8

PHASE EQUILIBRIA

A system is said to be in a state of *equilibrium* if it shows no tendency to depart from that state either by energy transfer through the mechanism of heat and work or by mass transfer across the phase boundary. Since a change of state is caused by a driving force, we can describe a system at equilibrium as one in which there are no driving forces for energy or mass transfer. That is, for a system in a state of equilibrium, all forces are in exact balance. It may be noted here that the state of equilibrium is different from a steady state condition. Under *steady state* there exist net fluxes for material or energy transfer across a plane surface placed anywhere in the system. Under equilibrium the net flux is zero.

Transfer of material or energy across phase boundaries occurs till equilibrium is established between the phases. In our daily experience, we come across a number of processes in which materials are transferred from one phase to another. During breathing we take oxygen from the air through the lungs and dissolve it in the blood. During the preparation of tea or coffee we extract the soluble components in the powder into boiling water. Dilute aqueous solution of alcohol is concentrated by distillation in which a vapour rich in alcohol is produced from the boiling solution. The phase equilibrium thermodynamics is of fundamental importance in many branches of science, whether physical or biological. It is particularly important in chemical engineering, because majority of manufacturing processes involve transfer of mass between phases either during the preparation of the raw materials or during the purification of the finished products. Gas–liquid absorption, distillation, liquid–liquid extraction, leaching, adsorption, etc., are some of the important separation techniques employing mass transfer between phases. In addition to these, many industrial chemical reactions are carried out under conditions where more than one phase exist. A good foundation in phase equilibrium thermodynamics is essential for the analysis and design of these processes.

In this chapter due emphasis is given to the development of the relationship between the various properties of the system such as pressure, temperature and composition when a state of equilibrium is attained between the various phases constituting the system. The temperature–pressure-composition relationships in multiphase system at equilibrium form the basis for the quantitative treatment of all separation processes. The two types of phase equilibrium problems that are frequently encountered are:

1. The determination of composition of phases which exist in equilibrium at a known temperature and pressure
2. The determination of conditions of temperature and pressure required to obtain equilibrium between phases of specified compositions.

The present chapter tries to provide solutions to these problems.

8.1 CRITERIA OF PHASE EQUILIBRIUM

Consider a homogeneous closed system in a state of internal equilibrium. The criteria of internal thermal and mechanical equilibrium are that the temperature and pressure be uniform throughout the system. For a system to be in thermodynamic equilibrium, additional criteria are to be satisfied. Consider a closed system consisting of two phases of a binary solution, for example, the vapour and liquid phases of an alcohol–water solution. The requirement of uniformity of temperature and pressure does not preclude the possibility of transfer of mass between the phases. If the system is in thermodynamic equilibrium, mass transfer also should not occur. It means that additional criteria are necessary for establishing the state of thermodynamic equilibrium.

A system can interact with the surroundings reversibly or irreversibly. In the *reversible process,* a state of equilibrium is maintained throughout the process. So it can be treated as a process connecting a series of equilibrium states. The driving forces are only infinitesimal in magnitude and the process can be reversed by an infinitesimal change (either increase or decrease) in the potential for the system or the surroundings. The *irreversible process,* in contrast, occurs with a finite driving force, and it can not be reversed by infinitesimal changes in the external conditions. However, all irreversible processes tend towards a state of equilibrium. We have shown in Chapter 4 under 'Clausius inequality',

$$dS \geq \frac{dQ}{T} \tag{4.44}$$

In this equation, the equality sign refers to a reversible process which can be treated as a succession of equilibrium states and the inequality refers to the entropy change for a spontaneous process whose ultimate result would be an equilibrium state. The first law of thermodynamics expressed mathematically by Eq. (2.5) can be rewritten as

$$dQ = dU + dW \tag{8.1}$$

Substituting Eq. (8.1) into Eq. (4.44), we get

$$T\,dS \geq dU + dW$$

$$dU \leq T\,dS - dW \tag{8.2}$$

dW in Eq. (8.2) may be replaced by $P\,dV$ so that

$$dU \leq T\,dS - P\,dV \tag{8.3}$$

Equation (8.3) is valid for cases where external pressure is the only force and the work is, therefore, the work of expansion only. By this, we exclude other effects like those due to gravitational and electromagnetic fields and surface and tensile forces. Equation (8.3) can be treated as the combined statement of the first and second law of thermodynamics applied to a closed system which interact with its surroundings through heat transfer and work of volume displacement. This equation is utilised for deriving the criteria of equilibrium under various sets of constraints, each set corresponding to a physically realistic or commonly encountered situation. These different criteria are discussed now.

Constant U and V. An isolated system does not exchange mass, heat or work with the surroundings. In Eq. (8.1), $dQ = 0$, $dW = 0$ and hence $dU = 0$. A well-insulated vessel of constant volume would closely approximate this behaviour. Thus in Eq. (8.3) $dU = 0$ and $dV = 0$ so that

$$\boxed{dS_{U,V} \geq 0} \tag{8.4}$$

The entropy is constant in a reversible process and increases in a spontaneous process occurring in a system of constant U and V. Since an irreversible process leads the system to an equilibrium state, the entropy is maximum at equilibrium when no further spontaneous processes are possible.

Constant T and V. Helmholtz free energy is defined by Eq. (6.1).

$$A = U - TS$$

Rearranging Eq. (6.1), we get

$$U = A + TS$$

$$dU = dA + T\,dS + S\,dT$$

Substitute this result in Eq. (8.3) and rearrange the resulting expression to the following form

$$dA \leq -P\,dV - S\,dT \tag{8.5}$$

Under the restriction of constant temperature and volume, the latter implying no work, the equation simplifies to

$$\boxed{dA_{T,V} \leq 0} \tag{8.6}$$

Equation (8.6) means that the spontaneous process occurring at constant temperature and volume is accompanied by a decrease in the work function and consequently, in a state of thermodynamic equilibrium under these conditions the Helmholtz free energy or the work function is a minimum.

Constant P and T. Equation (6.6) defines Gibbs free energy as

$$G = H - TS$$

Since $H = U + PV$ we can write Eq. (6.6) as

$$G = U + PV - TS$$

Taking the differentials

$$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT$$

rearranging these as

$$dU = dG - P\,dV - V\,dP + T\,dS + S\,dT$$

and combining this result with Eq. (8.3), we obtain

$$dG \leq V\,dP - S\,dT \tag{8.7}$$

At constant temperature and pressure, Eq. (8.7) reduces to

$$\boxed{dG_{T,P} \leq 0} \tag{8.8}$$

Equation (8.8) means that the free energy either decreases or remains unaltered depending upon whether the process is spontaneous or reversible. It implies that for a system in equilibrium at a given temperature and pressure the free energy must be minimum.

Since most chemical reactions and many physical changes are carried out under conditions of constant temperature and pressure, Eq. (8.8) is the commonly used criterion of thermodynamic equilibrium. It also provides a very convenient and simple test for the feasibility of a proposed process. No process is possible which results in an increase in the Gibbs free energy of the system, because according to Eq. (8.8) the Gibbs free energy always decreases in a spontaneous process and in the limit of the reversible process, the free energy doesn't change at all.

In the equilibrium state, differential variations can occur in the system at constant temperature and pressure without producing any change in the Gibbs function. Thus, the equality in Eq. (8.8) can be used as the general criterion of equilibrium or as a thermodynamic statement that characterises the equilibrium state.

$$dG = 0 \quad \text{(at constant } T \text{ and } P\text{)} \tag{8.9}$$

To apply this criterion for phase equilibrium problems we need formulate an expression for dG as function of the number of moles of the components in various phases and set it equal to zero. This equation along with the mass conservation equations provides the solutions to phase equilibrium problems.

8.2 CRITERION OF STABILITY

It can be shown that the criterion of equilibrium [Eq. (8.8)] can be used to formulate the criterion of stability for a binary mixture. When two pure liquids at a given temperature T and pressure P are mixed together, the resulting mixture should have a lower free energy at the same temperature and pressure. This is because the mixed state is an equilibrium state or stable state compared to the unmixed state. The molar free energy of the mixture is thus less than the sum of the molar free energies of the constituents for all possible concentrations. That is,

$$G - \Sigma x_i G_i < 0 \tag{8.10}$$

The left-hand side in the above equation is the free energy change on mixing ΔG. Therefore,

$$\Delta G < 0 \tag{8.11}$$

When the free energy change on mixing ΔG is plotted against x_1—the mole fraction of constituent 1 in the binary mixture—the resulting curve is one of the two types shown in Fig. 8.1. The upper curve is for a binary mixture, which is miscible for the entire concentration range. Assume that the points A and B represent two binary mixtures of composition x_A and x_B respectively. Points on the dotted line AB represent the composition as well as ΔG of the mixture of two phases obtained when solutions represented by the points A and B are mixed together. Since the line AB is above the solid curve that represents the free energy of the miscible solution, the free energy of the mixture in the miscible state is the minimum and the mixture exists as a single homogeneous phase. However, this argument is not valid for the lower curve in Fig. 8.1. The dotted line MN represents the free energy of the two-phase mixture obtained when two binary mixtures of composition x_M and x_N, respectively, are mixed together. It lies below the ΔG curve of the homogeneous solution. Any point on the line MN represents the ΔG that would result for systems consisting of two phases of mole fraction x_M and x_N. Thus, when the system moves from the solid curve to the dotted line MN, there is a decrease in the free energy. That is, the system attains stability when it moves from a homogeneous to a heterogeneous state. Therefore, for mixtures of composition lying

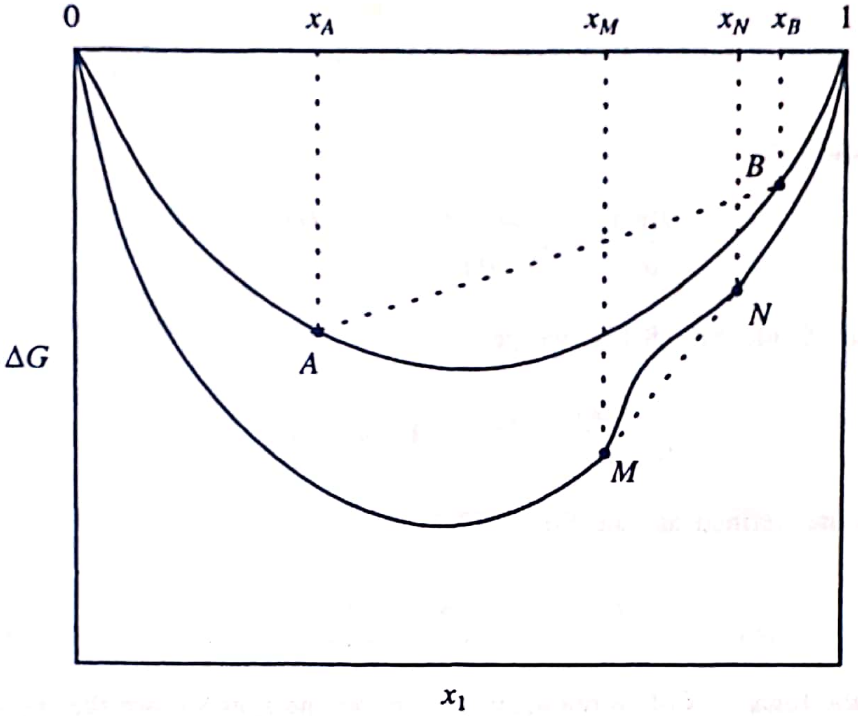

Fig. 8.1 Free energy of mixing plotted as a function of composition.

between points M and N, the equilibrium or stable state consists of two immiscible phases. We see that the second derivative of ΔG with respect to x_1 is always positive for stable liquid phase and if it becomes zero or negative, phase separation occurs. The criterion of stability is that *at constant temperature and pressure the free energy change on mixing* ΔG*, its first and second derivatives are all continuous functions of the concentration x and*

$$\frac{d^2 \Delta G}{dx_1^2} > 0 \qquad \text{(at constant } T \text{ and } P\text{)} \tag{8.12}$$

***EXAMPLE* 8.1** Show that for a stable liquid phase, the fugacity of each component in a binary mixture always increases with increase in concentration at constant temperature and pressure.

Solution The excess free energy of mixing was defined in Chapter 7. It was shown there that

$$\Delta G^E = \Delta G - \Delta G^{id}$$

$$\Delta G^E = G^E = RT \sum x_i \ln \gamma_i$$

$$\Delta G^{id} = RT \sum x_i \ln x_i$$

Combining these three equations we find that

$$\Delta G = RT \sum x_i \ln (\gamma_i x_i)$$

$$\frac{\Delta G}{RT} = \sum x_i \ln (\gamma_i x_i) = x_1 \ln (\gamma_1 x_1) + x_2 \ln (\gamma_2 x_2)$$

Differentiating this with respect to x_1,

$$\frac{d}{dx_1}\left(\frac{\Delta G}{RT}\right)=\frac{d}{dx_1}[x_1\ln(\gamma_1x_1)+x_2\ln(\gamma_2x_2)]=\ln(x_1\gamma_1)-\ln(x_2\gamma_2)+x_1\frac{\partial\ln\gamma_1}{\partial x_1}+x_2\frac{\partial\ln\gamma_2}{\partial x_1}\quad(8.13)$$

By Gibbs–Duhem equations,

$$x_1\frac{\partial\ln\gamma_1}{\partial x_1}=x_2\frac{\partial\ln\gamma_2}{\partial x_2}=-x_2\frac{\partial\ln\gamma_2}{\partial x_1}$$

When this is substituted into Eq. (8.13), we get

$$\frac{d}{dx_1}\left(\frac{\Delta G}{RT}\right)=\ln(\gamma_1x_1)-\ln(\gamma_2x_2)\quad(8.14)$$

Activity coefficients are defined as [see Eq. (7.77)],

$$\gamma_1=\frac{\bar{f}_1}{x_1f_1},\quad \gamma_2=\frac{\bar{f}_2}{x_2f_2}$$

where $\bar{f}_1$ and $\bar{f}_2$ are the fugacities of components in solution and f_1 and f_2 are the fugacities of pure components. Substituting these into Eq. (8.14), we get

$$\frac{d}{dx_1}\left(\frac{\Delta G}{RT}\right)=\ln\frac{\bar{f}_1}{f_1}-\ln\frac{\bar{f}_2}{f_2}\quad(8.15)$$

Differentiating Eq. (8.14) again with respect to x_1 and noting that fugacities of pure components are independent of concentration, we get

$$\frac{d^2}{dx_1^2}\left(\frac{\Delta G}{RT}\right)=\frac{d}{dx_1}\ln\bar{f}_1-\frac{d}{dx_1}\ln\bar{f}_2\quad(8.16)$$

According to Gibbs–Duhem equations, the fugacities in a binary mixture are interrelated as indicated below.

$$x_1\frac{\partial\ln\bar{f}_1}{\partial x_1}=x_2\frac{\partial\ln\bar{f}_2}{\partial x_2}=-x_2\frac{\partial\ln\bar{f}_2}{\partial x_1}$$

Therefore,

$$\frac{d}{dx_1}\ln\bar{f}_2=-\frac{x_1}{x_2}\frac{d\ln\bar{f}_1}{dx_1}$$

Using this equation, Eq. (8.16) can be written as

$$\frac{d^2}{dx_1^2}\left(\frac{\Delta G}{RT}\right)=\frac{d}{dx_1}\ln\bar{f}_1+\frac{x_1}{x_2}\frac{d}{dx_1}\ln\bar{f}_1=\frac{1}{x_2}\frac{d}{dx_1}\ln\bar{f}_1$$

$$\frac{d^2\Delta G}{dx_1^2}=\frac{RT}{x_2}\frac{d}{dx_1}\ln\bar{f}_1$$

Equation (8.12) reveals that the left-hand side of the above equation is greater than zero. Therefore,

$$\frac{RT}{x_2}\frac{d}{dx_1}\ln \bar{f}_1 > 0$$

$$\frac{d}{dx_1}\ln \bar{f}_1 > 0$$

In a similar way, we can show that

$$\frac{d}{dx_2}\ln \bar{f}_2 > 0$$

The last two equations imply that fugacity of components in a stable solution always increase with increase in concentration.

✓8.3 PHASE EQUILIBRIA IN SINGLE-COMPONENT SYSTEMS

Consider the thermodynamic equilibrium in a system consisting of two or more phases of a single substance. Though the individual phases can exchange mass with each other and are therefore open, the system as a whole is closed. As an example, we can treat the equilibrium between vapour and liquid phases of a single substance at a constant temperature and pressure. Applying the criterion of equilibrium [see Eqs. (8.8) and (8.9)] to this closed system,

$$dG = 0$$

$$dG^a + dG^b = 0 \tag{8.17}$$

where the dG^a and dG^b are the changes in free energies of the phases 'a' and 'b' respectively. Since each phase is open, the change in its free energy may be due to the changes in temperature, pressure and the number of moles of the components that constitute the phase. Equation (7.35) expresses this mathematically as

$$dG = V\,dP - S\,dT + \Sigma \overline{G}_i\,dn_i$$

Applying this equation to the phases 'a' and 'b', we can write

$$dG^a = V^a\,dP^a - S^a\,dT^a + G^a\,dn^a, \qquad dG^b = V^b\,dP^b - S^b\,dT^b + G^b\,dn^b$$

At constant temperature and pressure,

$$dG^a = G^a\,dn^a, \qquad dG^b = G^b\,dn^b \tag{8.18}$$

As the system as a whole is closed,

$$dn^a + dn^b = 0, \text{ or } dn^a = -\,dn^b \tag{8.19}$$

Substituting Eqs. (8.18) and (8.19) into Eq. (8.17), we get

$$(G^a - G^b)dn^a = 0 \tag{8.20}$$

Equation (8.20) means that

$$G^a = G^b \tag{8.21}$$

Whenever two phases of the same substance are in equilibrium under a given temperature and pressure, the molar free energy is the same in each phase.

We can verify the above result easily by considering the example of boiling water. As long as both phases are present, an appreciable transfer of material from one phase to the other at constant temperature and pressure would not disturb the equilibrium. The change in the free energy for the equilibrium process (or reversible process) of evaporating a mole of liquid water is

$$\Delta G = \Delta H - T\Delta S \tag{8.22}$$

As pressure is constant, $\Delta H = Q$, and the process being reversible, $Q = T\Delta S$. Equation (8.22) gives

$$\Delta G = 0$$

For vaporisation of 1 mol of liquid, $\Delta G = G^V - G^L$, where G^L and G^V are the molar free energy of water in the liquid and vapour states at the given T and P. Therefore, under equilibrium

$$G^V = G^L \tag{8.23}$$

As the molar free energies are related to the fugacity of the substance by

$$G = RT \ln f + C$$

Equation (8.21) can be expressed in terms of fugacity of the phases.

$$f^a = f^b \tag{8.24}$$

where f^a and f^b are the fugacities in phases a and b respectively. It is convenient to work with fugacities of substances as these have absolute values in contrast to free energies, which are usually expressed as differences.

The above conclusions can be extended to three phases, which is the maximum number of phases that can coexist under equilibrium in a system of one component.

***EXAMPLE* 8.2** Using the criterion of phase equilibrium, show that the change in entropy during phase changes can be calculated from the latent heat of phase change and the absolute temperature as $\Delta S = \Delta H/T$.

Solution Suppose that two phases a and b are in equilibrium. Using the definition of free energy [Eq. (6.6)],

$$G^a = H^a - TS^a, \qquad G^b = H^b - TS^b$$

Here, H and S denote the enthalpy and entropy of the substance. Substituting these results in Eq. (8.21),

$$H^a - TS^a = H^b - TS^b$$

This equation can be rearranged as,

$$S^b - S^a = \frac{H^b - H^a}{T}$$

The left-hand side of the above equation is the entropy change accompanying the phase change of one mole of the substance (ΔS), and the numerator on the right-hand side represents the enthalpy change for the phase change of one mole of the substance or the latent heat of phase change (ΔH). That is,

$$\Delta S = \frac{\Delta H}{T}$$

***EXAMPLE* 8.3** Deduce the Clapeyron equation using the criterion of equilibrium, Eq. (8.9).

Solution In Chapter 6 we have derived the Clapeyron equation, Eq. (6.25), using Maxwell's relations.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

The criterion of equilibrium provides an alternate route for its derivation. Consider any two phases a and b of the same substance under equilibrium. Since G^a and G^b are both functions of temperature and pressure, and these functional relationships are different for different phases, the two phases can coexist only at such values of the temperature and pressure that $G^a = G^b$. If the temperature and pressure are altered infinitesimally without disturbing the equilibrium, the change in the free energy must be the same in each phase.

$$dG^a = dG^b \tag{8.25}$$

In a phase change there is no work other than the work of expansion, so that

$$dG = V\,dP - S\,dT$$

Using this in Eq. (8.25),

$$V^a\,dP - S^a\,dT = V^b\,dP - S^b\,dT \tag{8.26}$$

V and S are the molar volume and molar entropy of the fluid with the superscript representing the phase for which the properties correspond to. Equation (8.26) can be rearranged to the following form.

$$\frac{dP}{dT} = \frac{S^a - S^b}{V^a - V^b} = \frac{\Delta S}{\Delta V} \tag{8.27}$$

In the above equation, ΔS and ΔV are the entropy change and volume change respectively, accompanying the phase change. Since the transition between phases is occurring reversibly, the entropy change can be evaluated if the latent heat of phase change is known.

$$\Delta S = \frac{\Delta H}{T} \tag{8.28}$$

where ΔH is the latent heat for the phase change. Substituting Eq. (8.28) into Eq. (8.27) the Clapeyron equation results.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{8.29}$$

This relation gives the increase in pressure that is necessary to maintain the equilibrium between phases for a pure substance when the temperature is increased. By using the following simplifications Eq. (8.29) can be modified to yield the Clausius–Clapeyron equation applicable for vapour–liquid equilibria.

1. The latent heat of vaporisation is constant and independent of temperature.
2. The molar volume of liquid is negligible compared to that of vapour.
3. The vapour behaves as ideal gas.

The Clausius–Clapeyron equation was derived [Eq. (6.28)] in Chapter 6 and is reproduced below.

$$\ln \frac{P_2^S}{P_1^S} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.30}$$

where P_1^S and P_2^S are the vapour pressures at temperatures T_1 and T_2 respectively.

8.4 PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS

The criterion of equal molar free energy [Eq. (8.21)] is applicable for equilibrium between phases of a single component. This criterion needs modification when dealing with heterogeneous multicomponent systems. A heterogeneous closed system is made up of two or more phases with each phase behaving as open system within the overall closed system. Because each phase consists of two or more components in different proportions, it is necessary that the criterion of multicomponent phase equilibrium be developed in terms of partial molar free energies or the chemical potentials of the components. The criteria of thermal and mechanical equilibrium are, as discussed earlier, the uniformity of temperature and pressure. For the system to be in equilibrium with respect to mass transfer, the driving force for mass transfer—the chemical potential—must have uniform values for each component in all phases. This criterion of internal equilibrium is derived in the following paragraphs.

Consider a heterogeneous system consisting of π phases indicated by the letters, α, β, γ, ..., π. The various components that constitute the system are 1, 2, 3, ..., C. The symbol μ_i^κ denotes the chemical potential of component 'i' in phase 'κ'. Suppose that small amounts of various components are transferred from one phase to another, the system being in equilibrium and the temperature and pressure kept constant. Since the system as a whole is closed, the proposed transfer should satisfy the following criterion.

$$dG = 0 \quad \text{(at constant } T \text{ and } P\text{)} \tag{8.9}$$

The free energy change in a multicomponent system is given by Eq. (7.35) as

$$dG = V\,dP - S\,dT + \Sigma\,\mu_i\,dn_i$$

At constant temperature and pressure, the above equation becomes

$$dG = \Sigma\,\mu_i\,dn_i$$

Substitute this into Eq. (8.9) to get

$$\Sigma\,\mu_i\,dn_i = 0 \tag{8.31}$$

Let dn_i^κ denote the increase in the number of moles of component i in phase κ. Equation (8.31) may then be written as

$$\sum_{i=1}^{C} \sum_{\kappa=\alpha}^{\pi} \mu_i^\kappa \, dn_i^\kappa = 0$$

Expanding this equation, we get

$$\begin{aligned}
&\mu_1^\alpha \, dn_1^\alpha + \mu_1^\beta \, dn_1^\beta + \ldots + \mu_1^\pi \, dn_1^\pi + \\
&\mu_2^\alpha \, dn_2^\alpha + \mu_2^\beta \, dn_2^\beta + \ldots + \mu_2^\pi \, dn_2^\pi + \\
&\vdots \qquad\qquad \vdots \qquad\qquad\qquad \vdots \\
&\mu_C^\alpha \, dn_C^\alpha + \mu_C^\beta \, dn_C^\beta + \ldots + \mu_C^\pi \, dn_C^\pi = 0
\end{aligned} \tag{8.32}$$

Since the system as a whole is closed, it should satisfy the mass conservation equation given below.

$$\begin{aligned}
&dn_1^\alpha + dn_1^\beta + \ldots + dn_1^\pi = 0 \\
&dn_2^\alpha + dn_2^\beta + \ldots + dn_2^\pi = 0 \\
&\vdots \qquad \vdots \qquad\qquad \vdots \\
&dn_C^\alpha + dn_C^\beta + \ldots + dn_C^\pi = 0
\end{aligned} \tag{8.33}$$

The variations in the number of moles dn_i are independent of each other. However, they are subject to the constraints imposed by Eq. (8.33). For all possible variations dn_i^κ, Eq. (8.32) is to be satisfied. This is possible only if

$$\begin{aligned}
&\mu_1^\alpha = \mu_1^\beta = \ldots = \mu_1^\pi \\
&\mu_2^\alpha = \mu_2^\beta = \ldots = \mu_2^\pi \\
&\vdots \qquad \vdots \qquad\quad \vdots \\
&\mu_C^\alpha = \mu_C^\beta = \ldots = \mu_C^\pi
\end{aligned} \tag{8.34}$$

Equation (8.34) means that *when a system consisting of several components distributed between various phases is in thermodynamic equilibrium at a definite temperature and pressure, the chemical potential of each component is the same in all the phases.* If they are different, the component for which such a difference exists will show a tendency to pass from the region of higher to the region of lower chemical potential. Thus the equality of chemical potential along with the requirement of uniformity of temperature and pressure serves as the general criterion of thermodynamic equilibrium in a closed heterogeneous multicomponent system. In short, we can write

$$\boxed{\begin{array}{ll} T = \text{constant}; & P = \text{constant} \\ \mu_i^\alpha = \mu_i^\beta = \ldots = \mu_i^\pi & \text{for } i = 1, 2, 3, \ldots, C \end{array}} \tag{8.35}$$

Since the chemical potential is related to fugacity as

$$\mu_i = RT \ln \bar{f}_i + C$$

where C is a constant, an alternative and equally general criterion of equilibrium can be written in terms of fugacities as

$$\boxed{\begin{array}{ll} T = \text{constant}; & P = \text{constant} \\ \bar{f}_i^{\alpha} = \bar{f}_i^{\beta} = \ldots = \bar{f}_i^{\pi} & \text{for } i = 1, 2, 3, \ldots, C \end{array}} \tag{8.36}$$

Fugacity is a more useful property than chemical potential for defining equilibrium since it can be expressed in absolute values, whereas chemical potential can be expressed only relative to some arbitrary reference state. Equation (8.36) is therefore widely used for the solution of phase equilibrium problems.

***EXAMPLE* 8.4** Using the criterion of phase equilibrium show that the osmotic pressure over an ideal solution can be evaluated as

$$P_{\text{osmotic}} = \frac{RTx_A}{V_B}$$

where x_A is the mole fraction of solute and V_B is the molar volume of the solvent.

Solution Consider a vessel which is divided into two compartments by a semi-permeable membrane. Pure solvent (say, water) is taken in one of the compartments and a solution (say, sucrose in water) is taken in the other. Let T be the temperatures on both sides of the membrane and P be the pressure. While the membrane is impermeable to the flow of the solute, it permits the flow of solvent into the solution. This phenomenon of a solvent diffusing through a membrane which is permeable to it, but is impermeable to the solute, is known as *osmosis*.

Osmosis is caused by the difference in the chemical potentials of the solvent on the two sides of the membrane. At a given pressure, the chemical potential of a pure solvent is greater than that of the solvent in the solution. By increasing the pressure at the solution side of the membrane, the chemical potential of the solvent in the solution can be increased. When the pressure is increased to P' keeping the temperature constant, the chemical potential of the solvent in the solution would become equal to that of the pure solvent at pressure P, and the diffusion would stop. If the pressure is increased above P', the direction of diffusion would be reversed. In that event, the solvent would diffuse from the solution to the pure solvent. This process is known as *reverse osmosis*. The excess pressure $P' - P$ to be applied over the solution at constant temperature to arrest the process of osmosis is known as the *osmotic pressure*. Thus, osmotic pressure is

$$P_{\text{osmotic}} = P' - P$$

Let the mole fraction of the solutes constituting the solution be represented by x_A and the mole fraction of the solvent be represented by x_B. Let μ'_B denotes the chemical potential of the solvent at pressure P'. Equation (7.51) relates the chemical potential of a component in a solution to its fugacity. Thus

$$\mu'_B = RT \ln \bar{f}_B + C$$

The chemical potential of the pure solvent at pressure P' is given by

$$\mu'_{B*} = RT \ln f_B + C$$

Combining the preceding two equations, we get

$$\mu'_B = \mu'_{B*} + RT \ln \frac{\bar{f}_B}{f_B}$$

In this equation, μ'_{B*} is the chemical potential of pure solvent at pressure P', f_B is its fugacity and $\bar{f}_B$ is its fugacity in the solution. Since the solution is ideal, the above equation may be simplified utilising the Lewis–Randall rule which relates f_B and that $\bar{f}_B$ as $\bar{f}_B = x_B f_B$. Now we get the following result for the chemical potential of the solvent in the solution at pressure P'.

$$\mu'_B = \mu'_{B*} + RT \ln x_B$$

Under equilibrium this should be equal to the chemical potential of the solvent in the pure state at pressure P which may be denoted by μ_{B*}. That is

$$\mu'_{B*} + RT \ln x_B = \mu_{B*}$$

Rearranging this, we obtain

$$\mu'_{B*} - \mu_{B*} = -RT \ln x_B$$

The left-hand-side of this equation involves the chemical potentials of pure B at pressures P and P'. Since the temperature is constant, we can use Eq. (6.18) to replace the chemical potential in terms of the pressure and volume. Equation (6.18) leads to $dG = d\mu = V\,dP$. Thus

$$\int_P^{P'} V dP = -RT \ln x_B$$

Since volume of a liquid is not affected by change in pressure, the integral in this equation can be easily determined in terms of the molar volume V_B. Thus

$$V_B (P' - P) = -RT \ln x_B$$

Noting the definition of the osmotic pressure, the preceding equation may be written as

$$P_{\text{osmotic}} = -\frac{RT \ln x_B}{V_B} = -\frac{RT \ln (1 - x_A)}{V_B}$$

For small values of x_A, we can use the approximation $\ln (1 - x_A) = -x_A$. Thus we get

$$P_{\text{osmotic}} = \frac{RT x_A}{V_B}$$

8.5 PHASE RULE FOR NON-REACTING SYSTEMS

The essence of a phase equilibrium problem is to express quantitatively the relationship between the variables that describe the state of equilibrium of two or more homogeneous phases, which are free to interchange energy and matter. For a homogeneous phase at equilibrium the intensive properties are the same everywhere. In phase equilibrium studies, the intensive properties of interest are pressure, temperature, density and composition.

between the number of variables and the number of equations is therefore two indicating that only two independent variables need be fixed to define the state of the system completely. These may be either intensive or extensive. If $F < 2$, at least one extensive variable must be fixed for complete determination of the system. For example, for water and water vapour in equilibrium, since the number of degrees of freedom is one, the intensive state of the system is specified by fixing either the pressure or the temperature. But the total properties can be evaluated only if the amount of liquid or vapour is also specified. However, for a binary mixture, say, water and alcohol, in vapour–liquid equilibrium, since the number of degrees of freedom is two, no additional specifications are needed to predict the amount of liquid and vapour present in equilibrium, provided, we know the amounts of the components from which the system is formed. Duhem's theorem is applicable to reacting systems as well (see Chapter 9).

8.7 VAPOUR–LIQUID EQUILIBRIA

The vapour–liquid equilibrium (VLE) data are essential for many engineering calculations, especially in the design and analysis of separation operations such as distillation, absorption, etc. Thermodynamics provides a system of equations relating the necessary experimental data and the unknown vapour–liquid equilibrium compositions, temperature and pressure.

The conditions of equilibrium [Eq. (8.36)] require that the fugacity of a component in the liquid phase be equal to that in the vapour phase. That is,

$$\bar{f}_i^L = \bar{f}_i^V \quad \text{for } i = 1, 2, 3, \ldots, C \tag{8.41}$$

$\bar{f}_i$ represents the fugacity of component i in the solution and the superscripts V and L represent the vapour and liquid phases respectively. Using this equation, the problem of determining the composition of the liquid and vapour phases in equilibrium is quite simple: it is necessary only to evaluate the compositions so that the fugacity of each component be the same in both phases. For example, for a binary mixture of ethanol and water in vapour–liquid equilibrium, at a definite temperature and pressure, the mole fractions in the liquid and vapour must be such that the fugacity of ethanol is the same in both phases. That is, $\bar{f}_E^L = \bar{f}_E^V$. Here, $\bar{f}_E$ is the fugacity of ethanol in the mixture. To evaluate quantitatively the equilibrium compositions, the fugacity of a component should be expressed in terms of its mole fraction in the mixture. Using the definition of activity coefficient, the fugacity of a substance in the vapour phase can be written in terms of its mole fraction y_i in the mixture and the fugacity of pure i as a vapour at the system temperature and pressure.

$$\bar{f}_i^V = \gamma_i^V y_i f_i^V \tag{8.42}$$

If the stable state for i at the given temperature and pressure is not a vapour, evaluating f_i^V requires the introduction of a hypothetical state. The use of the concept of fugacity coefficient helps to overcome this difficulty. The fugacity of a component in a gas mixture can be written as

$$\bar{f}_i^V = y_i \bar{\phi}_i P \tag{8.43}$$

where $\bar{\phi}_i$ is the fugacity coefficient of i in the mixture. The fugacity coefficient $\bar{\phi}_i$ may be evaluated from an equation of state for the mixture.

For the liquid phase, the fugacity of a component can be expressed as the product of its mole fraction x_i in the solution, the activity coefficient γ_i and the fugacity of the component in the standard state.

$$\bar{f}_i^L = x_i \gamma_i^L f_i^0 \tag{8.44}$$

Substituting Eqs. (8.43) and (8.44) into Eq. (8.41) and dropping the superscript L from the activity coefficient, we get

Fugacity co-eff. → Activity co-eff.

$$\boxed{y_i \bar{\phi}_i P = \gamma_i x_i f_i^0} \tag{8.45}$$

Equation (8.45) is the fundamental relationship in the study of vapour–liquid equilibrium. Vapour–liquid equilibrium problems may be solved, by dividing them into the following grouping for convenience.

Case 1: Ideal gas-phase, ideal liquid solution. For mixtures of ideal gases, $\bar{\phi}_i = 1$. For ideal liquid solutions, $\gamma_i = 1$, and the fugacity, f_i^0 at low pressures, is equal to the saturation pressure of pure liquid P_i^S at the temperature of interest. Equation (8.45) becomes

$$y_i P = x_i P_i^S \tag{8.46}$$

Case 2: Low-pressure VLE problems. If the pressure is low enough that the assumption of ideal gas behaviour for the gas phase would not introduce any significant errors in practical calculations, Eq. (8.45) can be modified as

$$y_i P = \gamma_i x_i P_i^S \tag{8.47}$$

Case 3: High-pressure VLE problems. In the general case where ideal behaviour cannot be assumed for the gas and liquid phases, the fugacity coefficient $\bar{\phi}_i$ and the activity coefficient γ_i should first be determined for solving vapour–liquid equilibrium problems using Eq. (8.45). These are normally complex functions of temperature, pressure and compositions and can be written as

$$\bar{\phi}_i = F'(T, P, y_1, y_2, \ldots, y_{n-1})$$

$$\gamma_i = F''(T, P, x_1, x_2, \ldots, x_{n-1})$$

The fugacity in the reference state f_i^0 is the fugacity of pure i at the same T, P and state of aggregation as the mixture. To calculate this, it is convenient to determine first the fugacity of pure i in the liquid state at T under its equilibrium vapour pressure P_i^S and then apply a correction term for the fact that $P \neq P_i^S$. The fugacity of the liquid under its equilibrium vapour pressure is equal to the vapour pressure times the fugacity coefficient ϕ_i^S. (ϕ_i^S tends to unity if the vapour behaves as an ideal gas.) Using Eq. (6.31), we can write

$$\ln \frac{f_i^0}{\phi_i^S P_i^S} = \frac{1}{RT} \int_{P_i^S}^{P} V_i \, dP \tag{8.48}$$

Here the liquid phase molar volume V_i can be assumed not to change appreciably with pressure so that the above equation can be written as

$$\ln \frac{f_i^0}{\phi_i^S P_i^S} = \frac{V_i}{RT}(P - P_i^S)$$

Therefore,

$$f_i^0 = \phi_i^S P_i^S \exp\left[\frac{V_i (P - P_i^S)}{RT}\right]$$

This result is substituted into Eq. (8.45).

$$y_i \overline{\phi}_i P = \gamma_i x_i \phi_i^S P_i^S \exp\left[\frac{V_i (P - P_i^S)}{RT}\right] \tag{8.49}$$

This is the general equation for vapour–liquid equilibria. The exponential in the above equation is known as the *Poynting correction* and it is approximately unity when pressure is low. Also at low pressures when gas behaves ideally, $\overline{\phi}_i = \phi_i^S = 1$ and the above equation reduces to Eq. (8.47).

Therefore,

$$f_i^0 = \phi_i^S P_i^S \exp\left[\frac{V_i (P - P_i^S)}{RT}\right]$$

This result is substituted into Eq. (8.45).

$$y_i \bar{\phi}_i P = \gamma_i x_i \phi_i^S P_i^S \exp\left[\frac{V_i (P - P_i^S)}{RT}\right] \tag{8.49}$$

This is the general equation for vapour–liquid equilibria. The exponential in the above equation is known as the *Poynting correction* and it is approximately unity when pressure is low. Also at low pressures when gas behaves ideally, $\bar{\phi}_i = \phi_i^S = 1$ and the above equation reduces to Eq. (8.47).

8.8 PHASE DIAGRAMS FOR BINARY SOLUTIONS

8.8.1 Constant-pressure Equilibria

$F = C - P + 2$

Consider a binary system made up of components A and B. Component A is assumed to be more volatile than B, i.e. the vapour pressure of A is greater than that of B at any given temperature. For a binary liquid mixture in equilibrium with its vapour, according to the Gibbs Phase rule, the number of degrees of freedom is two. When the pressure is fixed, only one variable, say liquid phase composition, can be changed independently and other properties such as the temperature and the vapour phase compositions get uniquely determined. Vapour–liquid equilibrium data at constant pressure are usually represented by means of either the temperature-composition diagrams (the T-x-y diagrams or the boiling point diagrams) or the distribution diagrams (x-y diagrams or equilibrium curves).

Boiling-point diagram. The boiling point diagrams are plots of temperature as ordinate against composition of liquid and vapour as abscissa. The composition of liquid is usually indicated by the mole fraction of more volatile component in the liquid, x, and the composition of the vapour is indicated by the mole fraction of the more volatile component in the vapour, y. Therefore, the boiling point diagrams are also called T-x-y diagrams. The upper curve in Fig. 8.2 gives the temperature versus vapour composition (y), and is known as the 'dew-point curve'. The lower curve in the figure is temperature versus liquid composition (x), also called the 'bubble-point curve'. Below the bubble-point curve the mixture is subcooled liquid and above the dew-point curve the mixture is superheated vapour. Between the bubble-point and dew-point curves the mixture cannot exist as a single phase, it spontaneously separates into saturated liquid and vapour phases that are in equilibrium.

To make these points clearer, consider a mixture whose temperature and composition (x_1) are such that it is represented by point A in Fig. 8.2. Since the point A lies below the bubble-point curve, the solution is entirely liquid. The mixture is taken in a closed container and the pressure over the system is maintained at a constant value by a piston. The mixture is heated slowly so that its temperature increases along the vertical line passing through point A till point B on the bubble-point curve is reached. The temperature T_1 corresponding to point B, is the bubble point of the original mixture. The first bubble of the vapour is produced at this temperature and it will have the

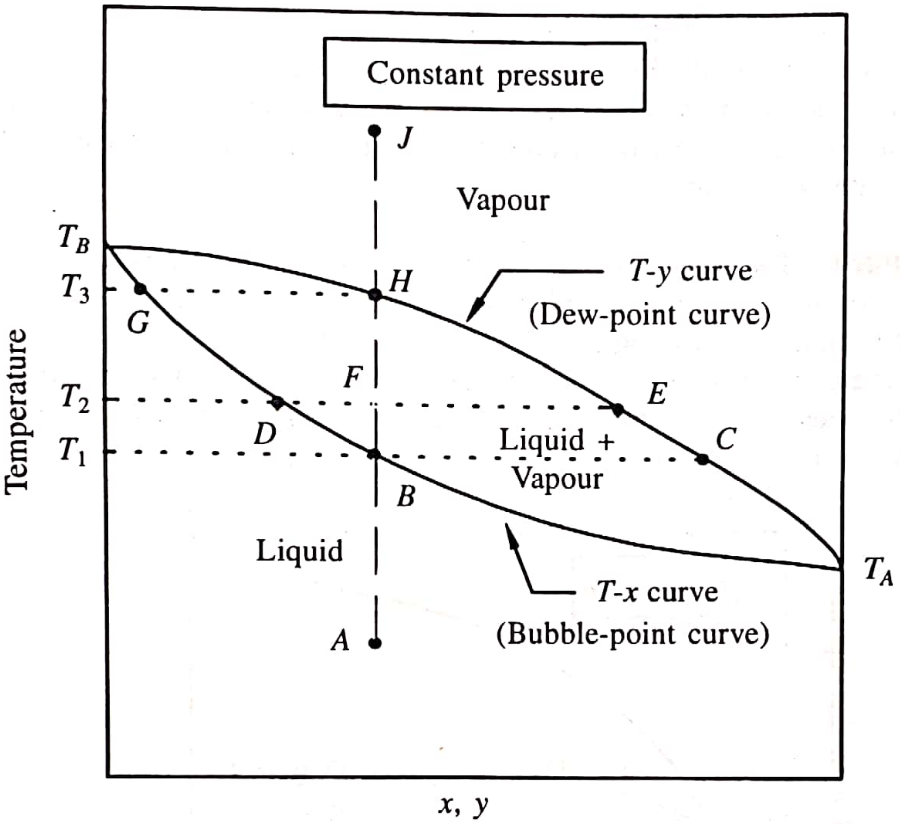

Fig. 8.2 *T-x-y* diagram (boiling-point diagram).

composition (y_1) represented by point C on the upper curve. The vapour is richer in the more volatile component. Therefore $y_1 > x_1$, and the dew-point curve lies above the bubble-point curve. The mixtures at points B and C are the liquid and vapour at equilibrium at the system pressure and temperature T_1. Since both are at the same temperature, they can be joined by a horizontal line BC, known as a 'tie line'. Further heating will result in the vaporisation of more liquid, and at temperature T_2 the system will consist of saturated liquid represented by point D and saturated vapour represented by point E, which are in equilibrium. Since the vapour formed is not removed from the system, the overall composition of the combined mixture of liquid and vapour will be same as x_1, the composition of the original mixture. However, the relative amounts of the liquid and the vapour change as the temperature is changed.

These relative amounts are given by the ratio in which the point representing the combined mixture (in this case, point F) divides the tie line DE. By material balance consideration, it can be easily verified that

$$\frac{\text{Amount of liquid}}{\text{Amount of vapour}} = \frac{\text{Line } EF}{\text{Line } DF}$$

If heating is continued, eventually a temperature T_3 is reached when almost all liquid is vaporised. The last drop of liquid getting vaporised at this temperature has a composition denoted by point G and the equilibrium vapour has the composition at H same as the original mixture. Temperature T_3 is the dew point of the original mixture. The mixture temperature increases along the vertical line HJ on further heating. On cooling the superheated mixture at point J, the first drop of condensate appears when the temperature drops to T_3, the dew point of the mixture and the composition of the liquid is given by point G.

We have seen that the mixture at point A has vaporised over a temperature range from T_1 (the bubble point) to T_3 (the dew point), unlike a pure substance, which vaporises at a single temperature known as the boiling point of the substance. For a solution, the term 'boiling point' has no meaning, because, at a given pressure the temperature during vaporisation of a solution varies from the bubble point to the dew point.

Equilibrium diagram. The vapour–liquid equilibrium data at constant pressure can be represented on a x versus y plot or an equilibrium distribution diagram. If the vapour composition is taken as the ordinate and the liquid composition is taken as the abscissa, a tie line such as line BC on the boiling point diagram gives rise to a point such as point P on the distribution diagram (Fig. 8.3). Since the vapour is richer in the more volatile component, the curve lies above the diagonal on which $x = y$.

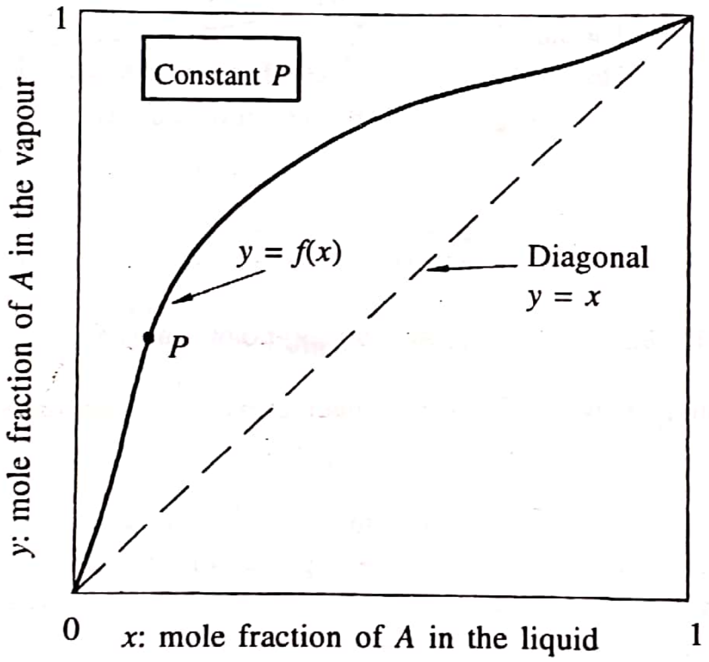

Fig. 8.3 *x-y* diagram (Equilibrium distribution diagram).

A liquid–vapour equilibrium curve very close to the diagonal means that the composition of the vapour is not much different from the composition of the liquid with which it is in equilibrium; when the curve coincides with the diagonal, x and y are equal.

Effect of pressure on VLE. On the boiling point diagram the temperatures corresponding to $x = 0$ and $x = 1$ are the boiling points of pure substances B and A respectively. The boiling points of pure substances increase with pressure. This is true for the bubble and dew points of a mixture of given composition. Consequently the boiling point diagrams at higher pressures will be above the boiling point diagrams at lower pressures as shown in Fig. 8.4. Since the relative volatility decreases as pressure is increased, the closed loop formed by the dew-point and bubble-point curves become narrow at high pressures. Figure 8.5 indicates the effect of pressure on the distribution diagram. In Fig. 8.4, P_3 is the *critical pressure* for component A and above this pressure, the looped curves are shorter.

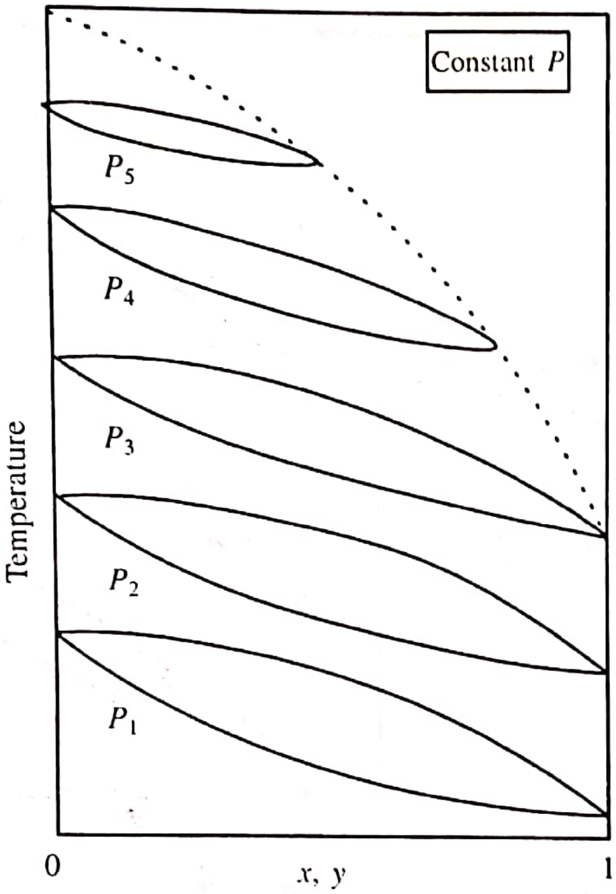

Fig. 8.4 Effect of increasing pressure on *T-x-y* diagram.

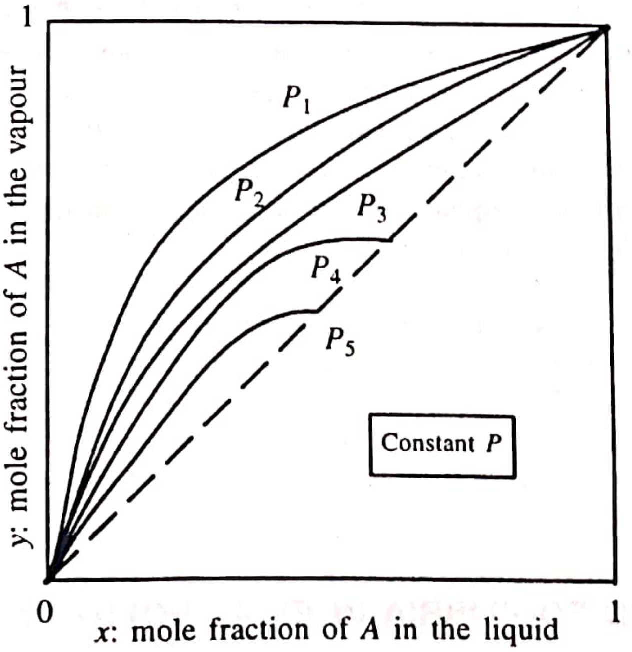

Fig. 8.5 Effect of varying the pressure on the equilibrium diagram.

8.8.2 Constant-temperature Equilibria

Vapour–liquid equilibrium data at constant temperature are represented by means of *P-x-y* diagrams; Fig. 8.6 shows a typical *P-x-y* diagram.

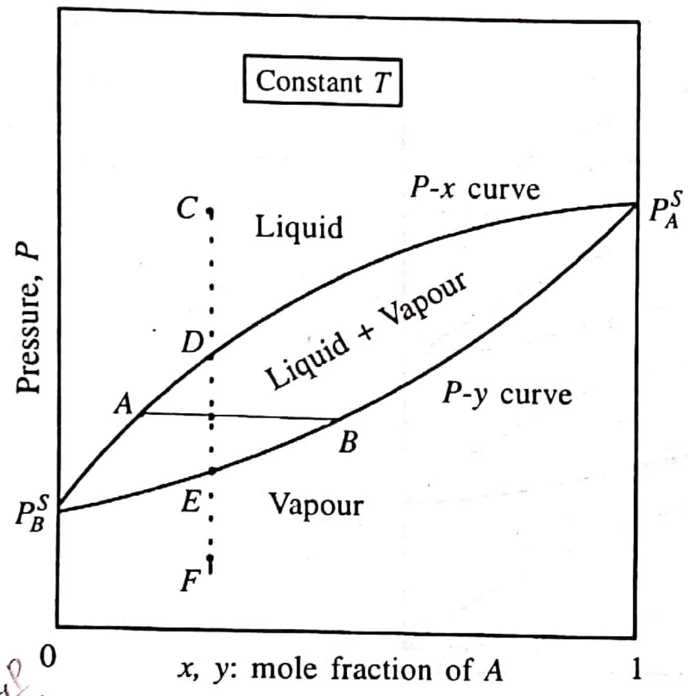

Fig. 8.6(a) *P-x-y* diagram.

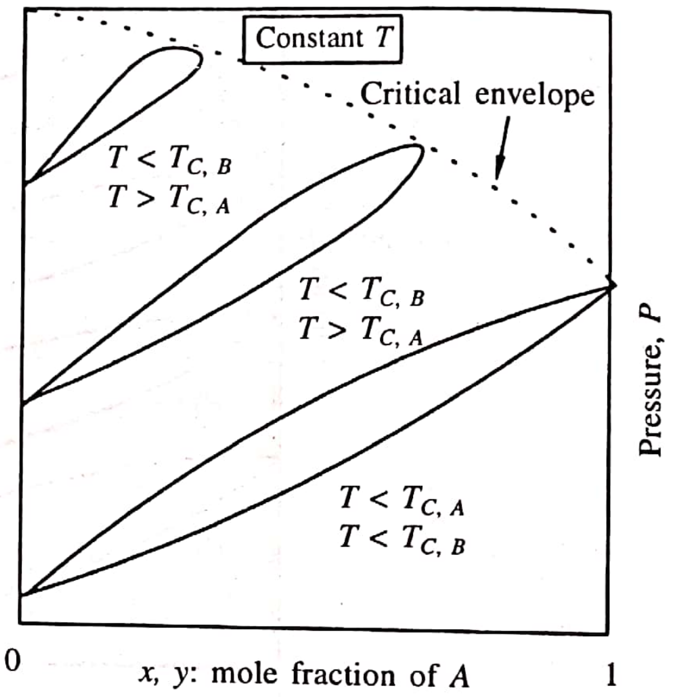

Fig. 8.6(b) Effect of temperature on *P-x-y* diagram near the critical point.

$y_1 = x_1 P / P_1^S$

$x_1 = y_1 \cdot P_1^S / P$

$y_2 \cdot P_2^S / P$

x_2

$= y_2 \cdot P_2^S / P_1$

The pressure at $x = 0$ is the vapour pressure of pure $B(P_B^S)$ and the pressure at $x = 1$ is the vapour pressure of pure $A(P_A^S)$. Since component A is assumed to be more volatile, $P_A^S > P_B^S$ and therefore, the *P-x-y* diagram slopes upwards as shown in the figure. The *P-y* curve lies below the *P-x* curve so that for any given pressure, $y > x$. A solution lying above the *P-x* curve is in the liquid region and that lying below the *P-y* curve is in the vapour region. In between *P-x* and *P-y* curves the solution is a mixture of saturated liquid and vapour. A horizontal line such as *AB* connects the liquid and vapour phases in equilibrium and is therefore, a tie line. Assume that a liquid mixture whose conditions may be represented by the point *C* in Fig. 8.6, is taken in a closed container. When the pressure over this system is reduced at constant temperature, the first bubble of vapour forms at point *D*, and vaporisation goes to completion at point *E*. Further reduction in pressure leads to the production of superheated vapour represented by point *F.* The effect of temperature on *P-x-y* diagram is shown in Fig. 8.6(b). When the temperature is less than the critical temperature of both components, the looped curve such as the one shown at the bottom of Fig. 8.6(b) results. The other two curves refer to temperatures greater than the critical temperature of *A*.

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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 ($\Delta V = 0$) 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 ($\Delta H = 0$); 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.

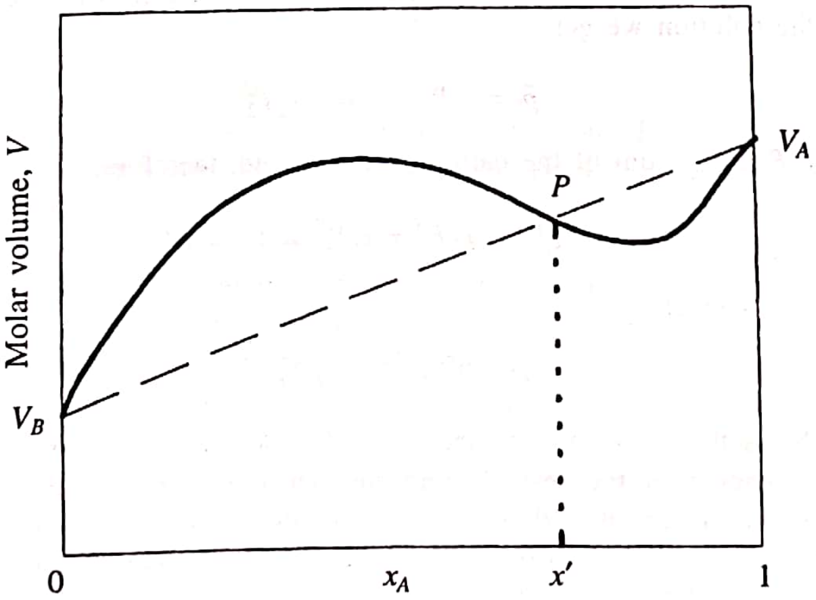


Fig. 8.7 A real solution with no volume change of mixing at point P.

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

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

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

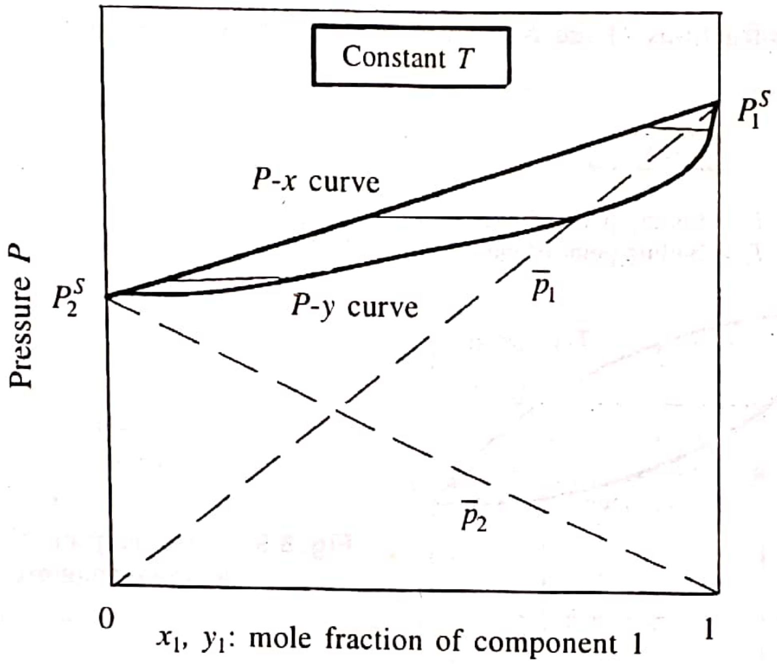


Fig. 8.8 Pressures over ideal solution.

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.

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.

x_1, y_1: mole fractions of the component 1

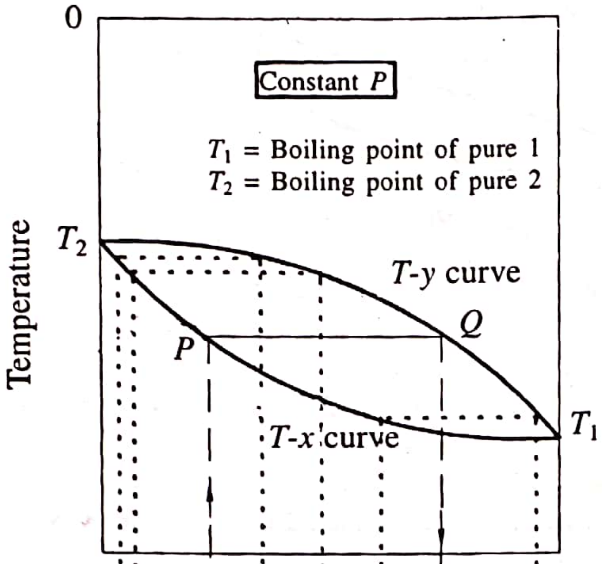


Fig. 8.9 *T-x-y* diagram of an ideal solution.

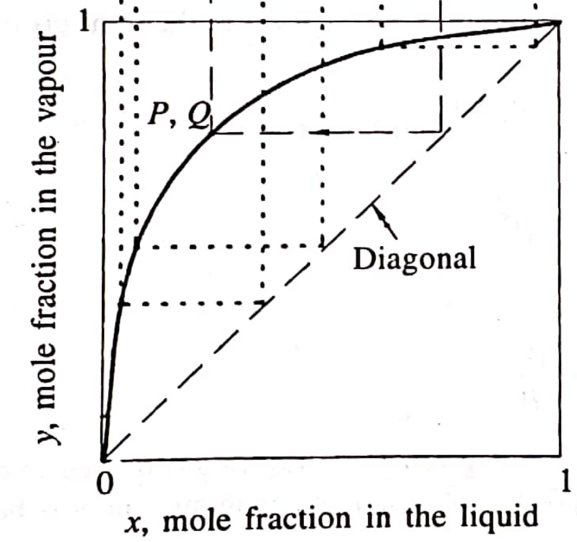


Fig. 8.10 Equilibrium diagram.

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

$$\alpha = \frac{P_1^S}{P_2^S}, \text{ a constant}$$

The quantity α is designated as the relative volatility of the system.

From Eq. (8.54),

$$y_1 = x_1 \frac{P_1^S}{P}, \qquad y_2 = x_2 \frac{P_2^S}{P}$$

Taking the ratio of the above two equations and noting that $y_2 = 1 - y_1$ and $x_2 = 1 - x_1$ we get

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

which can be written in the following form.

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

Although Eq. (8.55) is not exact over a wide range of temperatures, the effect of variation in α is so small that an average α 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 whole concentration range, it must also apply to the other constituent.

Solution Assume that Raoult's law is obeyed by component 1 in a binary mixture. Then

$$\bar{p}_1 = x_1 P_1^S$$

As pointed out earlier, Raoult's law is obeyed by ideal solutions when the vapour phase behaves as an ideal gas whereas Lewis–Randall rule is obeyed by ideal solutions irrespective of whether the gas phase is ideal or not. So for component 1, we can write

$$\bar{f}_1 = x_1 f_1$$

Differentiating this equation and noting that f_1 is constant at the given conditions

$$d(\ln \bar{f}_1) = d(\ln x_1)$$

which on rearrangement gives

$$\frac{d(\ln \bar{f}_1)}{d(\ln x_1)} = 1 \tag{8.56}$$

Gibbs–Duhem equation relates fugacities of components in a binary mixture as

$$x_1 \frac{d(\ln \bar{f}_1)}{dx_1} = x_2 \frac{d(\ln \bar{f}_2)}{dx_2}$$

which on rearrangement gives

$$\frac{d(\ln \bar{f}_1)}{d(\ln x_1)} = \frac{d(\ln \bar{f}_2)}{d(\ln x_2)} \tag{8.57}$$

This equation is sometimes referred to as *Duhem–Margules equation*. Comparing Eq. (8.56) with Eq. (8.57) we see that

$$\frac{d(\ln \bar{f}_2)}{d(\ln x_2)} = 1$$

i.e.

$$d(\ln \bar{f}_2) = d(\ln x_2)$$

Noting that $\bar{f}_2 = f_2$ when $x_2 = 1$ the above equation can be integrated.

$$\int_{f_2}^{\bar{f}_2} d(\ln \bar{f}_2) = \int_1^{x_2} d(\ln x_2)$$

$$\ln \frac{\bar{f}_2}{f_2} = \ln \frac{x_2}{1}$$

or

$$\frac{\bar{f}_2}{f_2} = x_2$$

That is, $\bar{f}_2 = x_2 f_2$, which is the Lewis–Randall rule for component 2. If the vapour is an ideal gas, this can be equally written as

$$\bar{p}_2 = x_2 P_2^S$$

This is Raoult's law for component 2. The conclusion to be drawn from the above derivation is that if Raoult's law is applicable to one of the constituents of a liquid mixture at all concentrations, it must be applicable to the other constituent as well.

***EXAMPLE* 8.6** *n*-Heptane and toluene form ideal solution. At 373 K, their vapour pressures are 106 and 74 kPa respectively. Determine the composition of the liquid and vapour in equilibrium at 373 K and 101.3 kPa.

Solution Refer Eq. (8.51). Then,

$$P_1^S = 106; \ P_2^S = 74, \quad P = 101.3$$

$$101.3 = 74 + (106 - 74)x$$

where x is the mole fraction of heptane in the liquid. On solving this, we get $x = 0.853$

From Eq. (8.54),

$$y = 0.853 \times 106/101.3 = 0.893$$

The liquid and the vapour at the given conditions contain respectively 85.3% (mol) and 89.3% (mol) heptane.

***EXAMPLE* 8.7** An equimolar solution of benzene and toluene is totally evaporated at a constant temperature of 363 K. At this temperature, the vapour pressures of benzene and toluene are 135.4 and 54 kPa respectively. What are the pressures at the beginning and at the end of the vaporisation process?

Solution Put $x = 0.5$ in Eq. (8.51). Then $P = 94.7$ kPa. This is the pressure at the beginning of vaporisation. Equation (8.51) can be written as

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

Substitute this in Eq. (8.54). Then,

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

On rearranging this equation, we get

$$P = \frac{P_1^S P_2^S}{P_1^S - y(P_1^S - P_2^S)}$$

Put $y = 0.5$ in this. Thus, we get $P = 77.2$ kPa. (This is the pressure at the end of vaporisation).

***EXAMPLE* 8.8** 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

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

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)

$$y_1 = 0.4 \times 85.12/57.63 = 0.5908$$

(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

$$1 \times 0.7 = f \times 0.5608 + (1 - f) \times 0.7344$$

Solving this, we get $f = 0.1982$. That is, 19.82% (mol) of the given mixture is liquid.

EXAMPLE 8.9 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 α value.

T, K	371.4	378	383	388	393	398.6
P_A, kPa	101.3	125.3	140.0	160.0	179.9	205.3
P_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; $P_A = 125.3$ kPa; $P_B = 55.6$ 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

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

Relative volatility is

$$\alpha = P_A/P_B = 125.3/55.6 = 2.25$$

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
α	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 $\alpha = 2.16$. Use this value of α 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.

The non-ideal behaviour of liquid mixtures arises due to the dissimilarity among molecules. The dissimilarities arise from the difference in the molecular structure or from the difference in the molecular weight. The non-ideal behaviour of light hydrocarbons such as methane, ethylene, etc., in mixtures of heavier paraffin or crude oil is due to the difference in the molecular weights. In contrast, it is a type of intermolecular attraction called hydrogen bonding, that is responsible for the non-ideal behaviour resulting from the difference in the molecular structure. Molecules, which

$$\left[\frac{0.2634}{1-[0.842\,\Lambda_{12}/(0.842+0.158\,\Lambda_{12})]+5.329\ln(0.8639+0.1621\,\Lambda_{12})]}\right]^{0.1876}$$
$$\times\,(0.8639+0.1621\,\Lambda_{12})=1$$

$\Lambda_{12} = 0.935$. Substitute this value in Eq. (8.72) and calculate Λ_{21}. So, $\Lambda_{21} = 0.467$

8.12 VAPOUR-LIQUID EQUILIBRIA INVOLVING HIGH PRESSURES AND MULTICOMPONENT SYSTEMS

8.12.1 Vaporisation Equilibrium Constants

For high-pressure vapour–liquid equilibrium (VLE) calculations, it is convenient to express the phase equilibrium relations in terms of vaporisation equilibrium constants or K factors. It is defined as the ratio of mole fraction in the vapour phase y to that in the liquid x or $K = (y/x)$. Since the fugacities in the liquid and vapour are equal, we can combine Eqs. (8.42) and (8.44) as

$$f_i^{0,V}\gamma_i^V y_i = x_i\gamma_i^L f_i^{0,L}$$

Using this we can write the K factor as

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L f_i^{0,L}}{\gamma_i^V f_i^{0,V}} \qquad (8.82)$$

K factor is also obtained from Eq. (8.49) assuming a Poynting factor of unity.

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^S}{\bar{\phi}_i}\,\frac{\gamma_i^L P_i^S}{P} = \frac{\Phi_i\gamma_i P_i^S}{P} \qquad (8.83)$$

where $\Phi_i = (\phi_i^S/\bar{\phi}_i)$. If the Poynting factor is not unity, it should also be included in Φ_i. The K factors contain all the thermodynamic information needed for VLE calculations and are complex functions of temperature, pressure and the vapour phase and liquid phase compositions.

If the vapour phase is assumed to behave as an ideal gas $(\phi_i^S/\bar{\phi}_i) = 1$ and $K_i = (y_i/x_i) = (\gamma_i P_i^S/P)$. In addition, if the liquid phase behaves as an ideal solution $\gamma_i = 1$ and $K_i = y_i/x_i = P_i^S/P$. For ideal solutions, K factors depend only on temperature and pressure and are readily correlated as function of these two variables. DePriester nomographs [C.L. DePriester, *Chem. Eng. Progr., Symposium Ser.* 7, 49 (1953)] provide such correlations for many hydrocarbons. These nomographs can be found reproduced in *Chemical Engineers Handbook.*

8.12.2 Bubble-point Equilibria

The *bubble-point temperature* is the one at which the first bubble of vapour is produced from the liquid on heating at constant pressure. At the bubble point the liquid has the same composition as the original mixture. Therefore, in problems where bubble-point temperature is to be determined, the x_i are known. Assume a temperature and get the K_i values at this temperature. Calculate y_i using $y_i = K_i x_i$. If the assumed temperature is correct then

$$\Sigma\, y_i = \Sigma\, K_i x_i = 1 \qquad (8.84)$$

Otherwise, repeat the calculations with another temperature. To find the *bubble-point pressure*, a similar procedure as above is adopted by assuming various values of pressure until $\Sigma K_i x_i = 1$.

8.12.3 Dew-point Equilibria

The *dew-point temperature* is the one at which the first drop of condensate is formed on cooling a vapour at constant pressure. The vapour in equilibrium with the liquid at the dew point has the same composition as the original mixture. In order to find the dew-point temperature, a temperature is assumed arbitrarily and K_i is determined. Then,

$$x_i = \frac{y_i}{K_i}$$

At the dew point,

$$\Sigma x_i = \Sigma \frac{y_i}{K_i} = 1.00 \tag{8.85}$$

Otherwise, repeat the calculation by assuming another temperature till this equation is satisfied. Determination of the *dew-point pressure* involves a similar procedure assuming pressure instead of temperature.

8.12.4 Flash Vaporisation

The general *flash vaporisation* problem can be stated as: Given a mixture of known overall composition z_i at temperature T and pressure P, what is the fraction that is vapour (V) and what are the composition of the liquid and vapour phases in equilibrium? The overall material balance for the system is

$$F = V + L \tag{8.86}$$

where F is the total number of moles of the initial mixture. The component-i balance for the system is

$$Fz_i = Vy_i + Lx_i \tag{8.87}$$

Since $y_i = K_i x_i$, it can be eliminated from Eq. (8.87) to get the following:

$$x_i = \frac{Fz_i}{K_i V + L} = \frac{F}{V}\,\frac{z_i}{K_i + (L/V)} \tag{8.88}$$

Since $\Sigma x_i = 1$, we have

$$\Sigma \frac{z_i}{K_i + (L/V)} = \frac{V}{F} \tag{8.89}$$

The above equation can be used for the calculation of T, P or fractional vaporisation in an iterative procedure. Alternatively, x_i can be eliminated from Eq. (8.87) which leads to

$$y_i = \frac{Fz_i}{V + (L/K_i)} = \frac{F}{V}\,\frac{z_i}{1 + [L/(VK_i)]} \tag{8.90}$$

As $\Sigma\, y_i = 1$, we have

$$\Sigma \frac{z_i}{1 + L/(VK_i)} = \frac{V}{F} \tag{8.91}$$

Equation (8.91) can also be utilised in an iterative procedure to estimate T, P or the fraction of the initial mixture that is vaporised.

EXAMPLE 8.21 A mixture contains 45% (mol) methanol (A), 30% (mol) ethanol (B) and the rest n-propanol (C). Liquid solution may be assumed to be ideal and perfect gas law is valid for the vapour phase. Calculate at a total pressure of 101.3 kPa.

(a) The bubble point and the vapour composition

(b) The dew point and the liquid composition.

The vapour pressures of the pure liquids are given below:

Temperature, K	333	343	353	363
P_A, kPa	81.97	133.29	186.61	266.58
P_B, kPa	49.32	73.31	106.63	166.61
P_C, kPa	39.32	62.65	93.30	133.29

Solution The vapour pressures of the components are plotted against temperature so that interpolation of vapour pressure can be done easily.

(a) If the vapour phase can be treated as an ideal gas and liquid phase, an ideal solution, the K-values can be written as $K_i = y_i/x_i = P_i^S/P$. Equation (8.84) can be written as

$$\Sigma y_i = \Sigma K_i x_i = \Sigma \frac{x_i P_i^S}{P} = 1$$

Draw graph for each component individully

Now temperatures are assumed till the above equality is satisfied. It is seen that at 344 K,

$$\frac{\Sigma x_i P_i^S}{P} = 0.98$$

and at 345 K,

$$\Sigma \frac{x_i P_i^S}{P} = 1.015$$

344 345

$\underbrace{0{\cdot}98 \qquad 1{\cdot}00}_{0{\cdot}02}\;\underbrace{\qquad 1{\cdot}015}_{0{\cdot}015}$

$T = \dfrac{345 \times 0{\cdot}02 + 344 \times 0{\cdot}015}{(0{\cdot}02 + 0{\cdot}015)} = 344{\cdot}57$

The bubble-point lies between 344 and 345 K. By interpolation, the bubble-point is obtained as 344.6 K. At this temperature the vapour pressures are obtained from the P vs T plots. P_A^S = 137.3 kPa, P_B^S = 76.20 kPa and P_C^S = 65.40 kPa.

Component	x_i	P_i^S	$K_i = P_i^S/P$	$y_i = K_i x_i$
Methanol	0.45	137.30	1.355	0.610
Ethanol	0.30	76.20	0.752	0.226
Propanol	0.25	65.40	0.646	0.162
$\Sigma\, K_i x_i$				0.998

The equilibrium vapour contains 61% methanol, 22.6% ethanol and 16.2% propanol.

(b) Equation (8.85) for the present case becomes

$$\Sigma x_i = \Sigma \frac{y_i}{K_i} = \frac{y_i P}{P_i^S} = 1.00$$

The dew-point temperature is to be determined by trial such that the above relation is satisfied. By trial, it can be seen that at 347.5 K, P_A^S = 153.28 kPa, P_B^S = 85.25 kPa and P_C^S = 73.31 kPa.

Component	y_i	P_i^S	$K_i = P_i^S/P$	$x_i = y_i/K_i$
Methanol	0.45	153.28	1.5131	0.2974
Ethanol	0.30	85.25	0.8416	0.3565
Propanol	0.25	73.31	0.7237	0.3454
$\Sigma y_i/K_i$				0.9993

The values in the last column are the liquid composition at the dew point. Thus, liquid contains 29.7% methanol, 35.7% ethanol, and 34.5% propanol.

***EXAMPLE* 8.22** A hydrocarbon mixture contains 25% (mol) propane, 40% (mol) *n*-butane and 35% (mol) *n*-pentane at 1447.14 kPa. Assume ideal solution behaviour and calculate

(a) The bubble-point temperature and composition of the vapour
(b) The dew-point temperature and the composition of the liquid
(c) The temperature and the composition of the liquid and vapour in equilibrium when 45% (mol) of the initial mixture is vaporised. (The values of K_i can be obtained from Fig. 13.6 of *Chemical Engineer's Handbook*, 5th ed.)

Solution (a) Assume temperature, say 355.4 K, and the K_i values are found out from the nomograph [Fig. 13.6(b) in *Chemical Engineer's Handbook*]. The products of K_i and x_i are calculated and their sum Σx_iK_i is found out. The results for two temperatures 355.4 K and 366.5 K are shown below.

		T = 355.4 K		T = 366.5 K	
Component	x_i	K_i	K_ix_i	K_i	K_ix_i
Propane	0.25	2.000	0.500	2.30	0.575
n-Butane	0.40	0.780	0.312	0.90	0.360
n-Pentane	0.35	0.330	0.116	0.40	0.140
ΣK_ix_i			0.928		1.075

The bubble-point temperature lies between 355.4 K and 366.5 K. By interpolation, the temperature is found out to be 361 K. The calculations are carried out at this temperature and the results are as follows:

Component	x_i	K_i	K_ix_i
Propane	0.25	2.12	0.530
n-Butane	0.40	0.85	0.340
n-Pentane	0.35	0.37	0.130
$\Sigma\ K_ix_i$			1.000

Since $\Sigma\ x_iK_i$ is approximately 1.00, the bubble-point temperature is 361 K. The values in the last column are the mole fraction of various components in the vapour. At the bubble-point, the vapour contains 53% propane, 34% butane and 13% pentane.

(b) At the dew-point temperature, $\Sigma\ y_i/K_i = 1$. At 377.6 K, this value is 1.1598 and at 388.8 K it is 0.9677.

		$T = 377.6$ K		$T = 388.8$ K	
Component	y_i	K_i	y_i/K_i	K_i	y_i/K_i
Propane	0.25	2.6	0.0962	2.9	0.0862
n-Butane	0.40	1.1	0.3636	1.3	0.3077
n-Pentane	0.35	0.5	0.7000	0.61	0.5738
$\Sigma y_i/K_i$			1.1598		0.9677

By interpolation, the dew-point temperature is found to be 387 K. The calculations for this temperature is given below.

Component	y_i	K_i	y_i/K_i
Propane	0.25	2.85	0.0877
n-Butane	0.40	1.25	0.3200
n-Pentane	0.35	0.59	0.5932
$\Sigma\ y_i/K_i$			1.0009

The last column in the above table is the liquid compositions. The equilibrium liquid at the dew point contains 8.77% propane, 32.0% butane and 59.32% pentane.

(c) In the following calculations, temperature is assumed so as to satisfy Eq. (8.91). For a basis of 100 mol of the initial mixture, $F = 100$ mol, $V = 45$ mol and $L = 55$ mol. Equation (8.91) becomes

$$\Sigma \frac{z_i}{1 + L/(VK_i)} = 0.45$$

Component	z_i	$T = 366.5$ K		$T = 377.6$ K	
		K_i	$z_i/[1 + L/(VK_i)]$	K_i	$z_i/[1 + L/(VK_i)]$
Propane	0.25	2.30	0.1632	2.6	0.1701
n-Butane	0.40	0.90	0.1696	1.1	0.1895
n-Pentane	0.35	0.40	0.0863	0.5	0.1016
$\Sigma\, z_i/[1 + L/(VK_i)]$			0.4191		0.4612

From the calculations given above, we see that the equilibrium temperature is between 366.5 K and 377.6 K. By interpolation, $T = 374.6$ K.

Component	z_i	$T = 374.6$ K	
		K_i	$z_i/[1 + L/(VK_i)]$
Propane	0.25	2.50	0.1679
n-Butane	0.40	1.08	0.1876
n-Pentane	0.35	0.48	0.0987
$\Sigma\, z_i/[1 + L/(VK_i)]$			0.4542

Comparing Eqs. (8.90) and (8.91), we can see that

$$y_i = \frac{z_i/[1 + L/(VK_i)]}{\Sigma z_i/[1 + L/(VK_i)]}$$

These are calculated using the values in the last column. Corresponding x_i values are found out using the material balance [Eq. (8.87)].

$$Fz_i = Vy_i + Lx_i$$

The results of the calculation are given below:

Component	y_i	x_i
Propane	0.3697	0.1521
n-Butane	0.4130	0.3894
n-Pentane	0.2173	0.4586

8.13 CONSISTENCY TESTS FOR VLE DATA

Many practical cases like distillation calculations are dependent on vapour–liquid equilibrium data and such data should be reasonably accurate if the results are to be reliable. As the VLE measurements are prone to inaccuracies, it is essential that we have some means for checking the consistency of the measured results. Thermodynamics provides tests for consistency of experimental VLE data. Almost all these tests are based on the Gibbs–Duhem equations written in terms of activity coefficients [Eq. (7.101)].

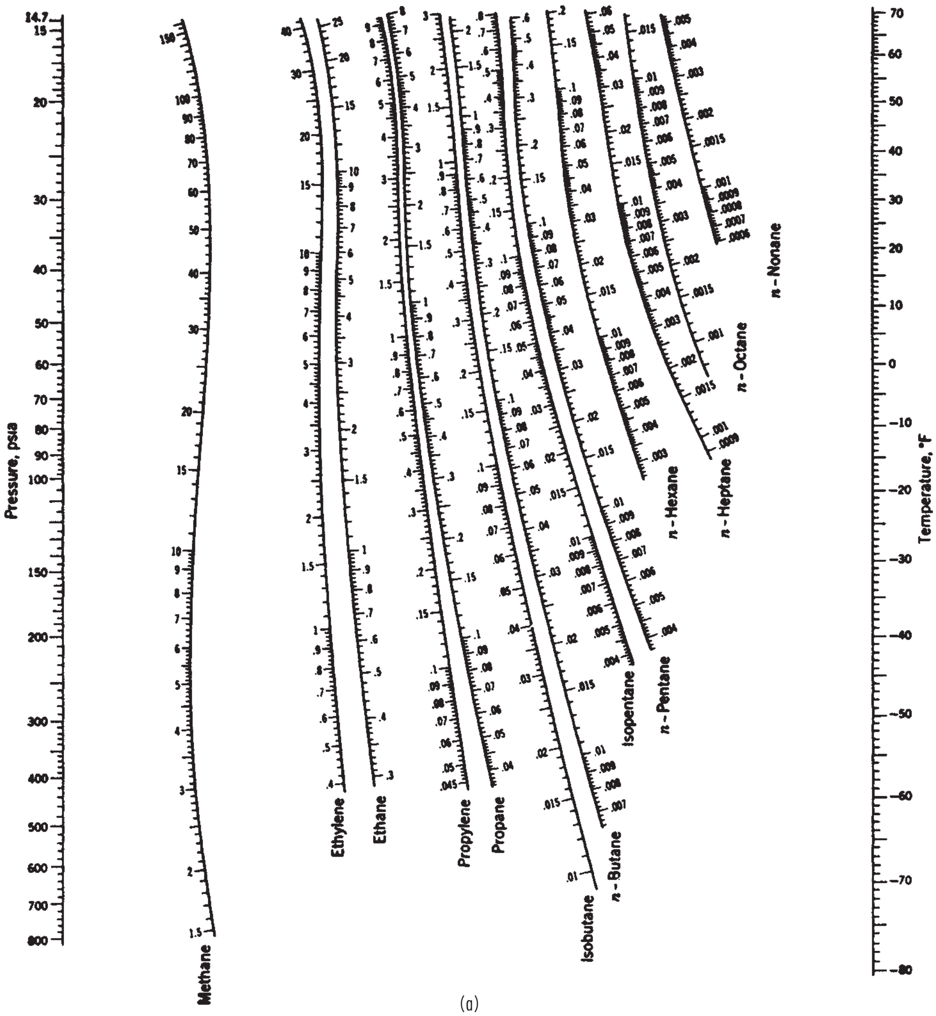


FIG. 13-14 K values ($K = y/x$) in light-hydrocarbon systems. (*a*) Low-temperature range. [*DePriester,* Chem. Eng. Prog. Symp. Sec. 7, ***49,*** *1 (1953).*]

Preferred analytical correlations are less empirical in nature and most often are theoretically based on one of two exact thermodynamic formulations, as derived in Sec. 4. When a single pressure-volume-temperature (*PVT*) equation of state is applicable to both vapor and liquid phases, the formulation used is

$$K_i = \hat{\Phi}_i^L / \hat{\Phi}_i^V \qquad (13\text{-}3)$$

where the mixture fugacity coefficients $\hat{\Phi}_i^L$ for the liquid and $\hat{\Phi}_i^V$ for the vapor are derived by classical thermodynamics from the *PVT* expression. Consistent equations for enthalpy can similarly be derived.

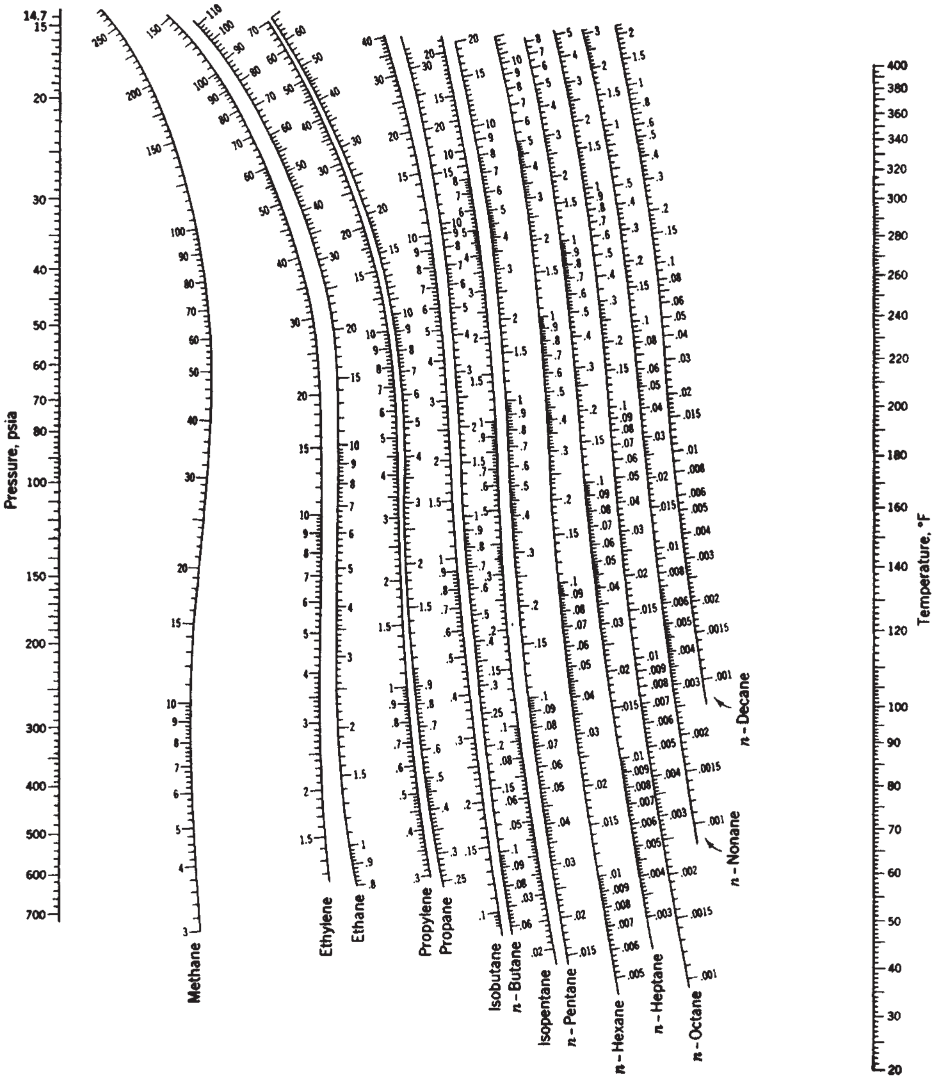
Until recently, equations of state that have been successfully applied to Eq. (13-3) have been restricted to mixtures of nonpolar compounds, namely, hydrocarbons and light gases. These equations include those of Benedict-Webb-Rubin (BWR), Soave (SRK) [*Chem. Eng. Sci.*, **27,** 1197 (1972)], who extended the remarkable Redlich-Kwong equation, and Peng-Robinson (PR) [*Ind. Eng. Chem. Fundam.*, **15,** 59 (1976)]. The SRK and PR equations belong to a family of so-called cubic equations of state. The Starling extension of the BWR equation (*Fluid Thermodynamic Properties for Light Petroleum Systems,* Gulf, Houston, 1973) predicts K values and enthalpies of the normal paraffins up through n-octane, as well as isobutane, isopentane, ethylene, propylene, nitrogen, carbon dioxide, and hydrogen sulfide, including the cryogenic region. Computer programs for K values derived from the SRK, PR and other equations of state are widely available in all computer-aided process design and simulation programs. The ability of the SRK correlation to predict K values even when the pressure approaches the convergence pressure is shown for a multicomponent system in Fig. 13-18. Similar results are achieved with the PR correlation. The Wong-Sandler mixing rules for cubic equations of state now permit such equations to be extended to mixtures of organic chemicals, as shown in a reformulated version by Orbey and Sandler [*AIChE J.*, **41,** 683 (1995)].

An alternative K-value formulation that has received wide application to mixtures containing polar and/or nonpolar compounds is

$$K_i = \gamma_i^L \Phi_i^L / \hat{\Phi}_i^V \qquad (13\text{-}4)$$

where different equations of state may be used to predict the pure-component liquid fugacity coefficient Φ_i^L and the vapor-mixture fugacity coefficient, and any one of a number of mixture free-energy models may be used to obtain the liquid activity coefficient γ_i^L. At low to moderate pressures, accurate prediction of the latter is crucial to the application of Eq. (13-4).

When either Eq. (13-3) or Eq. (13-4) can be applied, the former is generally preferred because it involves only a single equation of state



(b)

FIG. 13-14 (*Continued*) *K* values (*K* = *y*/*x*) in light-hydrocarbon systems. (*b*) High-temperature range. [*DePriester,* Chem. Eng. Prog. Symp. Sec. 7, ***49,*** *1 (1953).*]

applicable to both phases and thus would seem to offer greater consistency. In addition, the quantity Φ_i^L in Eq. (13-4) is hypothetical for any components that are supercritical. In that case, a modification of Eq. (13-4) that uses Henry's law is sometimes applied.

For mixtures of hydrocarbons and light gases, Chao and Seader (CS) [*AIChE,* **7,** 598 (1961)] applied Eq. (13-4) by using an empirical expression for Φ_i^L based on the generalized corresponding-states *PVT* correlation of Pitzer et al., the Redlich-Kwong equation of state for $\hat{\Phi}_i^V$, and the regular solution theory of Scatchard and Hildebrand for γ_i^L. The predictive ability of the last-named theory is exhibited in Fig. 13-19 for the heptane-toluene system at 101.3 kPa (1 atm). Five pure-component constants for each species (T_c, P_c, ω, δ, and v^L) are required to use the CS method, which when applied within the restrictions discussed by Lenoir and Koppany [*Hydrocarbon Process.,* **46**(11), 249 (1967)] gives good results. Revised coefficients of Grayson and Streed (GS) (Pap. 20-P07, Sixth World Pet. Conf., Frankfurt, June, 1963) for the Φ_i^L expression permit application of the CS correlation to higher temperatures and pressures and give improved predictions for hydrogen. Jin, Greenkorn, and Chao [*AIChE J,* **41,** 1602 (1995)] present a revised correlation for the standard-state liquid fugacity of hydrogen, applicable from 200 to 730 *K.*

For mixtures containing polar substances, more complex predictive equations for γ_i^L that involve binary-interaction parameters for each pair of components in the mixture are required for use in Eq. (13-4), as discussed in Sec. 4. Six popular expressions are the Margules, van Laar, Wilson, NRTL, UNIFAC, and UNIQUAC equations. Extensive listings of binary-interaction parameters for use in all but the UNIFAC equation are given by Gmehling and Onken (op. cit.). They obtained the parameters for binary systems at 101.3 kPa (1 atm) from best fits of the experimental *T*-*y*-*x* equilibrium data by setting Φ_i^V and Φ_i^L to their ideal-gas, ideal-solution limits of 1.0 and P^{sat}/P respectively, with the vapor pressure P^{sat} given by a three-constant Antoine equation, whose values they tabulate. Table 13-2 lists their parameters for some of the binary systems included in