

101.265 kN/m² is essentially 101.3 kN/m² and hence, at this pressure, the boiling or the bubble point of the equimolar mixture is 365.1 K which lies between the boiling points of pure benzene, 353.3 K, and pure toluene, 383.8 K.

Example 11.5

What is the dew point of a equimolar mixture of benzene and toluene at 101.3 kN/m²?

Solution

From Raoult's Law, equations 11.1 and 11.2:

$$P_B = x_B P_B^0 = y_B P$$

and:

$$P_T = x_T P_T^0 = y_T P$$

Since the total pressure is 101.3 kN/m², $P_B = P_T = 50.65$ kN/m² and hence:

$$x_B = P_B/P_B^0 = 50.65/P_B^0 \text{ and } x_T = 50.65/P_T^0$$

It now remains to estimate the saturation vapour pressures as a function of temperature, using the data of Example 11.3, and then determine, by a process of trial and error, when $(x_B + x_T) = 1.0$. The data, with pressures in kN/m² are:

$T(\text{K})$	P_B^0	x_B	P_T^0	x_T	$(x_B + x_T)$
373.2	180.006	0.2813	74.152	0.6831	0.9644
371.2	170.451	0.2872	69.760	0.7261	1.0233
371.7	172.803	0.2931	70.838	0.7150	1.0081
371.9	173.751	0.2915	71.273	0.7107	1.0021
372.0	174.225	0.2907	71.491	0.7085	0.9992

As 0.9992 is near enough to 1.000, the dew point may be taken as 372.0 K.

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:

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

Whilst α does vary somewhat with temperature, it remains remarkably steady for many systems, and a few values to illustrate this point are given in Table 11.1.

Table 11.1. Relative volatility of mixtures of benzene and toluene

Temperature (K)	353	363	373	383
α (-)	2.62	2.44	2.40	2.39

It may be seen that α increases as the temperature falls, so that it is sometimes worthwhile reducing the boiling point by operating at reduced pressure. When Equation 11.16 is used to construct the equilibrium curve, an average value of α must be taken over the whole column. As FRANK⁽¹³⁾ points out, this is valid if the relative volatilities at the top and bottom of the column differ by less than 15 per cent. If they differ by more than

this amount, the equilibrium curve must be constructed incrementally by calculating the relative volatility at several points along the column.

Another frequently used relationship for vapour–liquid equilibrium is the simple equation:

$$y_A = Kx_A \quad (11.18)$$

For many systems K is constant over an appreciable temperature range and Equation 11.11 may be used to determine the vapour composition at any stage. The method is particularly suited to multicomponent systems, discussed further in Section 11.7.1.

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.

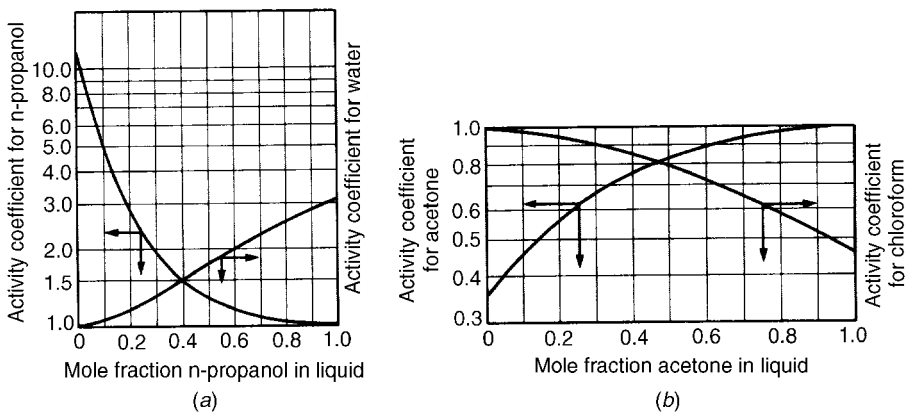


Figure 11.8. Activity coefficient data

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:

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

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

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

The four-suffix Margules binary equations are:

$$\log \gamma_1 = x_2^2 [\mathcal{A}_{12} + 2x_1 (\mathcal{A}_{21} - \mathcal{A}_{12} - \mathcal{A}_D) + 3\mathcal{A}_D x_1^2] \quad (11.24)$$

$$\log \gamma_2 = x_1^2 [\mathcal{A}_{21} + 2x_2 (\mathcal{A}_{12} - \mathcal{A}_{21} - \mathcal{A}_D) + 3\mathcal{A}_D x_2^2] \quad (11.25)$$

\mathcal{A}_{12} and \mathcal{A}_{21} have the same significance as before and \mathcal{A}_D is a third constant. Equations 11.24 and 11.25 are more complex than equations 11.22 and 11.23 though, because they contain an additional constant \mathcal{A}_D , they are more flexible. When \mathcal{A}_D becomes zero in equations 11.24 and 11.25, they become identical to the three-suffix equations.

The two-suffix van Laar binary equations are:

$$\log \gamma_1 = \frac{\mathcal{A}_{12}}{[1 + (\mathcal{A}_{12}x_1/\mathcal{A}_{21}x_2)]^2} \quad (11.26)$$

$$\log \gamma_2 = \frac{\mathcal{A}_{21}}{[1 + (\mathcal{A}_{21}x_2/\mathcal{A}_{12}x_1)]^2} \quad (11.27)$$

These equations become identical to the three-suffix Margules equations when $\mathcal{A}_{12} = \mathcal{A}_{21}$, and the functional form of these two types of equations is not greatly different unless the constants \mathcal{A}_{12} and \mathcal{A}_{21} differ by more than about 50 per cent.

The Margules and van Laar equations apply only at *constant temperature and pressure*, as they were derived from equation 11.21, which also has this restriction. The effect of pressure upon γ values and the constants \mathcal{A}_{12} and \mathcal{A}_{21} is usually negligible, especially at pressures far removed from the critical. Correlation procedures for activity coefficients have been developed by BALZHISER *et al.*⁽¹⁷⁾, FRENDENSLUND *et al.*⁽¹⁸⁾, PRAUNSLITZ *et al.*⁽¹⁹⁾, REID *et al.*⁽²⁰⁾, VAN NESS and ABBOTT⁽²¹⁾ and WALAS⁽²²⁾ and actual experimental data may be obtained from the PPDS system of the NATIONAL ENGINEERING LABORATORY, UK⁽²³⁾. When the liquid and vapour compositions are the same, that is $x_A = y_A$, point x_g in

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⁽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:

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

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/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.

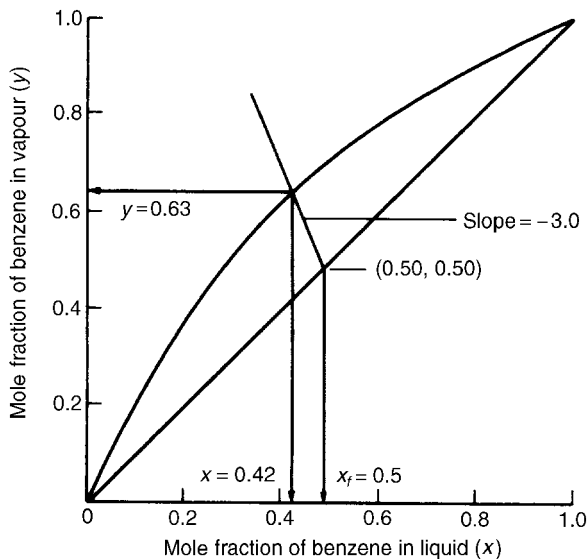


Figure 11.9. Equilibrium data for benzene–toluene for Example 11.6

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.

Example 11.6

An equimolar mixture of benzene and toluene is subjected to flash distillation at 100 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.

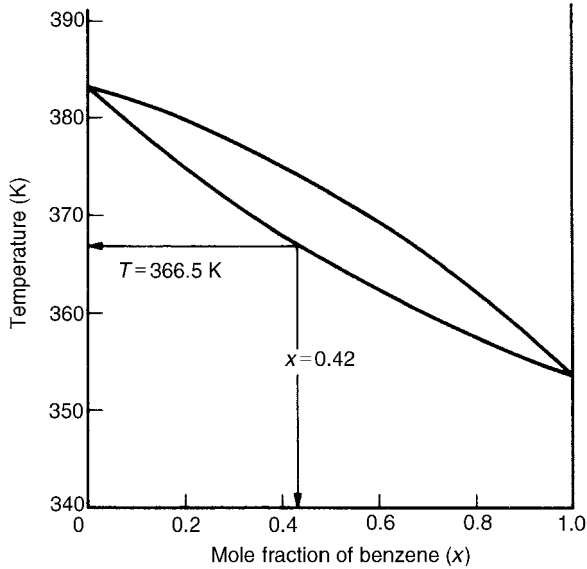


Figure 11.10. Boiling point diagram for benzene–toluene for Example 11.6

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 $x = \underline{0.42}$ and $y = \underline{0.63}$.

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

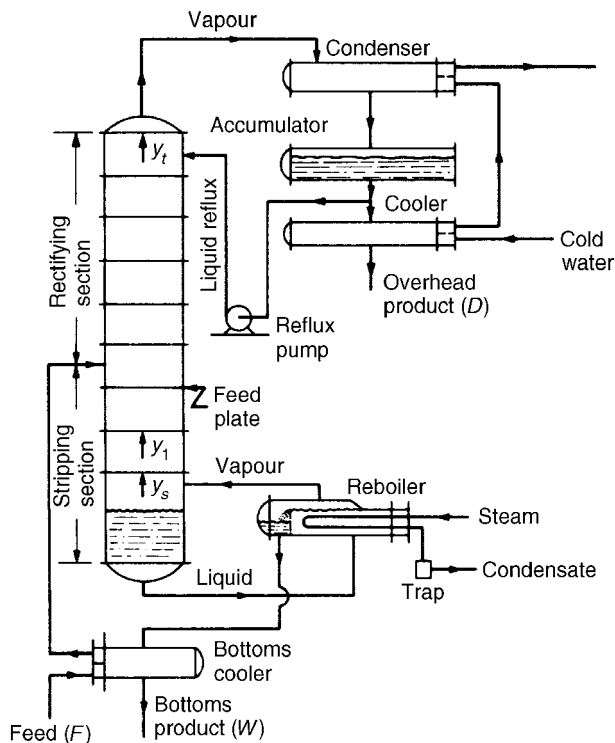


Figure 11.11. Continuous fractionating column with rectifying and stripping sections