

DISTILLATION PROCESS

Distillation is the **process of separating the components or substances from a liquid mixture by using selective boiling and condensation**. Distillation may result in essentially complete separation (nearly pure components), or it may be a partial separation that increases the concentration of selected components in the mixture. 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, to 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.

11.2.2. Partial pressures, and Dalton's, Raoult's and Henry's laws

The partial pressure P_A of component A in a mixture of vapours is the pressure that would be exerted by component A at the same temperature, if present in the same volumetric concentration as in the mixture.

By Dalton's law of partial pressures, $P = \Sigma P_A$, that is the total pressure is equal to the summation of the partial pressures. Since in an ideal gas or vapour the partial pressure is proportional to the mole fraction of the constituent, then:

$$P_A = y_A P \quad (11.1)$$

For an *ideal mixture*, the partial pressure is related to the concentration in the liquid phase by Raoult's law which may be written as:

$$P_A = P_A^\circ x_A \quad (11.2)$$

where P_A° is the vapour pressure of pure A at the same temperature. This relation is usually found to be true only for high values of x_A , or correspondingly low values of x_B , although mixtures of organic isomers and some hydrocarbons follow the law closely.

For low values of x_A , a linear relation between P_A and x_A again exists, although the proportionality factor is Henry's constant \mathcal{H}' , and not the vapour pressure P_A° of the pure material.

For a liquid solute A in a solvent liquid B, Henry's law takes the form:

$$P_A = \mathcal{H}' x_A \quad (11.3)$$

If the mixture follows Raoult's law, then the vapour pressure of a mixture may be obtained graphically from a knowledge of the vapour pressure of the two components.

Thus, in Figure 11.6. OA represents the partial pressure P_A of A in a mixture, and CB the partial pressure of B, with the total pressure being shown by the line BA. In a mixture of composition D, the partial pressure P_A is given by DE, P_B by DF, and the total pressure P by DG, from the geometry of Figure 11.6.

Figure 11.7 shows the partial pressure of one component A plotted against the mole fraction for a mixture that is not ideal. It is found that over the range OC the mixture follows Henry's law, and over BA it follows Raoult's law. Although most mixtures show wide divergences from ideality, one of the laws is usually followed at very high and very low concentrations.

If the mixture follows Raoult's law, then the values of y_A for various values of x_A may be calculated from a knowledge of the vapour pressures of the two components at

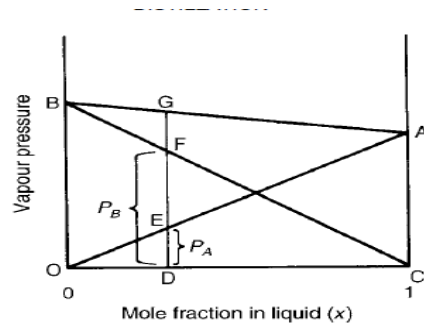


Figure 11.6. Partial pressures of ideal mixtures

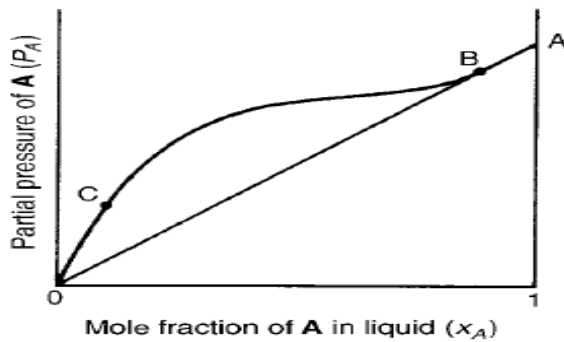


Figure 11.7. Partial pressures of non-ideal mixtures

various temperatures.

Thus:

$$P_A = P_A^\circ x_A$$

and:

$$P_A = P y_A$$

so that:

$$y_A = \frac{P_A^\circ x_A}{P}, \quad \text{and} \quad y_B = \frac{P_B^\circ x_B}{P} \quad (11.4)$$

But:

$$y_A + y_B = 1$$

$$\frac{P_A^\circ x_A}{P} + \frac{P_B^\circ (1 - x_A)}{P} = 1$$

giving:

$$x_A = \frac{P - P_B^\circ}{P_A^\circ - P_B^\circ} \quad (11.5)$$

Example 11.1

The vapour pressures of *n*-heptane and toluene at 373 K are 106 and 73.7 kN/m² respectively. What are the mole fractions of *n*-heptane in the vapour and in the liquid phase at 373 K if the total pressure is 101.3 kN/m²?

Solution

$$\text{At 373 K, } P_A^\circ = 106 \text{ kN/m}^2 \text{ and } P_B^\circ = 73.7 \text{ kN/m}^2$$

Thus, in equation 11.5:

$$x_A = (P - P_B^\circ) / (P_A^\circ - P_B^\circ) = \frac{(101.3 - 73.7)}{(106 - 73.7)} = \underline{\underline{0.856}}$$

and, in equation 11.4:

$$y_A = P_B^\circ x_B / P = \frac{(106 \times 0.856)}{101.3} = \underline{\underline{0.896}}$$

11.2.3. Relative volatility

The relationship between the composition of the vapour y_A and of the liquid x_A in equilibrium may also be expressed in a way, which is particularly useful in distillation calculations. If the ratio of the partial pressure to the mole fraction in the liquid is defined as the volatility, then:

$$\text{Volatility of A} = \frac{P_A}{x_A} \text{ and volatility of B} = \frac{P_B}{x_B}$$

The ratio of these two volatilities is known as the relative volatility α given by:

$$\alpha = \frac{P_A x_B}{x_A P_B}$$

Substituting $P y_A$ for P_A , and $P y_B$ for P_B :

$$\alpha = \frac{y_A x_B}{y_B x_A} \quad (11.13)$$

or:
$$\frac{y_A}{y_B} = \alpha \frac{x_A}{x_B} \quad (11.14)$$

This gives a relation between the ratio of **A** and **B** in the vapour to that in the liquid.

Since with a binary mixture $y_B = 1 - y_A$, and $x_B = 1 - x_A$ then:

$$\alpha = \left(\frac{y_A}{1 - y_A} \right) \left(\frac{1 - x_A}{x_A} \right)$$

or:
$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} \quad (11.15)$$

and:
$$x_A = \frac{y_A}{\alpha - (\alpha - 1)y_A} \quad (11.16)$$

This relation enables the composition of the vapour to be calculated for any desired value of x , if α is known. For separation to be achieved, α must not equal 1 and, considering the more volatile component, as α increases above unity, y increases and the separation becomes much easier. Equation 11.14 is useful in the calculation of plate enrichment and finds wide application in multicomponent distillation.

From the definition of the volatility of a component, it is seen that for an ideal system the volatility is numerically equal to the vapour pressure of the pure component. Thus the relative volatility α may be expressed as:

$$\alpha = \frac{P_A^\circ}{P_B^\circ} \quad (11.17)$$

This also follows by applying equation 11.1 from which $P_A/P_B = y_A/y_B$, so that:

$$\alpha = \frac{P_A x_B}{P_B x_A} = \frac{P_A^\circ x_A x_B}{P_B^\circ x_B x_A} = \frac{P_A^\circ}{P_B^\circ}$$

11.2.4. Non-ideal systems

Equation 11.4 relates x_A , y_A , P_A° and P . For a *non-ideal* system the term γ , the activity coefficient, is introduced to give:

$$y_A = \frac{\gamma_1 P_A^\circ x_A}{P} \quad \text{and} \quad y_B = \frac{\gamma_2 P_B^\circ x_B}{P} \quad (11.19)$$

or in Equation 11.18:

$$y_A = K \gamma_1 x_A \quad \text{and} \quad y_B = K \gamma_2 x_B \quad (11.20)$$

The liquid phase activity coefficients γ_1 and γ_2 depend upon temperature, pressure and concentration. Typical values taken from Perry's Chemical Engineers' Handbook⁽¹⁴⁾ are shown in Figure 11.8 for the systems *n*-propanol–water and acetone–chloroform. In the former, the activity coefficients are considered positive, that is greater than unity, whilst in the latter, they are fractional so that the logarithms of the values are negative. In both cases, γ approaches unity as the liquid concentration approaches unity and the highest values of γ occur as the concentration approaches zero.

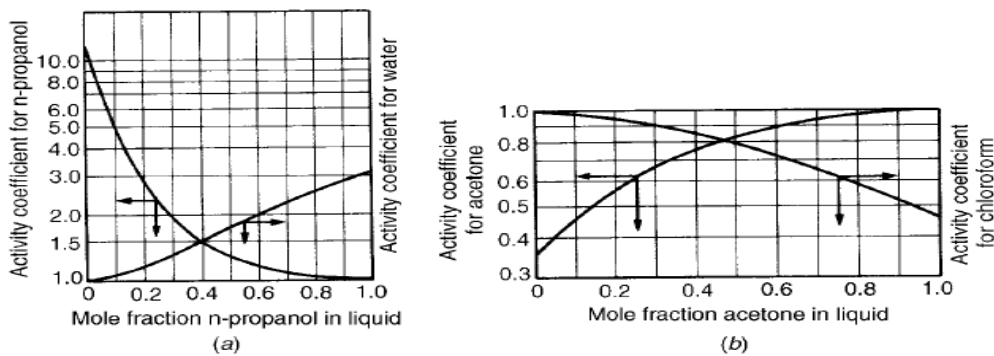


Figure 11.8. Activity coefficient data

The fundamental thermodynamic equation relating activity coefficients and composition is the *Gibbs–Duhem* relation which may be expressed as:

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} - x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} = 0 \quad (11.21)$$

This equation relates the slopes of the curves in Figure 11.8 and provides a means of testing experimental data. It is more convenient, however, to utilise integrated forms of these relations. A large number of different solutions to the basic Gibbs–Duhem equation are available, each of which gives a different functional relationship between $\log \gamma$ and x . Most binary systems may be characterised, however, by either the three- or four-suffix equations of Margules, or by the two-suffix van Laar equations, given as follows in the manner of WOHL^(15,16). The three-suffix Margules binary equations are:

$$\log \gamma_1 = x_2^2 [A_{12} + 2x_1(A_{21} - A_{12})] \quad (11.22)$$

$$\log \gamma_2 = x_1^2 [A_{21} + 2x_2(A_{12} - A_{21})] \quad (11.23)$$

Constants A_{12} and A_{21} are the limiting values of $\log \gamma$ as the composition of the component considered approaches zero. For example, in Equation 11.22, $A_{12} = \log \gamma_1$ when $x_1 = 0$.

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⁽²⁴⁾.

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:

$$\begin{aligned}y dS &= d(Sx) \\ &= S dx + x dS \\ \int_{S_0}^S \frac{dS}{S} &= \int_{x_0}^x \left(\frac{dx}{y-x} \right) \\ \text{and: } \ln \frac{S}{S_0} &= \int_{x_0}^x \left(\frac{dx}{y-x} \right) \quad (11.28)\end{aligned}$$

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/m², and leave at 520 K and 400 kN/m², 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.

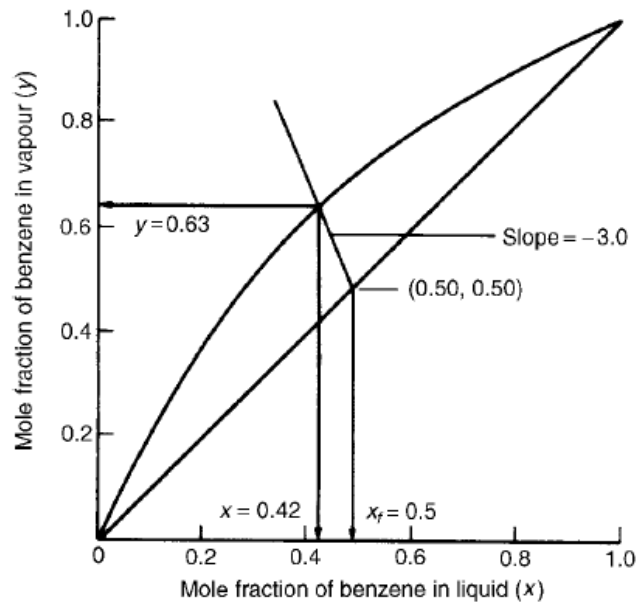


Figure 11.9. Equilibrium data for benzene–toluene for Example 11.6

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.

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.

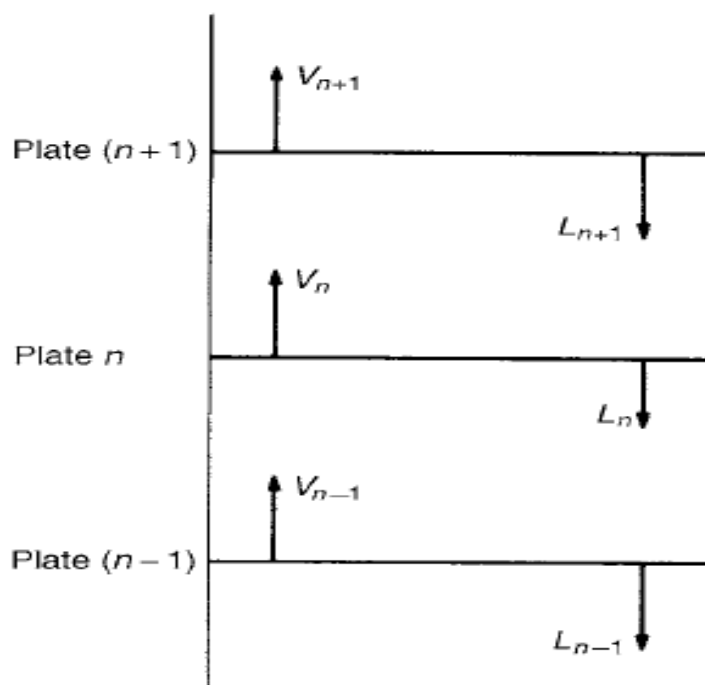


Figure 11.12. Material balance over a plate

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 .

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:

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

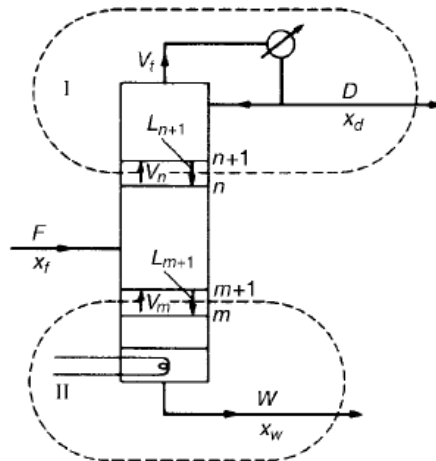


Figure 11.13. Material balances at top and bottom of column

Expressing this balance for the more volatile component gives:

$$y_n V_n = L_{n+1}x_{n+1} + Dx_d$$

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:

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