## 8.9 VAPOUR–LIQUID EQUILIBRIA IN IDEAL SOLUTIONS

It is possible to determine the vapour–liquid equilibrium (VLE) data of certain systems from the vapour pressures of pure components constituting the system. If the liquid phase is an ideal solution and the vapour behaves as an ideal gas, the VLE data can be estimated easily without resorting to direct experimentation. A solution conforming to the ideal behaviour has the following characteristics, all interrelated.

1. The components are chemically similar. The average intermolecular forces of attraction and repulsion in the pure state and in the solution are of approximately the same order of magnitude.
2. There is no volume change on mixing (D$V$ = 0) or the volume of the solution varies linearly with composition.
3. There is neither absorption nor evolution of heat on mixing the constituents that form an ideal solution (D$H$ = 0); that is, there is no temperature change on mixing.
4. The components in an ideal solution obey Raoult's law, which states that the partial pressure in the vapour in equilibrium with a liquid is directly proportional to the concentration in the liquid. That is, $\bar{p}_i = x_i P_i^S$, where $\bar{p}_i$ is the partial pressure of component $i$ and $x_i$ is its mole fraction in the liquid. $P_i^S$ is the vapour pressure of pure $i$. This criterion also implies that the total vapour pressure over an ideal solution is a linear function of its composition.

For an experimental test of an ideal solution, the last criterion is the safest one to use. For example, the solution formed by two chemically dissimilar materials like benzene and ethyl alcohol should definitely be non-ideal. It is found that for an equimolar mixture of benzene and ethyl alcohol, there is no change in volume during mixing at room temperature. This peculiar behaviour is because of the fact that when this solution is formed from its constituents, there is increase in volume up to certain concentration and thereafter the volume decreases as shown in Fig. 8.7. When the solution volume is plotted against the composition, the curve will intersect the broken line representing the volume of an ideal solution at a particular concentration represented in the figure by point $P$.

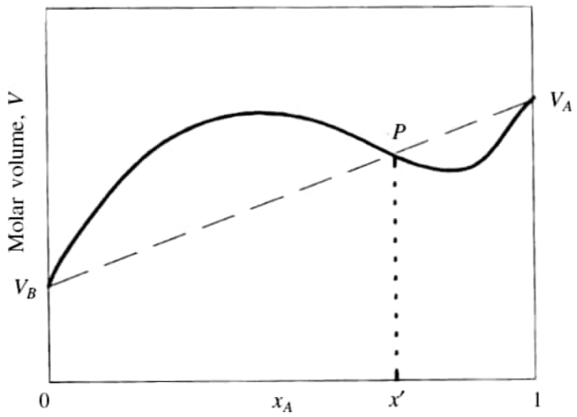

**Fig. 8.7** A real solution with no volume change of mixing at point $P$.

If the volume were measured for the concentration of the solution corresponding to point $P$, no change in volume would be observed. This may be the case for enthalpy change of mixing also at some particular composition. The conclusion to be drawn is that negligible volume change or temperature change for one particular composition of the mixture is not a safe criterion of an ideal solution. If these are to be used as the tests for ideal behaviour, then these tests should be done for more than one concentration of the solution. In contrast, the criterion that the total vapour pressure over an ideal solution varies linearly with composition is safe and reliable.

It should be understood that there exists no ideal solution in the strict sense of the word; but actual mixtures approach ideality as a limit. Ideality requires that the molecules of the constituents are similar in size, structure and chemical nature; only optical isomers of organic compounds meet these requirements. Thus a mixture of *ortho*-, *meta*- and *para*-xylene conforms very closely to the ideal solution behaviour. Practically, adjacent or nearly adjacent members of the homologous series of organic compounds can be expected to form ideal solutions. Thus mixtures of benzene and toluene, *n*-octane and *n*-hexane, ethyl alcohol and propyl alcohol, acetone and acetonitrile, paraffin hydrocarbons in paraffin oils, etc., can be treated as ideal solutions in engineering calculations.

Consider an ideal binary solution made up of component 1 and component 2. We have shown in Chapter 7 that all ideal solutions obey Lewis–Randall rule.

$$\bar{f}_i = x_i f_i \tag{7.66}$$

Here $\bar{f}_i$ is the fugacity of the component $i$ in the liquid and $f_i$ is the fugacity of pure $i$. Using the criterion of equilibrium $\bar{f}_i^L = \bar{f}_i^V$ and noting that if pressure is not too high, the vapour would not depart too greatly from ideal gas behaviour, it is possible to write

$$\bar{p}_i = x_i P_i^S \tag{7.67}$$

[redacted]

This is the mathematical statement of Raoult's law. Here $\bar{P}_i$ is the partial pressure and $P_i^S$ is the vapour pressure in the pure state for component $i$. Writing Eq. (7.67) for component 1 and component 2 in the solution we get

$$\bar{P}_1 = x_1 P_1^S, \quad \bar{P}_2 = x_2 P_2^S \tag{8.50}$$

The total pressure $P$ is the sum of the partial pressures and, therefore,

$$P = x_1 P_1^S + x_2 P_2^S = x_1 P_1^S + (1 - x_1) P_2^S$$

This on rearrangement gives

$$P = P_2^S + (P_1^S - P_2^S)\, x_1 \tag{8.51}$$

Equation (8.51) shows that at a given temperature, the total pressure over an ideal solution is a linear function of composition thus establishing the fourth criteria given above. When the partial pressures and total pressure are plotted against mole fraction $x_1$, we get according to Eq. (8.50) and Eq. (8.51) the straight lines shown in Fig. 8.8. The broken lines give the partial pressures and the continuous line gives the total pressure.

The $P$-$x$-$y$ diagram can be easily constructed. At any fixed temperature, the total pressure can be calculated using Eq. (8.51) for various $x$ values ranging from 0 to 1. The corresponding equilibrium vapour phase compositions are obtained by applying Dalton's law according to which the partial pressure in the vapour is equal to the mole fraction in the vapour ($y$) times the total pressure ($P$). That is

$$\bar{P}_1 = y_1 P, \qquad \bar{P}_2 = y_2 P \tag{8.52}$$

Combining Eqs. (8.50) and (8.52), we see that

$$y_1 P = x_1 P_1^S \tag{8.53}$$

Equation (8.53) can be rearranged as

$$y_1 = x_1 \frac{P_1^S}{P} \tag{8.54}$$

Thus Eq. (8.51) is used to calculate the total pressure at given $x$ and Eq. (8.54) is used to calculate the corresponding equilibrium vapour phase composition $y$. The $P$-$x$-$y$ diagram can now be plotted as shown in the Fig. 8.8.

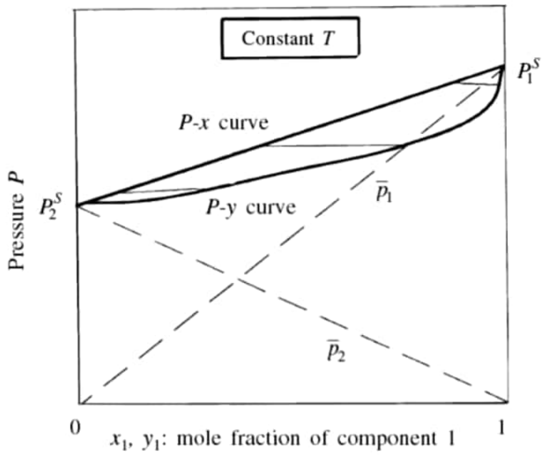

**Fig. 8.8** Pressures over ideal solution.

To prepare the $T$-$x$-$y$ diagrams at a given total pressure $P$ we can again use Eqs. (8.51) and (8.54). Assume temperatures lying between the boiling points of pure liquids at the given pressure. For the temperature assumed, find the vapour pressures of the pure liquids and calculate $x$ from Eq. (8.51). Use these in Eq. (8.54) and calculate the vapour composition $y$. Instead, if we attempt to find the equilibrium temperature for the solution of known concentration $x$, the temperature may be estimated by trial, such that the sum of the partial pressures is equal to the given total pressure. Once the temperature is thus known, the vapour phase composition is determined as before. The $T$-$x$ curve is the lower curve in the figure and is called the bubble-point curve. The $T$-$y$ curve is the upper curve and is called the dew-point curve.

The $y$-$x$ diagram is also prepared from the constant total pressure data. It can be constructed from the boiling point diagram by drawing horizontal tie lines. The intersections of these lines with the bubble-point curve give $x$ and the intersections with the dew-point curve give $y$. Figure 8.10 shows a typical equilibrium diagram.

There is an approximate method for the construction of the equilibrium diagram, and it is based on the assumption that the ratio of vapour pressures of the components is independent of temperature. This assumption may not introduce much error, as it is possible that the vapour pressures of both components vary with temperature and these variations are to the same extent that their ratio remains unaltered. Thus

[redacted]

$$\frac{y_1}{1-y_1} = \frac{x_1}{1-x_1}\frac{P_1^S}{P_2^S} = \alpha\frac{x_1}{1-x_1}$$

which can be written in the following form.

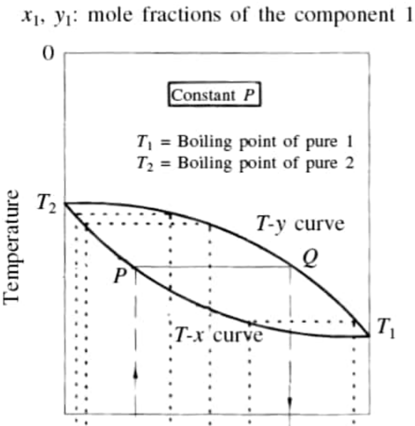

**Fig. 8.9** *T-x-y* diagram of an ideal solution.

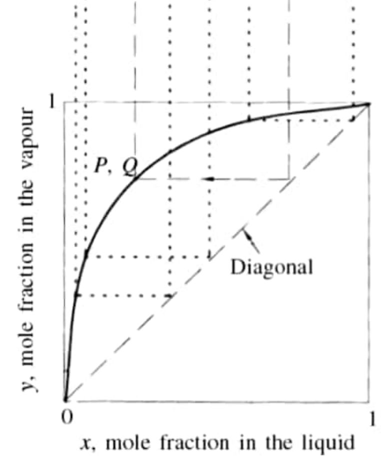

**Fig. 8.10** Equilibrium diagram.

$$y_1 = \frac{\alpha x_1}{1 + (\alpha - 1)x_1} \tag{8.55}$$

Although Eq. (8.55) is not exact over a wide range of temperatures, the effect of variation in $\alpha$ is so small that an average $\alpha$ value can be used in Eq. (8.55) and the whole $y$-$x$ data required for the preparation of the equilibrium curve can be evaluated.

***EXAMPLE 8.5*** Prove that if Raoult's law is valid for one constituent of a binary solution over the

***EXAMPLE* 8.8** A mixture of *A* and *B* conforms closely to Raoult's law. The pure component vapour pressures $P_A^S$ and $P_B^S$ in kPa at *T* K are given by

$$\ln P_A^S = 14.27 - \frac{2945}{T - 49}$$

$$\ln P_B^S = 14.20 - \frac{2973}{T - 64}$$

If the bubble point of a certain mixture of *A* and *B* is 349 K at a total pressure of 80 kPa, find the composition of the first vapour that forms.

***Solution*** At 349 K, the vapour pressures of the pure components are:

$$\ln P_A^S = 14.27 - \frac{2945}{349 - 49} = 4.4533. \qquad P_A^S = 85.9128 \text{ kPa}$$

$$\ln P_B^S = 14.20 - \frac{2973}{349 - 64} = 3.7684. \qquad P_B^S = 43.3116 \text{ kPa}$$

At a given temperature and pressure, the composition of the liquid and vapour phases in equilibrium is calculated using Eqs. (8.51) and (8.54), respectively. The composition of the vapour so calculated at the bubble-point temperature is the composition of the first vapour produced from a liquid on boiling.

Using Eq. (8.51),

Using Eq. (8.51),

$$x_A = \frac{P - P_B^S}{P_A^S - P_B^S} = \frac{80 - 43.3116}{85.9128 - 43.3116} = 0.8612$$

and using Eq. (8.54),

$$y_A = \frac{x_A P_A^S}{P} = 0.9249$$

The vapour formed contains 92.5% A.

***EXAMPLE* 8.9** The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations

$$\ln P_1^S = 14.5463 - \frac{2940.46}{T - 35.93}$$

$$\ln P_2^S = 14.2724 - \frac{2945.47}{T - 49.15}$$

where *T* is in K and *P* is in kPa. Assuming that the solutions formed by these are ideal, calculate

(a) $x_1$ and $y_1$ at 327 K and 65 kPa
(b) *T* and $y_1$ at 65 kPa and $x_1 = 0.4$
(c) *P* and $y_1$ at 327 K and $x_1 = 0.4$
(d) *T* and $x_1$ at 65 kPa and $y_1 = 0.4$
(e) *P* and $x_1$ at 327 K and $y_1 = 0.4$
(f) The fraction of the system that is liquid and the composition of the liquid and vapour in equilibrium at 327 K and 65 kPa when the overall composition of the system is 70 mole per cent acetone.

***Solution*** (a) From the Antoine equations, at 327 K,

$$\ln P_1^S = 14.5463 - \frac{2940.46}{327 - 35.93} = 4.4441, \quad P_1^S = 85.12 \text{ kPa}$$

$$\ln P_2^S = 14.2724 - \frac{2945.47}{327 - 49.15} = 3.6715, \quad P_2^S = 39.31 \text{ kPa}$$

Using Eq. (8.51),

$$65 = 39.31 + x_1(85.12 - 39.31) \qquad x_1 = 0.5608$$

Using Eq. (8.54),

$$y_1 = 0.5608 \times 85.12/65 = 0.7344$$

(b) Equation (8.51) can be written as

[redacted]

$$65 = P_2^S + 0.4\,(P_1^S - P_2^S)$$

The temperature is to be determined by trial so that this equation is satisfied. Assume $T = 340$ K. Antoine equations give $P_1^S = 131.1$ kPa and $P_2^S = 63.14$ kPa. Therefore,

$$P_2^S + 0.4\,(P_1^S - P_2^S) = 90.32 \text{ kPa} > 65 \text{ kPa}$$

Assume $T = 330$ K. At this temperature $P_1^S = 94.36$ kPa and $P_2^S = 44.02$ kPa. Thus,

$$P_2^S + 0.4\,(P_1^S - P_2^S) = 64.15 \text{ kPa} < 65 \text{ kPa}$$

Assume $T = 330.4$ K. $P_1^S = 95.65$ kPa and $P_2^S = 44.68$ kPa. Thus,

$$P_2^S + 0.4\,(P_1^S - P_2^S) = 65.07 \text{ kPa}$$

Thus, equilibrium temperature, $T = 330.4$ K. Using Eq. (8.54),

$$y_1 = 0.4 \times 95.65/65 = 0.5886$$

(c) At 327 K, we have $P_1^S = 85.12$ kPa and $P_2^S = 39.31$ kPa. Here $x_1 = 0.4$. Using these values in Eq. (8.51), we get $P = 57.63$ kPa. Using Eq. (8.54)

$y_1 = 0.4$ □ $85.12/57.63 = 0.5908$

(d) Equation (8.51) can be written as

$$x_1 = \frac{P - P_2^S}{P_1^S - P_2^S}$$

When this is substituted into Eq. (8.54), we get

$$y_1 = \frac{P_1^S}{P} \times \frac{P - P_2^S}{P_1^S - P_2^S}$$

Here $y_1 = 0.4$ and $P = 65$. Therefore,

$$\frac{P_1^S}{65} \times \frac{65 - P_2^S}{P_1^S - P_2^S} = 0.4$$

Assume a temperature and calculate the vapour pressures using Antoine equations. Substitute the vapour pressure values in the above equation. See whether the Left-hand side = 0.4. This is repeated till the left-hand side of the above equation becomes equal to 0.4.

At $T = 334$ K, $P_1^S = 107.91$ kPa and $P_2^S = 51.01$ kPa.

$$\frac{P_1^S}{65} \times \frac{65 - P_2^S}{P_1^S - P_2^S} = 0.408$$

As this is very close to the required value of 0.4, $T = 334$ K.

Using Eq. (8.54), we get

$$x_1 = \frac{y_1 P}{P_1^S} = \frac{0.4 \times 65}{107.91} = 0.241$$

(e) At 327 K, we have $P_1^S = 85.12$ kPa and $P_2^S = 39.31$ kPa. Here $y_1 = 0.4$

Equation (8.54) relates $y$ to $x$. When $P$ in Eq. (8.54) is eliminated using Eq. (8.51) we get

$$y_1 = \frac{x_1 P_1^S}{P_2^S + x_1\,(P_1^S - P_2^S)}$$

This can be rearranged to the following form.

$$x_1 = \frac{y_1 P_2^S}{P_1^S - y_1\,(P_1^S - P_2^S)}$$

Substituting the given values, we get $x_1 = 0.2354$.

From Eq. (8.54),

$$P = \frac{x_1 P_1^S}{y_1} = \frac{0.2354 \times 85.12}{0.4} = 50.09 \text{ kPa}$$

(f) The composition of the vapour and liquid in equilibrium at $P = 65$ kPa and $T = 327$ K were determined in part (a). They are $x_1 = 0.5608$ and $y_1 = 0.7344$. Let $f$ be the fraction of the mixture that is liquid. Then an acetone balance gives

1 □ 0.7 = $f$ □ 0.5608 + (1 – $f$) □ 0.7344

[redacted]

***EXAMPLE* 8.10** Mixtures of *n*-Heptane (*A*) and *n*-Octane (*B*) are expected to behave ideally. The total pressure over the system is 101.3 kPa. Using the vapour pressure data given below,

(a) Construct the boiling point diagram and
(b) The equilibrium diagram and
(c) Deduce an equation for the equilibrium diagram using an arithmetic average a value.

| $T$, K | 371.4 | 378 | 383 | 388 | 393 | 398.6 |
|---|---|---|---|---|---|---|
| $P^S_A$, kPa | 101.3 | 125.3 | 140.0 | 160.0 | 179.9 | 205.3 |
| $P^S_B$, kPa | 44.4 | 55.6 | 64.5 | 74.8 | 86.6 | 101.3 |

***Solution*** *Sample calculation:* Consider the second set of data. $T = 378$ K; $P^S_A = 125.3$ kPa; $P^S_B =$ 55.6 kPa.

Using Eq. (8.51),

$$101.3 = 55.6 + x_A(125.3 - 55.6)$$

Therefore, $x_A = 0.656$.

Using Eq. (8.54), we see

$$y_A = 0.656 \ \square\ 125.3/101.3 = 0.811$$

Relative volatility is

$$\text{a} = P^S_A/P^S_B = 125.3/55.6 = 2.25$$

These calculations are repeated for other temperatures. The results are tabulated below:

| $T$, K | 371.4 | 378 | 383 | 388 | 393 | 398.6 |
|---|---|---|---|---|---|---|
| $x_A$ | 1.000 | 0.656 | 0.487 | 0.312 | 0.157 | 0 |
| $y_A$ | 1.000 | 0.811 | 0.674 | 0.492 | 0.279 | 0 |
| a | 2.28 | 2.25 | 2.17 | 2.14 | 2.08 | 2.02 |

(a) Plot of $T$ versus $x$ and $y$ gives the boiling point diagram
(b) Plot of $y$ against $x$ gives the equilibrium diagram
(c) The average of the last row gives a = 2.16. Use this value of a in Eq. (8.55) to get the equation for the equilibrium curve.

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} = \frac{2.16\, x_A}{1 + 1.16\, x_A}$$

## 8.10 NON-IDEAL SOLUTIONS

We have seen that the partial pressure of a component in an ideal solution varies linearly with concentration in the solution. If the solution behaves ideally, the different molecules should be chemically similar. In that case, the molecules of a particular substance, when brought into solution with other components, would not experience any difference in the environment surrounding them from that existed in their pure state. The intermolecular forces in the pure state of the substance and that in the solution would then be approximately of the same order of magnitude. Therefore, the fugacity (or the partial pressure) of a substance, which is a measure of the tendency of the substance to escape from the solution, is not affected by the properties of the other components in the solution. It depends only on the number of molecules of the substance present, or its concentration. In short, the components in an ideal solution obey Raoult's law. But for non-ideal solutions, the partial pressures do not vary linearly with composition, as shown in Fig. 8.11 for the case of carbon disulphide–acetone system.