying these simplifications to equation 11.32, it is seen that  $L_n = L_{n+1}$ , so that the moles of liquid reflux are also constant in this section of the column. Thus  $V_n$  and  $L_n$  are constant over the rectifying section, and  $V_m$  and  $L_m$  are constant over the stripping section.

For these conditions there are two basic methods for determining the number of plates required. The first is due to SOREL<sup>(25)</sup> and later modified by LEWIS<sup>(26)</sup>, and the second is due to McCABE and THIELE<sup>(27)</sup>. The Lewis method is used here for binary systems, and also in Section 11.7.4 for calculations involving multicomponent mixtures. This method is also the basis of modern computerised methods. The McCabe–Thiele method is particularly

important since it introduces the idea of the operating line which is an important common concept in multistage operations. The best assessment of these methods and their various applications is given by UNDERWOOD<sup>(28)</sup>.

When the molar heat of vaporisation varies appreciably and the heat of mixing is no longer negligible, these methods have to be modified, and alternative techniques are discussed in Section 11.5.

### Calculation of number of plates using the Lewis–Sorel method

If a unit is operating as shown in Figure 11.13, so that a binary feed  $F$  is distilled to give a top product  $D$  and a bottom product  $W$ , with  $x_f$ ,  $x_d$ , and  $x_w$  as the corresponding mole fractions of the more volatile component, the vapour  $V_t$  rising from the top plate is condensed, and part is run back as liquid at its boiling point to the column as reflux, the remainder being withdrawn as product, then a material balance above plate  $n$ , indicated by the loop I in Figure 11.13 gives:

$$V_n = L_{n+1} + D \quad (11.33)$$

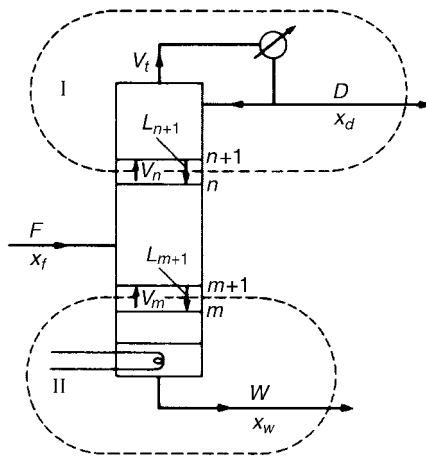


Figure 11.13. Material balances at top and bottom of column

Expressing this balance for the more volatile component gives:

$$y_n V_n = L_{n+1} x_{n+1} + D x_d$$

Thus:

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_d \quad (11.34)$$

This equation relates the composition of the vapour rising to the plate to the composition of the liquid on any plate above the feed plate. Since the molar liquid overflow is constant,  $L_n$  may be replaced by  $L_{n+1}$  and:

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D}{V_n} x_d \quad (11.35)$$

Similarly, taking a material balance for the total streams and for the more volatile component from the bottom to above plate  $m$ , as indicated by the loop II in Figure 11.13, and noting that  $L_m = L_{m+1}$  gives:

$$L_m = V_m + W \quad (11.36)$$

and:

$$y_m V_m = L_m x_{m+1} - W x_w$$

Thus:

$$y_m = \frac{L_m}{V_m} x_{m+1} - \frac{W}{V_m} x_w \quad (11.37)$$

This equation, which is similar to equation 11.35, gives the corresponding relation between the compositions of the vapour rising to a plate and the liquid on the plate, for the section below the feed plate. These two equations are the equations of the operating lines.

In order to calculate the change in composition from one plate to the next, the equilibrium data are used to find the composition of the vapour above the liquid, and the enrichment line to calculate the composition of the liquid on the next plate. This method may then be repeated up the column, using equation 11.37 for sections below the feed point, and equation 11.35 for sections above the feed point.

### Example 11.7

A mixture of benzene and toluene containing 40 mole per cent benzene is to be separated to give a product containing 90 mole per cent benzene at the top, and a bottom product containing not more than 10 mole per cent benzene. The feed enters the column at its boiling point, and the vapour leaving the column which is condensed but not cooled, provides reflux and product. It is proposed to operate the unit with a reflux ratio of 3 kmol/kmol product. It is required to find the number of theoretical plates needed and the position of entry for the feed. The equilibrium diagram at 100 kN/m<sup>2</sup> is shown in Figure 11.14.

### Solution

For 100 kmol of feed, an overall mass balance gives:

$$100 = D + W$$

A balance on the MVC, benzene, gives:

$$(100 \times 0.4) = 0.9 D + 0.1 W$$

Thus:

$$40 = 0.9(100 - W) + 0.1 W$$

and:

$$W = 62.5 \quad \text{and} \quad D = 37.5 \text{ kmol}$$

Using the notation of Figure 11.13 then:

$$L_n = 3D = 112.5$$

and:

$$V_n = L_n + D = 150$$

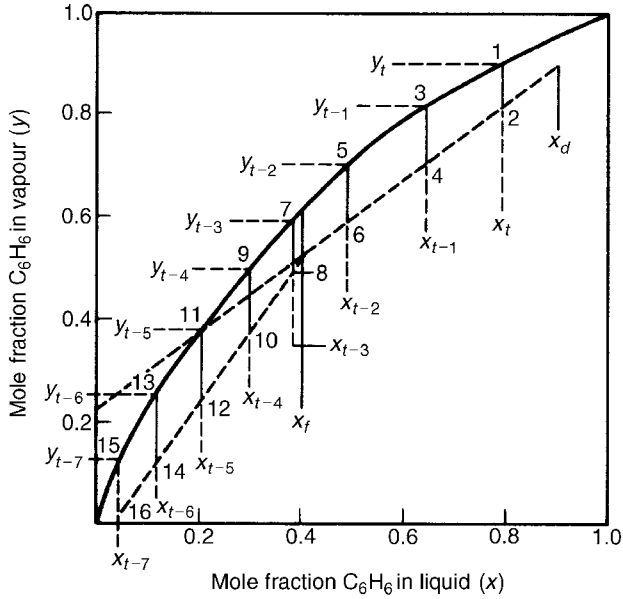


Figure 11.14. Calculation of the number of plates by the Lewis–Sorel method for Example 11.7

Thus, the top operating line from equation 11.35 is:

$$y_n = \left( \frac{112.5}{150} \right) x_{n+1} + \frac{(37.5 \times 0.9)}{150}$$

or: 
$$y_n = 0.75x_{n+1} + 0.225 \tag{i}$$

Since the feed is all liquid at its boiling point, this will all run down as increased reflux to the plate below.

Thus: 
$$L_m = L_n + F$$

$$= (112.5 + 100) = 212.5$$

Also: 
$$V_m = L_m - W$$

$$= 212.5 - 62.5 = 150 = V_n$$

Thus: 
$$y_m = \left( \frac{212.5}{150} \right) x_{m+1} - \left( \frac{62.5}{150} \right) \times 0.1 \tag{equation 11.37}$$

or: 
$$y_m = 1.415x_{m+1} - 0.042 \tag{ii}$$

With the two equations (i) and (ii) and the equilibrium curve, the composition on the various plates may be calculated by working either from the still up to the condenser, or in the reverse direction. Since all the vapour from the column is condensed, the composition of the vapour  $y_t$  from the top plate must equal that of the product  $x_d$ , and that of the liquid returned as reflux  $x_r$ . The composition  $x_t$  of the liquid on the top plate is found from the equilibrium curve and, since it is in equilibrium with vapour of composition,  $y_t = 0.90$ ,  $x_t = 0.79$ .

The value of  $y_{t-1}$  is obtained from equation (i) as:

$$y_{t-1} = (0.75 \times 0.79) + 0.225 = (0.593 + 0.225) = 0.818$$

$x_{t-1}$  is obtained from the equilibrium curve as 0.644

$$y_{t-2} = (0.75 \times 0.644) + 0.225 = (0.483 + 0.225) = 0.708$$

$x_{t-2}$  from equilibrium curve = 0.492

$$y_{t-3} = (0.75 \times 0.492) + 0.225 = (0.369 + 0.225) = 0.594$$

$x_{t-3}$  from the equilibrium curve = 0.382

This last value of composition is sufficiently near to that of the feed for the feed to be introduced on plate  $(t - 3)$ . For the lower part of the column, the operating line equation (ii) will be used.

Thus: 
$$y_{t-4} = (1.415 \times 0.382) - 0.042 = (0.540 - 0.042) = 0.498$$

$x_{t-4}$  from the equilibrium curve = 0.298

$$y_{t-5} = (1.415 \times 0.298) - 0.042 = (0.421 - 0.042) = 0.379$$

$x_{t-5}$  from the equilibrium curve = 0.208

$$y_{t-6} = (1.415 \times 0.208) - 0.042 = (0.294 - 0.042) = 0.252$$

$x_{t-6}$  from the equilibrium curve = 0.120

$$y_{t-7} = (1.415 \times 0.120) - 0.042 = (0.169 - 0.042) = 0.127$$

$x_{t-7}$  from the equilibrium curve = 0.048

This liquid  $x_{t-7}$  is slightly weaker than the minimum required and it may be withdrawn as the bottom product. Thus,  $x_{t-7}$  will correspond to the reboiler, and there will be seven plates in the column.

### ***The method of McCabe and Thiele***

The simplifying assumptions of constant molar heat of vaporisation, no heat losses, and no heat of mixing, lead to a constant molar vapour flow and a constant molar reflux flow in any section of the column, that is  $V_n = V_{n+1}$ ,  $L_n = L_{n+1}$ , and so on. Using these simplifications, the two enrichment equations are obtained:

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D}{V_n} x_d \quad (\text{equation 11.35})$$

and: 
$$y_m = \frac{L_m}{V_m} x_{m+1} - \frac{W}{V_m} x_w \quad (\text{equation 11.37})$$

These equations are used in the Lewis–Sorel method to calculate the relation between the composition of the liquid on a plate and the composition of the vapour rising to that plate. McCABE and THIELE<sup>(27)</sup> pointed out that, since these equations represent straight lines connecting  $y_n$  with  $x_{n+1}$  and  $y_m$  with  $x_{m+1}$ , they can be drawn on the same diagram as the equilibrium curve to give a simple graphical solution for the number of stages required. Thus, the line of equation 11.35 will pass through the points 2, 4 and 6 shown



in Figure 11.14, and similarly the line of equation 11.37 will pass through points 8, 10, 12 and 14.

If  $x_{n+1} = x_d$  in equation 11.35, then:

$$y_n = \frac{L_n}{V_n}x_d + \frac{D}{V_n}x_d = x_d \quad (11.38)$$

and this equation represents a line passing through the point  $y_n = x_{n+1} = x_d$ . If  $x_{n+1}$  is put equal to zero, then  $y_n = Dx_d/V_n$ , giving a second easily determined point. The top operating line is therefore drawn through two points of coordinates  $(x_d, x_d)$  and  $(0, (Dx_d/V_n))$ .

For the bottom operating line, equation 11.30, if  $x_{m+1} = x_w$ , then:

$$y_m = \frac{L_m}{V_m}x_w - \frac{W}{V_m}x_w \quad (11.39)$$

Since  $V_m = L_m - W$ , it follows that  $y_m = x_w$ . Thus the bottom operating line passes through the point C, that is  $(x_w, x_w)$ , and has a slope  $L_m/V_m$ . When the two operating lines have been drawn in, the number of stages required may be found by drawing steps between the operating line and the equilibrium curve starting from point A.

This method is one of the most important concepts in chemical engineering and is an invaluable tool for the solution of distillation problems. The assumption of constant molar overflow is not limiting since in very few systems do the molar heats of vapourisation differ by more than 10 per cent. The method does have limitations, however, and should not be employed when the relative volatility is less than 1.3 or greater than 5, when the reflux ratio is less than 1.1 times the minimum, or when more than twenty-five theoretical trays are required<sup>(13)</sup>. In these circumstances, the Ponchon–Savarit method described in Section 11.5 should be used.

### Example 11.8. The McCabe-Thiele Method

Example 11.7 is now worked using this method. Thus, with a feed composition,  $x_f = 0.4$ , the top composition,  $x_d$  is to have a value of 0.9 and the bottom composition,  $x_w$  is to be 0.10. The reflux ratio,  $L_n/D = 3$ .

### Solution

a) From a material balance for a feed of 100 kmol:

$$V_n = V_m = 150; L_n = 112.5; L_m = 212.5; D = 37.5 \text{ and } W = 62.5 \text{ kmol}$$

b) The equilibrium curve and the diagonal line are drawn in as shown in Figure 11.15.

c) The equation of the top operating line is:

$$y_n = 0.75x_{n+1} + 0.225 \quad (i)$$

Thus, the line AB is drawn through the two points A (0.9, 0.9) and B (0, 0.225).

d) The equation of the bottom operating line is:

$$y_m = 1.415x_{m+1} - 0.042 \quad (\text{ii})$$

This equation is represented by the line CD drawn through C (0.1, 0.1) at a slope of 1.415.

e) Starting at point A, the horizontal line is drawn to cut the equilibrium line at point 1. The vertical line is dropped through 1 to the operating line at point 2 and this procedure is repeated to obtain points 3–6.

f) A horizontal line is drawn through point 6 to cut the equilibrium line at point 7 and a vertical line is drawn through point 7 to the lower enrichment line at point 8. This procedure is repeated in order to obtain points 9–16.

g) The number of stages are then counted, that is points 2, 4, 6, 8, 10, 12, and 14 which gives the number of plates required as 7.

### Enrichment in still and condenser

Point 16 in Figure 11.15 represents the concentration of the liquor in the still. The concentration of the vapour is represented by point 15, so that the enrichment represented by the increment 16–15 is achieved in the boiler or still body. Again, the concentration on the top plate is given by point 2, but the vapour from this plate has a concentration given by point 1, and the condenser by completely condensing the vapour gives a product of equal concentration, represented by point A. The still and condenser together, therefore, provide enrichment (16 – 15) + (1 – A), which is equivalent to one ideal stage. Thus, the actual number of theoretical plates required is one less than the number of stages shown on the diagram. From a liquid in the still, point 16 to the product, point A, there are eight steps, although the column need only contain seven theoretical plates.

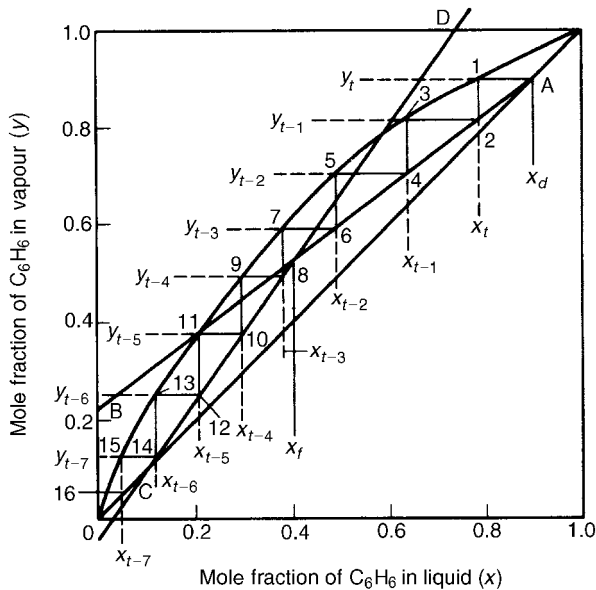


Figure 11.15. Determination of number of plates by the McCabe–Thiele method (Example 11.8)

### The intersection of the operating lines

It is seen from the example shown in Figure 11.15 in which the feed enters as liquid at its boiling point that the two operating lines intersect at a point having an  $X$ -coordinate of  $x_f$ . The locus of the point of intersection of the operating lines is of considerable importance since, as will be seen, it is dependent on the temperature and physical condition of the feed.

If the two operating lines intersect at a point with coordinates  $(x_q, y_q)$ , then from equations 11.35 and 11.37:

$$V_n y_q = L_n x_q + D x_d \quad (11.40)$$

and: 
$$V_m y_q = L_m x_q - W x_w \quad (11.41)$$

or: 
$$y_q (V_m - V_n) = (L_m - L_n) x_q - (D x_d + W x_w) \quad (11.42)$$

A material balance over the feed plate gives:

$$F + L_n + V_m = L_m + V_n$$

or: 
$$V_m - V_n = L_m - L_n - F \quad (11.43)$$

To obtain a relation between  $L_n$  and  $L_m$ , it is necessary to make an enthalpy balance over the feed plate, and to consider what happens when the feed enters the column. If the feed is all in the form of liquid at its boiling point, the reflux  $L_m$  overflowing to the plate below will be  $L_n + F$ . If however the feed is a liquid at a temperature  $T_f$ , that is less than the boiling point, some vapour rising from the plate below will condense to provide sufficient heat to bring the feed liquor to the boiling point.

If  $H_f$  is the enthalpy per mole of feed, and  $H_{fs}$  is the enthalpy of one mole of feed at its boiling point, then the heat to be supplied to bring feed to the boiling point is  $F(H_{fs} - H_f)$ , and the number of moles of vapour to be condensed to provide this heat is  $F(H_{fs} - H_f)/\lambda$ , where  $\lambda$  is the molar latent heat of the vapour.

The reflux liquor is then:

$$\begin{aligned} L_m &= L_n + F + \frac{F(H_{fs} - H_f)}{\lambda} \\ &= L_n + F \left( \frac{\lambda + H_{fs} - H_f}{\lambda} \right) \\ &= L_n + qF \end{aligned} \quad (11.44)$$

where: 
$$q = \frac{\text{heat to vaporise 1 mole of feed}}{\text{molar latent heat of the feed}}$$

Thus, from equation 11.43:

$$V_m - V_n = qF - F \quad (11.45)$$

A material balance of the more volatile component over the whole column gives:

$$F x_f = D x_d + W x_w$$

Thus, from equation 11.42:

$$F(q - 1)y_q = qFx_q - Fx_f$$

or:

$$y_q = \left( \frac{q}{q - 1} \right) x_q - \left( \frac{x_f}{q - 1} \right) \quad (11.46)$$

This equation is commonly known as the equation of the  $q$ -line. If  $x_q = x_f$ , then  $y_q = x_f$ . Thus, the point of intersection of the two operating lines lies on the straight line of slope  $q/(q - 1)$  passing through the point  $(x_f, x_f)$ . When  $y_q = 0$ ,  $x_q = x_f/q$ . The line may thus be drawn through two easily determined points. From the definition of  $q$ , it follows that the slope of the  $q$ -line is governed by the nature of the feed as follows.

(a) Cold feed as liquor	$q > 1$	$q$ line /
(b) Feed at boiling point	$q = 1$	$q$ line
(c) Feed partly vapour	$0 < q < 1$	$q$ line \
(d) Feed saturated vapour	$q = 0$	$q$ line —
(e) Feed superheated vapour	$q < 0$	$q$ line /

These various conditions are indicated in Figure 11.16.

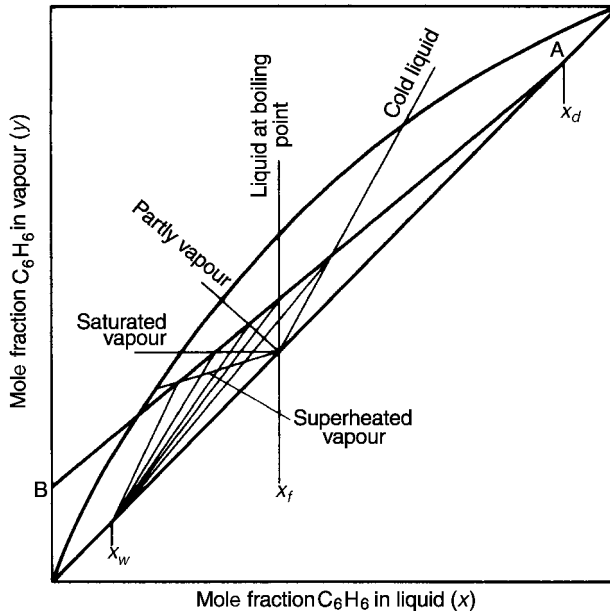


Figure 11.16. Effect of the condition of the feed on the intersection of the operating lines for a fixed reflux ratio

Altering the slope of the  $q$ -line will alter the liquid concentration at which the two operating lines cut each other for a given reflux ratio. This will mean a slight alteration in the number of plates required for the given separation. Whilst the change in the number of plates is usually rather small, if the feed is cold, there will be an increase in reflux flow

below the feed plate, and hence an increased heat consumption from the boiler per mole of distillate.

### 11.4.3. The importance of the reflux ratio

#### *Influence on the number of plates required*

The ratio  $L_n/D$ , that is the ratio of the top overflow to the quantity of product, is denoted by  $R$ , and this enables the equation of the operating line to be expressed in another way, which is often more convenient. Thus, introducing  $R$  in equation 11.35 gives:

$$y_n = \left( \frac{L_n}{L_n + D} \right) x_{n+1} + \left( \frac{D}{L_n + D} \right) x_d \quad (11.47)$$

$$= \left( \frac{R}{R + 1} \right) x_{n+1} + \left( \frac{x_d}{R + 1} \right) \quad (11.48)$$

Any change in the reflux ratio  $R$  will therefore modify the slope of the operating line and, as may be seen from Figure 11.15, this will alter the number of plates required for a given separation. If  $R$  is known, the top line is most easily drawn by joining point A ( $x_d, x_d$ ) to B ( $0, x_d/(R + 1)$ ) as shown in Figure 11.17. This method avoids the calculation of the actual flow rates  $L_n$  and  $V_n$ , when the number of plates only is to be estimated.

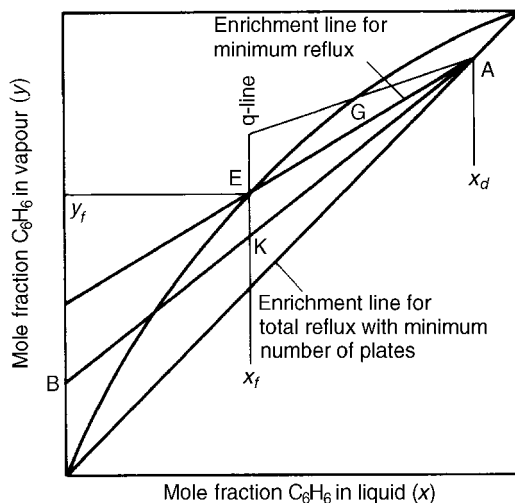


Figure 11.17. Influence of reflux ratio on the number of plates required for a given separation

If no product is withdrawn from the still, that is  $D = 0$ , then the column is said to operate under conditions of total reflux and, as seen from equation 11.47, the top operating line has its maximum slope of unity, and coincides with the line  $x = y$ . If the reflux ratio is reduced, the slope of the operating line is reduced and more stages are required to pass

from  $x_f$  to  $x_d$ , as shown by the line AK in Figure 11.17. Further reduction in  $R$  will eventually bring the operating line to AE, where an infinite number of stages is needed to pass from  $x_d$  to  $x_f$ . This arises from the fact that under these conditions the steps become very close together at liquid compositions near to  $x_f$ , and no enrichment occurs from the feed plate to the plate above. These conditions are known as *minimum reflux*, and the reflux ratio is denoted by  $R_m$ . Any small increase in  $R$  beyond  $R_m$  will give a workable system, although a large number of plates will be required. It is important to note that any line such as AG, which is equivalent to a smaller value of  $R$  than  $R_m$ , represents an impossible condition, since it is impossible to pass beyond point G towards  $x_f$ . Two important deductions may be made. Firstly that the minimum number of plates is required for a given separation at conditions of total reflux, and secondly that there is a minimum reflux ratio below which it is impossible to obtain the desired enrichment, however many plates are used.

### Calculation of the minimum reflux ratio

Figure 11.17 represents conditions where the  $q$ -line is vertical, and the point E lies on the equilibrium curve and has co-ordinates  $(x_f, y_f)$ . The slope of the line AE is then given by:

$$\left( \frac{R_m}{R_m + 1} \right) = \left( \frac{x_d - y_f}{x_d - x_f} \right)$$

or:

$$R_m = \left( \frac{x_d - y_f}{y_f - x_f} \right) \quad (11.49)$$

If the  $q$ -line is horizontal as shown in Figure 11.18, the enrichment line for minimum reflux is given by AC, where C has coordinates  $(x_c, y_c)$ . Thus:

$$\left( \frac{R_m}{R_m + 1} \right) = \left( \frac{x_d - y_c}{x_d - x_c} \right)$$

or, since  $y_c = x_f$ :

$$R_m = \left( \frac{x_d - y_c}{y_c - x_c} \right) = \left( \frac{x_d - x_f}{x_f - x_c} \right) \quad (11.50)$$

### Underwood and Fenske equations

For ideal mixtures, or where over the concentration range concerned the relative volatility may be taken as constant,  $R_m$  may be obtained analytically from the physical properties of the system as discussed by UNDERWOOD<sup>(28)</sup>. Thus, if  $x_{nA}$  and  $x_{nB}$  are the mole fractions of two components **A** and **B** in the liquid on any plate  $n$ , then a material balance over the top portion of the column above plate  $n$  gives:

$$V_n y_{nA} = L_n x_{(n+1)A} + D x_{dA} \quad (11.51)$$

and:

$$V_n y_{nB} = L_n x_{(n+1)B} + D x_{dB} \quad (11.52)$$

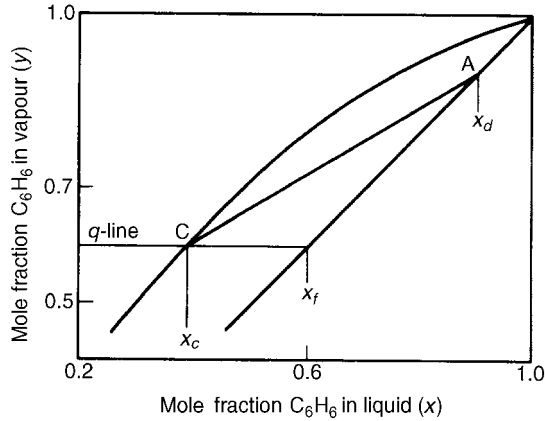


Figure 11.18. Minimum reflux ratio with feed as saturated vapour

Under conditions of minimum reflux, a column has to have an infinite number of plates, or alternatively the composition on plate  $n$  is equal to that on plate  $n + 1$ . Dividing equation 11.51 by equation 11.52 and using the relations  $x_{(n+1)A} = x_{nA}$  and  $x_{(n+1)B} = x_{nB}$ , then:

$$\frac{\alpha x_{nA}}{x_{nB}} = \frac{y_{nA}}{y_{nB}} = \frac{L_n x_{nA} + D x_{dA}}{L_n x_{nB} + D x_{dB}}$$

Thus:

$$R_m = \left(\frac{L_n}{D}\right)_{\min} = \frac{1}{\alpha - 1} \left[ \frac{x_{dA}}{x_{nA}} - \alpha \left(\frac{x_{dB}}{x_{nB}}\right) \right] \tag{11.53}$$

In this analysis,  $\alpha$  is taken as the volatility of **A** relative to **B**. There is, in general, therefore a different value of  $R_m$  for each plate. In order to produce any separation of the feed, the minimum relevant value of  $R_m$  is that for the feed plate, so that the minimum reflux ratio for the desired separation is given by:

$$R_m = \frac{1}{(\alpha - 1)} \left[ \frac{x_{dA}}{x_{fA}} - \alpha \frac{x_{dB}}{x_{fB}} \right] \tag{11.54}$$

For a binary system, this becomes:

$$R_m = \frac{1}{(\alpha - 1)} \left[ \frac{x_{dA}}{x_{fA}} - \alpha \frac{(1 - x_{dA})}{(1 - x_{fA})} \right] \tag{11.55}$$

This relation may be obtained by putting  $y = \alpha x/[1 + (\alpha - 1)x]$  from equation 11.15, in equation 11.49 to give:

$$R_m = \frac{x_d - \left(\frac{\alpha x_f}{1 + (\alpha - 1)x_f}\right)}{\left(\frac{\alpha x_f}{1 + (\alpha - 1)x_f}\right) - x_f} = \frac{1}{(\alpha - 1)} \left[ \frac{x_d}{x_f} - \frac{\alpha(1 - x_d)}{(1 - x_f)} \right] \tag{11.56}$$

### ***The number of plates at total reflux. Fenske's method***

For conditions in which the relative volatility is constant, FENSKE<sup>(29)</sup> derived an equation for calculating the required number of plates for a desired separation. Since no product is withdrawn from the still, the equations of the two operating lines become:

$$y_n = x_{n+1} \quad \text{and} \quad y_m = x_{m+1} \quad (11.57)$$

If for two components **A** and **B**, the concentrations in the still are  $x_{sA}$  and  $x_{sB}$ , then the composition on the first plate is given by:

$$\left(\frac{x_A}{x_B}\right)_1 = \left(\frac{y_A}{y_B}\right)_s = \alpha_s \left(\frac{x_A}{x_B}\right)_s$$

where the subscript outside the bracket indicates the plate, and  $s$  the still.

For plate 2: 
$$\left(\frac{x_A}{x_B}\right)_2 = \left(\frac{y_A}{y_B}\right)_1 = \alpha_1 \left(\frac{x_A}{x_B}\right)_1 = \alpha_1 \alpha_s \left(\frac{x_A}{x_B}\right)_s$$

and for plate  $n$ :

$$\left(\frac{x_A}{x_B}\right)_n = \left(\frac{y_A}{y_B}\right)_{n-1} = \alpha_1 \alpha_2 \alpha_3 \dots \alpha_{n-1} \alpha_s \left(\frac{x_A}{x_B}\right)_s$$

If an average value of  $\alpha$  is used, then:

$$\left(\frac{x_A}{x_B}\right)_n = \alpha_{av}^n \left(\frac{x_A}{x_B}\right)_s$$

In most cases total condensation occurs in the condenser, so that:

$$\begin{aligned} \left(\frac{x_A}{x_B}\right)_d &= \left(\frac{y_A}{y_B}\right)_n = \alpha_n \left(\frac{x_A}{x_B}\right)_n = \alpha_{av}^{n+1} \left(\frac{x_A}{x_B}\right)_s \\ n + 1 &= \frac{\log \left[ \left(\frac{x_A}{x_B}\right)_d \left(\frac{x_B}{x_A}\right)_s \right]}{\log \alpha_{av}} \end{aligned} \quad (11.58)$$

and  $n$  is the required number of theoretical plates in the column.

It is important to note that, in this derivation, only the relative volatilities of two components have been used. The same relation may be applied to two components of a multicomponent mixture, as is seen in Section 11.7.6.

### **Example 11.9**

For the separation of a mixture of benzene and toluene, considered in Example 11.7,  $x_d = 0.9$ ,  $x_w = 0.1$ , and  $x_f = 0.4$ . If the mean volatility of benzene relative to toluene is 2.4, what is the number of plates required at total reflux?



## Solution

The number of plates at total reflux is given by:

$$n + 1 = \frac{\log \left[ \left( \frac{0.9}{0.1} \right) \left( \frac{0.9}{0.1} \right) \right]}{\log 2.4} = 5.0 \quad (\text{equation 11.58})$$

Thus the number of theoretical plates in the column is 4, a value which is independent of the feed composition.

If the feed is liquid at its boiling point, then the minimum reflux ratio  $R_m$  is given by:

$$\begin{aligned} R_m &= \frac{1}{\alpha - 1} \left[ \frac{x_d}{x_f} - \alpha \frac{(1 - x_d)}{(1 - x_f)} \right] \quad (\text{equation 11.56}) \\ &= \frac{1}{2.4 - 1} \left[ \frac{0.9}{0.4} - \frac{(2.4 \times 0.1)}{0.6} \right] \\ &= \underline{\underline{1.32}} \end{aligned}$$

Using the graphical construction shown in Figure 11.18, with  $y_f = 0.61$ , the value of  $R_m$  is:

$$R_m = \frac{x_d - y_f}{y_f - x_f} = \frac{(0.9 - 0.61)}{(0.61 - 0.4)} = \underline{\underline{1.38}}$$

## Selection of economic reflux ratio

The cost of a distillation unit includes the capital cost of the column, determined largely by the number and diameter of the plates, and the operating costs, determined by the steam and cooling water requirements. The depreciation charges may be taken as a percentage of the capital cost, and the two together taken as the overall charges. The steam required will be proportional to  $V_m$ , which may be taken as  $V_n$  where the feed is liquid at its boiling point. From a material balance over the top portion of the column,  $V_n = D(R + 1)$ , and hence the steam required per mole of product is proportional to  $(R + 1)$ . This will be a minimum when  $R$  equals  $R_m$ , and will steadily rise as  $R$  is increased. The relationship between the number of plates  $n$  and the reflux ratio  $R$ , as derived by GILLILAND<sup>(30)</sup>, is discussed in Section 11.7.7.

The reduction in the required number of plates as  $R$  is increased beyond  $R_m$  will tend to reduce the cost of the column. For a column separating a benzene–toluene mixture, for example, where  $x_f = 0.79$ ,  $x_d = 0.99$  and  $x_w = 0.01$ , the numbers of theoretical plates as given by the McCabe–Thiele method for various values of  $R$  are given as follows. The minimum reflux ratio for this case is 0.81.

Reflux ratio $R$	0.81	0.9	1.0	1.1	1.2
Number of plates	$\infty$	25	22	19	18

Thus, an increase in  $R$ , at values near  $R_m$ , gives a marked reduction in the number of plates, although at higher values of  $R$ , further increases have little effect on the number of plates. Increasing the reflux ratio from  $R_m$  therefore affects the capital and operating costs of a column as follows:

- (a) The operating costs rise and are approximately proportional to  $(R + 1)$ .
- (b) The capital cost initially falls since the number of plates falls off rapidly at this stage.
- (c) The capital cost rises at high values of  $R$ , since there is then only a very small reduction in the number of plates, although the diameter, and hence the area, continually increases because the vapour load becomes greater. The associated condenser and reboiler will also be larger and hence more expensive.

The total charges may be obtained by adding the fixed and operating charges as shown in Figure 11.19, where curve A shows the steam costs and B the fixed costs. The final total is shown by curve C which has a minimum value corresponding to the economic reflux ratio. There is no simple relation between  $R_m$  and the optimum value, although practical values are generally 1.1–1.5 times the minimum, with much higher values being employed, particularly in the case of vacuum distillation. It may be noted that, for a fixed degree of enrichment from the feed to the top product, the number of trays required increases rapidly as the difficulty of separation increases, that is as the relative volatility approaches unity. A demand for a higher purity of product necessitates a very considerable increase in the number of trays, particularly when  $\alpha$  is near unity. In these circumstances only a limited improvement in product purity may be obtained by increasing the reflux ratio. The designer must be careful to consider the increase in cost of plant resulting from specification of a higher degree of purity of production and at the same time assess the highest degree of purity that may be obtained with the proposed plant.

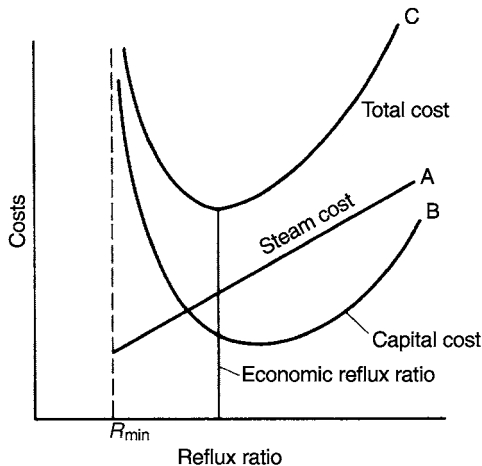


Figure 11.19. Influence of reflux ratio on capital and operating costs of a still

In general, the greater the reflux ratio, the lower is the number of plates or transfer units required although the requirements of steam in the reboiler and cooling water in the condenser are both increased and a column of larger diameter is required in order to achieve acceptable vapour velocities. An optimum value of the reflux ratio may be obtained by using the following argument which is based on the work of COLBURN<sup>(31)</sup>.

The annual capital cost of a distillation column,  $c_c$  per mole of distillate, including depreciation, interest and overheads, may be written as:

$$c_c = c_a A n / (E t_a D) \quad (11.59)$$

where  $c_a$  is the annual cost of the column per unit area of plate,  $A$  is the cross-sectional area of the column,  $n$  is the number of theoretical plates,  $E$  is the plate efficiency,  $t_a$  is the annual period of operation and  $D$  is the molar flowrate of distillate. The cross-sectional area of the column is given by:

$$A = V / u' \quad (11.60)$$

where  $V$  is the molar flow of vapour and  $u'$  is the allowable molar vapour velocity per unit area. Since  $V = D(R + 1)$ , where  $R$  is the reflux ratio, then the cost of the column is:

$$c_c = c_a n (R + 1) / (E t_a u') \quad (11.61)$$

The annual cost of the reboiler and the condenser,  $c_h$  per mole of distillate may be written as:

$$c_h = c_b A_h / (t_a D) \quad (11.62)$$

where  $c_b$  is the annual cost of the heat exchange equipment per unit area including depreciation and interest and  $A_h$  is the area for heat transfer.  $A_h = V / N''$  where  $N''$  is the vapour handling capacity of the boiler and condenser in terms of molar flow per unit area. Thus  $A_h = D(R + 1) / N''$  and the cost of the reboiler and the condenser is:

$$c_h = c_b (R + 1) / (t_a N'') \quad (11.63)$$

As far as operating costs are concerned, the important annual variable costs are that of the steam in the reboiler and that of the cooling water in the condenser. These may be written as:

$$c_w = c_d V / D = c_3 (R + 1) \quad (11.64)$$

where  $c_d$  is the annual cost of the steam and the cooling water. The total annual cost,  $c$  per mole of distillate, is the cost of the steam and the cooling water plus the costs of the column, reboiler and condenser, or:

$$c = (R + 1) [(c_a n / E t_a u') + (c_b / t_a N'') + c_d] \quad (11.65)$$

As the number of plates,  $n$ , is a function of  $R$ , equation 11.65 may be differentiated with respect to  $R$  to give:

$$dc/dR = c_a n / (E t_a V') + [(c_a n / (E t_a u'))(R + 1) dn/dR] + c_b / (t_a N'') + c_d \quad (11.66)$$

Equating to zero for minimum cost, the optimum value of the reflux ratio is:

$$R_{\text{opt}} + 1 = (n_{\text{opt}} + F) / (-dn/dR) \quad (11.67)$$

where  $n_{\text{opt}}$  is the optimum number of theoretical plates corresponding to  $R_{\text{opt}}$  and the cost factor,  $F$ , is:

$$F = [c_d + c_b / (t_a N'')][E t_a u' / c_a] \quad (11.68)$$

Because there is no simple equation relating  $n$  and  $dn/dR$ , it is not possible to obtain an expression for  $R_{\text{opt}}$  although a method of solution is given in the Example 11.18 which is based on the work of HARKER<sup>(32)</sup>.

In practice, values of 110–150 per cent of the minimum reflux ratio are used although higher values are sometimes employed particularly in vacuum distillation. Where a high purity product is required, only limited improvements can be obtained by increasing the reflux ratio and since there is a very large increase in the number of trays required, an arrangement by which the minimum acceptable purity is achieved in the product is usually adopted.

#### 11.4.4. Location of feed point in a continuous still

From Figure 11.20 it may be seen that, when stepping off plates down the top operating line AB, the bottom operating line CE cannot be used until the value of  $x_n$  on any plate is less than  $x_e$ . Again it is essential to pass to the lower line CE by the time  $x_n = x_b$ . The best conditions are those where the minimum number of plates is used. From the geometry of the figure, the largest steps in the enriching section occur down to the point of intersection of the operating lines at  $x = x_q$ . Below this value of  $x$ , the steps are larger on the lower operating line. Thus, although the column will operate for a feed composition between  $x_e$  and  $x_b$ , the minimum number of plates will be required if  $x_f = x_q$ . For a binary mixture at its boiling point, this is equivalent to making  $x_f$  equal to the composition of the liquid on the feed plate.

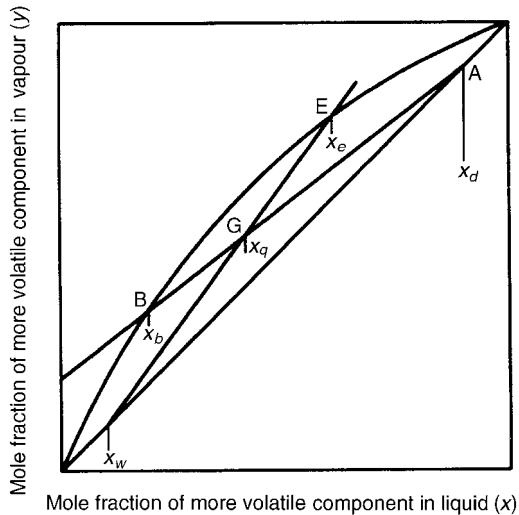


Figure 11.20. Location of feed point

#### 11.4.5. Multiple feeds and sidestreams

In general, a sidestream is defined as any product stream other than the overhead product and the residue such as the streams  $S'$ ,  $S''$ , and  $S'''$  in Figure 11.21. In a similar way,

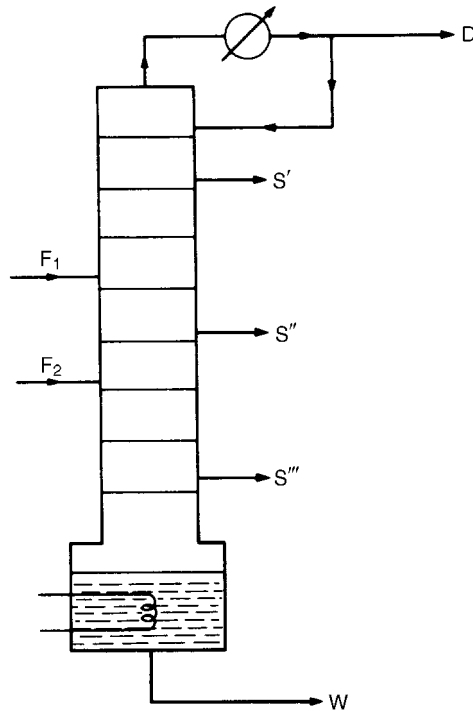


Figure 11.21. Column with multiple feeds and sidestreams

$F_1$  and  $F_2$  are separate feed streams to the column. Sidestreams are most often removed with multicomponent systems, although they may be used with binary mixtures. A binary system is now considered, with one sidestream, as shown in Figure 11.22.  $S'$  represents the rate of removal of the sidestream and  $x_{s'}$  its composition.

Assuming constant molar overflow, then for the part of the column above the sidestream the operating line is given by:

$$y_n = \frac{L_n}{V_n}x_{n+1} + \frac{Dx_d}{V_n} \quad (\text{equation 11.35})$$

as before. Balances for the part of the tower above a plate between the feed plate and the sidestream give:

$$V_s = L_s + S' + D \quad (11.69)$$

and: 
$$V_s y_n = L_s x_{n+1} + S' x_{s'} + D x_d \quad (11.70)$$

Thus: 
$$y_n = \frac{L_s}{V_s} x_{n+1} + \frac{S' x_{s'} + D x_d}{V_s} \quad (11.71)$$

Since the sidestream is normally removed as a liquid,  $L_s = (L_n - S')$  and  $V_s = V_n$ .

The line represented by equation 11.35 has a slope  $L_n/V_n$  and passes through the point  $(x_d, x_d)$ . Equation 11.71 represents a line of slope  $L_s/V_s$ , which passes through the point

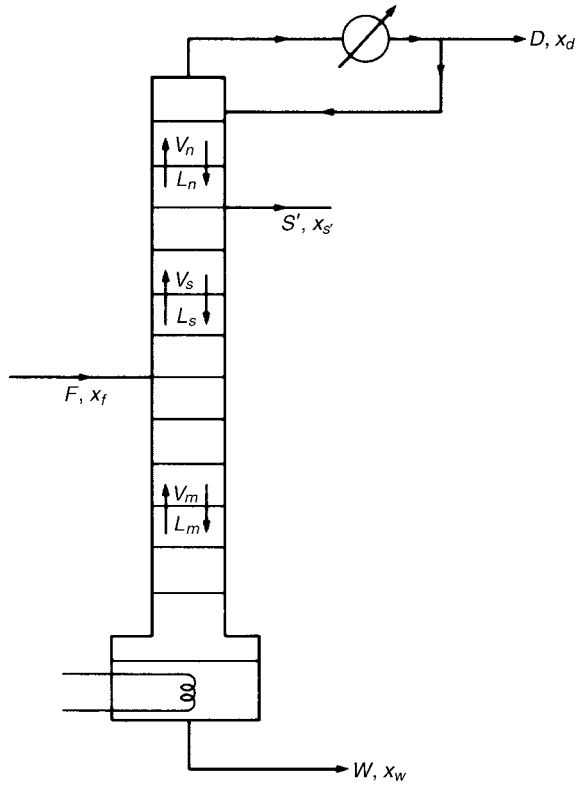


Figure 11.22. Column with a sidestream

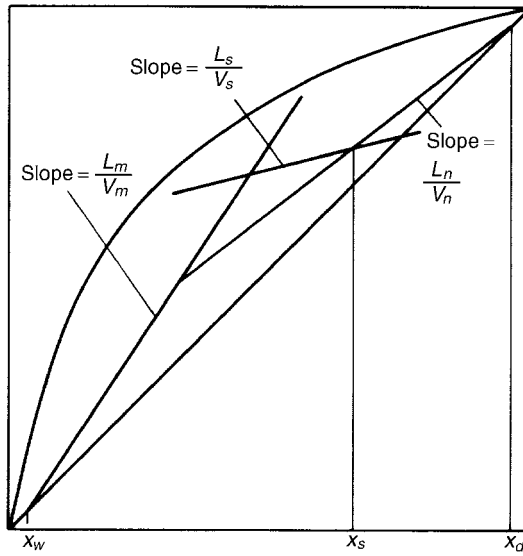


Figure 11.23. Effect of a sidestream

$y = x = (S'x_{s'} + Dx_d)/(S' + D)$ , which is the mean molar composition of the overhead product and sidestream. Since  $x_{s'} < x_d$ , and  $L_s < L_n$ , this additional operating line cuts the  $y = x$  line at a lower value than the upper operating line though it has a smaller slope, as shown in Figure 11.23. The two lines intersect at  $x = x_{s'}$ . Plates are stepped off as before between the appropriate operating line and the equilibrium curve. It may be seen that the removal of a sidestream increases the number of plates required, due to the decrease in liquid rate below the sidestream.

The effect of any additional sidestream or feed is to introduce an additional operating line for each stream. In all other respects the method of calculation is identical with that used for the straight separation of a binary mixture.

The Ponchon–Savarit method, using an enthalpy–composition diagram, may also be used to handle sidestreams and multiple feeds, though only for binary systems. This is dealt with in Section 11.5.

## 11.5. CONDITIONS FOR VARYING OVERFLOW IN NON-IDEAL BINARY SYSTEMS

### 11.5.1. The heat balance

In previous sections, the case of constant molar latent heat has been considered with no heat of mixing, and hence a constant molar rate of reflux in the column. These simplifying assumptions are extremely useful in that they enable a simple geometrical method to be used for finding the change in concentration on the plates and, whilst they are rarely entirely true in industrial conditions, they often provide a convenient start for design purposes. For a non-ideal system, where the molar latent heat is no longer constant and where there is a substantial heat of mixing, the calculations become much more tedious. For binary mixtures of this kind a graphical model has been developed by RUHEMANN<sup>(33)</sup>, PONCHON<sup>(34)</sup>, and SAVARIT<sup>(35)</sup>, based on the use of an enthalpy–composition chart. A typical enthalpy–composition or  $H - x$  chart is shown in Figure 11.24, where the upper curve V is the dew-point curve, and the lower curve L the boiling-point curve. The use of this diagram is based on the geometrical properties, as illustrated in Figure 11.25. A quantity of mixture in any physical state is known as a “phase” and is denoted by mass, composition and enthalpy. The phase is shown upon the diagram by a point which shows enthalpy and composition, though it does not show the mass. If  $m$  is the mass,  $x$  the composition and  $H$  the enthalpy per unit mass, then the addition of two phases A and B to give phase C is governed by:

$$m_A + m_B = m_C \quad (11.72)$$

$$m_A x_A + m_B x_B = m_C x_C \quad (11.73)$$

and:

$$m_A H_A + m_B H_B = m_C H_C \quad (11.74)$$

Similarly, if an amount  $Q$  of heat is added to a mass  $m_A$  of a phase, the increase in enthalpy from  $H_A$  to  $H_C$  will be given by:

$$H_A + \frac{Q}{m_A} = H_C \quad (11.75)$$

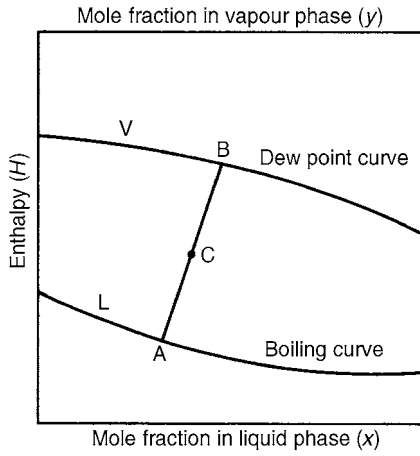


Figure 11.24. Enthalpy-composition diagram, showing the enthalpies of liquid and vapour

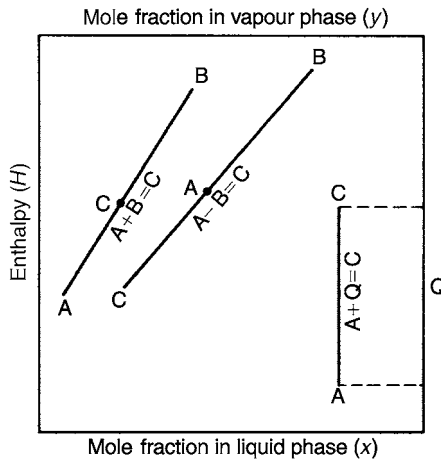


Figure 11.25. Combination and separation of a mixture on an enthalpy-composition diagram

Thus, the addition of two phases A and B is shown on the diagram by point C on the straight line joining the two phases, whilst the difference (A – B) is found by a point C on the extension of the line AB. If, as shown in Figure 11.24, a phase represented by C in the region between the dew-point and boiling-point curves is considered, then this phase will divide into two phases A and B at the ends of a tie line through the point C, so that:

$$\frac{m_A}{m_B} = \frac{CB}{CA} \tag{11.76}$$

The  $H - x$  chart, therefore, enables the effect of adding two phases, with or without the addition of heat, to be determined geometrically. The diagram may be drawn for unit mass or for one mole of material, although as a constant molar reflux does not



now apply, it is more convenient to use unit mass as the basis. Thus, working with unit mass of product, the mass of the individual streams as proportions of the product are calculated.

Figure 11.26 represents a continuous distillation unit operating with a feed  $F$  of composition  $x_f$ , and giving a top product  $D$  of composition  $x_d$  and a bottom product  $W$  of composition  $x_w$ . In this analysis, the quantities in the streams  $V$  of rising vapour and  $L$  of reflux are given in mass units, such as kg/s, and the composition of the streams as mass fractions,  $x$  referring to the liquid and  $y$  to the vapour streams as usual.

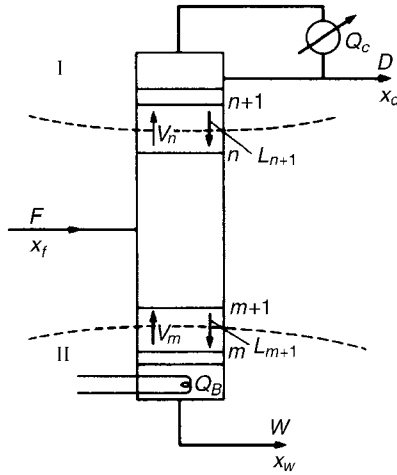


Figure 11.26. Continuous distillation column

The plates are numbered from the bottom upwards, subscript  $n$  indicating the rectifying and  $m$  the stripping section.

$H^V$  and  $H^L$  represent the enthalpy per unit mass of a vapour and liquid stream respectively.

$Q_C$  is the heat removed in the condenser. In this case no cooling of product is considered.

$Q_B$  is the heat added in the boiler.

The following relationships are then obtained by taking material and heat balances:

$$V_n = L_{n+1} + D$$

or: 
$$V_n - L_{n+1} = D \quad (11.77)$$

$$V_n y_n = L_{n+1} x_{n+1} + D x_d$$

or: 
$$V_n y_n - L_{n+1} x_{n+1} = D x_d \quad (11.78)$$

$$V_n H_n^V = L_{n+1} H_{n+1}^L + D H_d^L + Q_c$$

or: 
$$V_n H_n^V - L_{n+1} H_{n+1}^L = D H_d^L + Q_c \quad (11.79)$$

Putting  $H'_d = H_d^L + Q_C/D$ , then equation 11.79 may be written as:

$$V_n H_n^V = L_{n+1} H_{n+1}^L + D H'_d$$

or: 
$$V_n H_n^V - L_{n+1} H_{n+1}^L = D H'_d \quad (11.80)$$

From equations 11.77 and 11.78:

$$\frac{L_{n+1}}{D} = \frac{x_d - y_n}{y_n - x_{n+1}} \quad (11.81)$$

and from equations 11.77 and 11.80:

$$\frac{L_{n+1}}{D} = \frac{H'_d - H_n^V}{H_n^V - H_{n+1}^L} \quad (11.82)$$

or: 
$$\frac{H'_d - H_n^V}{H_n^V - H_{n+1}^L} = \frac{x_d - y_n}{y_n - x_{n+1}} \quad (11.83)$$

and: 
$$y_n = \left[ \frac{H'_d - H_n^V}{H'_d - H_{n+1}^L} \right] x_{n+1} + \left[ \frac{H_n^V - H_{n+1}^L}{H'_d - H_{n+1}^L} \right] x_d \quad (11.84)$$

Equation 11.84 represents any operating line relating the composition of the vapour  $y_n$  rising from a plate to the composition of the liquid reflux entering the plate, or alternatively it represents the relation between the composition of the vapour and liquid streams between any two plates. From equation 11.83, it may be seen that all such operating lines pass through a common pole N of coordinates  $x_d$  and  $H'_d$ .

Alternatively, noting that the right-hand side of equations 11.77, 11.78 and 11.79 are independent of conditions below the feed plate, a stream N may be defined with mass equal to the difference between the vapour and liquid streams between two plates, of composition  $x_d$  and of enthalpy  $H'_d$ . The three quantities  $V_n$ ,  $L_{n+1}$ , and N are then on a straight line passing through N, as shown in Figure 11.27.

Below the feed plate a similar series of equations for material and heat balances may be written as:

$$V_m + W = L_{m+1}$$

or: 
$$-V_m + L_{m+1} = W \quad (11.85)$$

$$V_m y_m + W x_w = L_{m+1} x_{m+1}$$

or: 
$$-V_m y_m + L_{m+1} x_{m+1} = W x_w \quad (11.86)$$

$$V_m H_m^V + W H_w^L = L_{m+1} H_{m+1}^L + Q_B$$

or: 
$$-V_m H_m^V + L_{m+1} H_{m+1}^L = W H_w^L - Q_B \quad (11.87)$$

Putting: 
$$H'_w = H_w^L - \frac{Q_B}{W} \quad (11.88)$$

then: 
$$-V H_m^V + L_{m+1} H_{m+1}^L = W H'_w \quad (11.89)$$

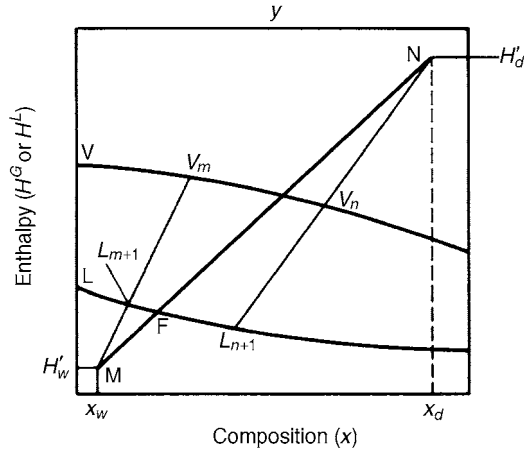


Figure 11.27. Enthalpy–composition diagram

Then: 
$$\frac{L_{m+1}}{W} = \frac{-x_w + y_m}{y_m - x_{m+1}} \tag{11.90}$$

and: 
$$\frac{L_{m+1}}{W} = \frac{-H'_w + H_m^V}{H_m^V - H_{m+1}^L} \tag{11.91}$$

Thus: 
$$\frac{-H'_w + H_m^V}{H_m^V - H_{m+1}^L} = \frac{-x_w + y_m}{y_m - x_{m+1}} \tag{11.92}$$

Equation 11.92 represents any operating line below the feed plate, and it shows that all such lines pass through a common pole  $M$  of coordinates  $x_w$  and  $H'_w$ . As with the rectifying section, a stream  $M$  may be defined by mass  $L_{m+1} - V_m$ , composition  $x_w$  and enthalpy  $H'_w$ . Thus:

$$F = M + N \tag{11.93}$$

and: 
$$F x_f = M x_w + N x_d \tag{11.94}$$

It therefore follows that phases  $F$ ,  $M$ , and  $N$  are on a straight line on the  $H - x$  chart, as shown in Figures 11.27 and 11.28.

### 11.5.2. Determination of the number of plates on the $H - x$ diagram

The determination of the number of plates necessary for a desired separation is shown in Figure 11.28. The position of the feed ( $F, x_f$ ) is shown at  $F$  on the boiling line and the pole  $N$  is located as  $(x_d, H'_d)$ , where:

$$H'_d = H_d^L + \frac{Q_C}{D} \tag{11.95}$$

Pole  $M$  is located as on the extension of  $NF$  cutting the ordinate at  $x_w$  in  $M$ .



From equations 11.83 and 11.95 and writing  $Q_C/D = q_c$ , then:

$$\frac{H_d^L + q_c - H_n^V}{H_n^V - H_{n+1}^L} = \frac{x_d - y_n}{y_n - x_{n+1}} \quad (11.96)$$

or: 
$$q_c = (H_n^V - H_{n+1}^L) \left( \frac{x_d - y_n}{y_n - x_{n+1}} \right) + H_n^V - H_d^L \quad (11.97)$$

and: 
$$(q_c)_{\min} = (H_f^V - H_{f+1}^L) \left( \frac{x_d - y_f}{y_f - x_{f+1}} \right) + H_f^V - H_d^L \quad (11.98)$$

The advantage of the  $H - x$  chart lies in the fact that the heat quantities required for the distillation are clearly indicated. Thus, the higher the reflux ratio the more heat must be removed per mole of product, and point N rises. This immediately shows that both  $q_c$  and  $Q_B$  are increased. The use of this method is illustrated by considering the separation of ammonia from an ammonia–water mixture, as occurs in the ammonia absorption unit for refrigeration.

### Example 11.10

It is required to separate 1 kg/s (3.6 tonnes/h) of a solution of ammonia in water, containing 30 per cent by mass of ammonia, to give a top product of 99.5 per cent purity and a weak solution containing 10 per cent by mass of ammonia.

Calculate the heat required in the boiler and the heat to be rejected in the condenser, assuming a reflux 8 per cent in excess of the minimum and a column pressure of 1000 kN/m<sup>2</sup>. The plates may be assumed to have an ideal efficiency of 60 per cent.

### Solution

Taking a material balance for the whole throughput and for the ammonia gives:

$$D + W = 1.0$$

$$0.995D + 0.1W = (1.0 \times 0.3)$$

Thus: 
$$D = 0.22 \text{ kg/s}$$

and: 
$$W = 0.78 \text{ kg/s}$$

The enthalpy–composition chart for this system is shown in Figure 11.29. It is assumed that the feed F and the bottom product W are both liquids at their boiling points.

### Location of the poles N and M

$N_m$  for minimum reflux is found by drawing a tie-line through F, representing the feed, to cut the line  $x = 0.995$  at  $N_m$ .

$$\begin{aligned} \text{The minimum reflux ratio, } R_m &= \frac{\text{length } N_m A}{\text{length } AL} \\ &= \frac{(1952 - 1547)}{(1547 - 295)} = 0.323 \end{aligned}$$

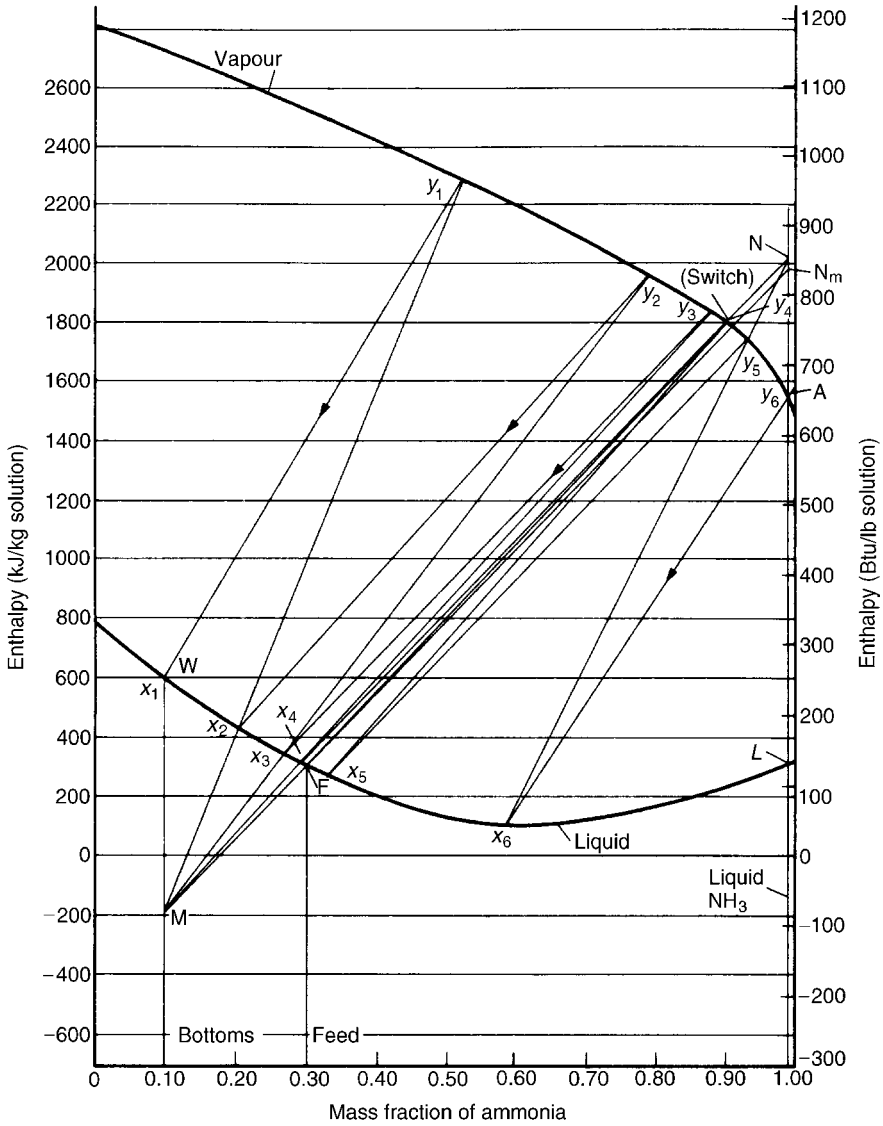


Figure 11.29. Enthalpy-composition diagram for ammonia-water at 1.0 MN/m<sup>2</sup> pressure (Example 11.10)

Since the actual reflux is 8 per cent above the minimum, then:

$$\begin{aligned}
 NA &= 1.08 N_m A \\
 &= (1.08 \times 405) = 437
 \end{aligned}$$

Point N therefore has an ordinate of (437 + 1547) = 1984 and an abscissa of 0.995. Point M is found by drawing NF to cut the line x = 0.10, through W, at M. The number of theoretical plates is found, as on the diagram, to be 5+.

The number of plates to be provided =  $(5/0.6) = 8.33$ , say 9.

The feed is introduced just below the third ideal plate from the top, or just below the fifth actual plate.

The heat input at the boiler per unit mass of bottom product is:

$$\frac{Q_B}{W} = 582 - (-209) = 791$$

$$\text{Heat input to boiler} = (791 \times 0.78) = \underline{\underline{617 \text{ kW}}}$$

$$\begin{aligned} \text{Condenser duty} &= \text{length } NL \times D \\ &= (1984 - 296) \times 0.22 \\ &= \underline{\underline{372 \text{ kW}}} \end{aligned}$$

### 11.5.4. Multiple feeds and sidestreams

The enthalpy–composition approach may also be used for multiple feeds and sidestreams for binary systems. For the condition of constant molar overflow, each additional sidestream or feed adds a further operating line and pole point to the system.

Taking the same system as used in Figure 11.22, with one sidestream only, the procedure is as shown in Figure 11.30.

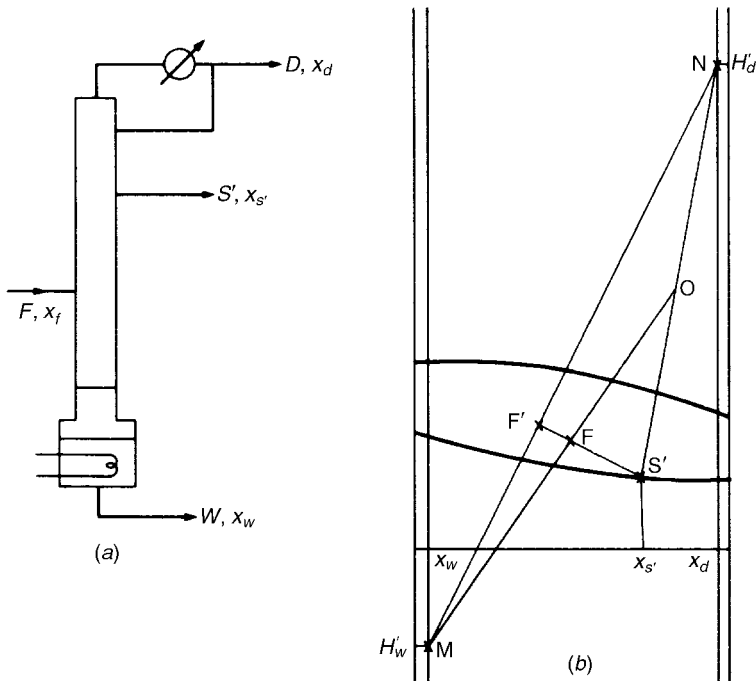


Figure 11.30. Enthalpy–composition diagram for a system with one sidestream

The upper pole point  $N$  is located as before. The effect of removing a sidestream  $S'$  from the system is to produce an effective feed  $F'$ , where  $F' = F - S'$  and where  $F'S'/F'F = F/S'$ . Thus, once  $S'$  and  $F$  have been located in the diagram, the position of  $F'$  may also be determined. The position of the lower pole point  $M$ , which must lie on the intersection of  $x = x_w$  and the straight line drawn through  $NF'$ , may then be found.  $N$  relates to the section of the column above the sidestream and  $M$  to that part below the feed plate. A third pole point must be defined to handle that part of the column between the feed and the sidestream.

The pole point for the intermediate section must be on the limiting operating line for the upper part of the column, that is  $NS'$ . This must also lie on the limiting operating line for the lower part of the column, that is  $MF$  or its extension. Thus the intersection of  $NS'$  and  $MF$  extended gives the position of the intermediate pole point  $O$ .

The number of stages required is determined in the same manner as before, using the upper pole point  $N$  for that part of the column between the sidestream and the top, the intermediate pole point  $O$  between the feed and the sidestream, and the lower pole point  $M$  between the feed and the bottom.

For the case of multiple feeds, the procedure is similar and may be followed by reference to Figure 11.31.

### Example 11.11

A mixture containing equal parts by mass of carbon tetrachloride and toluene is to be fractionated to give an overhead product containing 95 mass per cent carbon tetrachloride, a bottom product of 5 mass per cent carbon tetrachloride, and a sidestream containing 80 mass per cent carbon tetrachloride. Both the feed and sidestream may be regarded as liquids at their boiling points.

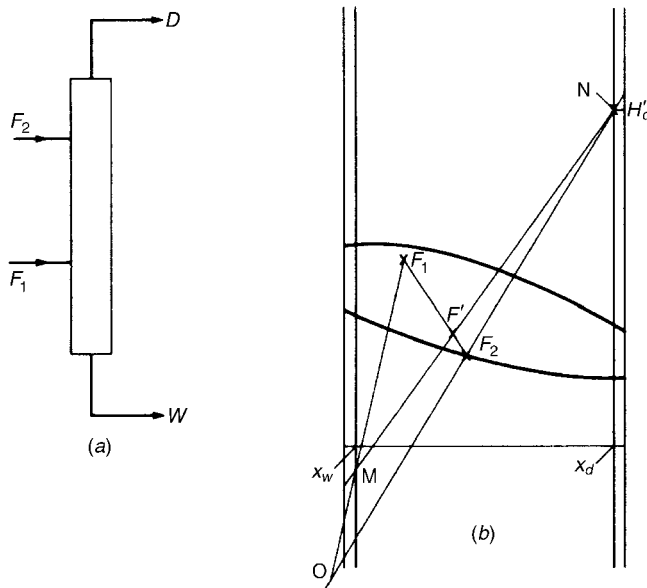


Figure 11.31. Enthalpy-composition diagram for a system with two feeds



The rate of withdrawal of the sidestream is 10 per cent of the column feed rate and the external reflux ratio is 2.5. Using the enthalpy composition method, determine the number of theoretical stages required, and the amounts of bottom product and distillate as percentages of the feed rate.

It may be assumed that the enthalpies of liquid and vapour are linear functions of composition. Enthalpy and equilibrium data are provided.

**Solution**

*Basis: 100 kg feed.*

An overall material balance gives:

$$F = D + W + S'$$

or:  $100 = D + W + 10$

$$F x_f = D x_d + W x_w + S' x_{s'}$$

and:  $50 = 0.95D + 0.05W + 8$

Thus:  $D = 41.7$  per cent;  $W = 48.3$  per cent

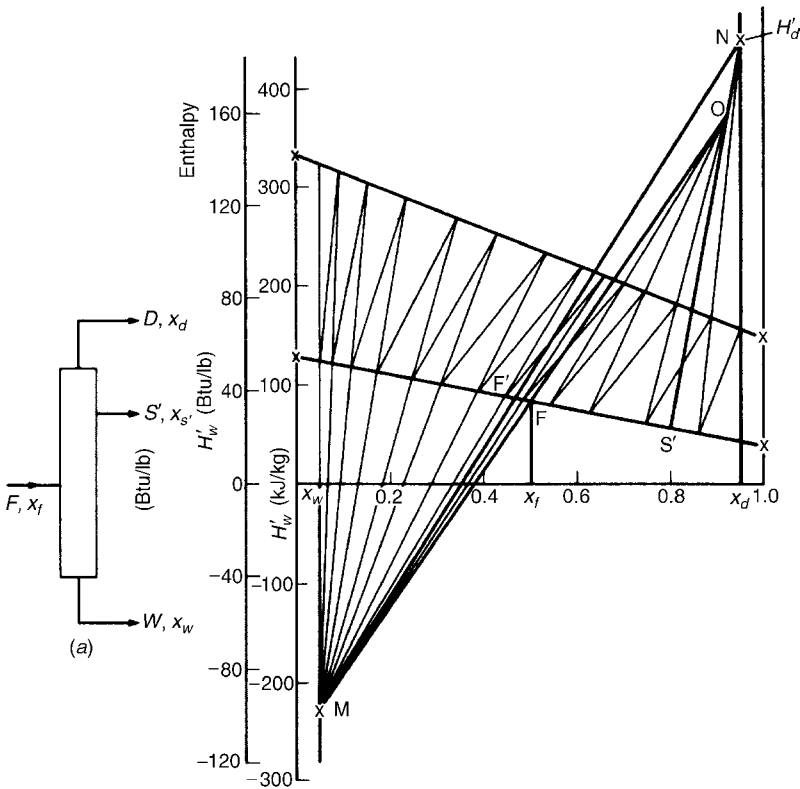


Figure 11.32. Enthalpy-composition diagram for carbon tetrachloride-toluene separation with one sidestream—Example 11.11

From the enthalpy data and the reflux ratio, the upper pole point M may be located as shown in Figure 11.32. Points F and S' are located on the liquid line, and the position of the effective feed, such that  $F'S'/F'F = 10$ . NF' is joined and extended to cut  $x = x_w$  at M, the lower pole point.

MF is joined and extended to cut NS' at O, the immediate pole point. The number of stages required is then obtained from the figure and

13 theoretical stages are required.

## 11.6. BATCH DISTILLATION

### 11.6.1. The process

In the previous sections conditions have been considered in which there has been a continuous feed to the still and a continuous withdrawal of products from the top and bottom. In many instances processes are carried out in batches, and it is more convenient to distil each batch separately. In these cases the whole of a batch is run into the boiler of the still and, on heating, the vapour is passed into a fractionation column, as shown in Figure 11.33. As with continuous distillation, the composition of the top product depends on the still composition, the number of plates in the column and on the reflux ratio used. When the still is operating, since the top product will be relatively rich in the more volatile component, the liquid remaining in the still will become steadily weaker in this component. As a result, the purity of the top product will steadily fall. Thus, the still may be charged with  $S_1$  mols of a mixture containing a mole fraction  $x_{s1}$  of the more volatile component. Initially, with a reflux ratio  $R_1$ , the top product has a composition

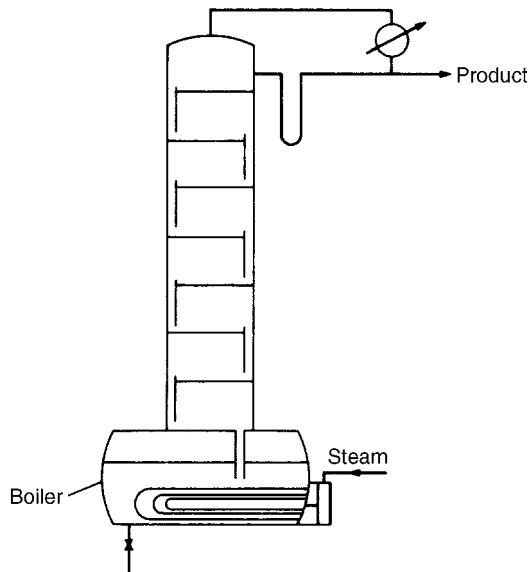


Figure 11.33. Column for batch distillation