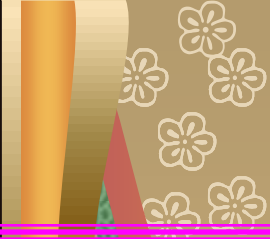


# *Distillation*

## **INTRODUCTION**

The separation of liquid mixtures into their various components is one of the major operations in the process industries, and distillation, the most widely used method of achieving this end, is the key operation in any oil refinery. In processing, the demand for purer products, coupled with the need for greater efficiency, has promoted continued research into the techniques of distillation. In engineering terms, distillation columns have to be designed with a larger range in capacity than any other types of processing equipment, with single columns 0.3–10 m in diameter and 3–75 m in height. Designers are required to achieve the desired product quality at minimum cost and also to provide constant purity of product even though there may be variations in feed composition. A distillation unit should be considered together with its associated control system, and it is often operated in association with several other separate units.

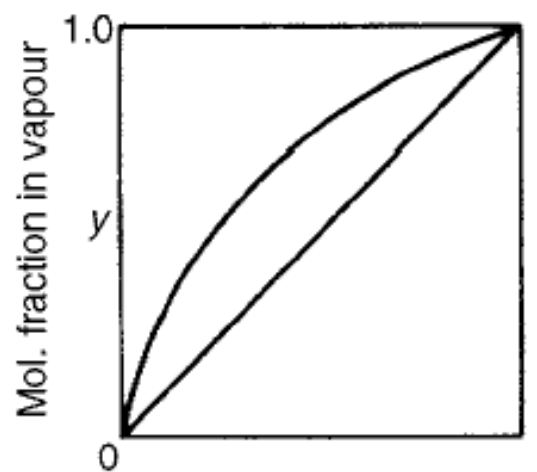


The vertical cylindrical column provides, in a compact form and with the minimum of ground requirements, a large number of separate stages of vaporisation and condensation. In this chapter the basic problems of design are considered and it may be seen that not only the physical and chemical properties, but also the fluid dynamics inside the unit, determine the number of stages required and the overall layout of the unit.

The separation of benzene from a mixture with toluene, for example, requires only a simple single unit as shown in Figure 11.1, and virtually pure products may be obtained. A more complex arrangement is shown in Figure 11.2 where the columns for the purification of crude styrene formed by the dehydrogenation of ethyl benzene are shown. It may be seen that, in this case, several columns are required and that it is necessary to recycle some of the streams to the reactor.

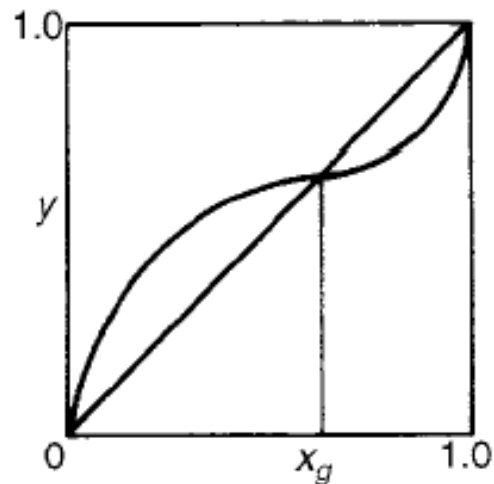
In this chapter consideration is given to the theory of the process, methods of distillation and calculation of the number of stages required for both binary and multicomponent systems, and discussion on design methods is included for plate and packed columns incorporating a variety of column internals.





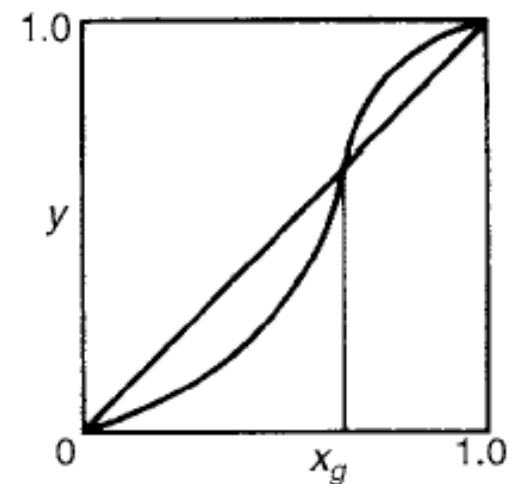
Mole fraction in liquid ( $x$ )

(a) Benzene–toluene



Mole fraction in liquid ( $x$ )

(b) Acetone–carbon disulphide



Mole fraction in liquid ( $x$ )

(c) Acetone–chloroform

Figure 11.4. Vapour composition as a function of liquid composition at constant pressure

## 11.2.1. Partial vaporisation and partial condensation

If a mixture of benzene and toluene is heated in a vessel, closed in such a way that the pressure remains atmospheric and no material can escape and the mole fraction of the more volatile component in the liquid, that is benzene, is plotted as abscissa, and the temperature at which the mixture boils as ordinate, then the boiling curve is obtained as shown by ABCJ in Figure 11.5. The corresponding dew point curve ADEJ shows the temperature at which a vapour of composition  $y$  starts to condense.

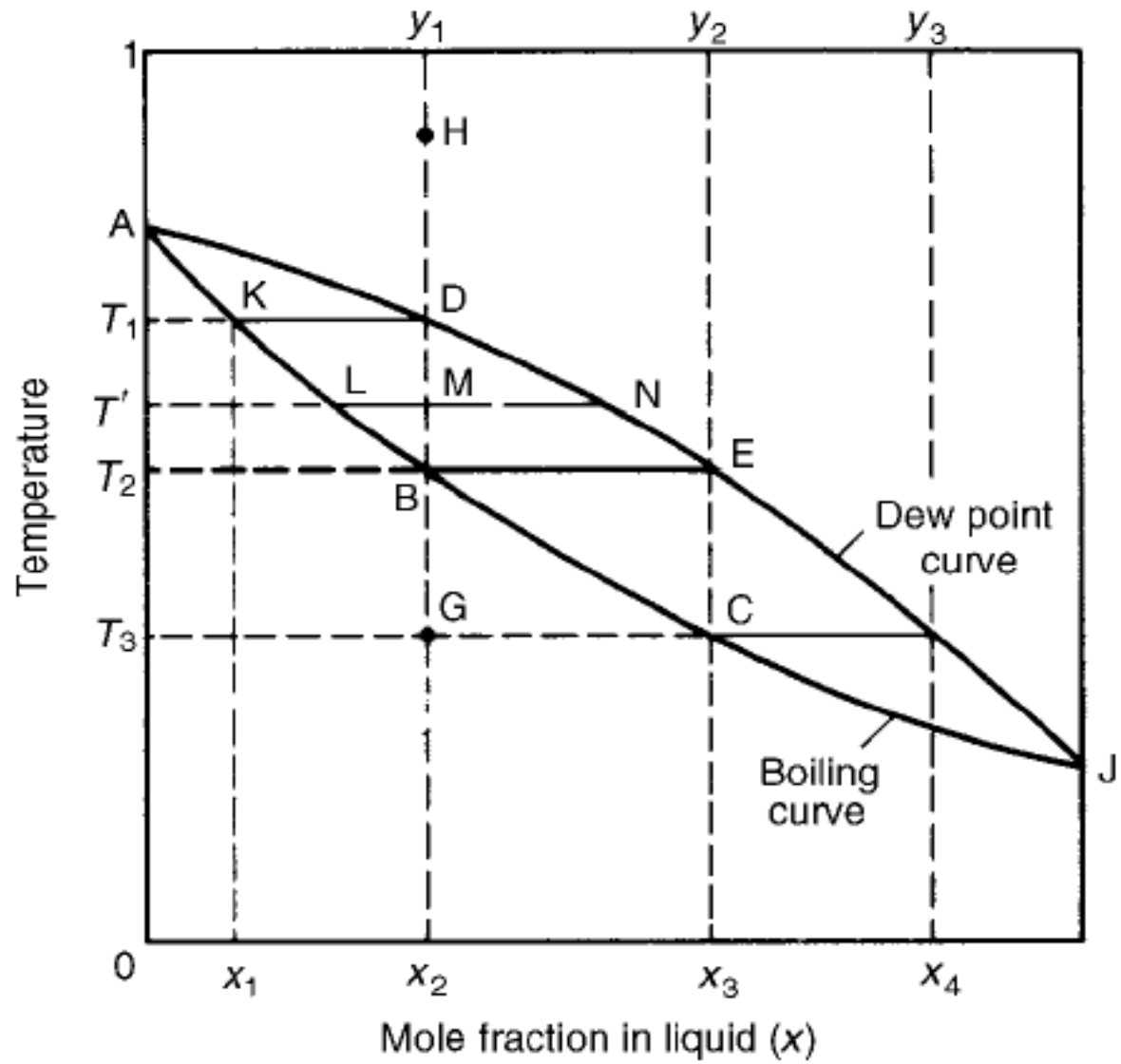


Figure 11.5. Effect of partial vaporisation and condensation at the boiling point

If a mixture of composition  $x_2$  is at a temperature  $T_3$  below its boiling point,  $T_2$ , as shown by point G on the diagram, then on heating at constant pressure the following changes will occur:

- (a) When the temperature reaches  $T_2$ , the liquid will boil, as shown by point B, and some vapour of composition  $y_2$ , shown by point E, is formed.
- (b) On further heating the composition of the liquid will change because of the loss of the more volatile component to the vapour and the boiling point will therefore rise to some temperature  $T'$ . At this temperature the liquid will have a composition represented by point L, and the vapour a composition represented by point N. Since no material is lost from the system, there will be a change in the proportion of liquid to vapour, where the ratio is:

$$\frac{\text{Liquid}}{\text{Vapour}} = \frac{\text{MN}}{\text{ML}}$$

- (c) On further heating to a temperature  $T_1$ , all of the liquid is vaporised to give vapour D of the same composition  $y_1$  as the original liquid.

It may be seen that partial vaporisation of the liquid gives a vapour richer in the more volatile component than the liquid. If the vapour initially formed, as for instance at point E, is at once removed by condensation, then a liquid of composition  $x_3$  is obtained, represented by point C. The step BEC may be regarded as representing an ideal stage, since the liquid passes from composition  $x_2$  to a liquid of composition  $x_3$ , which represents a greater enrichment in the more volatile component than can be obtained by any other single stage of vaporisation.

Figures 11.3 and 11.4, the system is said to form an azeotrope, a condition which is discussed in Section 11.8.

### **11.3. METHODS OF DISTILLATION – TWO COMPONENT MIXTURES**

From curve *a* of Figure 11.4 it is seen that, for a binary mixture with a normal  $y - x$  curve, the vapour is always richer in the more volatile component than the liquid from which it is formed. There are three main methods used in distillation practice which all rely on this basic fact. These are:

- (a) Differential distillation.
- (b) Flash or equilibrium distillation, and
- (c) Rectification.

Of these, rectification is much the most important, and it differs from the other two methods in that part of the vapour is condensed and returned as liquid to the still, whereas, in the other methods, all the vapour is either removed as such, or is condensed as product.



### 11.3.1. Differential distillation

The simplest example of batch distillation is a single stage, differential distillation, starting with a still pot, initially full, heated at a constant rate. In this process the vapour formed on boiling the liquid is removed at once from the system. Since this vapour is richer in the more volatile component than the liquid, it follows that the liquid remaining becomes steadily weaker in this component, with the result that the composition of the product progressively alters. Thus, whilst the vapour formed over a short period is in equilibrium with the liquid, the total vapour formed is not in equilibrium with the residual liquid. At the end of the process the liquid which has not been vaporised is removed as the bottom product. The analysis of this process was first proposed by RAYLEIGH<sup>(24)</sup>.

If  $S$  is the number of moles of material in the still,  $x$  is the mole fraction of component **A** and an amount  $dS$ , containing a mole fraction  $y$  of **A**, is vaporised, then a material balance on component **A** gives:

$$\begin{aligned}y \, dS &= d(Sx) \\ &= S \, dx + x \, dS \\ \int_{S_0}^S \frac{dS}{S} &= \int_{x_0}^x \left( \frac{dx}{y - x} \right)\end{aligned}$$

and:

$$\ln \frac{S}{S_0} = \int_{x_0}^x \left( \frac{dx}{y - x} \right) \quad (11.28)$$

The integral on the right-hand side of this equation may be solved graphically if the equilibrium relationship between  $y$  and  $x$  is available. In some cases a direct integration

is possible. Thus, if over the range concerned the equilibrium relationship is a straight line of the form  $y = mx + c$ , then:

$$\ln \frac{S}{S_0} = \left( \frac{1}{m-1} \right) \ln \left[ \frac{(m-1)x + c}{(m-1)x_0 + c} \right]$$

or:

$$\frac{S}{S_0} = \left( \frac{y-x}{y_0-x_0} \right)^{1/(m-1)}$$

and:

$$\left( \frac{y-x}{y_0-x_0} \right) = \left( \frac{S}{S_0} \right)^{m-1} \quad (11.29)$$

From this equation the amount of liquid to be distilled in order to obtain a liquid of given concentration in the still may be calculated, and from this the average composition of the distillate may be found by a mass balance.

Alternatively, if the relative volatility is assumed constant over the range concerned, then  $y = \alpha x / (1 + (\alpha - 1)x)$ , equation 11.15 may be substituted in equation 11.28. This leads to the solution:

$$\ln \frac{S}{S_0} = \left( \frac{1}{\alpha - 1} \right) \ln \left[ \frac{x(1-x_0)}{x_0(1-x)} \right] + \ln \left[ \frac{1-x_0}{1-x} \right] \quad (11.30)$$



As this process consists of only a single stage, a complete separation is impossible unless the relative volatility is infinite. Application is restricted to conditions where a preliminary separation is to be followed by a more rigorous distillation, where high purities are not required, or where the mixture is very easily separated.

### 11.3.2. Flash or equilibrium distillation

Flash or equilibrium distillation, frequently carried out as a continuous process, consists of vaporising a definite fraction of the liquid feed in such a way that the vapour evolved is in equilibrium with the residual liquid. The feed is usually pumped through a fired heater and enters the still through a valve where the pressure is reduced. The still is essentially a separator in which the liquid and vapour produced by the reduction in pressure have sufficient time to reach equilibrium. The vapour is removed from the top of the separator and is then usually condensed, while the liquid leaves from the bottom.

In a typical pipe still where, for example, a crude oil might enter at 440 K and at about 900 kN/m<sup>2</sup>, and leave at 520 K and 400 kN/m<sup>2</sup>, some 15 per cent may be vaporised in the process. The vapour and liquid streams may contain many components in such an application, although the process may be analysed simply for a binary mixture of **A** and **B** as follows:

If  $F$  = moles per unit time of feed of mole fraction  $x_f$  of **A**,

$V$  = moles per unit time of vapour formed with  $y$  the mole fraction of **A**, and

$S$  = moles per unit time of liquid with  $x$  the mole fraction of **A**,

then an overall mass balance gives:

$$F = V + S$$

and for the more volatile component:

$$Fx_f = Vy + Sx$$

Thus:

$$\frac{V}{F} = \left( \frac{x_f - x}{y - x} \right)$$

or:

$$y = \frac{F}{V}x_f - x \left( \frac{F}{V} - 1 \right) \quad (11.31)$$

Equation 11.31 represents a straight line of slope:

$$-\left( \frac{F - V}{V} \right) = \frac{-S}{V}$$

passing through the point  $(x_f, x_f)$ . The values of  $x$  and  $y$  required must satisfy, not only the equation, but also the appropriate equilibrium data. Thus these values may be determined graphically using an  $x - y$  diagram as shown in Figure 11.9.

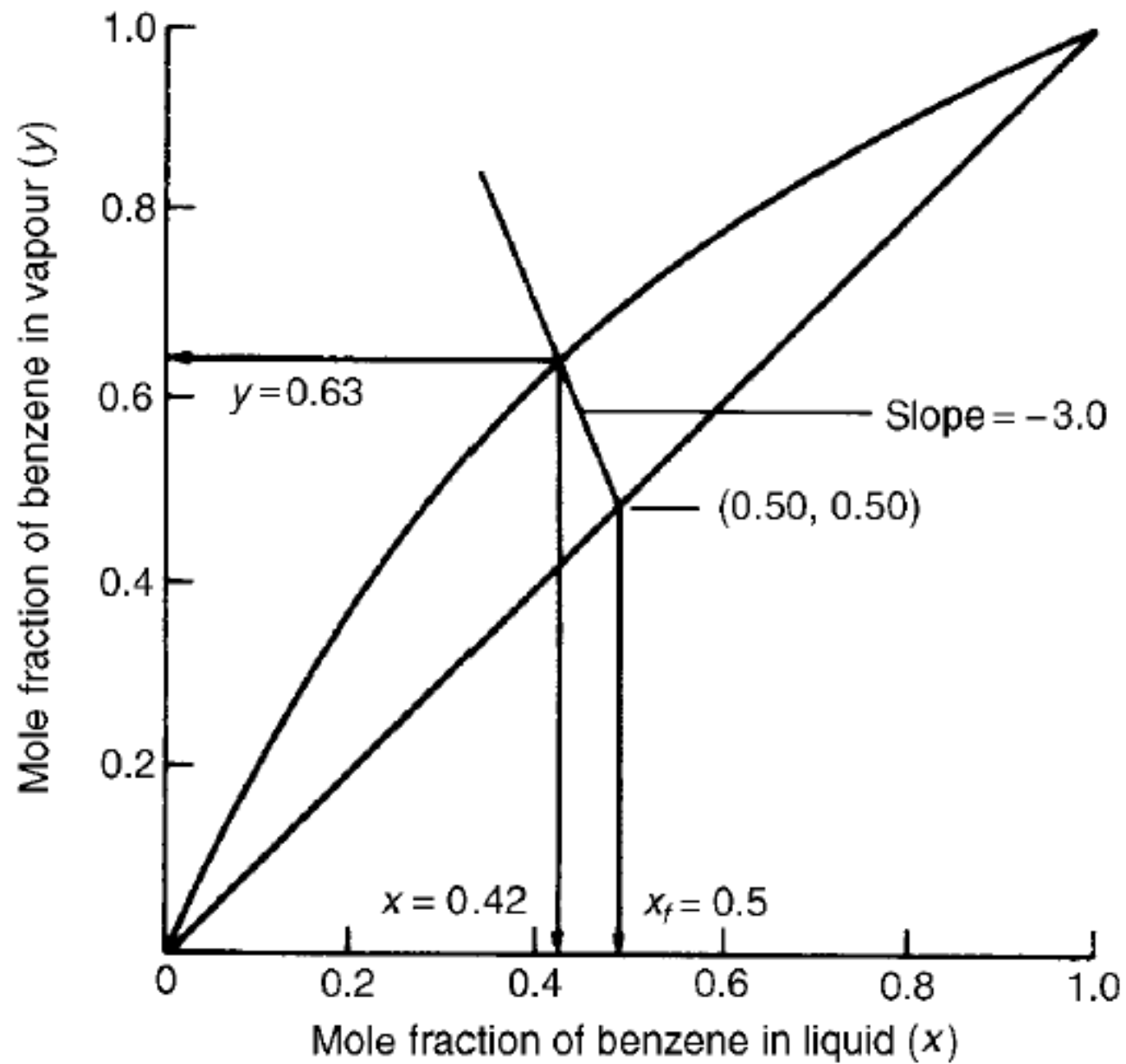


Figure 11.9. Equilibrium data for benzene–toluene for Example 11.6

In practice, the quantity vaporised is not fixed directly but it depends upon the enthalpy of the hot incoming feed and the enthalpies of the vapour and liquid leaving the separator. For a given feed condition, the fraction vaporised may be increased by lowering the pressure in the separator.

### **Example 11.6**

An equimolar mixture of benzene and toluene is subjected to flash distillation at  $100 \text{ kN/m}^2$  in the separator. Using the equilibrium data given in Figure 11.9, determine the composition of the liquid and vapour leaving the separator when the feed is 25 per cent vaporised. For this condition, the boiling point diagram in Figure 11.10 may be used to determine the temperature of the exit liquid stream.

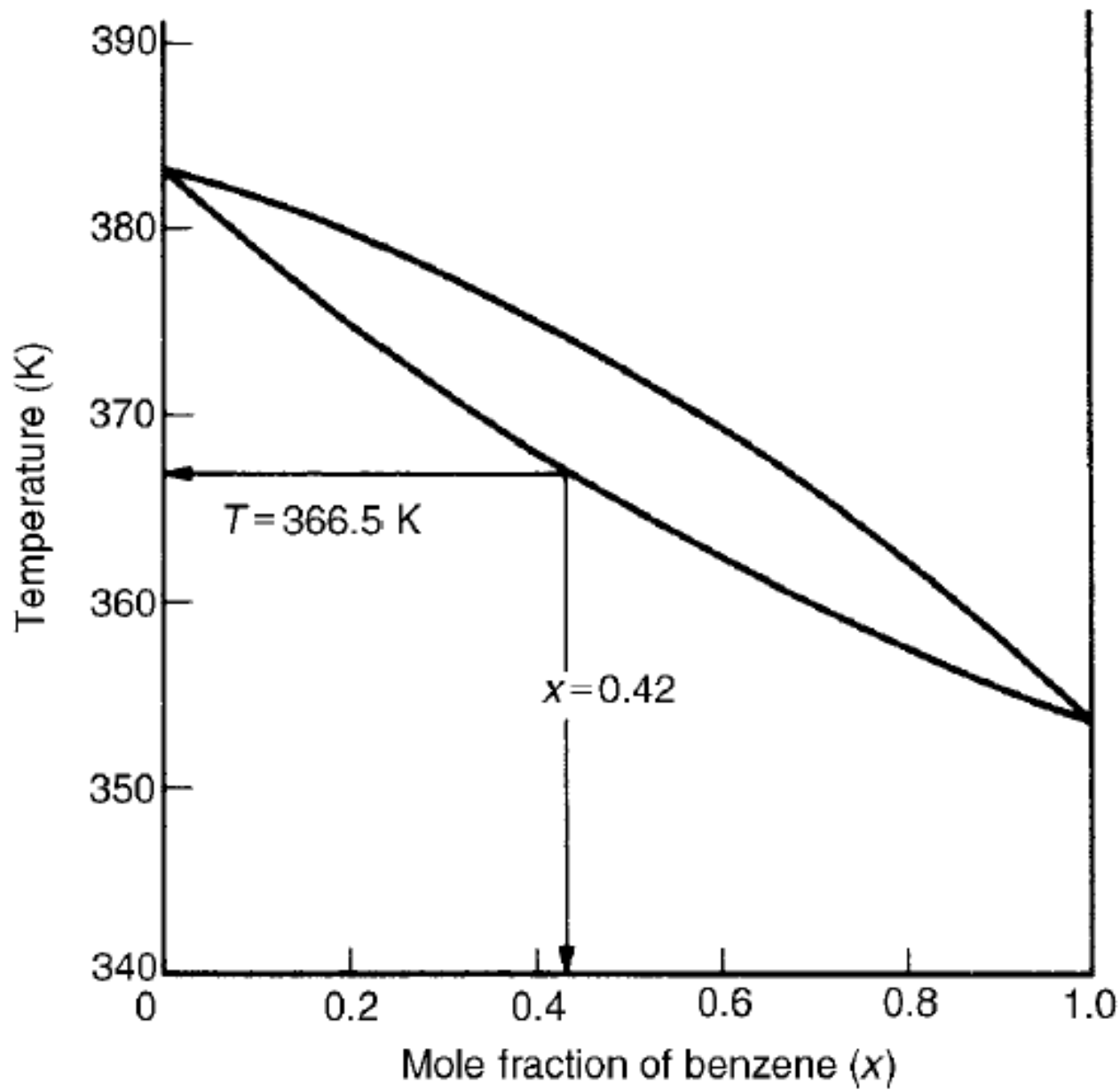


Figure 11.10. Boiling point diagram for benzene-toluene for Example 11.6

## Solution

The fractional vaporisation =  $V/F = f$  (say)

The slope of equation 11.31 is:

$$-\left(\frac{F - V}{V}\right) = -\left(\frac{1 - f}{f}\right)$$

When  $f = 0.25$ , the slope of equation 11.31 is therefore:

$$-(1 - 0.25)/0.25 = -3.0$$

and the construction is made as shown in Figure 11.9 to give  $x = \underline{\underline{0.42}}$  and  $y = \underline{\underline{0.63}}$ .

From the boiling point diagram, in Figure 11.10 the liquid temperature when  $x = 0.42$  is seen to be 366.5 K.



### **11.3.3. Rectification**

In the two processes considered, the vapour leaving the still at any time is in equilibrium with the liquid remaining, and normally there will be only a small increase in concentration of the more volatile component. The essential merit of rectification is that it enables a 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

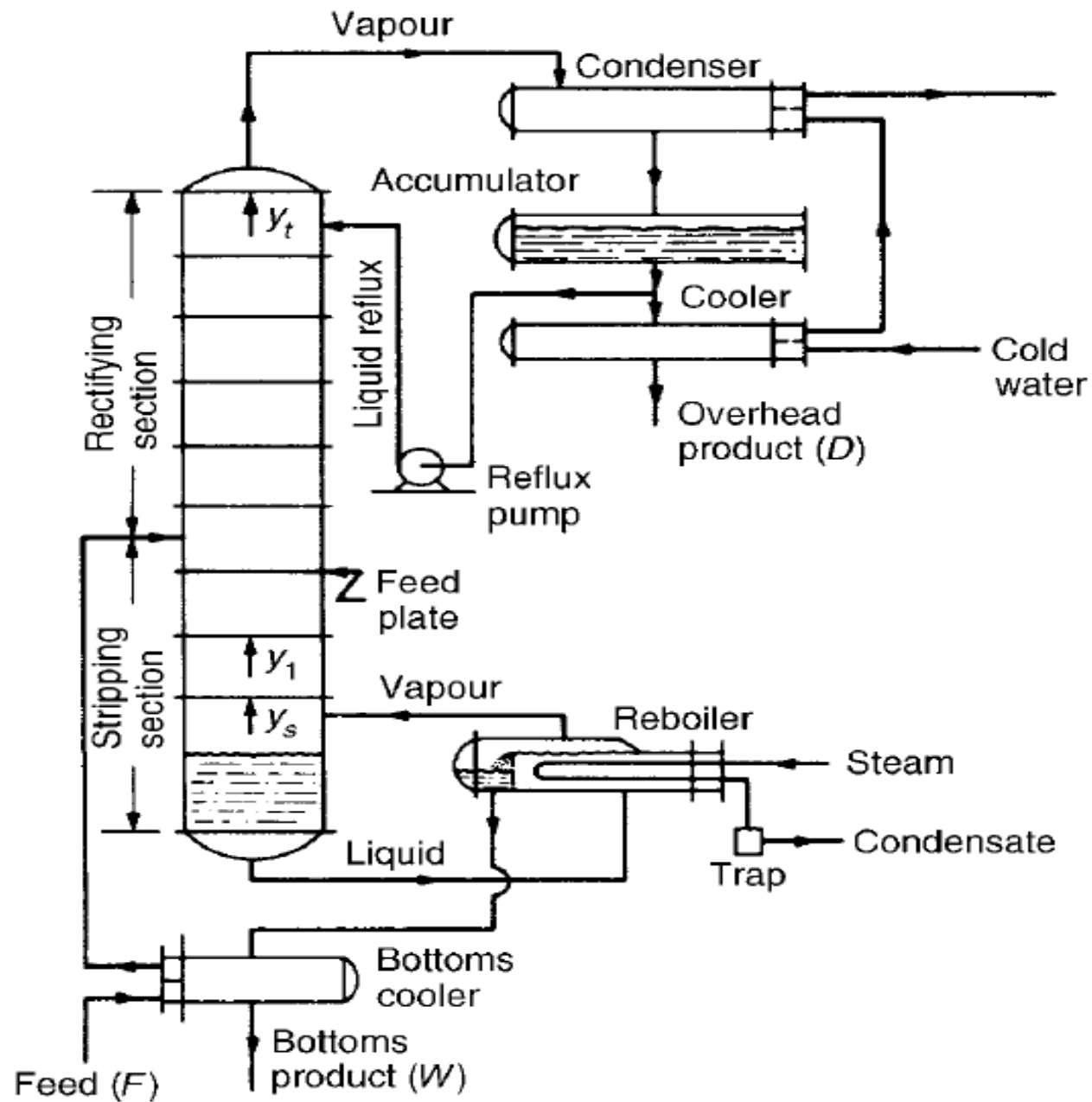


Figure 11.11. Continuous fractionating column with rectifying and stripping sections

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.

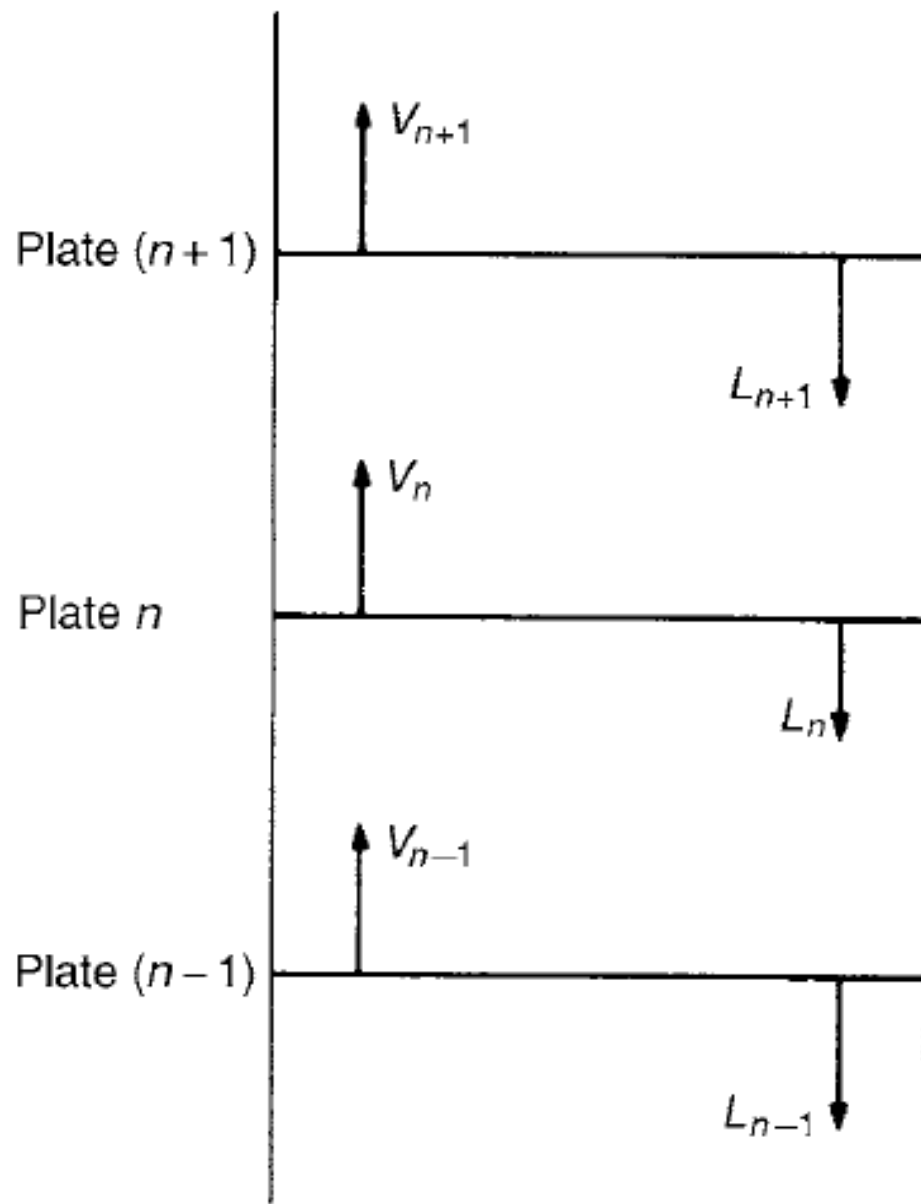


Figure 11.12. Material balance over a plate

## 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, and 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:

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

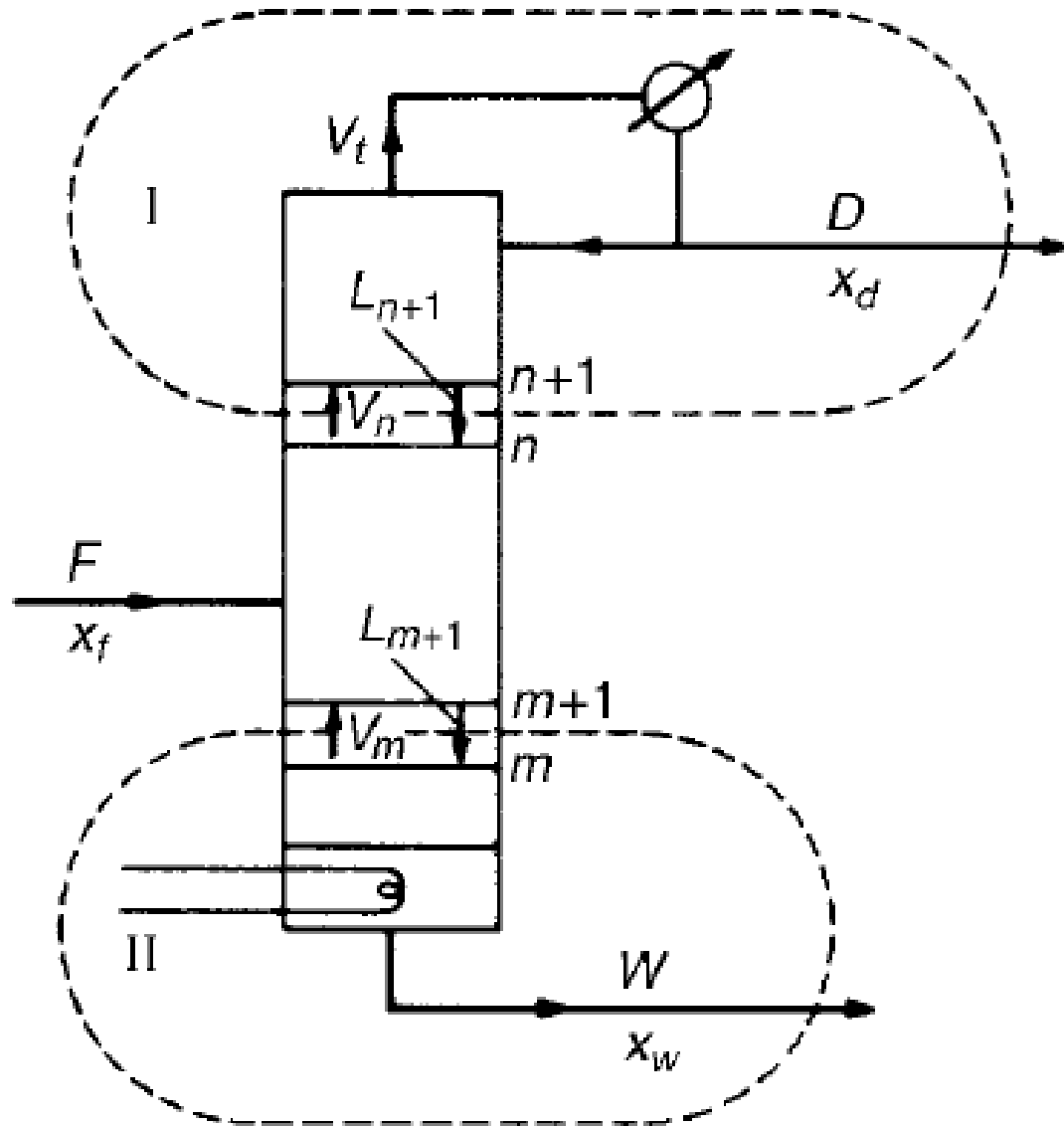


Figure 11.13. Material balances at top and bottom of column



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:

$$V_n = L_n + D = 150$$

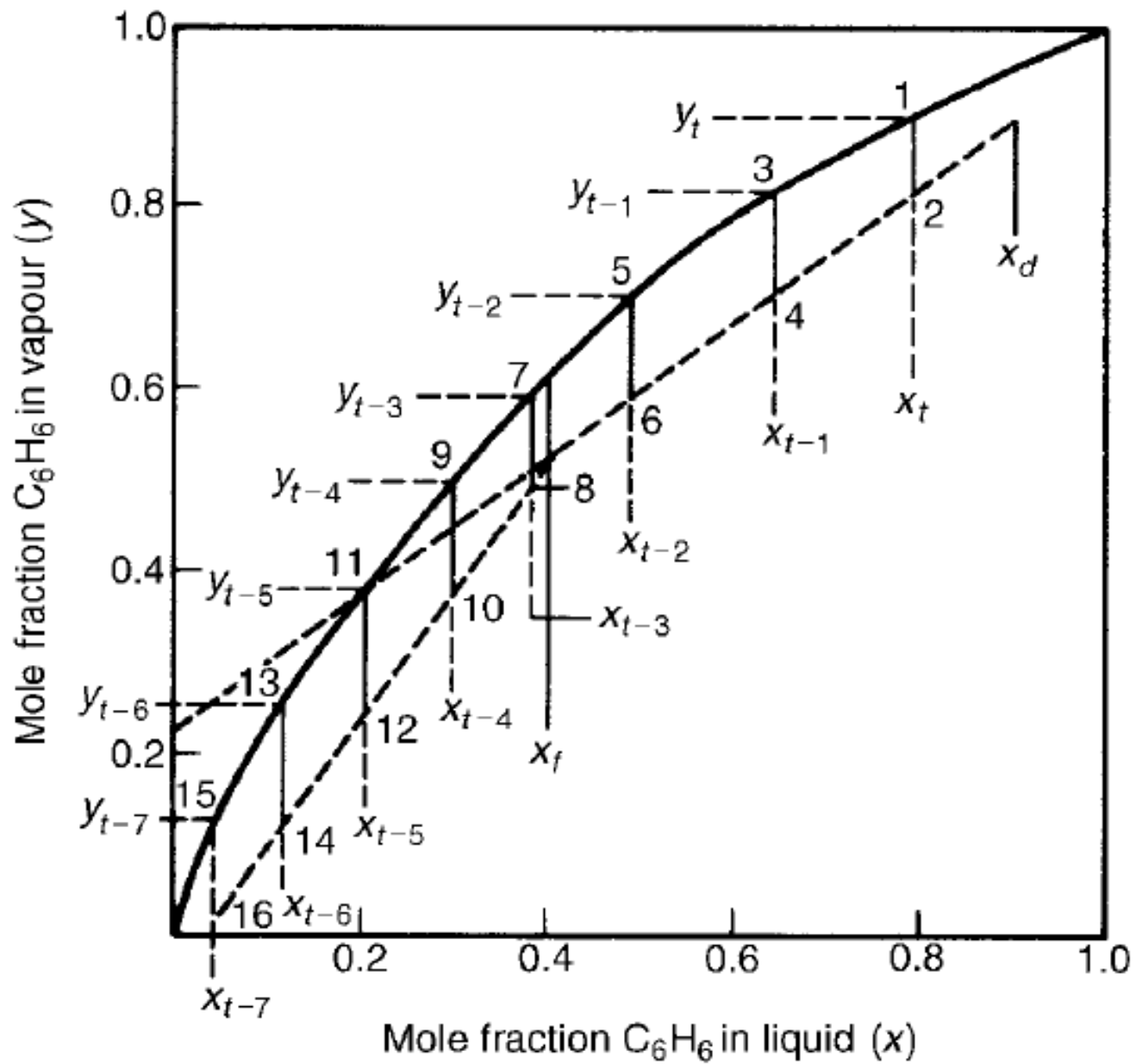


Figure 11.14. Calculation of the number of plates by the Lewis–Sorel method for Example 11.7

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

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

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

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

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

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

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

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

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

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

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

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 vaporisation 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:

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

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.

## ***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:

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

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

Thus, from equation 11.43:

$$V_m - V_n = qF - F \tag{11.45}$$

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

$$Fx_f = Dx_d + Wx_w$$

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.

These various conditions are indicated in Figure 11.16.

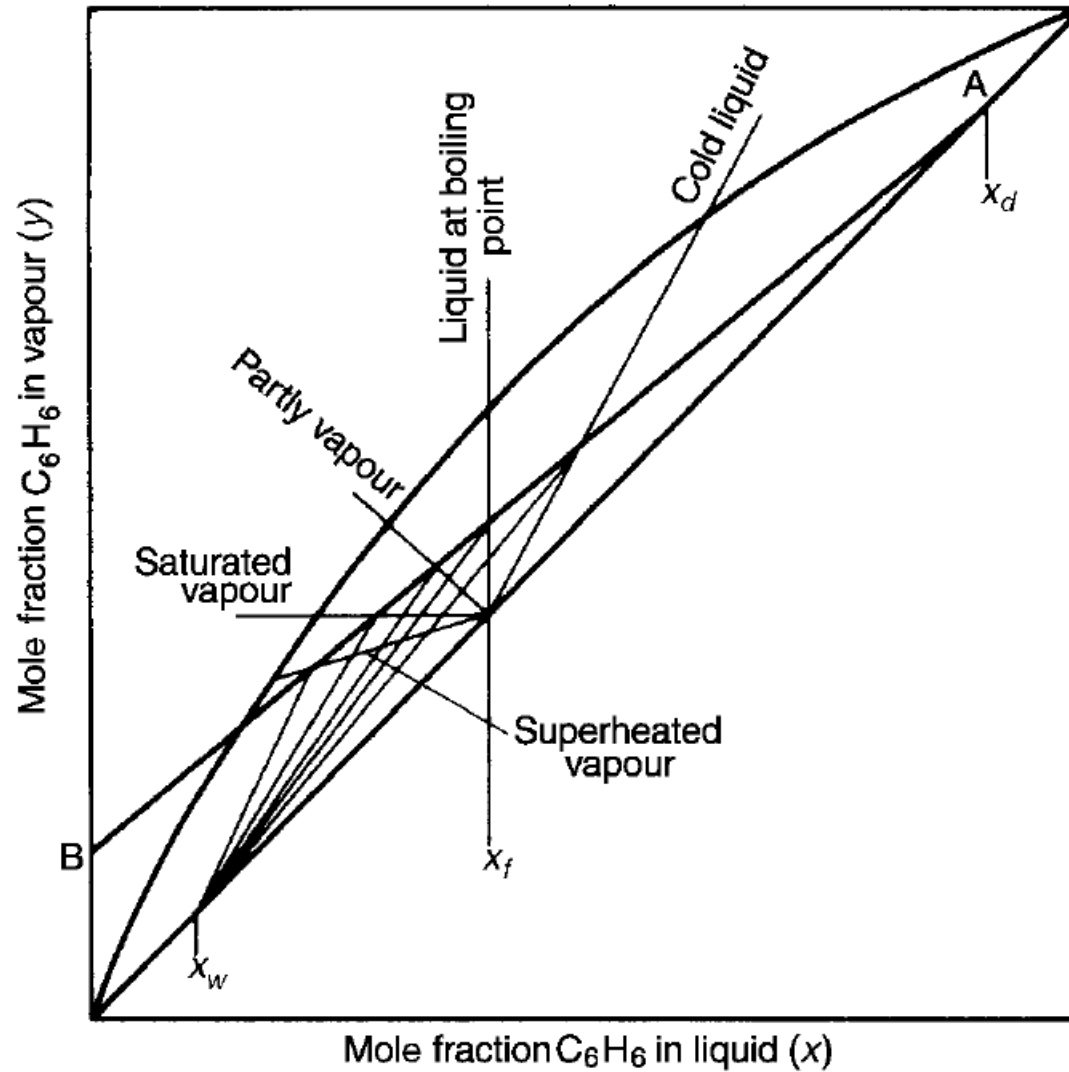


Figure 11.16. Effect of the condition of the feed on the intersection of the operating lines for a fixed reflux ratio

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.

### Home Work

A continuous fractionating column, operating at atmospheric pressure, is to be designed to separate a mixture containing 15.67 per cent  $\text{CS}_2$  and 84.33 per cent  $\text{CCl}_4$  into an overhead product containing 91 per cent  $\text{CS}_2$  and a waste of 97.3 per cent  $\text{CCl}_4$  all by mass. A plate efficiency of 70 per cent and a reflux of 3.16 kmol/kmol of product may be assumed. Using the following data, determine the number of plates required.

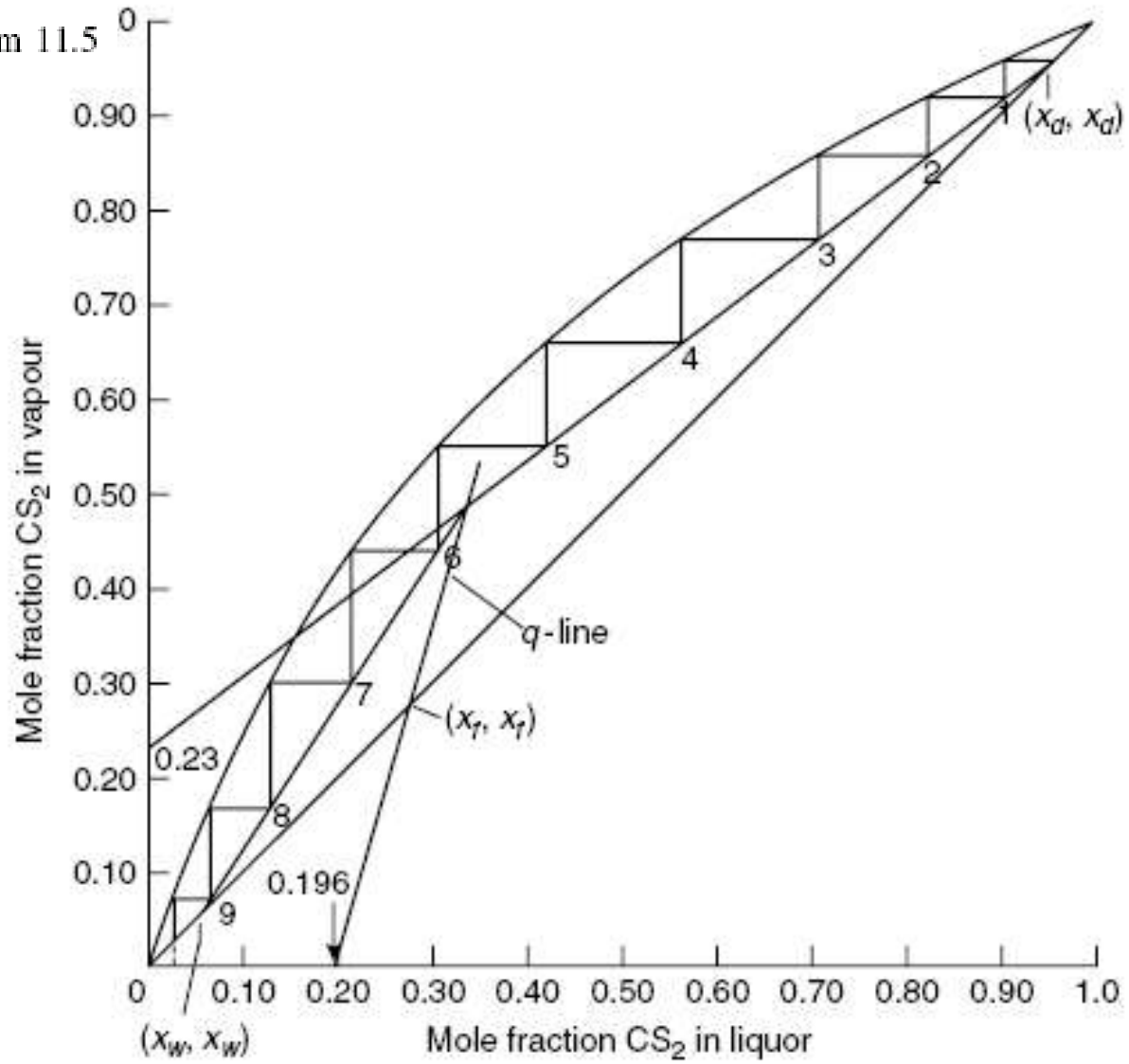
The feed enters at 290 K with a specific heat capacity of 1.7 kJ/kg K and a boiling point of 336 K. The latent heats of  $\text{CS}_2$  and  $\text{CCl}_4$  are 25.9 kJ/kmol.

CS <sub>2</sub> in the vapour (Mole per cent)	0	8.23	15.55	26.6	33.2	49.5	63.4	74.7	82.9	87.8	93.2
CS <sub>2</sub> in the liquid (Mole per cent)	0	2.36	6.15	11.06	14.35	25.85	33.0	53.18	66.30	75.75	86.04

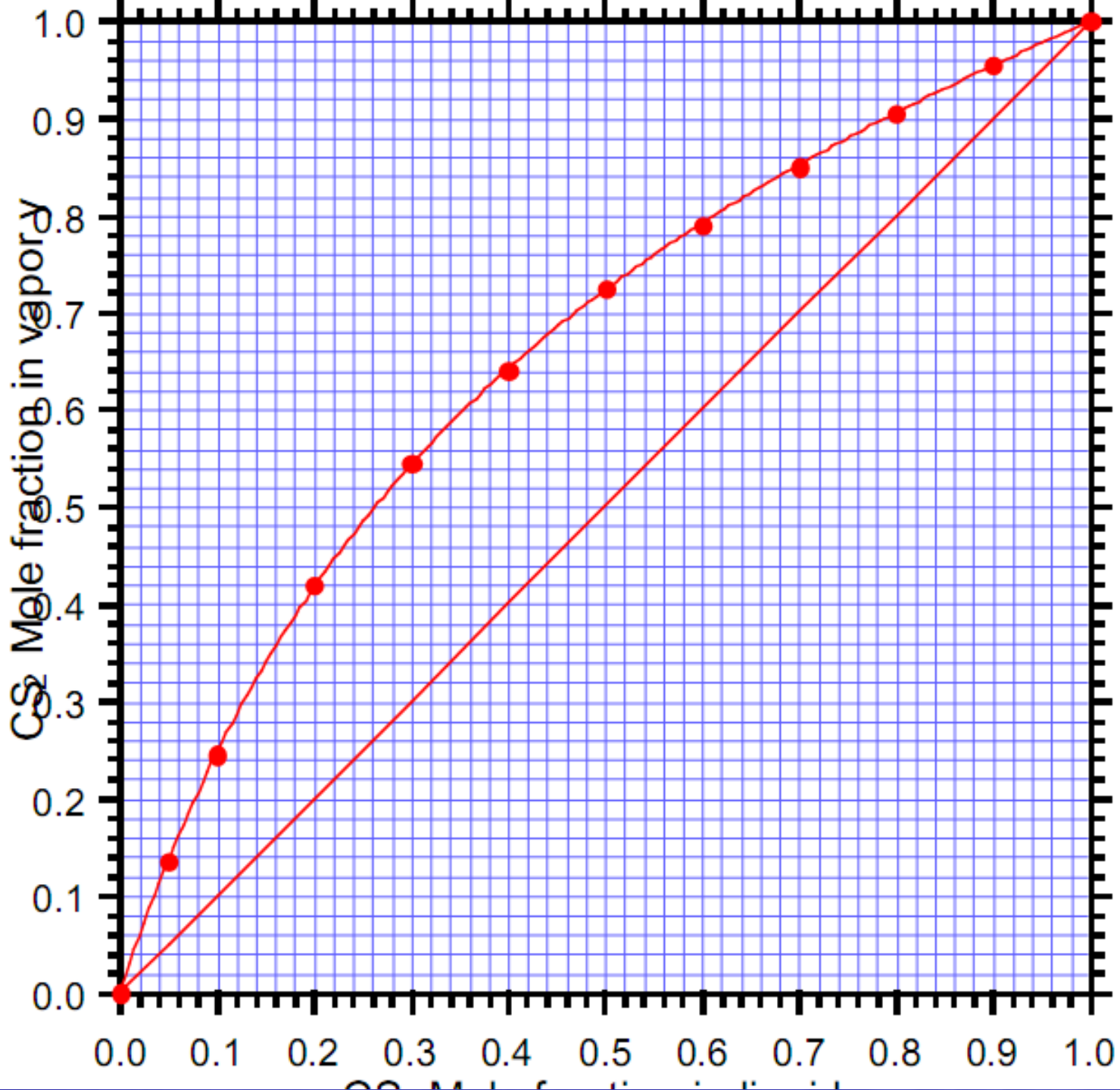
# Solution

The equilibrium data are shown in Figure 11c and the problem may be solved using the method of McCabe and Thiele. All compositions are in terms of mole fractions so that:

Figure 11c. Equilibrium data for Problem 11.5









Top product:  $x_d = \frac{(91/76)}{(91/76) + (9/154)} = 0.953$

Feed:  $x_f = \frac{(15.67/76)}{(15.67/76) + (84.33/154)} = 0.274$

Bottom product:  $x_w = \frac{(2.7/76)}{(2.7/76) + (97.3/154)} = 0.053$

In this problem, the feed is not at its boiling-point so the slope of the  $q$ -line must be determined in order to locate the intersection of the operating lines.

$q$  is defined as the heat required to vaporise 1 kmol of feed/molar latent heat of feed, or

$$q = (\lambda + H_{fs} - H_f)/\lambda$$

where  $\lambda$  is the molar latent heat.  $H_{fs}$  is the enthalpy of 1 kmol of feed at its boiling-point, and  $H_f$  is the enthalpy of 1 kmol of feed.

The feed composition is 27.4 per cent  $\text{CS}_2$  and 72.6 per cent  $\text{CCl}_4$  so that the mean molecular mass of the feed is given by:

$$(0.274 \times 76) + (0.726 \times 154) = 132.6 \text{ kg/kmol}$$

Taking a datum of 273 K:

$$H_f = 1.7 \times 132.6(290 - 273) = 3832 \text{ kJ/kmol}$$

$$H_{fs} = 1.7 \times 132.6(336 - 273) = 14,200 \text{ kJ/kmol}$$

$$\lambda = 25,900 \text{ kJ/kmol}$$

Thus:  $q = (25,900 + 14,200 - 3832)/25,900 = 1.4$

The intercept of the  $q$ -line on the  $x$ -axis is shown from equation 11.46 to be  $x_f/q$  or:

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

$$x_f/q = (0.274/1.4) = 0.196$$

Thus the  $q$ -line is drawn through  $(x_f, x_f)$  and  $(0.196, 0)$  as shown in Figure 11c. As the reflux ratio is given as 3.16, the top operating line may be drawn through  $(x_d, x_d)$  and  $(0, x_d/4.16)$ . The lower operating line is drawn by joining the intersection of the top operating line and the  $q$ -line with the point  $(x_w, x_w)$ .

The theoretical plates may be stepped off as shown and 9 theoretical plates are shown. If the plate efficiency is 70 per cent, the number of actual plates =  $(9/0.7) = 12.85$ ,

Thus: 13 plates are required

### 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.

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

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

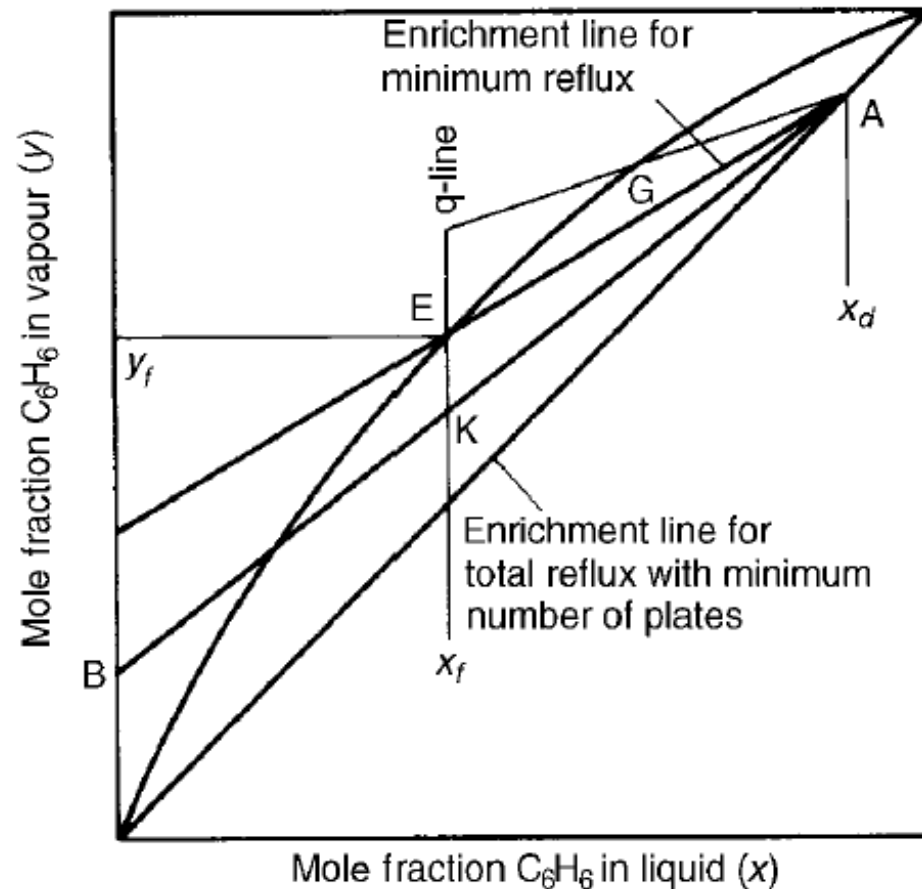


Figure 11.17. Influence of reflux ratio on the number of plates required for a given separation

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  $y_c = x_f$ :

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



## 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:

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

## 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:

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

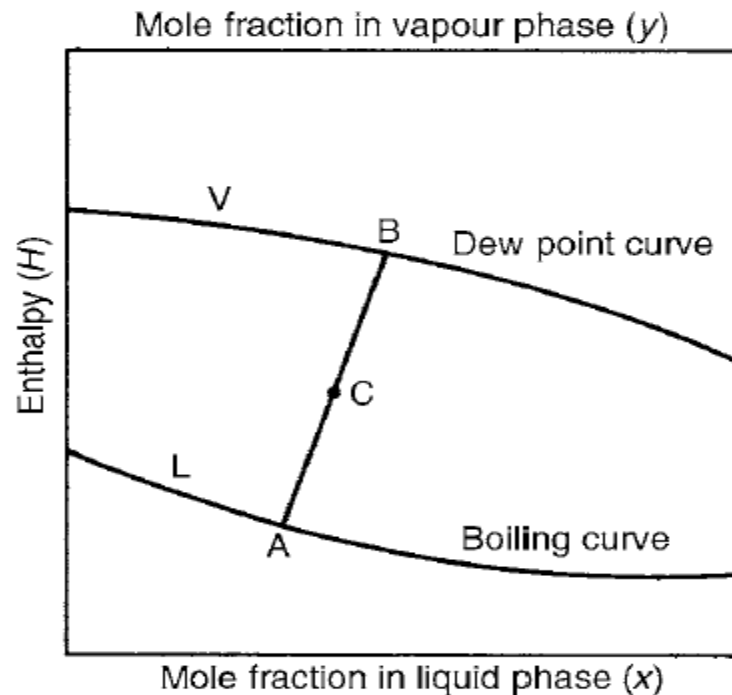


Figure 11.24. Enthalpy–composition diagram, showing the enthalpies of liquid and vapour

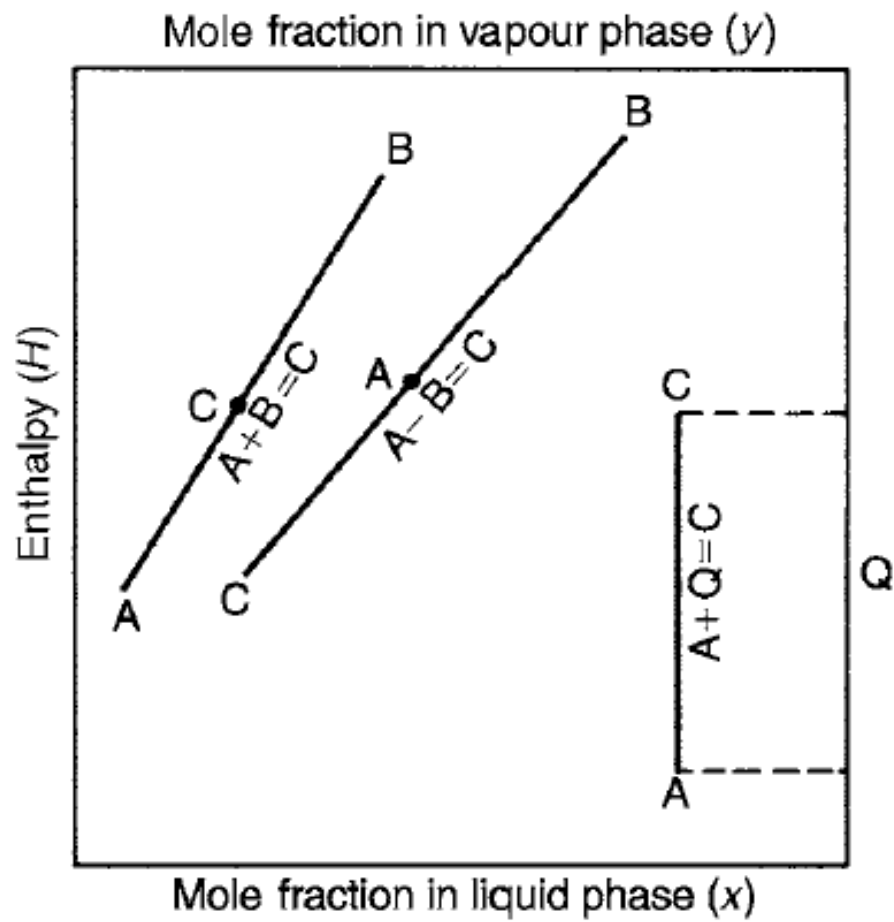


Figure 11.25. Combination and separation of a mixture on an enthalpy–composition diagram

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:

$$\frac{m_A}{m_B} = \frac{CB}{CA} \quad (11.76)$$

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.

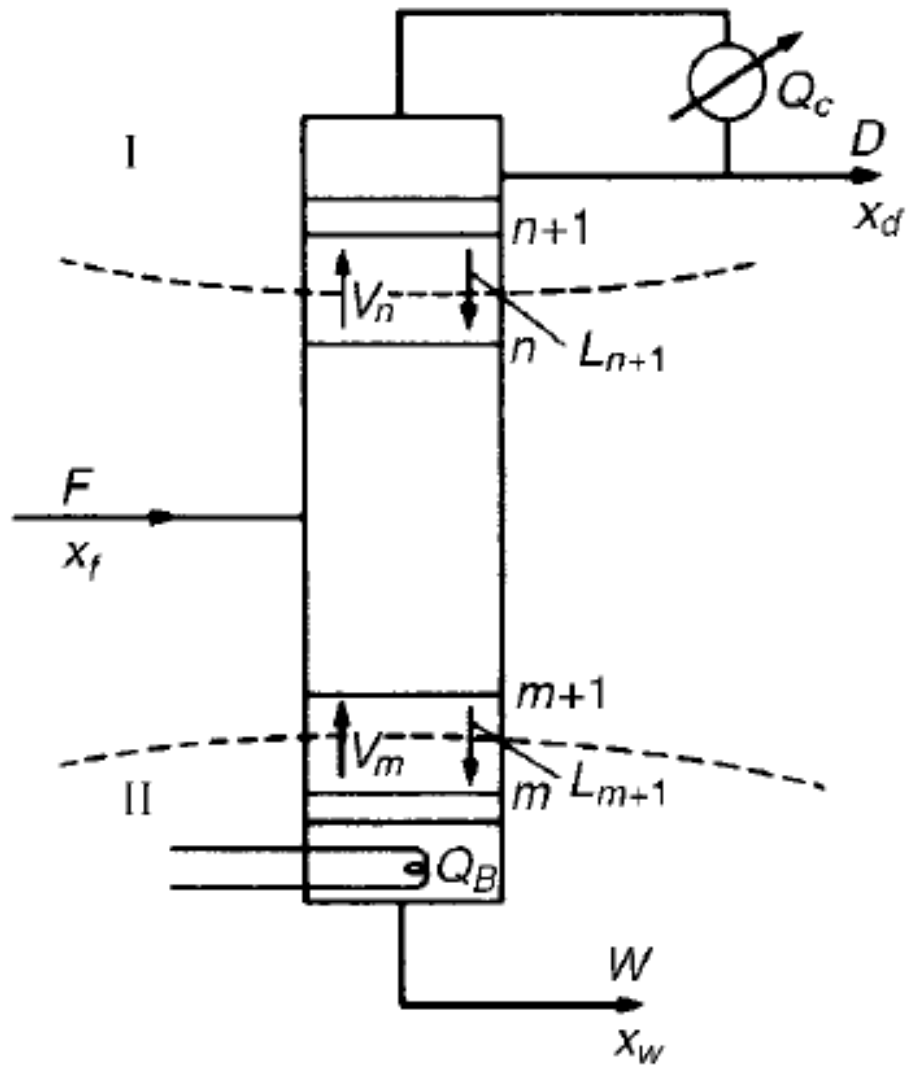


Figure 11.26. Continuous distillation column



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

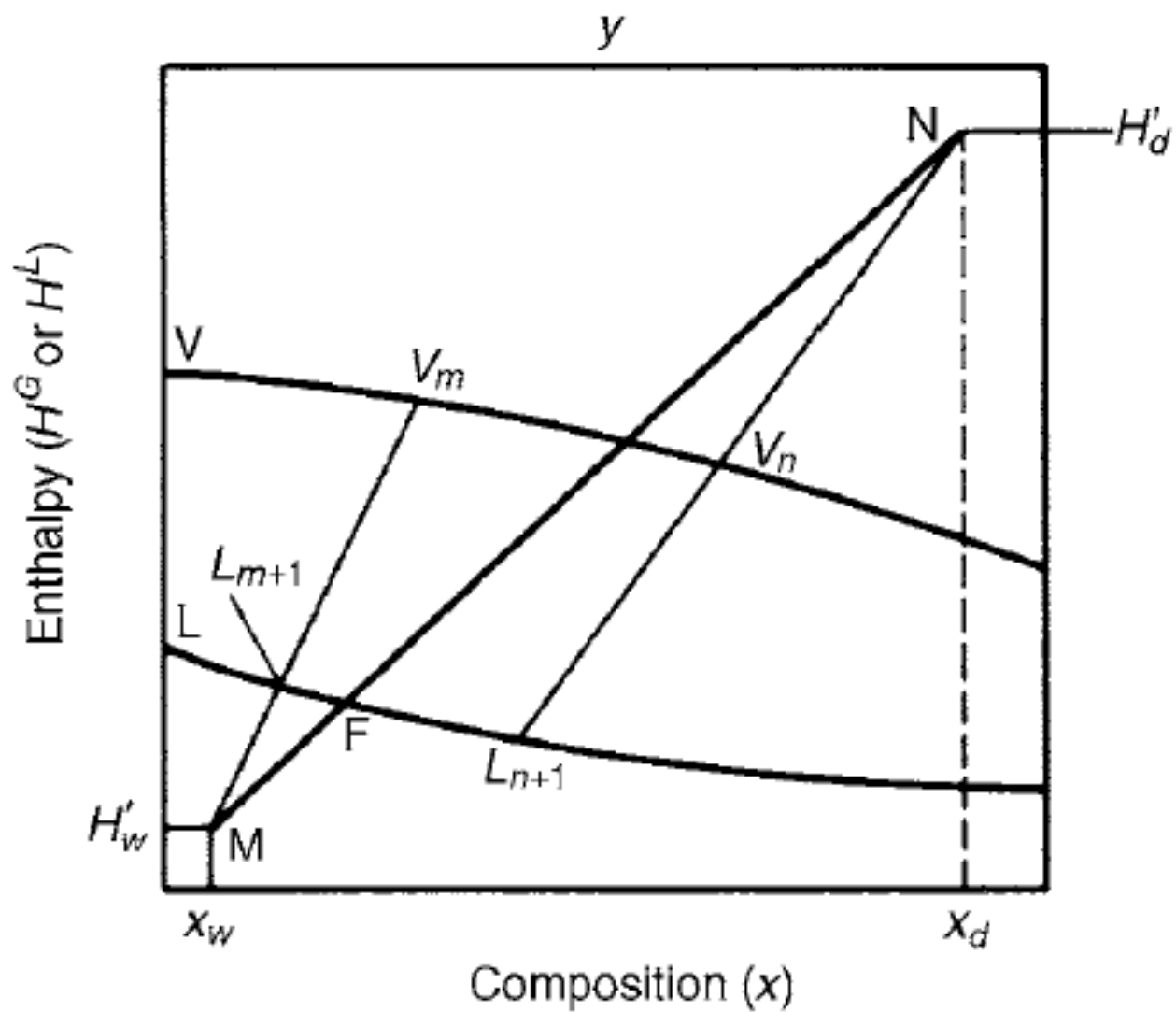


Figure 11.27. Enthalpy–composition diagram

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

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

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

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:

$$F = M + N \quad (11.93)$$

and: 
$$F x_f = M x_w + N x_d \quad (11.94)$$

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:

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

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



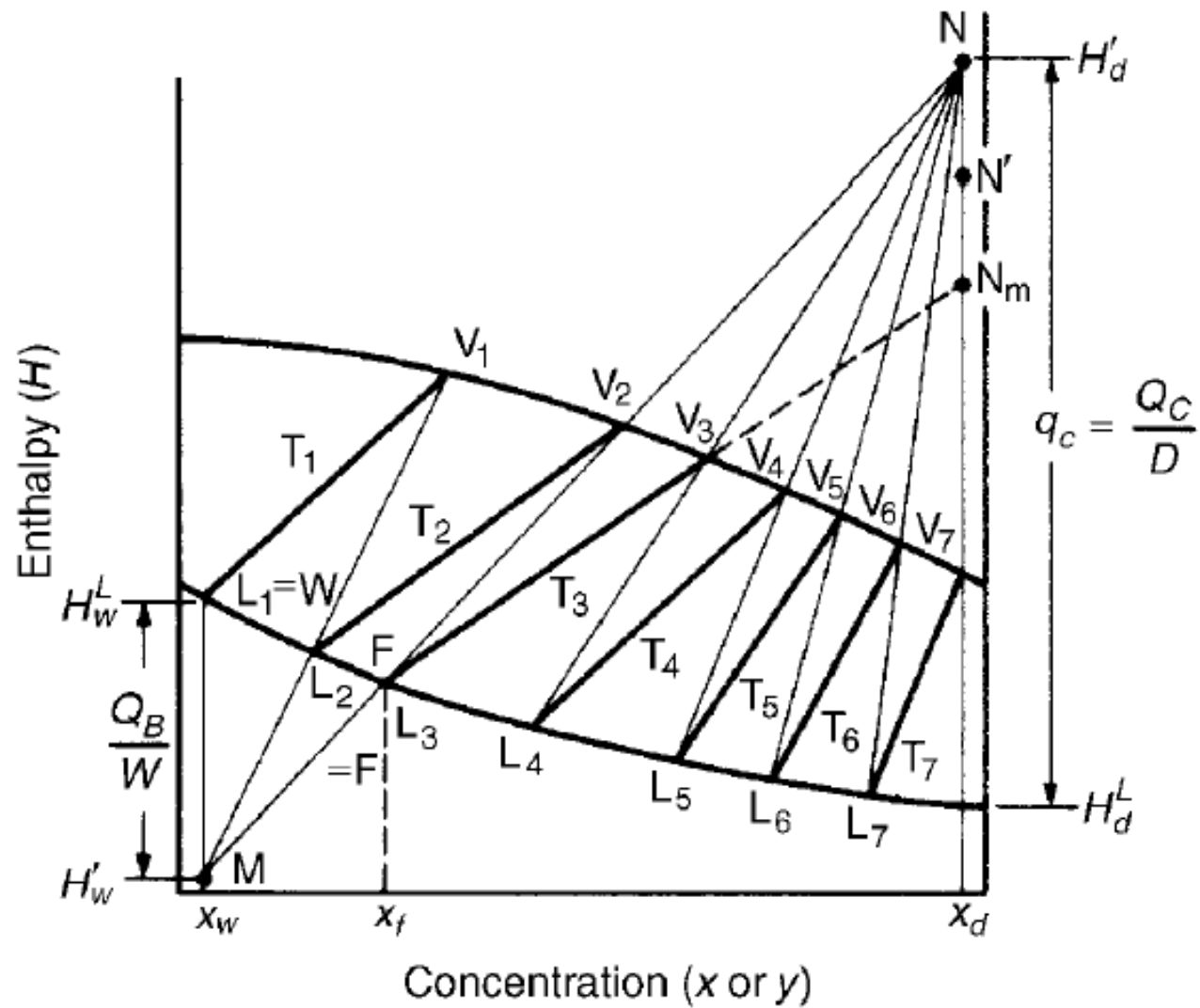


Figure 11.28. Determination of the number of plates using the enthalpy–composition diagram

The condition of the vapour leaving the top plate is shown at  $V_7$  on the dew-point curve with abscissa  $x_d$ . The condition of the liquid on the top plate is then found by drawing the tie line  $T_7$  from  $V_7$  to  $L_7$  on the boiling curve. The condition  $V_6$  of the vapour on the second plate is found, from equation 11.77, by drawing  $L_7N$  to cut the dew-point curve on  $V_6$ .  $L_6$  is then found on the tie line  $T_6$ . The conditions of vapour and liquid  $V_5, V_4, V_3$  and  $L_5, L_4$  are found in the same way. Tie line  $T_3$  gives  $L_3$ , which has the same composition as the feed.  $V_2$  is then found using the line  $MFV_2$ , as this represents the vapour on the top plate of the stripping section.  $L_2, L_1$  and  $V_1$  are then found by a similar construction.  $L_1$  has the required composition of the bottoms,  $x_w$ .

Alternatively, calculations may start with the feed condition and proceed up and down the column.

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

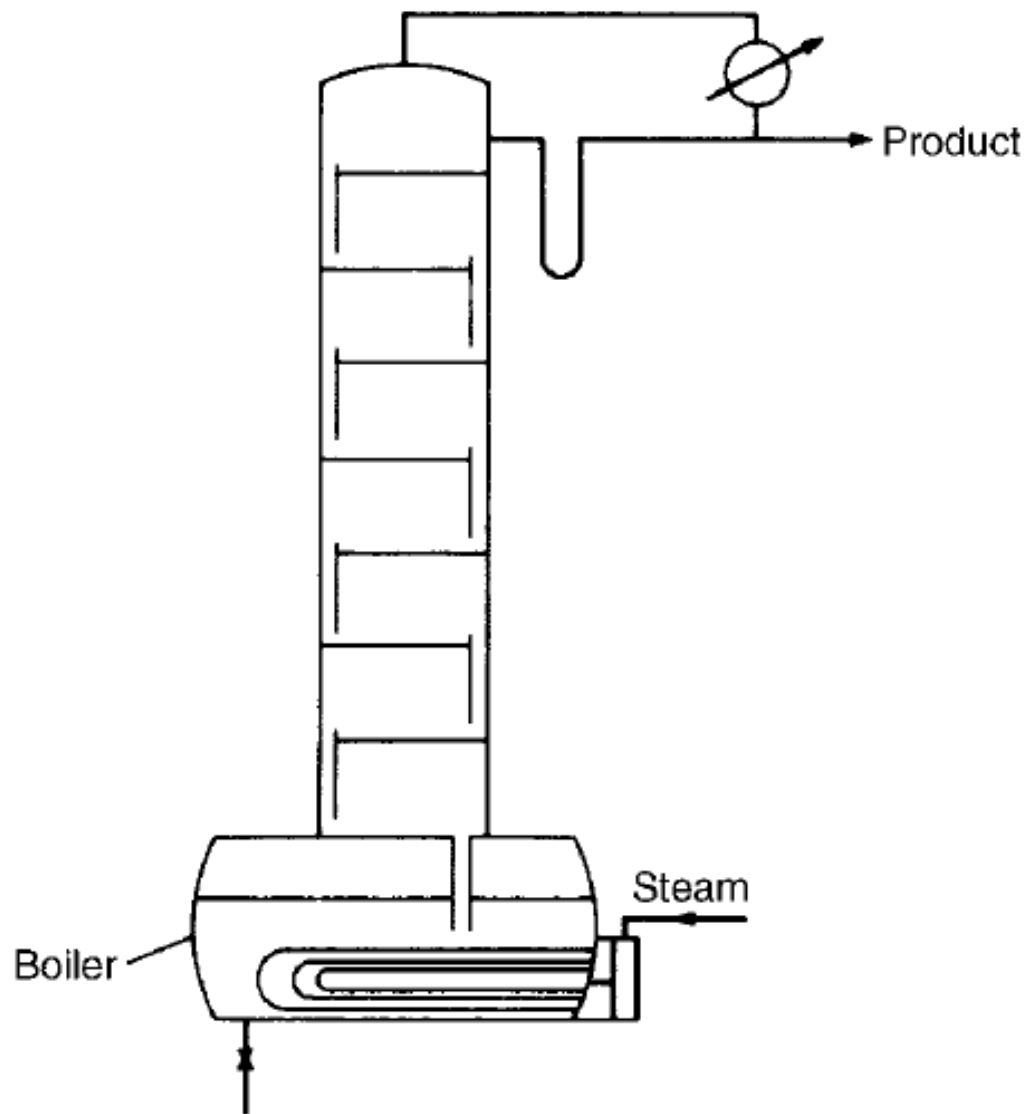
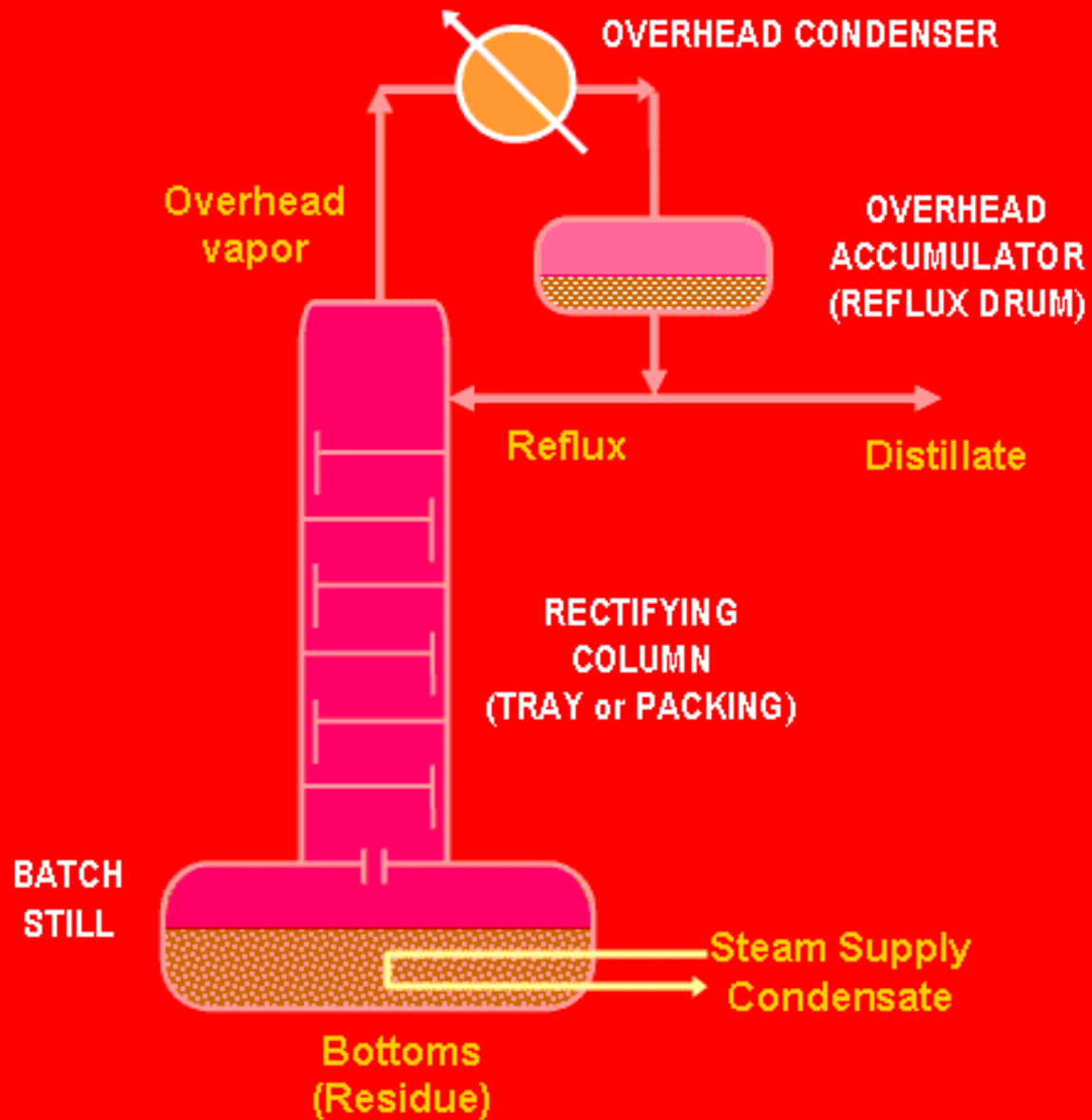
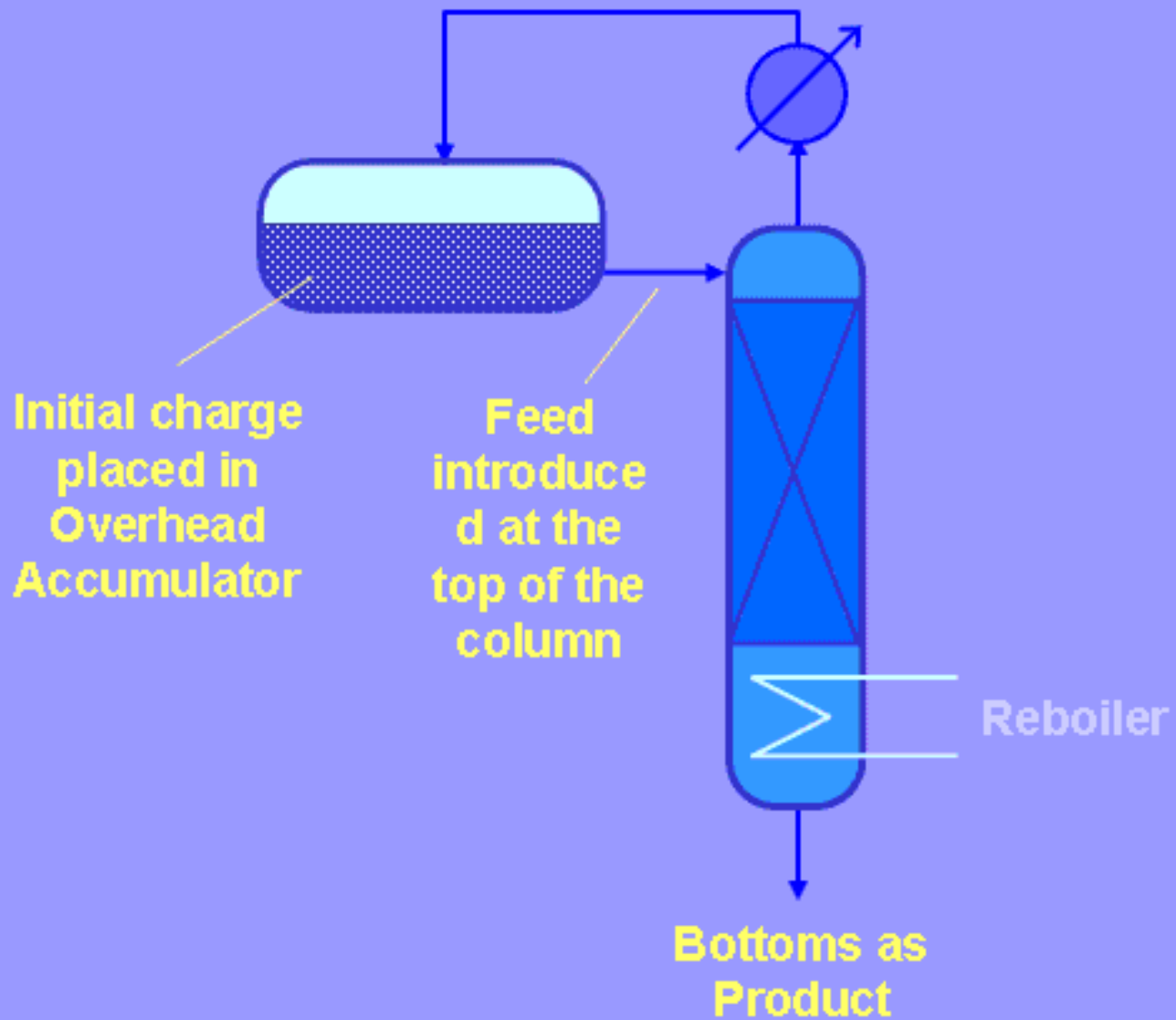


Figure 11.33. Column for batch distillation







$x_{d1}$ . If after a certain interval of time the composition of the top product starts to fall, then, if the reflux ratio is increased to a new value  $R_2$ , it will be possible to obtain the same composition at the top as before, although the composition in the still is weakened to  $x_{s2}$ . This method of operating a batch still requires a continuous increase in the reflux ratio to maintain a constant quality of the top product.

An alternative method of operation is to work with a constant reflux ratio and allow the composition of the top product to fall. For example, if a product of composition 0.9 with respect to the more volatile component is required, the composition initially obtained may be 0.95, and distillation is allowed to continue until the composition has fallen to some value below 0.9, say 0.82. The total product obtained will then have the required composition, provided the amounts of a given purity are correctly chosen.

One of the added merits of batch distillation is that more than one product may be obtained. Thus, a binary mixture of alcohol and water may be distilled to obtain initially a high quality alcohol. As the composition in the still weakens with respect to alcohol, a second product may be removed from the top with a reduced concentration of alcohol. In this way it is possible to obtain not only two different quality products, but also to reduce the alcohol in the still to a minimum value. This method of operation is particularly useful for handling small quantities of multi-component organic mixtures, since it is possible to obtain the different components at reasonable degrees of purity, in turn. To obtain the maximum recovery of a valuable component, the charge remaining in the still after the first distillation may be added to the next batch.

## 11.6.2. Operation at constant product composition

The case of a column with four ideal plates used to separate a mixture of ethyl alcohol and water may be considered. Initially there are  $S_1$  moles of liquor of mole fraction  $x_{s1}$  with respect to the more volatile component, alcohol, in the still. The top product is to contain a mole fraction  $x_d$ , and this necessitates a reflux ratio  $R_1$ . If the distillation is to be continued until there are  $S_2$  moles in the still, of mole fraction  $x_{s2}$ , then, for the same number of plates the reflux ratio will have been increased to  $R_2$ . If the amount of product obtained is  $D_b$  moles, then a material balance gives:

$$S_1 x_{s1} - S_2 x_{s2} = D_b x_d \quad (11.96)$$

and: 
$$S_1 - S_2 = D_b \quad (11.97)$$

Thus: 
$$S_1 x_{s1} - (S_1 - D_b) x_{s2} = D_b x_d$$

and: 
$$S_1 x_{s1} - S_1 x_{s2} = D_b x_d - D_b x_{s2}$$

and: 
$$D_b = S_1 \left[ \frac{x_{s1} - x_{s2}}{x_d - x_{s2}} \right] = \left( \frac{a}{b} \right) S_1 \quad (11.98)$$

where  $a$  and  $b$  are as shown in Figure 11.34. If  $\phi$  is the intercept on the  $Y$ -axis for any operating line, equation 11.48, then:

$$\left( \frac{R}{R+1} \right) x_{n+1} + \left( \frac{x_d}{R+1} \right) \quad \frac{x_d}{R+1} = \phi, \quad \text{or} \quad R = \frac{x_d}{\phi} - 1 \quad (11.99)$$



These equations enable the final reflux ratio to be determined for any desired end concentration in the still, and they also give the total quantity of distillate obtained. What is important, in comparing the operation at constant reflux ratio with that at constant product composition, is the difference in the total amount of steam used in the distillation, for a given quantity of product,  $D_b$ .

If the reflux ratio  $R$  is assumed to be adjusted continuously to keep the top product at constant quality, then at any moment the reflux ratio is given by  $R = dL_b/dD_b$ . During the course of the distillation, the total reflux liquor flowing down the column is given by:

$$\int_0^{L_b} dL_b = \int_{R=R_1}^{R=R_2} R dD_b \quad (11.100)$$

To provide the reflux  $dL_b$  the removal of a quantity of heat equal to  $\lambda dL_b$  in the condenser is required, where  $\lambda$  is the latent heat per mole. Thus, the heat to be supplied in the boiler to provide this reflux during the total distillation  $Q_R$  is given by:

$$Q_R = \lambda \int_0^{L_b} dL_b = \lambda \int_{R=R_1}^{R=R_2} R dD_b \quad (11.101)$$

This equation may be integrated graphically if the relation between  $R$  and  $D_b$  is known. For any desired value of  $R$ ,  $x_s$  may be obtained by drawing the operating line, and marking off the steps corresponding to the given number of stages. The amount of product  $D_b$  is then obtained from equation 11.88 and, if the corresponding values of  $R$  and  $D_b$  are plotted, graphical integration will give the value of  $\int R dD_b$ .

The minimum reflux ratio  $R_m$  may be found for any given still concentration  $x_s$  from equation 11.56.



### 11.6.3. Operation at constant reflux ratio

If the same column is operated at a constant reflux ratio  $R$ , the concentration of the more volatile component in the top product will continuously fall. Over a small interval of time  $dt$ , the top-product composition with respect to the more volatile component will change from  $x_d$  to  $x_d + dx_d$ , where  $dx_d$  is negative for the more volatile component. If in this time the amount of product obtained is  $dD_b$ , then a material balance on the more volatile component gives:

$$\text{More volatile component removed in product} = dD_b \left[ x_d + \frac{dx_d}{2} \right]$$

$$\text{which, neglecting second-order terms, gives: } = x_d dD_b \quad (11.102)$$

$$\text{and: } \quad x_d dD_b = -d(Sx_s)$$

$$\text{But } dD_b = -dS,$$

$$\text{and hence: } \quad -x_d dS = -S dx_s - x_s dS$$

$$\text{and: } \quad S dx_s = dS(x_d - x_s)$$

$$\text{Thus: } \quad \int_{S_1}^{S_2} \frac{dS}{S} = \int_{x_{s1}}^{x_{s2}} \frac{dx_s}{x_d - x_s}$$

$$\ln \frac{S_1}{S_2} = \int_{x_{s2}}^{x_{s1}} \frac{dx_s}{x_d - x_s} \quad (11.103)$$



The right-hand side of this equation may be integrated by plotting  $1/(x_d - x_s)$  against  $x_s$ . This enables the ratio of the initial to final quantity in the still to be found for any desired change in  $x_s$ , and hence the amount of distillate  $D_b$ . The heat to be supplied to provide the reflux is  $Q_R = \lambda R D_b$  and hence the reboil heat required per mole of product may be compared with that from the first method.

### Example 11.12

A mixture of ethyl alcohol and water with 0.55 mole fraction of alcohol is distilled to give a top product of 0.75 mole fraction of alcohol. The column has four ideal plates and the distillation is stopped when the reflux ratio has to be increased beyond 4.0.

What is the amount of distillate obtained, and the heat required per kmol of product?

$$D_b = S_1 \left[ \frac{x_{s1} - x_{s2}}{x_d - x_{s2}} \right] = \left( \frac{a}{b} \right) S_1$$

$$\frac{x_d}{R + 1} = \phi, \quad \text{or} \quad R = \frac{x_d}{\phi} - 1$$

### Solution

For various values of  $R$  the corresponding values of the intercept  $\phi$  and the concentration in the still  $x_s$  are calculated. Values of  $x_s$  are found as shown in Figure 11.35 for the two values of  $R$  of 0.85 and 4. The amount of product is then found from equation 11.98. Thus, for  $R = 4$ :

$$D_b = 100 \left[ \frac{0.55 - 0.05}{0.75 - 0.05} \right] = 100 \left( \frac{0.5}{0.7} \right) = \underline{\underline{71.4 \text{ kmol}}}$$

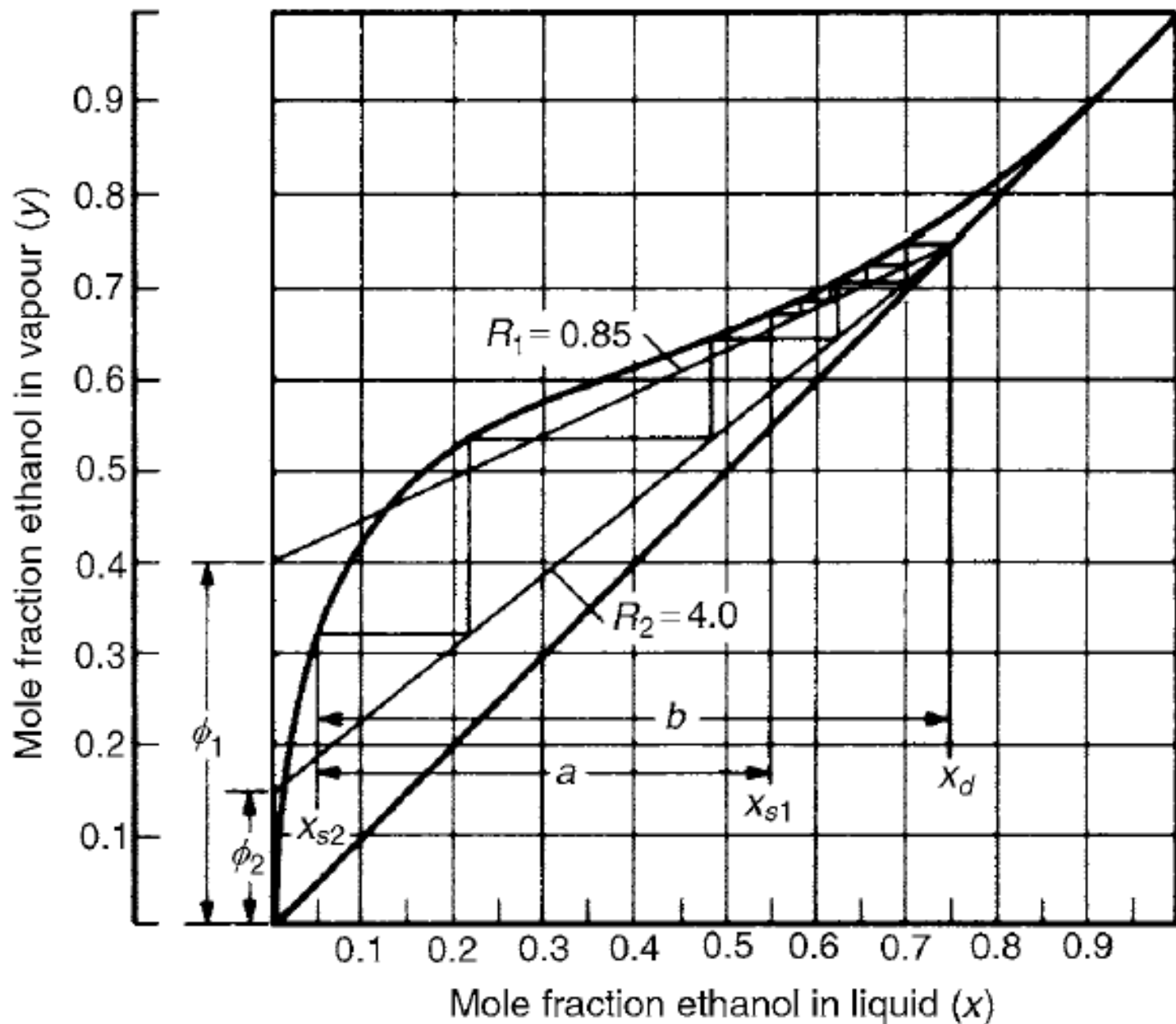


Figure 11.35. Batch distillation—constant product composition

Values of  $D_b$  found in this way are:

$R$	$\phi$	$x_s$	$D_b$
0.85	0.405	0.55	0
1.0	0.375	0.50	20.0
1.5	0.3	0.37	47.4
2.0	0.25	0.20	63.8
3.0	0.187	0.075	70.5
4.0	0.15	0.05	71.4

The relation between  $D_b$  and  $R$  is shown in Figure 11.36 and the  $\int_{R=0.85}^{R=4.0} R \, dD_b$  is given by area OABC as 96 kmol.

Assuming an average latent heat for the alcohol–water mixtures of 4000 kJ/kmol, the heat to be supplied to provide the reflux,  $Q_R$  is  $(96 \times 4000)/1000$  or approximately 380 MJ.

The heat to be supplied to provide the reflux per kmol of product is then  $(380/71.4) = 5.32$  MJ and the total heat is  $(5.32 + 4.0) = \underline{\underline{9.32}}$  MJ/kmol product.

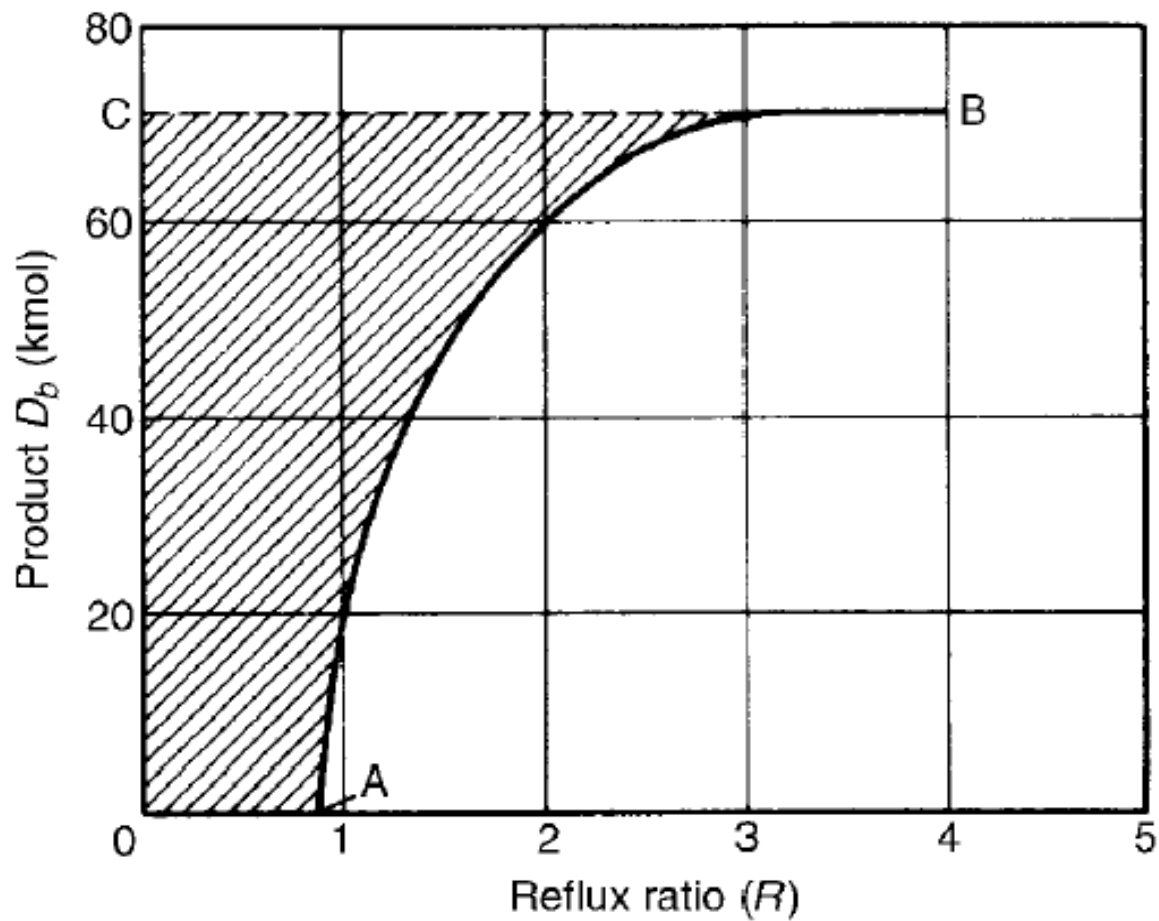


Figure 11.36. Graphical integration for Example 11.12

### Example 11.13

If the same batch as in Example 11.12 is distilled with a constant reflux ratio of  $R = 2.1$ , what will be the heat required and the average composition of the distillate if the distillation is stopped when the composition in the still has fallen to 0.105 mole fraction of ethanol?

### Example 11.13

If the same batch as in Example 11.12 is distilled with a constant reflux ratio of  $R = 2.1$ , what will be the heat required and the average composition of the distillate if the distillation is stopped when the composition in the still has fallen to 0.105 mole fraction of ethanol?

### Solution

The initial composition of the top product will be 0.78, as shown in Figure 11.37, and the final composition will be 0.74. Values of  $x_d$ ,  $x_s$ ,  $x_d - x_s$  and of  $1/(x_d - x_s)$  for various values of  $x_s$  and a constant reflux ratio are:

$x_s$	$x_d$	$x_d - x_s$	$1/(x_d - x_s)$
0.550	0.780	0.230	4.35
0.500	0.775	0.275	3.65
0.425	0.770	0.345	2.90
0.310	0.760	0.450	2.22
0.225	0.750	0.525	1.91
0.105	0.740	0.635	1.58

Values of  $x_s$  and  $1/(x_d - x_s)$  are plotted in Figure 11.38 from which  $\int_{0.105}^{0.55} (dx_s/(x_d - x_s)) = 1.1$ .

From equation 11.103:  $\ln(S_1/S_2) = 1.1$  and  $(S_1/S_2) = 3.0$ .

Product obtained,  $D_b = S_1 - S_2 = (100 - 100/3) = 66.7$  kmol.

Amount of ethanol in product =  $x_1 S_1 - x_2 S_2$

$$= (0.55 \times 100) - (0.105 \times 33.3) = 51.5 \text{ kmol}$$



Thus: average composition of product =  $(51.5/66.7) = \underline{\underline{0.77}}$  mole fraction ethanol.

The heat required to provide the reflux =  $(4000 \times 2.1 \times 66.7) = 560,380$  kJ.

Heat required to provide reflux per kmol of product =  $(560,380/66.7) = \underline{\underline{8400}}$  kJ.

Thus in Example 11.12 the total heat required per kmol of product is  $(5320 + 4000) = 9320$  kJ and at constant reflux ratio (Example 11.13) it is  $(8400 + 4000) = 12,400$  kJ, although the average quality of product is 0.77 for the second case and only 0.75 for the first.

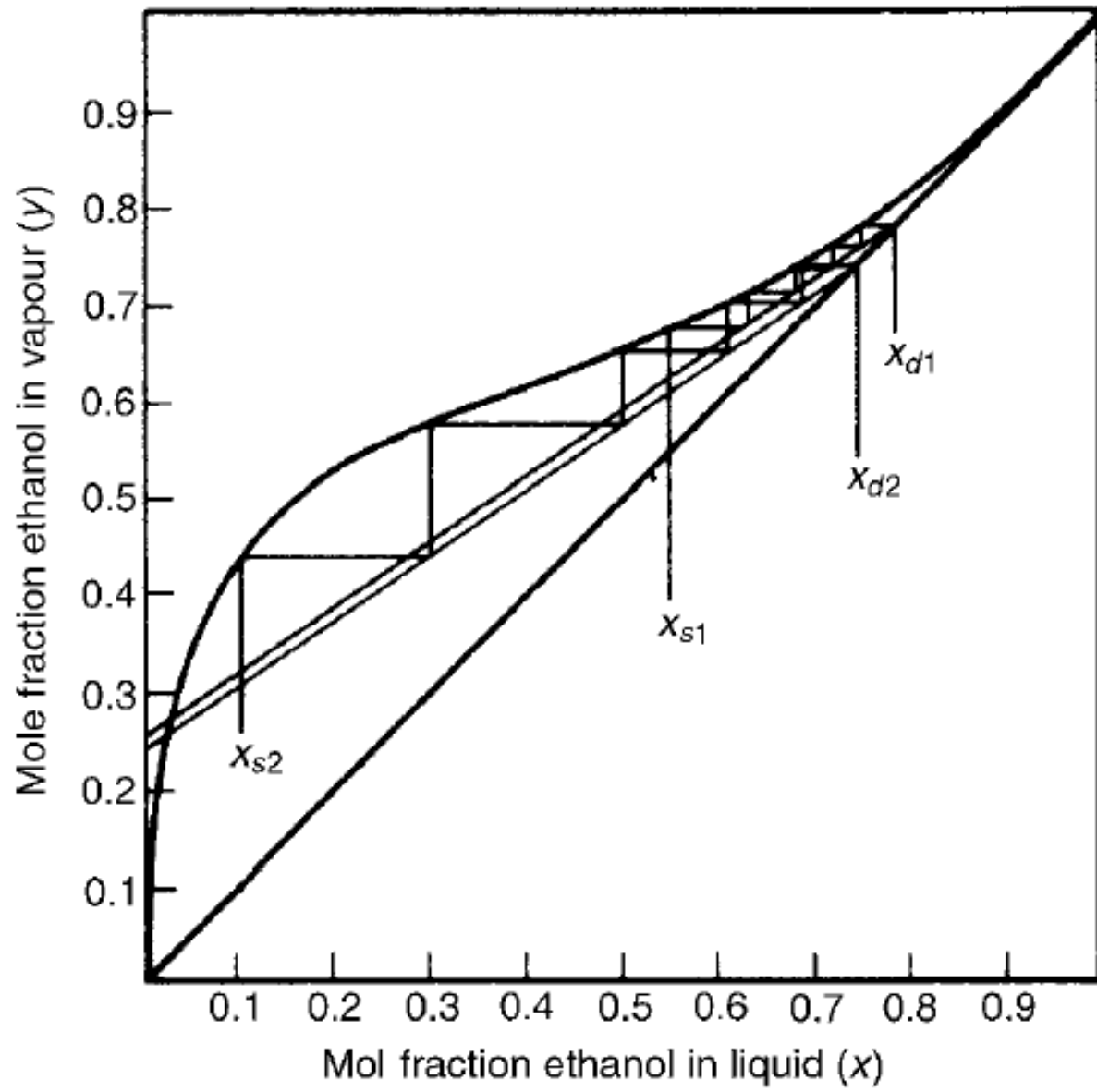


Figure 11.37. Batch distillation—constant reflux ratio (Example 11.13)

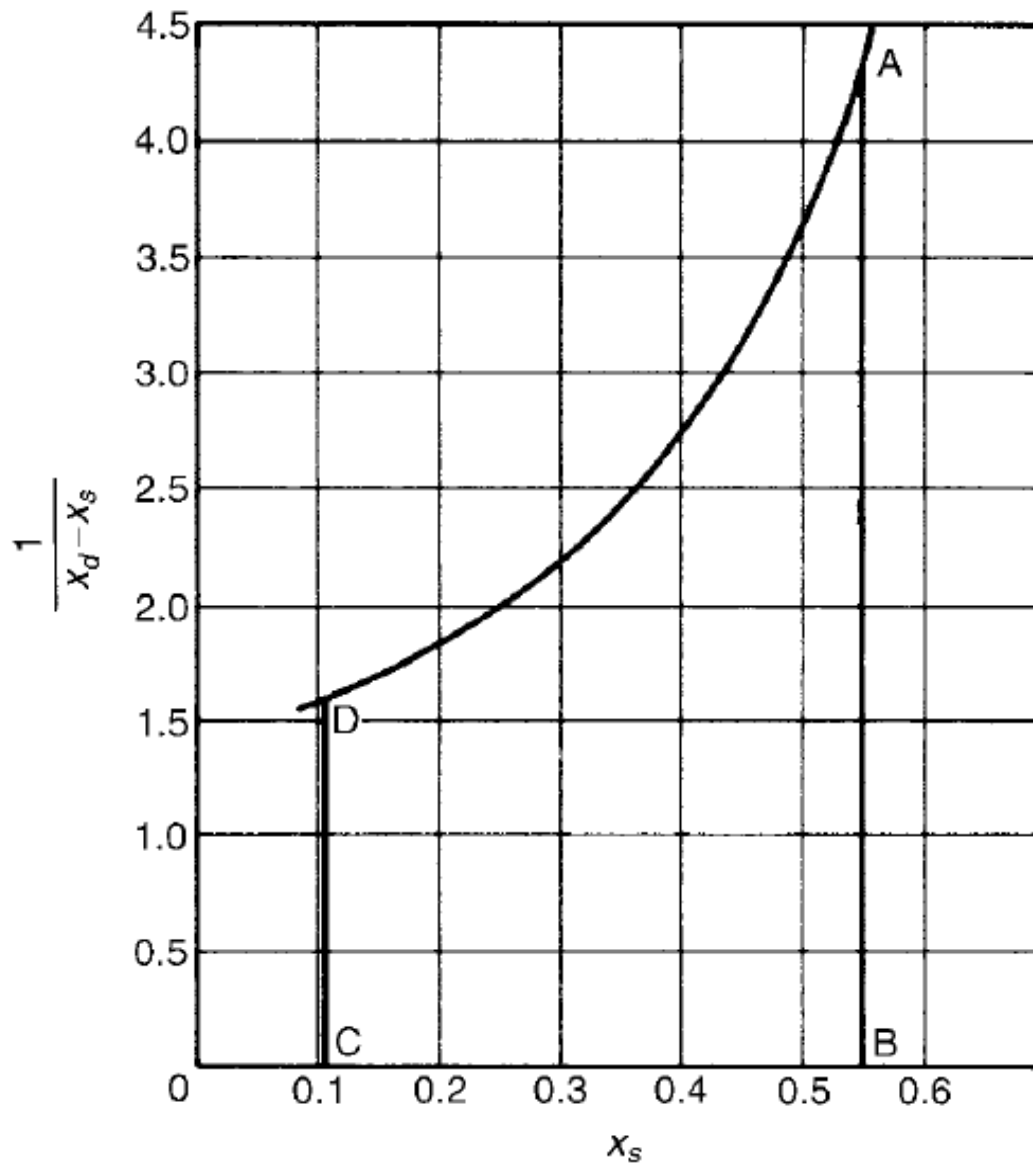


Figure 11.38. Graphical integration for Example 11.13