7 PROPERTIES OF SOLUTIONS

We have seen in Chapter 6 that the thermodynamic properties of homogeneous pure substances depend only on the state of the system. The relationships developed for pure fluids are not applicable to solutions and need modification. The thermodynamic properties of solutions and heterogeneous systems consisting of more than one phase are influenced by the addition and removal of matter. The term solution includes homogeneous mixtures of two or more components in the gas, liquid or solid phase. The pressure, temperature and the amount of various constituents present determine the extensive state of a solution; and pressure, temperature and composition determine the intensive state. In this chapter, we discuss how the thermodynamic properties of a solution are determined and introduce certain concepts that are essential to the study of phase equilibria and chemical reaction equilibria.

7.1 PARTIAL MOLAR PROPERTIES

The properties of a solution are not additive properties of its components. For example, the volume of a solution is not the sum of the volumes of the pure components constituting the solution. It means that when a substance becomes part of a solution it loses its identity. But it still contributes to the property of the solution as is evident from the fact that by changing the amount of substance, the solution property also changes. Thus we need a new set of concepts that enable us to apply thermodynamics to solutions of variable composition. In this connection, the concept of partial molar properties is of great use. The term partial molar property is used to designate the property of a component when it is in admixture with one or many components. To be more precise, the *partial molar property* of a particular component in a mixture measures the contribution of that component to the mixture property. If M^t is the total value of any extensive thermodynamic property of a solution, the partial molar property $\overline{M}_i$ of the component i in the solution is defined as

$$\overline{M}_i = \left(\frac{\partial nM}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial M^t}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{7.1}$$

In Eq. (7.1), n is the total number of moles and M is the molar property of the solution. n_i denotes the number of moles of component i in solution, so that $n = \Sigma n_i$.

In general, any partial molar property $\overline{M}_i$ is the increase, in the property M^t of the solution resulting from the addition at constant temperature and pressure, of one mole of that substance to such a large quantity of the system that its composition remains virtually unchanged. It is an intensive property and its value depends only on the composition at the given temperature and pressure. The subscript $n_{j \neq i}$ indicates that the number of moles of all components in the solution other than the number of moles of i are kept constant.

7.1.1 Physical Meaning of Partial Molar Properties

To understand the *physical meaning* of partial molar properties let us consider the partial molar volume, the simplest partial molar property to visualise. It is the contribution that a component in the solution makes to the total volume. Consider an open beaker containing a huge volume of water. Assume that one mole of water is added to it. The volume increases by 18×10^{-6} m^3, which is the molar volume of pure water. If the same amount of water is added to a large amount of pure ethanol taken in the beaker, the increase in volume will be approximately 14×10^{-6} m^3, which is the partial molar volume of water in pure ethanol. The difference in the increase in volumes can be explained thus: the volume occupied by a given number of water molecules depends on the molecules surrounding them. When water is mixed with a large volume of alcohol, there is so much alcohol present that each water molecule is surrounded by pure ethanol. Consequently, the packing of the molecules would be different from that in pure water, and the molecules occupy lesser volume.

If one mole water is added to an equimolar mixture of alcohol and water, the increase in volume of the solution would be different from that resulted when the same quantity were added to pure alcohol. The partial molar properties of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes. The intermolecular forces also get changed resulting in the changes in the thermodynamic properties of solutions with compositions. The variation of partial molar volumes with concentration is shown in Fig. 7.1 for ethanol (E) – water (W) system.

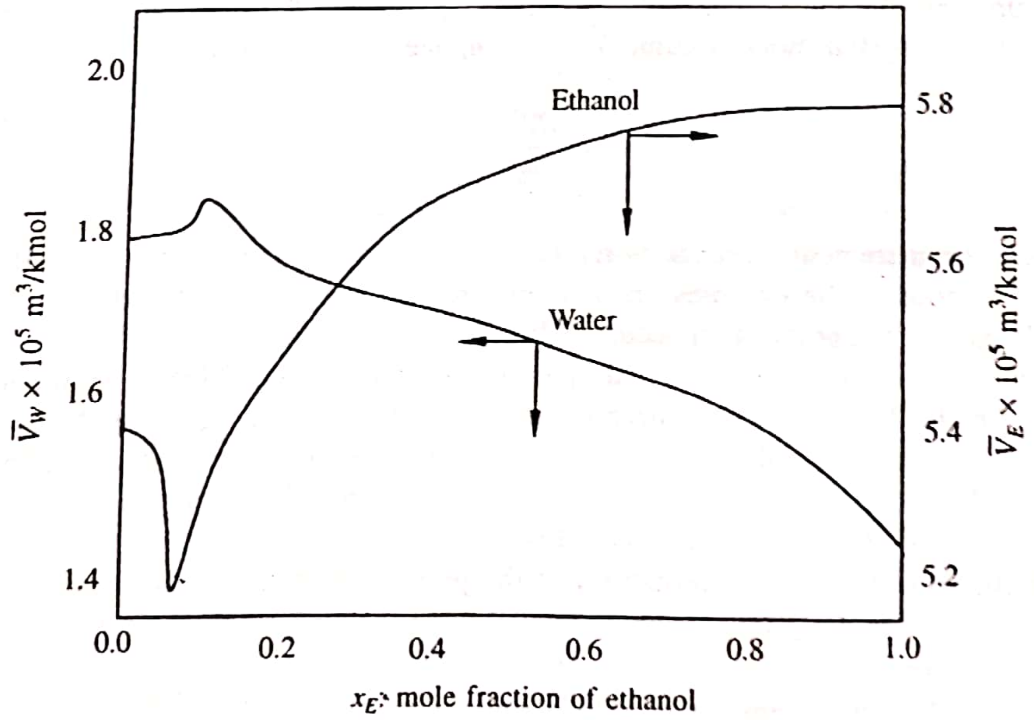

Fig. 7.1 Partial molar volumes in alcohol-water mixture.

We have seen that the effective molar volume of water added to the ethanol–water solution, i.e. the partial molar volume $\overline{V}_W$ in the solution is less than the molar volume V_W of pure water at the same temperature and pressure. To be specific, when pure water is added to an ethanol water solution of volume V^t and allowed sufficient time for heat exchange so that temperature remains the same as that before addition, the increase in volume of the solution $\Delta V^t \neq \Delta n_W V_W$, where Δn_W is the moles of water added. The increase in volume is given by

$$\Delta V^t = \Delta n_W \overline{V}_W \tag{7.2}$$

Equation (7.2) can be written as

$$\overline{V}_W = \frac{\Delta V^t}{\Delta n_W} \tag{7.3}$$

In this process, a finite drop of water was added which may cause a finite change in composition. If $\overline{V}_W$ were to represent a property of the solution, it must be based on data for the solution at this composition. For an infinitesimal amount of water added, Eq. (7.3) becomes

$$\overline{V}_W = \lim_{\Delta n_W \to 0} \frac{\Delta V^t}{\Delta n_W} = \left(\frac{\partial V^t}{\partial n_W}\right)$$

Since temperature, pressure and number of moles of alcohol are kept constant during addition of water,

$$\overline{V}_W = \left(\frac{\partial V^t}{\partial n_W}\right)_{T,P,n_E} \tag{7.4}$$

where n_E represents the number of moles of alcohol present in the solution.

In general, the partial molar volume $\overline{V}_i$ of component i is defined as

$$\overline{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{7.5}$$

and it denotes the incremental change in mixture volume which occurs when a small quantity of component i is added at constant pressure and temperature. The amount of i added is so small that no detectable change in composition occurs. While the molar volume is always positive, the partial molar volume may even be negative. The partial molar volume of $MgSO_4$ in water at infinite dilution (i.e. in the limit of zero concentration) is -1.4×10^{-6} m^3/mol which means that the addition of one mole of $MgSO_4$ to a large volume of water results in a decrease in volume of 1.4×10^{-6} m^3. The contraction may be due to the breaking up and subsequent collapse of the open structure of water as the ions become hydrated.

Though different from molar properties of the pure components, to get a physical picture of the concept of partial molar properties, we can treat them as the molar properties of the components in solution. However, it is to be borne in mind that the components of a solution are intimately intermixed and cannot have individual properties of their own. The partial molar properties in fact, represent the contribution of individual components constituting the solution to the total solution property as described in the following section.

7.1.2 Partial Molar Properties and Properties of Solution

Consider any thermodynamic *extensive* property (such as volume, free energy, heat capacity, etc.) its value, for a homogeneous system, being completely determined by the temperature, pressure and the amounts of various constituents present. Let M be the molar property of a solution and M^t be the total property. Then, $M^t = nM$, where n is $n_1 + n_2 + n_3 + \cdots$. Here, $n_1, n_2, n_3, \ldots$ are the number of moles of the respective components 1, 2, 3, . . . of the system. The solution property is a function represented by

$$M^t = f(P, T, n_1, n_2, \ldots, n_i, \ldots) \tag{7.6}$$

If there is a small change in the pressure, temperature and the amounts of various constituents, then

$$dM^t = \left(\frac{\partial M^t}{\partial P}\right)_{T,N} dP + \left(\frac{\partial M^t}{\partial T}\right)_{P,N} dT + \left(\frac{\partial M^t}{\partial n_1}\right)_{P,T,n_2,\ldots} dn_1 + \cdots + \left(\frac{\partial M^t}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i + \cdots \tag{7.7}$$

The subscript N in the first two partial derivatives indicate that the number of moles is kept constant, and the subscript $n_{j\neq i}$ indicates that the number of moles of all components other than that of component i is kept constant.

At constant temperature and pressure, dP and dT are zero, so that Eq. (7.7) reduces to

$$dM^t = \sum_{i=1}^{n} \left(\frac{\partial M^t}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i \tag{7.8}$$

The partial derivatives appearing on the right-hand side are, by Eq. (7.1), the partial molar properties $\overline{M}_i$. That is, at constant temperature and pressure,

$$dM^t = \sum_{i=1}^{n} \overline{M}_i \, dn_i \tag{7.9}$$

It is evident that the partial molar properties $\overline{M}_i$ are not extensive properties, but are intensive properties of the solution. They depend, therefore, not upon the total amount of each constituent, but only upon the composition, or the relative amounts of the constituents. If we add several constituents simultaneously to a given solution at constant temperature and pressure, keeping the ratio of the various constituents constant, the partial molar properties are not changed. Then, the change in property

$$dM^t = \overline{M}_1 dn_1 + \overline{M}_2 dn_2 + \cdots = (\overline{M}_1 x_1 + \overline{M}_2 x_2 + \cdots)\, dn \tag{7.10}$$

where x_i represents mole fraction of component i in the solution. Integration of Eq. (7.10) yields

$$M^t = (\overline{M}_1 x_1 + \overline{M}_2 x_2 + \cdots)\, n = \overline{M}_1 n_1 + \overline{M}_2 n_2 + \cdots \tag{7.11}$$

Therefore, M^t, the total property of the solution, is the sum of the partial molar properties of the constituents each weighted according to its number of moles. That is,

$$M^t = \Sigma n_i \overline{M}_i \tag{7.12}$$

This equation along with Eq. (7.9), which can be written in the following form serves as the relationship between partial molar properties and total solution property.

$$dM^t = \Sigma \overline{M}_i dn_i \tag{7.13}$$

For one mole of the solution it can be easily shown (see Example 7.1) that

$$M = \Sigma x_i \overline{M}_i \tag{7.14}$$

$$dM = \Sigma \overline{M}_i dx_i \tag{7.15}$$

Thus the molar volume V of a solution made up of components 1, 2, . . . can be written as

$$V = x_1\overline{V}_1 + x_2\overline{V}_2 + \dots$$

We see that the partial molar property $\overline{M}_i$ of any constituent may be regarded as the contribution of one mole of that constituent to the total value of the property under the specified conditions. In other words, the partial molar properties may be treated exactly as though they represent the molar properties of the components in the solution.

EXAMPLE 7.1 Give an alternative derivation for Eqs. (7.12) and (7.14) starting from Eq. (7.9)

Solution Equation (7.9) gives

$$dM^t = \Sigma \overline{M}_i dn_i$$

Using $x_i n = n_i$, $d(x_i n) = n\,dx_i + x_i\,dn$ and $dM^t = d(nM) = n\,dM + M\,dn$, where M, as pointed out earlier, is the molar property. Equation (7.9) becomes

$$n\,dM + M\,dn = \Sigma\, \overline{M}_i(x_i\,dn + n\,dx_i)$$

On rearranging the above result, we get

$$(M - \Sigma \overline{M}_i x_i)\,dn = (\Sigma \overline{M}_i\,dx_i - dM)\,n$$

n represents the total amount of various constituents and dn the changes in the total number of moles. One is free to choose any value for n as well as dn. In short, n and dn can be independently changed. For all possible values of n and dn, the above equation is to be satisfied. This is possible only if the terms in brackets reduce to zero.

$$M - \Sigma\, x_i\overline{M}_i = 0 \quad \text{or} \quad M = \Sigma\, x_i\overline{M}_i \tag{7.14}$$

$$\Sigma\, \overline{M}_i\, dx_i - dM = 0 \quad \text{or} \quad dM = \Sigma\, \overline{M}_i\, dx_i \tag{7.15}$$

Multiplying Eq. (7.14) by n, we get

$$nM = M^t = \Sigma\, n_i\overline{M}_i \tag{7.12}$$

EXAMPLE 7.2 Will it be possible to prepare 0.1 m^3 of alcohol-water solution by mixing 0.03 m^3 alcohol with 0.07 m^3 pure water? If not possible, what volume should have been mixed in order to prepare a mixture of the same strength and of the required volume? Density of ethanol and water are 789 and 997 kg/m^3 respectively. The partial molar volumes of ethanol and water at the desired compositions are: Ethanol = 53.6×10^{-6} m^3/mol; water = 18×10^{-6} m^3/mol.

Solution Let us first find out the number of moles of ethanol and water mixed and their mole fractions in the resultant mixture.

Moles of ethanol in the solution = $(0.03 \times 789 \times 10^3)/46 = 514.57$ mol

Moles of water in the solution = $(0.07 \times 997 \times 10^3)/18 = 3877.22$ mol

Mole fraction of ethanol desired = $514.57/(514.57 + 3877.22) = 0.1172$

Mole fraction of water = $1 - 0.1172 = 0.8828$

Actual volume of solution is

$$514.57 \times 53.6 \times 10^{-6} + 3877.22 \times 18 \times 10^{-6} = (0.02758 + 0.06979) = 0.09737 \text{ m}^3$$

That is, by mixing 0.03 m^3 alcohol with 0.07 m^3 water, we would get only 0.09737 m^3 of solution. To prepare 0.1 m^3 of solution the volumes to be mixed are:

Ethanol = $(0.03/0.09737) \times 0.1 = 0.03081$ m^3 and Water = $(0.07/0.09737) \times 0.1 = 0.07189$ m^3

***EXAMPLE* 7.3** A 30 per cent by mole methanol-water solution is to be prepared. How many cubic metres of pure methanol (molar volume, 40.727×10^{-6} m^3/mol) and pure water (molar volume, 18.068×10^{-6} m^3/mol) are to be mixed to prepare 2 m^3 of the desired solution? The partial molar volumes of methanol and water in a 30 per cent solution are 38.632×10^{-6} m^3/mol and 17.765×10^{-6} m^3/mol, respectively.

Solution Molar volume of the desired solution is

$$V = x_1\bar{V}_1 + x_2\bar{V}_2 = (0.3 \times 38.632 \times 10^{-6} + 0.7 \times 17.765 \times 10^{-6}) = 24.0251 \times 10^{-6} \text{ m}^3\text{/mol}$$

Therefore, 2 m^3 of the desired solution contains

$$2/(24.0251 \times 10^{-6}) = 83.2463 \times 10^3 \text{ mol}$$

Number of moles of methanol in 2 m^3 of solution = $83.2463 \times 10^3 \times 0.3 = 24.9739 \times 10^3$ mol

Number of moles of water in 2 m^3 of solution = $83.2463 \times 10^3 \times 0.7 = 58.2724 \times 10^3$ mol

Volume of methanol to be taken = $24.9739 \times 10^3 \times 40.727 \times 10^{-6}$ m^3 = 1.0171 m^3

Volume of water to be taken = $58.2724 \times 10^3 \times 18.068 \times 10^{-6}$ m^3 = 1.0529 m^3

***EXAMPLE* 7.4** Laboratory alcohol containing 96% alcohol and 4% water is to be diluted to a solution containing 56% alcohol and 44% water. All percentages are on weight basis. The partial specific volumes are as follows: In 96% alcohol solution, $\bar{V}_W = 0.816 \times 10^{-3}$ m^3/kg, $\bar{V}_E = 1.273 \times 10^{-3}$ m^3/kg. In 56% alcohol solution, $\bar{V}_W = 0.953 \times 10^{-3}$ m^3/kg, $\bar{V}_E = 1.243 \times 10^{-3}$ m^3/kg. The density of water may be taken as 0.997×10^3 kg/m^3.

(a) How much water should be added to 2×10^{-3} m^3 of the laboratory alcohol?
(b) What is the volume of the dilute alcohol obtained?

Solution Basis: 2×10^{-3} m^3 laboratory alcohol.

$$1 \text{ kg laboratory alcohol} \equiv (0.96 \times 1.273 + 0.04 \times 0.816) \times 10^{-3} = 1.255 \times 10^{-3} \text{ m}^3$$

$$2 \times 10^{-3} \text{ m}^3 \text{ of laboratory alcohol} \equiv 2 \times 10^{-3}/(1.255 \times 10^{-3}) = 1.594 \text{ kg}$$

(a) Let the mass of water added be m kg. Taking an alcohol balance, we get

$$1.594 \times 0.96 = (m + 1.594)\ 0.56$$

Thus mass of water added is,

$$m = (1.594 \times 0.96)/0.56 - 1.594 = 1.1386 \text{ kg}$$

and volume of water added is

$$1.1386/(0.997 \times 10^3) = 1.142 \times 10^{-3} \text{ m}^3$$

(b)

$$\text{Mass of dilute alcohol obtained} = 1.594 + 1.1386 = 2.7326 \text{ kg}$$

$$\text{Specific volume of 56\% alcohol} = (0.56 \times 1.243 + 0.44 \times 0.953) \times 10^{-3} = 1.115 \times 10^{-3} \text{ m}^3\text{/kg}$$

Therefore,

$$\text{Volume of dilute alcohol obtained} = 1.115 \times 10^{-3} \times 2.7326 = 3.0468 \times 10^{-3} \text{ m}^3$$

7.1.3 Determination of Partial Molar Properties

Method 1 (Analytical). If the volume of a solution is known as a function of its composition, the partial molar volume of a constituent may be found by partial differentiation with respect to the amount of that constituent.

$$\bar{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{P,T,n_j}$$

Method 2 (Graphical). Let V^t, the volume of the solution containing a fixed amount of one of the constituents (say, n_1) is known for several values of the amount of other constituent (say, n_2). We may plot V^t against n_2. See Fig. 7.2. The slope of the tangent to the curve is $(\partial V^t/\partial n_2)_{P,T,n_1}$ which, by definition is $\bar{V}_2$, the partial molar volume of component 2. The volume of solution is assumed

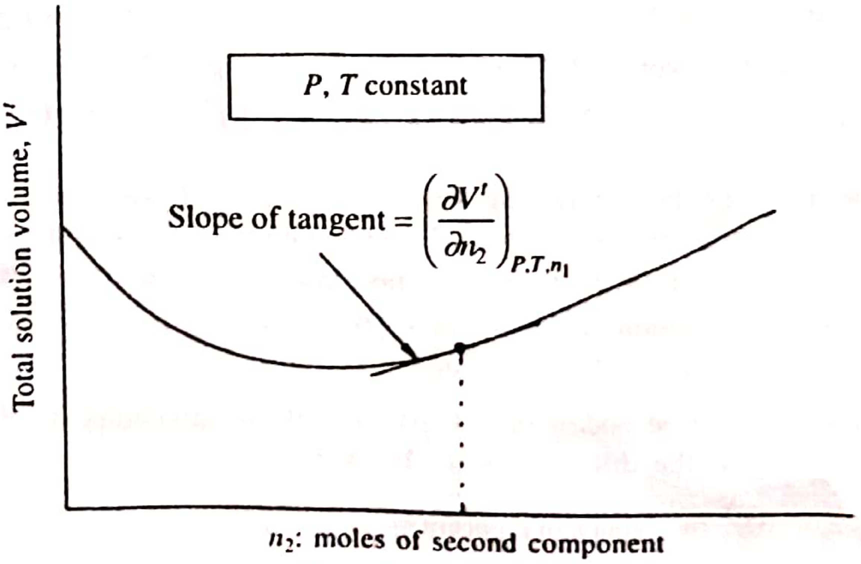

Fig. 7.2 Determination of partial molar properties by Method 2.

so large that no significant change in composition occurs when n_2 is changed. This method has limitation of not yielding values of $\overline{V_1}$ directly. Also, it is not advisable to use this method for determination of $\overline{V_2}$ when n_2 is large compared to n_1. The method of tangent intercepts is free from such limitations and is therefore preferred for the determination of partial molar properties.

***Method* 3 (*The tangent-intercept method*).** This is a graphical method widely used for the determination of partial molar properties of both components in a binary solution. The molar volume V is plotted against mole fraction of one of the components (say, x_2, the mole fraction of component 2). To determine the partial molar volumes, draw the tangent to the curve at the desired mole fraction. The intercept that this tangent makes with the vertical axis at $x_2 = 1$ gives $\overline{V_2}$ and the intercept on the vertical axis at $x_2 = 0$ (or $x_1 = 1$) gives $\overline{V_1}$. In Fig. 7.3, $BD = \overline{V_2}$ and $AC = \overline{V_1}$.

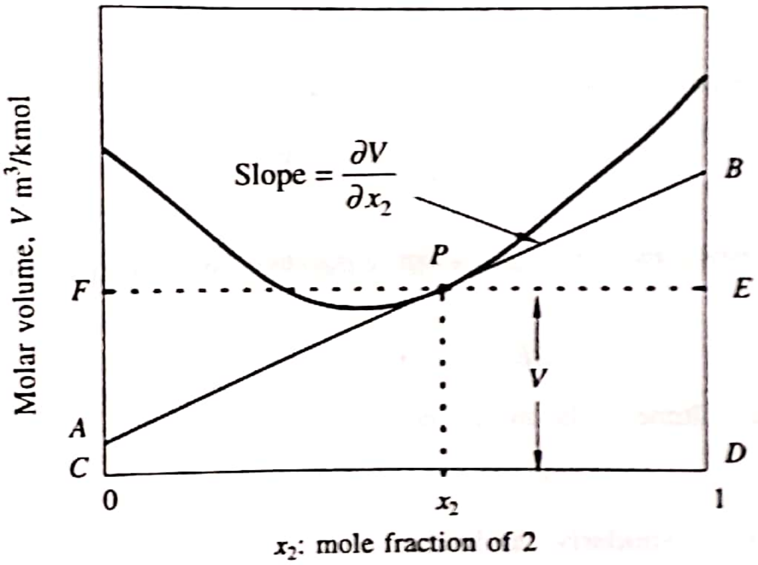

Fig. 7.3 The method of tangent-intercepts for the determination of partial molar properties.

To prove this result, consider a binary solution containing n_1 moles of component 1 and n_2 moles of component 2. Let the total volume be V^t and let V be the molar volume. Then

$$V^t = nV = (n_1 + n_2)\,V \tag{7.16}$$

Differentiating Eq. (7.16) with respect to n_1, keeping n_2, T and P constant

$$\left(\frac{\partial V^t}{\partial n_1}\right)_{T,P,n_2} = \overline{V_1} = V + (n_1 + n_2)\left(\frac{\partial V}{\partial n_1}\right)_{n_2} \tag{7.17}$$

The mole fraction x_2 is given by

$$x_2 = \frac{n_2}{n_1 + n_2} \tag{7.18}$$

Differentiating Eq. (7.18) with respect to n_1 keeping n_2 constant, we get

$$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = -\frac{n_2}{(n_1 + n_2)^2} = -\frac{x_2}{n_1 + n_2}$$

which can be rearranged as

$$\frac{n_1 + n_2}{dn_1} = -\frac{x_2}{dx_2} \tag{7.19}$$

Equation (7.19) can be substituted into Eq. (7.17) to yield the following:

$$\overline{V}_1 = V - x_2 \frac{\partial V}{\partial x_2} \tag{7.20}$$

Similarly it can be shown that

$$\overline{V}_2 = V - x_1 \frac{\partial V}{\partial x_1} \tag{7.21}$$

Since, for a binary solution, $x_1 = 1 - x_2$ and $dx_1 = -dx_2$, Eq. (7.21) can be put in another form:

$$\overline{V}_2 = V + (1 - x_2) \frac{\partial V}{\partial x_2} \tag{7.22}$$

In Fig. 7.3, the length $BD = BE + ED$, where BE is the slope of the tangent at P times the length PE. That is,

$$BE = (1 - x_2)\,(\partial V/\partial x_2)$$

and $ED = V$, the molar volume at the mole fraction x_2. Thus

$$BD = V + (1 - x_2)\,(\partial V/\partial x_2)$$

which, by Eq. (7.22) is $\overline{V}_2$. Similarly, the length

$$AC = FC - FA = V - x_2\,(\partial V/\partial x_2) = \overline{V}_1$$

The above methods are applicable for the determination of various other partial molar properties also. Of the various mixture properties, only the volume can be determined absolutely. For the determination of other properties like $\overline{G}_i, \overline{H}_i$, etc., it becomes necessary to work with property changes on mixing (discussed later in this chapter) like ΔG, ΔH, etc. The method of tangent intercept for the determination of, say $\overline{G}_1$ and $\overline{G}_2$, requires the plot of ΔG per mole versus x_2.

EXAMPLE 7.5 At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by $V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x - 2.64 \times 10^{-6}x^2$, where x is the mole fraction of benzene and V has the units of m^3/mol. Find expressions for the partial molar volumes of benzene and cyclohexane.

Solution The molar volume of the solution as a function of composition is given:

$$V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x_1 - 2.64 \times 10^{-6}x_1^2 \tag{7.23}$$

where x_1 = mole fraction of component 1 (in this case, benzene). By Eq. (7.20),

$$\overline{V}_1 = V - x_2 \frac{\partial V}{\partial x_2} \tag{7.24}$$

$$\overline{V_1} = V + (1 - x_1)\frac{\partial V}{\partial x_1} \tag{7.25}$$

Differentiating Eq. (7.23), we get

$$\frac{\partial V}{\partial x_1} = -16.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1$$

Substitute this in Eq. (7.25), we get

$$\overline{V_1} = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.64 \times 10^{-6} x_1^2 + (1 - x_1)(-16.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1)$$

$$= 92.6 \times 10^{-6} - 5.28 \times 10^{-6} x_1 + 2.64 \times 10^{-6} x_1^2$$

Using Eq. (7.21), $\overline{V_2}$ can be found out.

$$\overline{V_2} = V - x_1 \frac{\partial V}{\partial x_1}$$

$$\overline{V_2} = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.64 \times 10^{-6} x_1^2 - x_1(-16.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1)$$

$$= 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2$$

The partial molar volume of benzene:

$$\overline{V_1} = 92.6 \times 10^{-6} - 5.28 \times 10^{-6} x_1 + 2.64 \times 10^{-6} x_1^2$$

The partial molar volume of cyclohexane:

$$\overline{V_2} = 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2$$

EXAMPLE 7.6 The enthalpy at 300 K and 1 bar of a binary liquid mixture is

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where H is in J/mol. For the stated temperature and pressure, determine:

(a) Expressions for $\overline{H_1}$ and $\overline{H_2}$ in terms of x_1
(b) Numerical values for the pure component enthalpies H_1 and H_2
(c) Numerical values for the partial molar enthalpies at infinite dilution $\overline{H_1^\infty}$ and $\overline{H_2^\infty}$.

Solution The molar enthalpy of the solution as function of concentrations of the constituents is given:

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) \tag{7.26}$$

(a) Differentiating Eq. (7.26), we get

$$\frac{\partial H}{\partial x_1} = 400 + 600\frac{\partial x_2}{\partial x_1} + x_1x_2\left(40 + 20\frac{\partial x_2}{\partial x_1}\right) + (40x_1 + 20x_2)\left(x_1\frac{\partial x_2}{\partial x_1} + x_2\right)$$

Since $x_1 = 1 - x_2$, $dx_1 = -dx_2$ and $\partial x_2/\partial x_1 = -1$, the above equation simplifies to

$$\frac{\partial H}{\partial x_1} = 400 - 600 + x_1x_2(40 - 20) + (40x_1 + 20x_2)(x_2 - x_1) = -200 + 40x_1x_2 - 40x_1^2 + 20x_2^2$$

$$\overline{H}_1 = H + (1 - x_1)\frac{\partial H}{\partial x_1}$$

$$= 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) + (1 - x_1)(-200 + 40x_1x_2 - 40x_1^2 + 20x_2^2)$$

$$= 420 - 60x_1^2 + 40x_1^3 \qquad (7.27)$$

$$\overline{H}_2 = H - x_1\frac{\partial H}{\partial x_1}$$

$$= 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) - x_1(-200 + 40x_1x_2 - 40x_1^2 + 20x_2^2)$$

$$= 600 + 40x_1^3 \qquad (7.28)$$

(b) $H_1 = \overline{H}_1$ when $x_1 = 1$. Using Eq. (7.27), we get,

$$H_1 = 420 - 60 + 40 = 400 \text{ J/mol}$$

$H_2 = \overline{H}_2$ when $x_2 = 1$ or $x_1 = 0$. Using Eq. (7.28), $\overline{H}_2 = 600$ J/mol

[Alternatively, $H_1 = H$, when $x_1 = 1$, $x_2 = 0$. $H_1 = 400$ J/mol, using Eq. (7.25) $H_2 = H$, when $x_1 = 0$, $x_2 = 1 = 600$ J/mol using Eq. (7.23).]

(c) $\overline{H}_1^\infty = \overline{H}_1$ as $x_1 \to 0$ and $\overline{H}_2^\infty = \overline{H}_2$ as $x_2 \to 0$ (or $x_1 \to 1$)

Put $x_1 = 0$ in Eq. (7.27). $\overline{H}_1^\infty = 420$ J/mol

Put $x_1 = 1$ in Eq. (7.28). $\overline{H}_2^\infty = 640$ J/mol

EXAMPLE 7.7 The volume of an aqueous solution of NaCl at 298 K was measured for a series of molalities (moles of solute per kg of solvent) and it was found that the volume varies with molality according to the following expression.

$$V = 1.003 \times 10^{-3} + 0.1662 \times 10^{-4}m + 0.177 \times 10^{-5}m^{1.5} + 0.12 \times 10^{-6}m^2$$

where m is the molality and V is in m^3. Calculate the partial molar volumes of the components at $m = 0.1$ mol/kg.

Solution The partial molar volume of NaCl:

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} = \left(\frac{\partial V}{\partial m}\right)_{n_2}$$

$$V = 1.003 \times 10^{-3} + 0.1662 \times 10^{-4}m + 0.177 \times 10^{-5}m^{1.5} + 0.12 \times 10^{-6}m^2 \qquad (7.29)$$

Differentiating Eq. (7.29) with reference to m,

$$\overline{V}_1 = 0.1662 \times 10^{-4} + 0.177 \times 1.5 \times 10^{-5} m^{0.5} + 0.12 \times 2 \times 10^{-6} m$$

$$= 0.1662 \times 10^{-4} + 0.2655 \times 10^{-5} m^{0.5} + 0.24 \times 10^{-6} m$$

Substituting $m = 0.1$, this equation gives $\overline{V}_1 = 0.1748 \times 10^{-4}$ m³/mol. Substituting $m = 0.1$ in Eq. (7.29), $V = 1.0047 \times 10^{-3} m^3$. But,

$$V = n_1\overline{V}_1 + n_2\overline{V}_2 = m\overline{V}_1 + \frac{1000}{18}\overline{V}_2$$

Rearranging this equation and substituting the values, we find

$$\overline{V}_2 = (1.0047 \times 10^{-3} - 0.1 \times 0.1748 \times 10^{-4}) \times \frac{18}{1000} = 18.05 \times 10^{-6} \text{ m}^3\text{/mol}$$

Partial molar volume of water = 18.05×10^{-6} m³/mol
Partial molar volume of NaCl = 17.48×10^{-6} m³/mol

7.2 CHEMICAL POTENTIAL

The *chemical potential*, denoted by the symbol μ, is a widely used thermodynamic property. It is used as an index of chemical equilibrium in the same manner as temperature and pressure are used as indices of thermal and mechanical equilibrium. The chemical potential μ_i of component i in a solution is the same as its partial molar free energy in the solution, $\overline{G}_i$. That is, chemical potential of a component i in a solution can be defined as

$$\mu_i = \overline{G}_i = \left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_j} \tag{7.30}$$

The total free energy G^t of a solution is a function of pressure, temperature and number of moles of various components.

$$G^t = f(P, T, n_1, n_2, \ldots, n_i, \ldots) \tag{7.31}$$

The total differential dG^t is

$$dG^t = \left(\frac{\partial G^t}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G^t}{\partial T}\right)_{P,N} dT + \Sigma\left(\frac{\partial G^t}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i \tag{7.32}$$

Then using Eq. (7.30),

$$dG^t = \left(\frac{\partial G^t}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G^t}{\partial T}\right)_{P,N} dT + \Sigma\mu_i\, dn_i \tag{7.33}$$

We have shown that for a closed system, when there is no change in the amount of various constituents,

$$dG = V\,dP - S\,dT \tag{6.18}$$

Considering the total properties of the system,

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

from which, it follows that

$$\left(\frac{\partial G^t}{\partial T}\right)_{P,N} = -S^t, \quad \left(\frac{\partial G^t}{\partial P}\right)_{T,N} = V^t \tag{7.34}$$

Equation (7.33) can be written as

$$\boxed{dG^t = V^t\,dP - S^t\,dT + \Sigma\mu_i\,dn_i} \tag{7.35}$$

This is the fundamental relationship for changes in the free energy of a solution. At constant temperature and pressure, the change in the free energy is due entirely to the changes in the number of moles and is given by

$$\boxed{dG^t_{T,P} = \Sigma\mu_i\,dn_i} \tag{7.36}$$

By reasoning analogous to that used in the derivation of Eq. (7.12), we have, at constant temperature and pressure,

$$G^t = \Sigma\,\mu_i n_i$$

For a binary solution, the molar free energy of the solution is

$$G = x_1\mu_1 + x_2\mu_2$$

The chemical potential of a component is thus seen to be the contribution of that component to the Gibbs free energy of the solution. The chemical potential is an important property of solution extensively used in the study of phase and chemical equilibria.

7.2.1 Effect of Temperature and Pressure on Chemical Potential

Effect of temperature. Consider Eqs. (7.30) and (7.34). Differentiate Eq. (7.30) with respect to temperature. Then

$$\left[\frac{\partial\mu_i}{\partial T}\right]_{P,N} = \frac{\partial^2 G^t}{\partial T\,\partial n_i} \tag{7.37}$$

Differentiating Eq. (7.34) with respect to n_i, we get

$$-\left[\frac{\partial S^t}{\partial n_i}\right]_{P,T,n_j} = \frac{\partial^2 G^t}{\partial n_i\,\partial T} \tag{7.38}$$

Equations (7.37) and (7.38) imply that

$$\left[\frac{\partial\mu_i}{\partial T}\right]_{P,N} = -\left[\frac{\partial S^t}{\partial n_i}\right]_{P,T,n_j} = -\bar{S}_i \tag{7.39}$$

where $\overline{S}_i$ is the partial molar entropy of the component i in the solution. This result, though gives the variation of chemical potential with temperature, can be put in a more useful form [compare with Eq. (6.73)] as follows: Since

$$G = H - TS, \quad \overline{G}_i = \overline{H}_i - T\overline{S}_i, \quad \mu_i = \overline{H}_i - T\overline{S}_i$$

we can write

$$-\overline{S}_i = \frac{\mu_i - \overline{H}_i}{T} \tag{7.40}$$

We know that

$$\left[\frac{\partial(\mu_i/T)}{\partial T}\right]_{P,N} = \frac{T(\partial\mu_i/\partial T) - \mu_i}{T^2}$$

Substituting Eqs. (7.39) and (7.40) into the above equation, we get,

$$\left[\frac{\partial(\mu_i/T)}{\partial T}\right]_{P,N} = -\frac{\overline{H}_i}{T^2} \tag{7.41}$$

Equation (7.41) predicts the effect of temperature on chemical potential.

✓ **Effect of pressure.** Equations (7.30) and (7.34) are further differentiated to develop equations that predict the effect of pressure on chemical potential. Differentiating Eq. (7.30) with respect to pressure, we obtain

$$\left[\frac{\partial\mu_i}{\partial P}\right]_{T,N} = \frac{\partial^2 G^t}{\partial P\,\partial n_i} \tag{7.42}$$

Differentiating Eq. (7.34) with respect to n_i,

$$\frac{\partial^2 G^t}{\partial n_i\,\partial P} = \left[\frac{\partial V^t}{\partial n_i}\right]_{P,T,n_{j\neq i}} = \overline{V}_i \tag{7.43}$$

Compare Eq. (7.42) with Eq. (7.43)

$$\left(\frac{\partial\mu_i}{\partial P}\right)_{T,N} = \overline{V}_i \tag{7.44}$$

The rate of change of chemical potential with pressure is thus equal to the partial molar volume of the constituent.

***EXAMPLE* 7.8** Prove the alternative definition of chemical potential that $\mu_i = (\partial U/\partial n_i)_{S,V,n_j}$.

Solution The internal energy of a system may be expressed as a function of thermodynamic state and moles of the components like the Gibb's free energy. For the present purpose, it is convenient to express it as

$$U^t = f(S^t, V^t, n_1, n_2, \ldots, n_i, \ldots)$$

which gives

$$dU^t = \left(\frac{\partial U^t}{\partial S^t}\right)_{V,N} dS^t + \left(\frac{\partial U^t}{\partial V^t}\right)_{S,N} dV^t + \Sigma\left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i \tag{7.45}$$

Since $dU = T\,dS - P\,dV$ for a closed system,

$$\left(\frac{\partial U^t}{\partial S^t}\right)_{V,N} = T; \quad \left(\frac{\partial U^t}{\partial V^t}\right)_{S,N} = -P \tag{7.46}$$

Combining these with Eq. (7.45)

$$dU^t = T\,dS^t - P\,dV^t + \Sigma\left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i \tag{7.47}$$

But, we know that

$$G = H - TS = U + PV - TS$$

so that

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

The change in the total free energy at constant temperature and pressure is therefore,

$$dG^t_{T,P} = dU^t + P\,dV^t - T\,dS^t \tag{7.48}$$

Combining Eqs. (7.47) and (7.48)

$$dG^t_{T,P} = \Sigma\left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i \tag{7.49}$$

Compare Eq. (7.49) with Eq. (7.36). We now have

$$\Sigma \mu_i\,dn_i = \Sigma\left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i$$

Since dn_1, dn_2, etc., are independent of one another, it follows that

$$\boxed{\mu_i = \left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}}} \tag{7.50}$$

Equation (7.50) is an *alternative definition of chemical potential.* But it should be understood that $(\partial U^t/\partial n_i)_{S,V,n_{j\neq i}}$ is not partial molar internal energy, for it refers to constant entropy and volume and not to constant temperature and pressure. Partial molar internal energy is not equal to chemical potential.

$$\mu = \frac{[T, H]}{[P, H]} \tag{6.114}$$

Using Eq. (6.87),

$$[H, T] = T[S, T] + V[P, T]$$

$$[H, P] = T[S, P] + V[P, P] = T[S, P]$$

Substituting these in Eq. (6.114), we get

$$\mu = \frac{[H, T]}{[H, P]} = \frac{T[S, T] + V[P, T]}{T[S, P]} \tag{6.115}$$

Using Eqs. (6.90) and (6.91), Eq. (6.115) becomes

$$\mu = -\frac{T[V, P] + V[P, T]}{C_P[T, P]} = \frac{T(\partial V/\partial T)_P - V}{C_P} \tag{6.116}$$

Equation (6.116) may be rearranged as

$$C_P \mu = T\left(\frac{\partial V}{\partial T}\right)_P - V \tag{6.70}$$

6.6 FUGACITY

The concept of *fugacity* was introduced by G.N. Lewis (1901) and is widely used in solution thermodynamics to represent the behaviour of real gases. The name fugacity is derived from the Latin for 'fleetness' or the 'escaping tendency'. It has been used extensively in the study of phase and chemical reaction equilibria involving gases at high pressures. Though the 'fugacity' is mainly applied to mixtures, the present discussion is limited to pure gases.

For an infinitesimal reversible change occurring in the system under isothermal conditions, Eq. (6.18) reduces to

$$dG = V\,dP$$

For one mole of an ideal gas V in the above equation may be replaced by RT/P, so that

$$dG = RT\frac{dP}{P} = RT\,d(\ln P) \tag{6.117}$$

Equation (6.117) is applicable only to ideal gases. If, however, we represent the influence of pressure on Gibbs free energy of real gases by a similar relationship, then the true pressure in the above equation should be replaced by an 'effective' pressure, which we call fugacity f of the gas. The following equation, thus, provides the partial definition of fugacity.

$$\boxed{dG = RT\,d(\ln f)} \tag{6.118}$$

Equation (6.118) is satisfied by all gases whether ideal or real. Integration of this equation gives

$$G = RT \ln f + C \tag{6.119}$$

where C is a constant of integration that depends upon the temperature and nature of the gas. Fugacity has the same dimension as pressure, usually atmosphere or bar.

6.6.1 Standard State for Fugacity

Consider the molar free energies of a gas in two states both at the same temperature. Let G_1 and G_2 be the free energies and f_1 and f_2 be the corresponding fugacities in these states. By Eq. (6.119), the change in free energy is

$$\Delta G = G_2 - G_1 = RT \ln \frac{f_2}{f_1} \tag{6.120}$$

The free energy change can be experimentally measured and by the above equation the measured free energy change gives the ratio of fugacities f_2/f_1. The fugacity in any state can be evaluated if the fugacity is assigned a specific value in a particular reference state.

For an ideal gas integration of Eq. (6.117) gives the free energy change as

$$\Delta G = G_2 - G_1 = RT \ln \frac{P_2}{P_1} \tag{6.121}$$

Whereas Eq. (6.121) is applicable only to ideal gases, Eq. (6.120) is valid for all fluids, ideal or real. It follows that in the case of ideal gases, $f_2/f_1 = P_2/P_1$, or fugacity is directly proportional to pressure. The proportionality constant is chosen to be unity for convenience. That is, $f/P = 1$ or $f = P$, for ideal gases. The fugacity is always equal to the pressure for an ideal gas. However, for real gases, fugacity and pressure are not proportional to one another, and f/P is not constant. As the pressure of the gas is reduced, the behaviour of the real gas approaches that of an ideal gas. That is, at very low pressures, the fugacity of a real gas should be the same as its pressure. So the gas at a very low pressure P^0 is chosen as the reference state and it is postulated that the ratio of fugacity to pressure at this state is unity. Thus the definition of fugacity is completed by stating that

$$\boxed{\lim_{P \to 0} \frac{f}{P} = 1 \quad \text{or} \quad \frac{f}{P} \to 1 \quad \text{as } P \to 0} \tag{6.122}$$

Thus, the standard state of a real gas is a hypothetical state in which the gas is at a pressure P^0 where it behaves perfectly. By this choice, the standard state has the simple properties of an ideal gas. If the standard state were chosen as the one for which f is equal to say, 1 bar, the standard state of different gases would have different and complex properties. If the standard state chosen were the gas at zero pressure, the free energy would have become $-\infty$ at the standard state. The choice of the hypothetical standard state standardises the interaction between the particles by setting them to zero. Since all intermolecular forces are absent in the standard state chosen, the differences in the standard free energies of different gases arise solely from the internal structure and properties of the molecules, and not from the way they interact with each other.

Equation (6.122), which sets the fugacity of the real gas equal to its pressure at low pressures, permits the evaluation of absolute values for fugacities at various pressures. It is this property that makes fugacity a widely accepted thermodynamic property in practical calculations.

6.6.2 Fugacity Coefficient

The ratio of fugacity to pressure is referred to as *fugacity coefficient* and is denoted by ϕ. It is dimensionless and depends on nature of the gas, the pressure, and the temperature. Integrating Eq. (6.118) between pressures P and P^0,

$$G - G^0 = RT \ln \frac{f}{f^0} \tag{6.123}$$

Since $f^0 = P^0$ and $f = \phi P$, we can write the above equation as

$$G = G^0 + RT \ln \frac{P}{P^0} + RT \ln \phi \tag{6.124}$$

For ideal gases, by Eq. (6.120), $G = G^0 + RT \ln P/P^0$. Combining this result with Eq. (6.124) we see that the free energy of a real gas = free energy of an ideal gas + $RT \ln \phi$. The quantity $RT \ln \phi$, therefore, expresses the entire effect of intermolecular interaction.

Since all gases becomes ideal as pressure approaches zero, we can say that

$$f \to P \quad \text{as} \quad P \to 0$$

$$\phi \to 1 \quad \text{as} \quad P \to 0$$

6.6.3 Effect of Temperature and Pressure on Fugacity

In Eq. (6.123), G^0 and f^0 refer to the molar free energy and fugacity respectively at a very low pressure where the gas behaves ideally. This equation can be rearranged as

$$R \ln \frac{f}{f^0} = \frac{G}{T} - \frac{G^0}{T}$$

Differentiate this with respect to temperature at constant pressure.

$$R\left[\left(\frac{\partial \ln f}{\partial T}\right)_P - \left(\frac{\partial \ln f^0}{\partial T}\right)_P\right] = \left(\frac{\partial (G/T)}{\partial T}\right)_P - \left(\frac{\partial (G^0/T)}{\partial T}\right)_P$$

Substituting the Gibbs–Helmholtz equation, Eq. (6.73), into the above result and observing that f^0 is equal to the pressure and is independent of temperature, we get

$$\boxed{\left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{H^0 - H}{RT^2}} \tag{6.125}$$

H is the molar enthalpy of the gas at the given pressure and H^0 is the enthalpy at a very low pressure. $H^0 - H$ can be treated as the increase of enthalpy accompanying the expansion of the gas from pressure P to zero pressure at constant temperature. Equation (6.125) indicates the *effect of temperature on the fugacity*.

The effect of pressure on fugacity is evident from the defining equation for fugacity [Eq. (6.118)].

$$dG = V\,dP = RT\,d(\ln f) \tag{6.118}$$

which on rearrangement gives:

$$\boxed{\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}} \tag{6.126}$$

6.6.4 Determination of Fugacity of Pure Gases

Using compressibility factor, Z. The *compressibility factor* Z of a real gas is the ratio of its volume to the volume of an ideal gas at the same temperature and pressure.

$$Z = \frac{PV}{RT} \quad \text{or} \quad \frac{V}{RT} = \frac{Z}{P}$$

Introducing this in Eq. (6.126) and rearranging, the following result is obtained.

$$d(\ln f) = \frac{V}{RT}\,dP = \frac{Z}{P}\,dP$$

The above result, as such, is of not much use for the determination of fugacity, because as $P \to 0$, $Z/P \to \infty$. This difficulty can be overcome if we add and subtract dP/P on the right-hand side of the preceding equation.

$$d(\ln f) = \frac{dP}{P} + (Z-1)\frac{dP}{P} = d\,(\ln P) + (Z-1)\frac{dP}{P}$$

$$d\left(\ln \frac{f}{P}\right) = (Z-1)\frac{dP}{P}$$

When this is integrated between 0 and P we get

$$\boxed{\ln \frac{f}{P} = \int_0^P \left(\frac{Z-1}{P}\right) dP} \tag{6.127}$$

As $(Z-1)/P$ is finite as pressure approaches zero, there is no difficulty in using Eq. (6.127) for the evaluation of f. The values of the compressibility factor, Z, from zero pressure to pressure P are calculated from the volume of the gas at the corresponding pressures. The integral in Eq. (6.127) is found out graphically by plotting $(Z-1)/P$ against P.

EXAMPLE 6.21 Derive an expression for the fugacity coefficient of a gas obeying the equation of state $P(V-b) = RT$ and estimate the fugacity of ammonia at 10 bar and 298 K, given that $b = 3.707 \times 10^{-5}$ m^3/mol.

Solution Since, $P(V-b) = RT$, we have,

$$PV = RT + Pb, \qquad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

***EXAMPLE* 7.9** Show that for an ideal gas,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \frac{RT}{P}$$

Solution For a mixture of ideal gases,

$$V^t = (n_1 + n_2 + \ldots)\frac{RT}{P}$$

where n_1, n_2, etc., are the moles of various constituents. Differentiating this with respect to n_i, we get

$$\left(\frac{\partial V^t}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \overline{V}_i = \frac{RT}{P_i}$$

By Eq. (7.44),

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \overline{V}_i = \frac{RT}{P}$$

7.3 FUGACITY IN SOLUTIONS

The concept of fugacity was discussed in Chapter 6 with reference to pure substances. It was pointed out that *fugacity* is a useful concept in dealing with mixtures. For pure fluids, the definition of fugacity is provided by Eq. (6.118) and (6.122):

$$dG = RT\, d(\ln f)$$

$$\lim_{P\to 0}\frac{f}{P} = 1$$

The fugacity of a component i in a solution (gaseous, liquid or solid) is defined analogously by

$$d\mu_i = RT\, d(\ln \bar{f}_i) \tag{7.51}$$

$$\lim_{P\to 0}\frac{\bar{f}_i}{\bar{p}_i} = 1 \tag{7.52}$$

Here μ_i is the chemical potential, $\bar{f}_i$ the fugacity and $\bar{p}_i$ is the partial pressure of component i in the solution. For an ideal gas mixture, the fugacity of a component is equal to its partial pressure. All gaseous mixtures behave ideally on approaching zero pressure. The partial pressure is defined as product of total pressure and mole fraction of $i(y_i)$ in the mixture.

$$\bar{p}_i = y_i P \tag{7.53}$$

7.3.1 Fugacity in Gaseous Solutions

The fugacity of a component i in a gaseous solution is given by Eq. (7.51). Equation (7.44) gives the effect of pressure on chemical potential.

dG = VdP - SdT

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{V}_i$$

where $\overline{V}_i$ is the partial molar volume of the component in the solution. Rearranging this equation

$$d\mu_i = \overline{V}_i\, dP \tag{7.54}$$

Compare Eq. (7.54) with Eq. (7.51). We get

$$RT\, d\,(\ln \bar{f}_i) = \overline{V}_i\, dP \tag{7.55}$$

$$d\,(\ln \bar{f}_i) = \frac{\overline{V}_i}{RT}\, dP$$

Subtracting $d(\ln \bar{p}_i)$, where $\bar{p}_i$ is the partial pressure of component i in the gas mixture, from both sides,

$$d\left(\ln \frac{\bar{f}_i}{\bar{p}_i}\right) = \frac{1}{RT}\,[\overline{V}_i\, dP - RT\, d\,(\ln \bar{p}_i)] \tag{7.56}$$

Since $\bar{p}_i = y_i P$, where y_i is the mole fraction,

$$d(\ln \bar{p}_i) = d(\ln P) + d(\ln y_i)$$

At constant composition, $d(\ln y_i) = 0$, so that the above equation reduces to

$$d(\ln \bar{p}_i) = d(\ln P) = \frac{dP}{P}$$

Substituting this in Eq. (7.56) we obtain,

$$d\left(\ln \frac{\bar{f}_i}{\bar{p}_i}\right) = \frac{1}{RT}\left(\overline{V}_i - \frac{RT}{P}\right) dP$$

As $P \to 0$, $\bar{f}_i = \bar{p}_i$, and the above equation can be readily integrated to give

$$\boxed{\left(\ln \frac{\bar{f}_i}{\bar{p}_i}\right) = \ln \bar{\phi}_i = \frac{1}{RT}\int_0^P \left(\overline{V}_i - \frac{RT}{P}\right) dP} \tag{7.57}$$

where $\bar{\phi}_i$ denotes the *fugacity coefficient* of a component in solution.

$$\bar{\phi}_i = \frac{\bar{f}_i}{\bar{p}_i} = \frac{\bar{f}_i}{y_i P} \tag{7.58}$$

For a mixture of ideal gases, we have the following simple equation of state:

$$PV^t = (n_1 + n_2 + n_3 + \cdots)\, RT$$

$$\boxed{\overline{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{T,P,n_j} = \frac{RT}{P}}$$

Substituting this into Eq. (7.57), it follows that

$$\bar{f}_i = \bar{p}_i = y_i P \tag{7.59}$$

which states that the fugacity of a component in a mixture of ideal gases is equal to the partial pressure of that component in the mixture. However, this is not true for real gases. Equation (7.57) provides the means for computing fugacities in the real gaseous solution. But this requires the evaluation of $\overline{V}_i$ as a function of pressure, which in turn requires the knowledge of how the solution volume varies with composition at each pressure. These types of data are rarely available, and hence rigorous calculation of fugacities in gaseous mixtures using Eq. (7.57) is rarely done.

7.3.2 Lewis–Randall Rule

As the calculation of fugacity in a mixture of gases through the general equation [Eq. (7.57)] is very difficult, we devise a model for mixtures known as the *ideal solution model* the fugacity of which can be easily evaluated. The fugacity in actual solution is then determined by taking into account the deviation of the actual solution from this ideal model behaviour. As an ideal gaseous solution we can consider a gas mixture formed without any volume change on mixing the components. A gas mixture that follows the Amagat's law is an ideal gaseous solution. For such solutions, the volume of the mixture is a linear function of the mole numbers at a fixed temperature and pressure. That is,

$$V^t = \Sigma\, n_i V_i \quad \text{(Amagat's Law)} \tag{7.60}$$

where V_i is the molar volume of pure i at the same temperature and pressure. For such ideal solutions,

$$\overline{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{T,P,n_j} = V_i \tag{7.61}$$

Note that the right-hand side of Eq. (7.57) reduces to the same result as that given by Eq. (6.128) where the residual volume for the pure component is given by $\alpha = V_i - RT/P$. That is, for pure components at a temperature T and pressure P,

$$\ln\frac{f_i}{P} = \frac{1}{RT}\int_0^P \left(V_i - \frac{RT}{P}\right) dP \tag{7.62}$$

and for component i in a gas mixture at the same temperature and pressure,

$$\ln\frac{\bar{f}_i}{\bar{p}_i} = \frac{1}{RT}\int_0^P \left(\overline{V}_i - \frac{RT}{P}\right) dP \tag{7.63}$$

Subtracting Eq. (7.62) from Eq. (7.63),

$$\ln \frac{\bar{f}_i P}{f_i \bar{p}_i} = \frac{1}{RT}\int_0^P (\bar{V}_i - V_i)\, dP \qquad (7.64)$$

Since $\bar{p}_i = y_i P$, we can simplify the above equation to the following form:

$$\ln \frac{\bar{f}_i}{y_i f_i} = \frac{1}{RT}\int_0^P (\bar{V}_i - V_i)\, dP$$

On substitution of Eq. (7.61), in the preceding equation, we get,

$$\ln \frac{\bar{f}_i}{y_i f_i} = 0 \quad \text{or} \quad \boxed{\bar{f}_i = y_i f_i} \quad \text{(Lewis-Randall rule)} \qquad (7.65)$$

which is commonly known as *Lewis–Randall* rule or *Lewis fugacity rule*. It states that fugacity of a component in an ideal solution is directly proportional to the mole fraction of the component in the solution. In Eq. (7.65), $\bar{f}_i$ is the fugacity of the species *i* in an ideal gaseous solution, and f_i is the fugacity of pure *i* evaluated at the temperature and pressure of the mixture. Thus, we have now, $\boxed{\bar{f}_i = y_i f_i \text{ for ideal gaseous solution}}$ and, $\boxed{\bar{f}_i = \bar{p}_i = y_i P \text{ for ideal (perfect) gases.}}$

For a gas mixture to behave as an ideal solution, it requires only that the molar volume in the pure state and the partial molar volume in the solution be the same, or $\bar{V}_i = V_i$. For the mixture to be an ideal gas it requires that $\bar{V}_i = V_i = RT/P$, which means that the molar volumes of all the components are the same whether in the mixture or in the pure state. For ideal solutions, the volumes of components may differ from one another. In short, the concept of an ideal gaseous solution is less restrictive than that of a mixture of ideal gases.

The Lewis–Randall rule is a simple equation and is therefore widely used for evaluating fugacities of components in gas mixtures. It allows the fugacity of a component in the mixture to be calculated without any information about the solution except its composition. However, it is not reliable because of the severe simplification inherent in Amagat's law of additive volumes. But at high pressures it is often a very good assumption, because, at liquid like densities, fluids tend to mix with little or no change in volume (J.M. Prausnitz et al., 1986). Lewis fugacity rule is valid for systems where the intermolecular forces in the mixture are similar to those in the pure state. Thus, it can be said that this rule is valid

1. At low pressures when the gas phase behaves ideally
2. At any pressure if the component is present in excess
3. If the physical properties of the components are nearly the same
4. At moderate and high pressures, the Lewis–Randall rule will give incorrect results if the molecular properties of the components are widely different and the component under consideration is not present in excess.

7.3.3 Fugacities in Liquid Solutions

Calculation of fugacity of a component in a liquid solution using Eq. (7.57) is not practical because the volumetric data at constant temperature and composition are rarely available. These data are required for the integration over the entire range of pressures from the ideal gas state to the pressure of the solution including the two-phase region. For calculation of fugacities in liquid solutions, another approach is used. We define an ideal solution whose fugacity can be easily calculated knowing its composition and measure the departure from ideal behaviour for the real solution. A quantitative measure of the deviation from ideality is provided by the function known as the *activity coefficient* which will be discussed in Section 7.6.

7.3.4 Ideal Solutions and Raoult's Law

A solution in which the partial molar volumes of the components are the same as their molar volumes in the pure state is called an *ideal solution*. There is no volume change when the components are mixed together to form an ideal solution. That is, for an ideal solution $V = \sum x_i \bar{V}_i = \sum x_i V_i$, where V is the molar volume of the solution, V_i and $\bar{V}_i$ are the molar volume and partial molar volume respectively of the component i, and x_i is the mole fraction of component i in the solution. If a mixture of two liquids is to behave ideally, theoretical considerations reveal that the two types of molecules must be similar. The environment of any molecule and hence the force acting on it is then not appreciably different from that existing in the pure state. We have shown that for ideal gaseous solutions, the Lewis–Randall rule is applicable which states that fugacity of each constituent is directly proportional to the number of moles of the constituent in the solution. The Lewis–Randall rule is applicable to ideal liquid solutions also. It can be written as

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

where $\bar{f}_i$ is the fugacity of component i in the solution, f_i is the fugacity of i in the pure state, and x_i is the mole fraction of component i in the solution.

While the ideal solution model is adequate for many gas mixtures for reasonable temperature and pressure, the same is not true for the case of liquid solutions. Very few solutions follow Eq. (7.66) over the entire composition range. Ideal liquid solution behaviour is often approximated by solutions comprised of molecules not too different in size and chemical nature. Thus a mixture of isomers (e.g. *ortho*-, *meta*- and *para*-xylene), adjacent members of homologous series of organic compounds (e.g. *n*-hexane and *n*-heptane, ethanol and propanol, benzene and toluene, ethyl bromide and ethyl iodide) etc., are expected to form ideal solutions.

Raoult's Law. The criterion of phase equilibria permit us to replace the liquid phase fugacities $\bar{f}_i$ and f_i with fugacities in the gas phase with which the liquid is in equilibrium. Thus, $\bar{f}_i^L = \bar{f}_i^V$ under equilibrium. Here superscripts V and L refer to the vapour phase and the liquid phase respectively. Thus, fugacity $\bar{f}_i$ in Eq. (7.66) is equal to the fugacity of constituent i in the vapour phase. If the vapour phase is assumed to be ideal gas, which is true if the pressure is not too high, the vapour phase fugacity $\bar{f}_i^V$ is the same as partial pressure $\bar{p}_i$ of component i in the vapour. If the liquid phase is pure i, the fugacity of pure i in the vapour phase can be replaced with the vapour pressure P_i^S. Under these conditions the Lewis–Randall rule, Eq. (7.66), becomes

$$\bar{p}_i = x_i P_i^S \quad \text{(Raoult's Law)} \tag{7.67}$$

This expression is known as Raoult's Law. This is a simplified form of the Lewis–Randall rule. Whereas the Lewis–Randall rule is obeyed by all ideal solutions, the Raoult's law is applicable to ideal solutions if the vapour phase with which it is in equilibrium is an ideal gas.

Raoult's law provides a very simple expression for calculating the fugacity of a component in the liquid mixture which is the same as the partial pressure of the component in the vapour.

It says that the partial pressure is directly proportional to the mole fraction in the liquid solution. Ideal solutions which conform to Raoult's law over the entire range of concentrations are rare. A frequently cited example for ideal solutions is mixtures of optical isomers of organic compounds. Raoult's law applies as fair approximation to mixtures of hydrocarbons showing a reasonable similarity in molecular structure such as are encountered in petroleum industry. In most other cases Raoult's law applies only over a limited concentration range.

7.4 HENRY'S LAW AND DILUTE SOLUTIONS

Solutions conforming to Raoult's law over the entire concentration range are rare as pointed out earlier. A solution, any of whose components does not obey Raoult's law is designated as *non-ideal solution*. Even non-ideal solutions exhibit a common form of ideal behaviour over a limited concentration range where the fugacity $\bar{f}_i$ (or, the partial pressure $\bar{P}_i$) is directly proportional to the concentration in the liquid. This behaviour is exhibited by the constituent as its mole fraction approaches zero, and is generalised by *Henry's law*.

$$\bar{f}_i = x_i K_i \tag{7.68}$$

$$\bar{P}_i = x_i K_i \tag{7.69}$$

Often, the solute portion of the non-ideal liquid solution can be assumed to follow Henry's law. $\bar{P}_i$ is the partial pressure of the solute over the solution, x_i is its mole fraction in the solution and K_i is a proportionality constant known as Henry's law constant. K_i may be greater or less than P_i^S, the vapour pressure of the solute at the temperature and total pressure in question. When K_i and P_i^S are equal, Henry's law and Raoult's law are identical. Henry's law may be thought of as a general rule of which Raoult's law is a special case. Henry's law is obeyed in all solutions by the solute at extremely low concentrations. Essentially all liquids will obey Henry's law close to mole fraction zero, but many will deviate from the law above 0.01–0.02 mole fraction. And almost all liquids deviate above 0.1 mole fraction. But in some exceptional cases, Henry's law is found to be obeyed quite well up to $x_i = 0.5$.

For ideal solutions, the partial fugacity (or partial pressure) of a component is proportional to its mole fraction. For a real solution it has been found experimentally that as the mole fraction of the component approaches unity, its fugacity approximates to the value for an ideal solution, though at lower mole fractions, the behaviour departs markedly from ideal behaviour.

In Fig. 7.4, the fugacity curve becomes asymptotic to the straight line showing ideal behaviour as mole fraction approaches unity. In a dilute solution, the component present in larger proportions designated as solvent, obeys Raoult's law even though it may depart from ideal solution behaviour in a more concentrated solution. As the mole fraction of the solute—the component present in smaller proportions—approaches zero, it will conform to the ideal behaviour predicted by Henry's law. Thus, we can generalise by saying that *the solute in a dilute solution obeys Henry's law and the solvent obeys Raoult's law*. It can be shown that over the range of compositions where the solvent obeys Raoult's law, the solute obeys Henry's law (see Example 7.15).

7.4.1 Ideal Behaviour of Real Solutions

The ideal behaviour exhibited by non-ideal solutions can be summarised by the following mathematical statements.

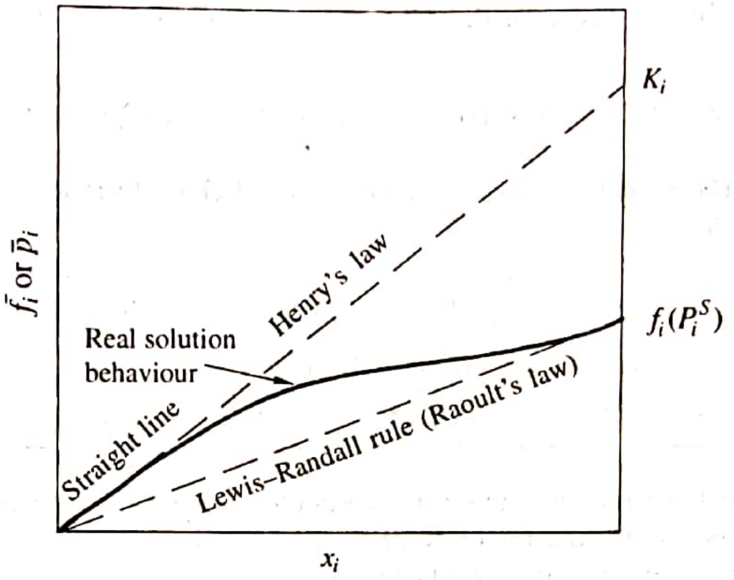

Fig. 7.4 Fugacity (partial pressure) versus concentration of real solutions.

$$\lim_{x_i \to 1} \frac{\bar{f}_i}{x_i} = f_i \qquad \text{[Lewis–Randall rule]} \tag{7.70}$$

$$\lim_{x_i \to 0} \frac{\bar{f}_i}{x_i} = K_i \qquad \text{[Henry's law]} \tag{7.71}$$

7.4.2 Henry's Law and Gas Solubility

Since the solubility of the gases in liquids is usually very low, the mole fraction of a gas in a saturated liquid solution is very small. The solute gas obeys Henry's law and therefore its fugacity (or the partial pressure) would be directly proportional to its mole fraction, the proportionality constant being the Henry's law constant [Eq. (7.69)]. In other words, the mole fraction or the solubility of the gas in the liquid is proportional to the partial pressure of the gas over the liquid as given by

$$x_i = \frac{\bar{p}_i}{K_i} \tag{7.72}$$

where K_i is the Henry's law constant.

***EXAMPLE* 7.10** The Henry's law constant for oxygen in water at 298 K is 4.4×10^4 bar. Estimate the solubility of oxygen in water at 298 K for a partial pressure of oxygen at 0.25 bar.

Solution Equation (7.72) gives the solubility of a gas in liquid in terms of its mole fraction. Substituting the values $K_i = 4.4 \times 10^4$ bar, and $\bar{p}_i = 0.25$ bar in Eq. (7.72) we get $x_i = 0.0568 \times 10^{-4}$. For very dilute solutions, we can write

$$x_{O_2} = \frac{\text{Moles of oxygen}}{\text{Moles of oxygen + moles of water}} \approx \frac{\text{Moles of oxygen}}{\text{Moles of water}}$$

Therefore, the solubility of oxygen is 0.0568×10^{-4} moles per mole of water. In mass units, it can be written as

$$0.0568 \times 10^{-4} \times 32 \times 1/18 = 0.101 \times 10^{-4} \text{ kg oxygen per kg water}$$

***EXAMPLE* 7.11** The partial pressure of acetone (A) and chloroform (B) were measured at 298 K and are reported below:

x_B	0	0.2	0.4	0.6	0.8	1.0
$\bar{p}_A$, bar	0.457	0.355	0.243	0.134	0.049	0
$\bar{p}_B$, bar	0	0.046	0.108	0.187	0.288	0.386

(a) Confirm that the mixture conforms to Raoult's law for the component present in excess and Henry's law for the minor component.

(b) Determine the Henry's law constants.

Solution The partial pressures are plotted against mole fraction x_A as shown in Fig. 7.5.

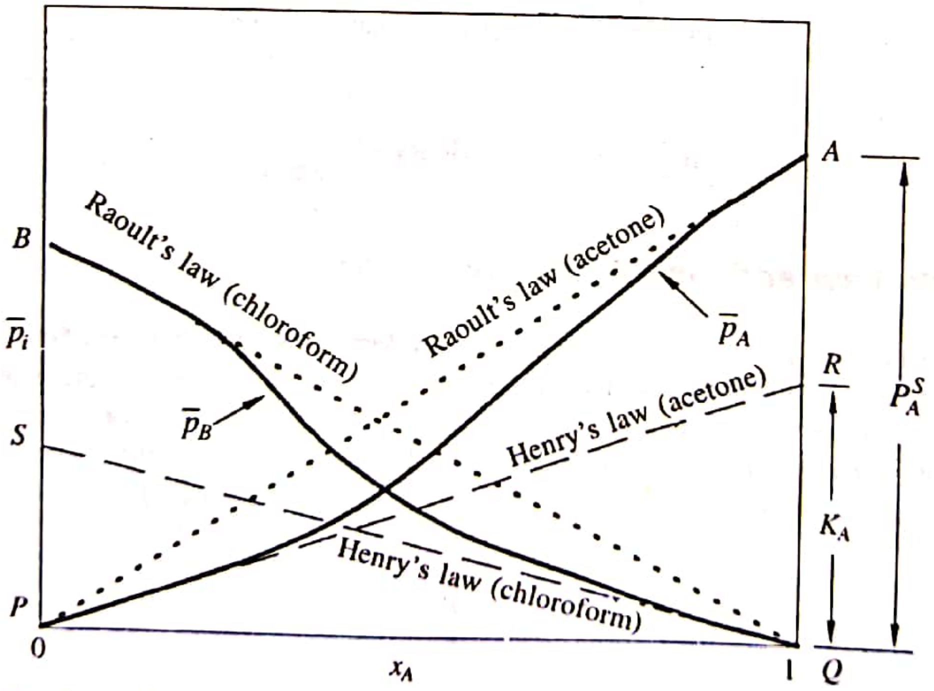

Fig. 7.5 Partial pressure versus mole fraction data for Example 7.11.

From the data given, it can be seen that $P_A^S = 0.457$ and $P_B^S = 0.386$ bar. The dotted line representing the ideal behaviour (Raoult's law) of component A is drawn by joining the origin and ($x = 1$, $p = 0.457$) by a straight line. Raoult's law for component B is also drawn. The dotted lines PA and QB represent the ideal behaviour. The Henry's law line PR is drawn tangential to the curve $\bar{p}_A$ versus x_A as x_A tends to 0 and the line QS is drawn tangential to the $\bar{p}_B$ versus x_A curve as x_A tends to 1.

(a) We see that the partial pressure curve for component A coincides with the Raoult's law line in the region where mole fraction of component A approaches unity and in this region, the partial pressure of component B coincides with the Henry's law line. Thus, in the region where Raoult's law is obeyed by A, Henry's law is obeyed by B, and vice versa.

(b) The slopes of the Henry's law line PR gives K_A, the Henry's law constant for A. $K_A = 0.23$ bar. Similarly slope of QS is K_B. $K_B = 0.217$ bar.

6.6.5 Fugacities of Solids and Liquids

Every solid or liquid has a definite vapour pressure although it may be immeasurably small, in some cases. At this pressure, the solid (or the liquid) will be in equilibrium with its vapour. When two phases of a substance are in thermodynamic equilibrium, the molar free energies in both phases should be equal. This follows from the criterion of phase equilibrium, which will be discussed in detail in Chapter 8. By this criterion the molar free energy of the liquid (or the solid) in equilibrium with its vapour is equal to the molar free energy of the vapour. That is, $G^L = G^V$ and $G^S = G^V$, where the superscripts L, S and V refer to liquid, solid and gas respectively. Since the molar free energy is related to the fugacity as $G = RT \ln f + C$, where C is constant that depends only on temperature, it follows that

$$f^L = f^V, \quad f^S = f^V \tag{6.143}$$

Equation (6.143) means that the fugacity of solid (or liquid) is equal to the fugacity of the vapour with which it is in equilibrium, provided that the reference state is taken to be the same in each case. If the vapour pressure is not very high, the fugacity of the vapour would be equal to the vapour pressure; hence, the fugacity of a liquid (or a solid) is approximately equal to its vapour pressure.

If the vapour pressure is very high and the vapour cannot be treated as ideal gas its fugacity is related to the saturation pressure as in Eq. (6.142)

$$f^{sat} = \frac{V{P^{S}}^{2}}{RT} \tag{6.142}$$

P^S is the saturation pressure of the gas and f^{sat} is the saturation fugacity. The latter should in turn be equal to the fugacity of solid or liquid at the desired temperature and the saturation pressure, by Eq. (6.143). Since, $RT\, d(\ln f) = V\, dP$ and the liquid can be assumed to be incompressible, the fugacity of the liquid at any other pressure P is readily obtained as

$$\ln \frac{f}{f^{sat}} = \frac{V}{RT}(P - P^S) \tag{6.144}$$

where V is the molar volume of the liquid.

EXAMPLE 6.28 Calculate the fugacity of liquid water at 303 K and 10 bar if the saturation pressure at 303 K is 4.241 kPa and the specific volume of liquid water at 303 K is 1.004×10^{-3} m^3/kg.

Solution The molar volume is

$$V = 1.004 \times 10^{-6} \times 18 = 18.072 \times 10^{-6} \text{ m}^3/\text{mol}$$

Assuming that the vapour behaves as an ideal gas, we have

$$P^S = 4.241 \text{ kPa} = 0.0424 \text{ bar} = f^{sat}$$

Using Eq. (6.144),

$$\ln \frac{f}{f^{sat}} = \frac{18.072 \times 10^{-6}}{8.314 \times 303}(10 - .0424) \times 10^5 = 7.1435 \times 10^{-3}$$

Therefore, $f = 0.0427$ bar.

EXAMPLE 6.29 Calculate the fugacity of *n*-butane in the liquid state at 350 K and 60 bar. The vapour pressure of *n*-butane at 350 K is 9.35 bar. The molar volume of saturated liquid at 350 K is 0.1072×10^{-3} m^3/mol. The fugacity coefficient for the saturated vapour at 350 K is 0.834.

Solution The fugacity of saturated vapour at 350 K = $0.834 \times 9.35 = 7.798$ bar. Therefore, fugacity of saturated liquid at 350 K = 7.798 bar = f^{sat}. Using Eq. (6.144),

$$\ln \frac{f}{f^{\text{sat}}} = \frac{0.1072 \times 10^{-3}}{8.314 \times 350}(60 - 9.35) \times 10^5 = 0.18659$$

Thus the fugacity of the liquid at 60 bar and 350 K, $f = 9.4$ bar.

6.7 ACTIVITY

The vapour pressures of relatively non-volatile solids and liquids may be extremely low, so, an experimental determination of their fugacity is impractical. When dealing with such substances, it would be convenient to work with another function called *activity* rather than with fugacity itself. 'Activity' is, in fact, relative fugacity and is defined as the ratio of fugacity to fugacity in the standard state. It finds wide application in the study of homogeneous chemical reaction equilibria involving solids and liquids. Activity is denoted by the letter *a*, where

$$a = \frac{f}{f^0} \tag{6.145}$$

The standard state at which fugacity is f^0 is chosen arbitrarily, but the temperature in the standard state is the same as the temperature in the given conditions. For gases, the standard state fugacity is chosen by convenience to be unity, and therefore, fugacity and activity are numerically equal.

The change in the free energy accompanying the process in which the substance is undergoing a change of state from the standard state to the given conditions is related to the activity of the substance as

$$\Delta G = RT \ln \frac{f}{f^0} = RT \ln a \tag{6.146}$$

Since $dG = V\,dP - S\,dT$, the change in the free energy when the substance is compressed isothermally is given by

$$\Delta G = \int V\,dP \tag{6.147}$$

Assuming that the substance is incompressible between the standard state pressure P^0 and the given pressure P, Eq. (6.147) can be integrated as

$$\Delta G = V(P - P^0) \tag{6.148}$$

The assumption of constant V is a good approximation and will not introduce much error for solids and liquids up to very high pressures, provided the temperature is well below the critical value. Comparison of Eqs. (6.146) and (6.148) shows that

$$\ln a = \frac{V}{RT}(P - P^0) \tag{6.149}$$

The concept of activity is particularly useful in the study of solutions. The commonly used standard states and their properties are discussed in detail in Chapter 7.

***EXAMPLE* 6.30** Determine the activity of solid magnesium (MW = 24.32) at 300 K and 10 bar if the reference state is 300 K and 1 bar. The density of magnesium at 300 K is 1.745×10^3 kg/m^3 and is assumed constant over this pressure range.

Solution Using Eq. (6.149), we obtain

$$\ln a = \frac{24.32 \times (10 - 1) \times 10^5}{1.745 \times 10^6 \times 8.314 \times 300} = 5.029 \times 10^{-3}$$

Therefore, $a = 1.00504$.

6.7.1 Effect of Pressure and Temperature on Activity

From Eq. (6.146) we see that,

$$\Delta G = G - G^0 = RT \ln a$$

$$R \ln a = \frac{G}{T} - \frac{G^0}{T} \tag{6.150}$$

Differentiating with respect to T at constant pressure,

$$R\left(\frac{\partial \ln a}{\partial T}\right)_P = \left(\frac{\partial (G/T)}{\partial T}\right)_P - \left(\frac{\partial (G^0/T)}{\partial T}\right)_P \tag{6.151}$$

Using Gibbs–Helmholtz equation [Eq. (6.73)] in the above equation, we see that

$$\left(\frac{\partial \ln a}{\partial T}\right)_P = \frac{H^0 - H}{RT^2} \tag{6.152}$$

Equation (6.152) predicts the effect of temperature on activity. Combining Eqs. (6.146) and (6.147) we get, for constant temperature,

$$RT\, d \ln a = V\, dP \tag{6.153}$$

$$\left(\frac{\partial \ln a}{\partial P}\right)_T = \frac{V}{RT} \tag{6.154}$$

Equation (6.154) predicts the effect of pressure on activity.

6.8 DEPARTURE FUNCTIONS AND GENERALISED CHARTS

The methods for the evaluation of thermodynamic properties from experimental *P-V-T* data or region, the partial pressure of component B coincides with the Henry's law line. Thus, in the region where Raoult's law is obeyed by A, Henry's law is obeyed by B, and vice versa.

(b) The slopes of the Henry's law line PR gives K_A, the Henry's law constant for A. $K_A = 0.23$ bar. Similarly slope of QS is K_B. $K_B = 0.217$ bar.

7.5 ACTIVITY IN SOLUTIONS

The activity with reference to pure substance was defined [see Eq. (6.145)] and the concept was discussed in Chapter 6. The *activity* of a component in a solution can be defined in a similar way. It is the ratio of fugacity of a component in the solution in a given condition to the fugacity of that component in the standard state. It is denoted by a_i.

$$a_i = \frac{\bar{f}_i}{f_i^0} \tag{7.73}$$

Since the fugacities are related to the chemical potential as

$$\mu_i = RT \ln \bar{f}_i + C, \qquad \mu_i^0 = RT \ln f_i^0 + C$$

it follows that

$$\Delta\mu_i = RT \ln \frac{\bar{f}_i}{f_i^0} = RT \ln a_i \tag{7.74}$$

$\Delta\mu_i = \mu_i - \mu_i^0$ is the increase in the chemical potential of species i when it is brought into solution from its standard state.

The concept of activity plays an important role in solution thermodynamics because activity can be related to compositions directly. For example, let the standard state for a substance be the pure component at the temperature and pressure of the solution. Then the activity of that component becomes equal to its mole fraction in the case of ideal solutions and is a strong function of mole fraction in the case of real solutions.

$$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{f_i}$$

For ideal solutions as $\bar{f}_i = x_i f_i$, the activity $a_i = x_i$. For real solutions, the activity can be shown to be equal to the product of activity coefficient and mole fraction. The activity coefficient is discussed later in this chapter.

The term activity is a ratio without dimensions. It is a widely used function in solution thermodynamics, particularly in dealing with property changes of mixing. The relationship between property change of mixing and activity is discussed later in this chapter.

7.5.1 Selection of Standard States

The numerical values of activity depend upon the choice of the standard state, this choice being based largely on experimental convenience and reproducibility. For all such standard states, the temperature is the same as the temperature of the solution under study and it is not a fixed value. Following are the commonly accepted standard states:

Gases. Two standard states are common:

1. The pure component gas in its ideal state at 1 bar. At this state, the fugacity is unity if expressed in bar. The activity becomes

$$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{1} = \bar{f}_i$$

   That is, the activity of a component in a mixture of gases is equal to its fugacity, numerically. If the mixture behaves as an ideal gas at the given conditions the activity and partial pressure are the same. This standard state is used in the study of chemical reaction equilibrium.

2. The pure component gas at the pressure of the system. With this choice the activity of each component in ideal gas solution becomes equal to its mole fraction.

$$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{f_i} = \frac{x_i f_i}{f_i} = x_i$$

   This standard state becomes hypothetical at temperatures where the total pressure exceeds the saturation pressure of the component gas in the pure state. Vapour–liquid equilibrium studies conventionally use this standard state.

Liquids. Two standard states are common for liquids also.

1. The pure component liquid at a pressure of 1 bar. This state is hypothetical if the vapour pressure of the pure liquid exceeds 1 bar.
2. The pure liquid at the pressure of the system. This state becomes hypothetical at temperatures above the critical or saturation temperature of the pure liquid. This standard state is used in vapour–liquid equilibrium studies.

Solids. The standard state chosen for solid is usually the pure component in the solid state at a pressure of 1 bar.

7.6 ACTIVITY COEFFICIENTS

We have already seen that the concept of ideal solution enables us to calculate the fugacity of a component in the liquid solution from the knowledge of its concentration in the solution and its fugacity in the pure state. The calculation of fugacity of a component in a real solution should take into account the degree of departure from ideal behaviour. *Activity coefficients* measure the extent to which the real solution departs from ideality. Activity coefficient of the component i in solution is denoted by γ_i and is defined by the following relationship.

$$\bar{f}_i = \gamma_i x_i f_i^0 \tag{7.75}$$

where f_i^0 is the fugacity in the standard state. For ideal solutions $\gamma_i = 1$, and we have

$$\bar{f}_i = x_i f_i^0 \tag{7.76}$$

which is same as the Lewis–Randall rule [Eq. (7.66)] with the pure liquid at the system pressure as the standard state.

Two types of ideal behaviour are observed; the first conforms to Lewis–Randall rule (or Raoult's law) in which case $f_i^0 = f_i$, the fugacity of the pure species at the system pressure and the second type conforms to an ideal dilute solution behaviour (the Henry's law), in which case $f_i^0 = K_i$, the Henry's law constant. Depending upon the standard states on which they are based, the activity coefficients can take different numerical values. For the standard state in the sense of Lewis–Randall rule or Raoult's law,

$$\bar{f}_i = \gamma_i x_i f_i \tag{7.77}$$

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i} = \frac{a_i}{x_i} \tag{7.78}$$

$$a_i = \gamma_i x_i \tag{7.79}$$

where a_i is the activity of i in the solution. Equation (7.77) is, in fact, Lewis fugacity rule modified by the factor γ_i to correct for deviation from ideality. This equation should reduce to Raoult's law as x approaches unity and to Henry's law as x approaches zero. For this to be possible, γ must equal unity as mole fraction approaches unity (Raoult's law region) and K_i/f_i, as mole fraction, approaches zero (Henry's law region). In terms of partial pressures, Eq. (7.77) may well be written as

$$\bar{p}_i = \gamma_i x_i P_i^S \tag{7.80}$$

If the hypothetical state, where the pure component fugacity = Henry's law constant, is chosen as the standard state, we get,

$$\bar{f}_i = \gamma_i' x_i K_i \tag{7.81}$$

$$\bar{p}_i = \gamma_i' x_i K_i \tag{7.82}$$

Then the activity coefficient approaches unity as x approaches zero. In Eqs. (7.81) and (7.82), γ_i' is the activity coefficient referred to infinite dilution.

When activity coefficients are defined with reference to an ideal solution in the sense of Raoult's law, then for each component i,

$$\gamma_i \to 1 \quad \text{as} \quad x_i \to 1$$

On the other hand, if activity coefficients are defined with reference to an ideal dilute solution, then

$$\gamma_1 \to 1 \quad \text{as} \quad x_1 \to 1 \quad \text{(solvent)}$$

$$\gamma_2' \to 1 \quad \text{as} \quad x_2 \to 0 \quad \text{(solute)}$$

Activity coefficients with reference to ideal dilute solution would be useful when dealing with liquid mixtures that cannot exist over the entire composition range as happens, for example, in a liquid mixture containing gaseous solute. If the critical temperature of the solute is lower than the temperature of the mixture, then a liquid phase cannot exist as $x_2 \rightarrow 1$, and the relations based on an ideal mixture in the sense of Raoult's law can be used only by introducing a hypothetical standard state for component 2. However, relations based on an ideal dilute solution eliminate this difficulty.

Activity coefficients are very strong functions of concentration of solution. The variation of γ with x over the entire range of composition is usually complex, but can often be roughly approximated in binary solutions by the empirical equations such as the one proposed by Porter:

$$\ln \gamma_1 = bx_2^2, \quad \ln \gamma_2 = bx_1^2$$

where b is an empirical constant. These relationships apply best when the components are not too dissimilar in structure and polarity.

7.6.1 Effect of Pressure on Activity Coefficients

The effect of pressure on fugacity was derived in Chapter 6 [Eq. (6.126)].

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_T = \frac{V_i}{RT}$$

Here f_i is the fugacity of pure i and V_i is its molar volume. In a similar way it can be shown that, $\bar{f}_i$, the fugacity of i in solution varies with pressure according to

$$\left(\frac{\partial \ln \bar{f}_i}{\partial P}\right)_T = \frac{\bar{V}_i}{RT} \tag{7.83}$$

Combining Eq. (6.126) with Eq. (7.83), we get

$$\left(\frac{\partial \ln \bar{f}_i / f_i}{\partial P}\right)_T = \frac{\bar{V}_i - V_i}{RT} \tag{7.84}$$

According to Eq. (7.77) $\bar{f}_i / f_i = \gamma_i x_i$, so that Eq. (7.84) can be written as

$$\left(\frac{\partial \ln \gamma_i x_i}{\partial P}\right)_T = \frac{\bar{V}_i - V_i}{RT} \tag{7.85}$$

As the mole fraction x_i is independent of pressure $(\partial \ln x_i / \partial P) = 0$, and hence

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T = \frac{\bar{V}_i - V_i}{RT} \tag{7.86}$$

The molar volumes $\bar{V}_i$ and V_i correspond to the particular phase under consideration. For liquid solutions, the effect of pressure on activity coefficients is negligible at pressures below atmospheric. For gaseous mixtures, activity coefficients are nearly unity at reduced pressures below 0.8.

7.6.2 Effect of Temperature on Activity Coefficients

The effect of temperature on fugacity of a pure substance was given by Eq. (6.125) as

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_P = \frac{H_i^0 - H_i}{RT^2}$$

Similarly, for the substance in the solution

$$\left(\frac{\partial \ln \bar{f}_i}{\partial T}\right)_P = \frac{H_i^0 - \bar{H}_i}{RT^2} \tag{7.87}$$

Combining the above two equations, and noting that $\bar{f}_i/f_i = \gamma_i x_i$, where x_i is independent of temperature,

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P = \frac{H_i - \bar{H}_i}{RT^2} \tag{7.88}$$

Equation (7.88) gives the effect of temperature on activity coefficients. The term $(\bar{H}_i - H_i)$ is the partial heat of mixing of component i from its pure state to the solution of given composition both in the same state of aggregation and pressure. For gaseous mixtures, this term is negligible at low pressures.

***EXAMPLE* 7.12** The partial pressures of acetone (A) and chloroform (B) were measured at 298 K and are reported below:

x_A	0	0.2	0.4	0.6	0.8	1.0
$\bar{p}_A$, bar	0	0.049	0.134	0.243	0.355	0.457
$\bar{p}_B$, bar	0.386	0.288	0.187	0.108	0.046	0

Calculate the activity and activity coefficient of chloroform in acetone at 298 K,

(a) Based on the standard state as per Lewis–Randall rule

(b) Based on Henry's law.

Solution The Henry's law constant was determined in Example 7.11. $K_B = 0.217$ bar. The vapour pressure of pure chloroform, $P_B^S = 0.386$ bar. The activity was defined by Eq. (7.73) and activity coefficient by Eq. (7.75). Combining these two we get,

$$a_i = \gamma_i x_i$$

Based on the Lewis–Randall rule, the activity,

$$a_i = \frac{\bar{p}_i}{P_i^S} \tag{7.89}$$

Based on the Henry's law, the activity,

$$a_i' = \frac{\bar{p}_i}{K_i} \tag{7.90}$$

The activity coefficient based on the Lewis–Randall rule is

$$\gamma_i = \frac{\bar{f}_i}{f_i^0 x_i} = \frac{a_i}{x_i} \tag{7.91}$$

The activity coefficient based on the Henry's law is

$$\gamma_i' = \frac{\bar{f}_i}{K_i x_i} = \frac{a_i'}{x_i} \tag{7.92}$$

The above equations are used to calculate the activity and activity coefficients for different concentrations. A sample calculation is provided below for the second set where

$$x_A = 0.2,\ x_B = 0.8,\ \bar{p}_A = 0.049 \text{ bar},\ \bar{p}_B = 0.288 \text{ bar},\ K_B = 0.217 \text{ bar},\ P_B^S = 0.386 \text{ bar}$$

(a) For the standard state referred to the Lewis–Randall rule:

$$a_B = \frac{\bar{p}_B}{P_B^S} = \frac{0.288}{0.386} = 0.75$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.75}{0.8} = 0.94$$

(b) For the standard state referred to the Henry's law:

$$a_B' = \frac{\bar{p}_B}{K_B} = \frac{0.288}{0.217} = 1.33$$

$$\gamma_B' = \frac{a_B'}{x_B} = \frac{1.33}{0.8} = 1.66$$

The above calculations are repeated for other concentrations and the results are given below:

x_B	0	0.2	0.4	0.6	0.8	1.0
a	0	0.12	0.28	0.48	0.75	1.0
a'	0	0.21	0.50	0.86	1.33	1.78
γ		0.60	0.70	0.80	0.94	1.0
γ'	1.0	1.05	1.25	1.43	1.66	1.78

***EXAMPLE* 7.13** The fugacity of component 1 in binary liquid mixture of components 1 and 2 at 298 K and 20 bar is given by

$$\bar{f}_1 = 50\,x_1 - 80\,x_1^2 + 40\,x_1^3$$

where $\bar{f}_1$ is in bar and x_1 is the mole fraction of component 1. Determine:

(a) The fugacity f_1 of pure component 1

(b) The fugacity coefficient ϕ_1

(c) The Henry's law constant K_1

(d) The activity coefficient γ_1.

Solution (a) When the mole fraction approaches unity, the fugacity of a component in the solution becomes equal to the fugacity of the pure component. That is,

$f_1 = \bar{f}_1$ when $x_1 = 1$. Therefore, $f_1 = 50 - 80 + 40 = 10$ bar

(b)

$$\phi_1 = f_1/P = 10/20 = 0.5$$

(c) By Eq. (7.71), the Henry's law constant is

$$K_1 = \lim_{x_1 \to 0} \frac{\bar{f}_1}{x_1} = \lim_{x_1 \to 0} (50 - 80\,x_1 + 40\,x_1^2) = 50 \text{ bar}$$

(d)

$$\gamma_1 = \frac{\bar{f}_1}{x_1 f_1} = \frac{50\,x_1 - 80\,x_1^2 + 40\,x_1^3}{10\,x_1} = 5 - 8\,x_1 + 4\,x_1^2$$

7.7 GIBBS–DUHEM EQUATIONS

In a mixture, the partial molar properties of the components are related to one another by one of the most useful equations in thermodynamics, the Gibbs–Duhem equations. It tells us how the partial molar properties change with compositions at constant temperature and pressure.

We have seen that at constant temperature and pressure, the property M^t of the solution is the sum of the partial molar properties of the constituents, each weighted according to the number of moles of the respective constituents.

$$M^t = \Sigma n_i \overline{M}_i \tag{7.12}$$

The total derivative dM^t gives the change in the property of the solution at constant T and P.

$$dM^t = \Sigma n_i d\overline{M}_i + \Sigma \overline{M}_i \, dn_i \tag{7.93}$$

where M is the molar value of the property of the solution M^t. But, since $M^t = f(T, P, n_1, n_2, \ldots)$, at constant T and P we have Eq. (7.13), which gives

$$dM^t = \Sigma \overline{M}_i \, dn_i \tag{7.13}$$

Comparing Eq. (7.93) with Eq. (7.13) we get the important result,

$$\Sigma n_i \, d\overline{M}_i = 0 \tag{7.94}$$

This result is the general form of the *Gibbs–Duhem equation*. If the property under consideration is the Gibbs free energy of the solution, then the above equation becomes

$$\Sigma \, n_i \, d\mu_i = 0 \tag{7.95}$$

Dividing throughout by n, the total number of moles in the solution, we get

$$\Sigma\, x_i\, d\mu_i = 0 \tag{7.96}$$

Here x_i is the mole fraction of component i in the solution and μ_i is the chemical potential of the component.

Other forms of Gibbs–Duhem equation. Consider a binary solution made up of components 1 and 2 whose mole fractions in the solution are x_1 and x_2 respectively. Equation (7.96) can be written as

$$x_1\, d\mu_1 + x_2\, d\mu_2 = 0 \tag{7.97}$$

where μ_1 and μ_2 are the chemical potentials of components 1 and 2 respectively. This can be rearranged as

$$x_1\, d\mu_1 = -\,x_2\, d\mu_2$$

Dividing by dx_1 and noting that $dx_1 = -\,dx_2$ in binary mixtures, the above result gives

$$\boxed{x_1 \frac{\partial \mu_1}{\partial x_1} = x_2 \frac{\partial \mu_2}{\partial x_2}} \tag{7.98}$$

Introducing the relationship between chemical potential and the fugacity [Eq. (7.51)] into the above, we get

$$\boxed{x_1 \frac{\partial \ln \bar{f}_1}{\partial x_1} = x_2 \frac{\partial \ln \bar{f}_2}{\partial x_2}} \tag{7.99}$$

Since activity $a_i = \bar{f}_i / f_i^0$, fugacities in Eq. (7.99) may be replaced in terms of activity as

$$x_1 \frac{\partial \ln (a_1 f_1^0)}{\partial x_1} = x_2 \frac{\partial \ln (a_2 f_2^0)}{\partial x_2}$$

Since f_i^0, the fugacity in the standard state, is independent of the composition of the solution,

$$\frac{\partial \ln (f_i^0)}{\partial x_i} = 0$$

Thus the Gibbs–Duhem equation in terms of activity is

$$\boxed{x_1 \frac{\partial \ln a_1}{\partial x_1} = x_2 \frac{\partial \ln a_2}{\partial x_2}} \tag{7.100}$$

By Eq. (7.79), $a_i = \gamma_i x_i$. Substitute this into Eq. (7.100) and thus the most important and widely used form of the Gibbs–Duhem equation, that involving the activity coefficients, is obtained.

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

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

The second terms on both sides of the above equation vanish, as they are equal to unity. Therefore,

$$\boxed{x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2}} \tag{7.101}$$

As the activity coefficients directly measure the departure from the ideal solution behaviour, Eq. (7.101) is the most useful form of the *Gibbs–Duhem equation.*

The various forms of Gibbs–Duhem equations are rigorous thermodynamic relations that are valid for conditions of constant temperature and pressure. They tell us that the partial molar properties of a mixture cannot change independently; in a binary mixture, if the partial molar property of one of the component increases, the partial molar properties of the other should decrease.

Gibbs–Duhem equations find wide applications in solution thermodynamics. These include:

(a) In the absence of complete experimental data on the properties of the solution, Gibbs–Duhem equations may be used to calculate additional properties. For example, if experimental data are available for the activity coefficient of one of the components in a binary solution over certain concentration range, the activity coefficient of the other component over the same composition range can be estimated using Gibbs–Duhem equations. This is particularly useful wherever the volatilities of the two components differ markedly. The measurements usually give the activity coefficient of the more volatile component whereas that of the less volatile component is calculated using Eq. (7.101). Thermodynamic properties of some high-boiling liquids (e.g. polymers) dissolved in a volatile liquid (say, benzene) can be computed by measuring the partial pressure of the latter in the solution.

(b) Thermodynamic consistency of experimental data can be tested using Gibbs–Duhem equations. If the data on the partial molar property of each component measured directly in experiments satisfy the Gibbs–Duhem equation, it is likely that they are reliable, but if they do not satisfy the Gibbs–Duhem equation, it is certain that they are incorrect.

(c) Gibbs–Duhem equations can be used for the calculation of partial pressure from isothermal total pressure data. Suppose that in an experimental investigation of vapour–liquid equilibrium, the total pressures are measured as a function of composition of one of the phases (usually the liquid phase) and the composition of the other phase is not measured. The Gibbs–Duhem equation facilitates the calculation of the composition of other phase thereby reducing the experimental work considerably.

(d) Partial pressure data can be obtained from isobaric boiling point data using Gibbs–Duhem equations. The isobaric *T-x* data can be easily converted to *x-y* data.

These equations find application in various other situations such as in the derivation of the relationship between Henry's law and Raoult's law for a real solution (see Example 7.15), in proving the essential criterion that the vapour and liquid compositions are the same for an azeotropic mixture (see Example 8.10) etc.

***EXAMPLE* 7.14** Show that in a binary solution, if the molar volume of one of the components increases with concentration, the molar volume of the other must decrease.

Solution When Eq. (7.94) is written for one mole of the solution with M replaced by V, we get

$$\Sigma\, x_i\, d\bar{V}_i = 0$$

For a binary solution,

$$x_1\, d\overline{V}_1 + x_2\, d\overline{V}_2 = 0$$

This is rearranged as

$$d\overline{V}_1 = -\frac{x_2}{x_1}\, d\overline{V}_2$$

It means that if $d\overline{V}_1$ is positive, $d\overline{V}_2$ must be negative. That is, if partial molar volume of component 1 increases the partial molar volume of component 2 must decrease.

EXAMPLE 7.15 Prove that if Henry's law is obeyed by component 1 in a binary solution over certain concentration range, Lewis–Randall rule (Raoult's law) will be obeyed by component 2 over the same concentration range.

Solution Equation (7.99) gives Gibbs–Duhem equations in terms of fugacities

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

Since $dx_2 = -dx_1$, Eq. (7.99) becomes

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

$$d \ln \bar{f}_2 = -\frac{x_1}{x_2}\, d \ln \bar{f}_1 \tag{7.102}$$

If component 1 obeys Henry's law, we can write $\bar{f}_1 = K_1 x_1$ and hence Eq. (7.102) gives

$$d \ln \bar{f}_2 = -\frac{x_1}{x_2}\, d \ln (K_1 x_1) = -\frac{x_1}{x_2}\frac{K_1\, dx_1}{K_1\, x_1} = -\frac{dx_1}{x_2} = \frac{dx_2}{x_2} = d \ln x_2$$

Integrating this equation, we get

$$\ln \bar{f}_2 = \ln x_2 + C \tag{7.103}$$

where C is a constant of integration.

Since $\bar{f}_2 = f_2$ when $x_2 = 1$, $C = \ln f_2$ and Eq. (7.103) becomes

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

or

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

which is the Lewis–Randall rule for component 2.

In Fig. 7.6, Henry's law applies to component 1 in a binary system over the range 0 to x_1'. Lewis–Randall rule will be applicable to component 2 over the same composition range.

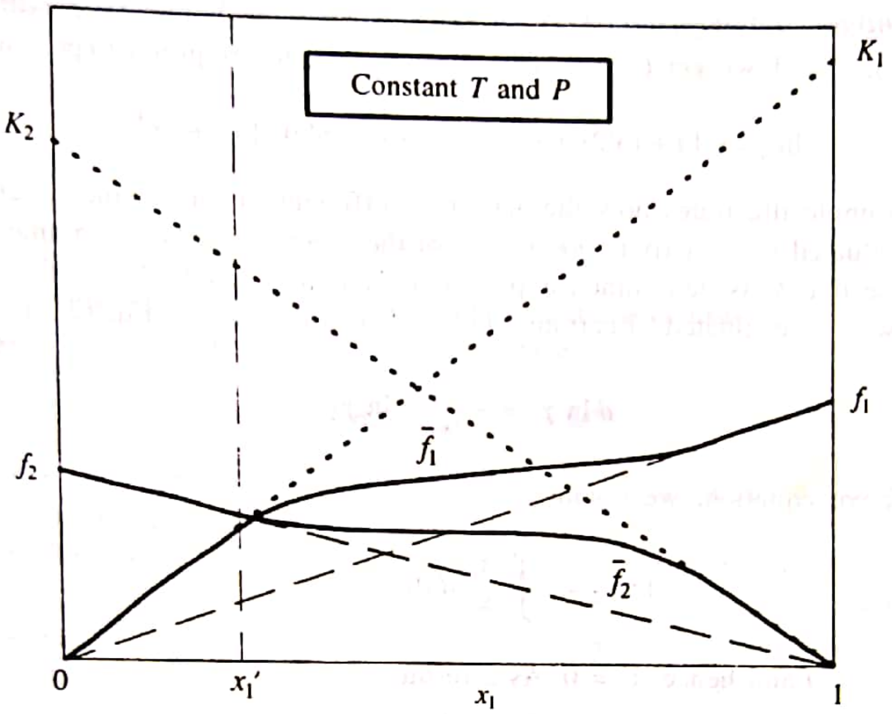

Fig. 7.6 Plot of fugacity versus mole fraction for Example 7.15.

***EXAMPLE* 7.16** The activity coefficient of component 1 in a binary solution is given by

$$\ln \gamma_1 = ax_2^2 + bx_2^3 + cx_2^4$$

where a, b, c are constants independent of concentrations. Obtain an expression for γ_2 in terms of x_1.

Solution Using the Gibbs–Duhem equation [Eq. (7.101)], we get

$$x_2 \frac{\partial \ln \gamma_2}{\partial x_2} = -x_1 \frac{\partial \ln \gamma_1}{\partial x_2} = -x_1 (2ax_2 + 3bx_2^2 + 4cx_2^3)$$

which may be rewritten as

$$\frac{\partial \ln \gamma_2}{\partial x_2} = -x_1 (2a + 3bx_2 + 4cx_2^2)$$

Replacing x_2 in the preceding equation by $(1 - x_1)$, we get

$$\frac{\partial \ln \gamma_2}{\partial x_1} = -x_1 (2a + 3b + 4c) + x_1^2 (-3b - 8c) + x_1^3 (4c)$$

Integrating the above equation,

$$\ln \gamma_2 = \int [x_1(2a + 3b + 4c) + x_1^2(-3b - 8c) + x_1^3(4c)]\, dx_1 + C'$$

where C' is a constant of integration. Integrating and using the boundary condition that when $x_2 = 1$ (or $x_1 = 0$), $\gamma_2 = 1$ we get $C' = 0$. Therefore, we get the required expression:

$$\ln \gamma_2 = [a + (3/2)\, b + 2c]\, x_1^2 - [b + (8/3)\, c]\, x_1^3 + c x_1^4$$

The above example illustrates how the activity coefficient of one of the species in a binary mixture can be evaluated if the activity coefficient of the other is known as an analytical equation in x. Now, suppose that γ_1 is determined experimentally and is reported as a function of x in a tabular form. How is γ_2 evaluated? Rearrange Gibbs–Duhem equation, Eq. (7.101) in the form

$$d \ln \gamma_2 = -\frac{x_1}{x_2}\, d \ln \gamma_1 \tag{7.104}$$

Integrating the above equation, we obtain

$$\ln \gamma_2 = -\int \frac{x_1}{x_2}\, d(\ln \gamma_1) + C \tag{7.105}$$

When $x_1 = 0$, $\ln \gamma_2 = 0$ and hence, $C = 0$. As a result,

$$\ln \gamma_2 = -\int_{(\ln \gamma_1) \text{ at } x_1 = 0}^{(\ln \gamma_1) \text{ at } x_1} \frac{x_1}{x_2}\, d(\ln \gamma_1) \tag{7.106}$$

The integral in Eq. (7.106) is to be evaluated graphically. For this, plot a graph taking x_1/x_2 along the y-axis and $\ln \gamma_1$ on the x-axis. The area under the curve from $\ln \gamma_1$ at $x_1 = 0$ to the $\ln \gamma_1$ value at the desired concentration x_1 will give the integral in Eq. (7.106). The negative of this is the value of $\ln \gamma_2$ at x_1.

8.11.1 Activity Coefficient Equations

Wohl's three-suffix equations. The relationship between excess free energy and activity coefficient was discussed in Chapter 7. Most of the equations relating activity coefficient and concentration of the solution were derived from these excess free energy relationships. Wohl proposed, statistically, a general method for expressing excess free energy and provided some rough physical significance to the various parameters appearing in the equations. Wohl's equation for excess free energy contained terms for compositions, effective molal volumes and effective volumetric fraction of the separate constituents of the solution. From these equations, the following empirical relations for activity coefficient could be written.

$$\ln \gamma_1 = z_2^2\left[A + 2\left(B\frac{q_1}{q_2} - A\right)z_1\right]; \quad \ln \gamma_2 = z_1^2\left[B + 2\left(A\frac{q_2}{q_1} - B\right)z_2\right] \tag{8.65}$$

z_1 and z_2 are the effective volume fraction of the separate components in the solution and q_1 and q_2 are the effective molal volumes. z and q are related as

$$z_1 = \frac{x_1}{x_1 + x_2(q_2/q_1)}; \quad z_2 = \frac{x_2}{x_2 + x_1(q_1/q_2)}$$

Equation (8.65) is known as *Wohl's three-suffix equation*. It involves three parameters, A, B and (q_1/q_2) which are characteristics of the binary system.

Margules equation. When the term (q_1/q_2) is unity in Eq. (8.65), we get the following expression, which is known as the *Margules three-suffix equation*.

$$\ln \gamma_1 = x_2^2[A + 2(B - A)x_1] = (2B - A)x_2^2 + 2(A - B)x_2^3 \tag{8.66}$$

$$\ln \gamma_2 = x_1^2[B + 2(A - B)x_2] = (2A - B)x_1^2 + 2(B - A)x_1^3$$

The constant A in the above equation is the terminal value of $\ln \gamma_1$ at $x_1 = 0$ and the constant B is the terminal value of $\ln \gamma_2$ at $x_2 = 0$. The three-suffix Margules equation adequately represents the VLE data of systems like acetone–methanol, acetone–chloroform, chloroform–methanol, etc.

When $A = B$ in Eq. (8.66), the Margules equation takes the following simple form:

$$\ln \gamma_1 = Ax_2^2; \quad \ln \gamma_2 = Ax_1^2 \tag{8.67}$$

Equation (8.67) is called the *Margules two-suffix equation*. It represents sufficiently and accurately the activity coefficients of simple liquid mixtures, i.e. mixtures of molecules, which are similar in size, shape and chemical nature. The constant A may be positive or negative. While in general, the constant depends on temperature, for many systems it is a weak function of temperature. Vapour–liquid equilibrium data of argon–oxygen, benzene–cyclohexane, etc., are well represented by the Margules equation [Eq. (8.67)].

van Laar equation. Let $(q_1/q_2) = (A/B)$ in Eq. (8.65). The resulting two-parameter equation is known as the *van Laar equation*. The van Laar equations can be written as

$$\ln \gamma_1 = Az_2^2 = \frac{Ax_2^2}{[(A/B)x_1 + x_2]^2}; \quad \ln \gamma_2 = Bz_1^2 = \frac{Bx_1^2}{[x_1 + (B/A)x_2]^2} \tag{8.68}$$

The constant A is the terminal value of $\ln \gamma_1$ at $x_1 = 0$ and B is the terminal value of $\ln \gamma_2$ at $x_2 = 0$. When A and B are equal, the van Laar equations simplify to the Margules equation, Eq. (8.67). The van Laar equation (8.68) may be rearranged to the following forms, which are very convenient for the evaluation of constants A and B.

$$A = \ln \gamma_1\left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2; \quad B = \ln \gamma_2\left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 \tag{8.69}$$

Strictly speaking, van Laar equations are applicable only for solutions of relatively simple, preferably non-polar liquids. But empirically, it has been found that these are applicable for more complex mixtures. The van Laar equations are widely used for vapour–liquid equilibrium calculations because of their flexibility and mathematical simplicity. Activity coefficients in benzene–isooctane system, *n*-propanol–water system, etc., are accurately represented by the van Laar equations.

The selection of a proper equation for VLE data correlation depends on the molecular complexity of the system and the precision of the experimental data. When an equation is selected that fits the experimental data well, the constants for the constant pressure conditions will be different from those applicable for constant temperature conditions. The effect of pressure on the constants is usually negligibly small, whereas the effect of temperature is appreciable and cannot be neglected. The van Laar constants vary with temperatures unless the temperature range involved is small. However, in vapour–liquid equilibrium calculations, the effect of temperature on the activity coefficient is usually ignored (Prausnitz, 1985).

The Margules three-suffix equation is suited for symmetrical systems, i.e. where the constants A and B are nearly the same. The van Laar equations can be used for unsymmetrical solutions, where the ratio A/B does not exceed 2. Though many systems follow van Laar equations, they cannot represent maxima or minima in the $\ln \gamma$ curve. Margules three-suffix equation should be used in such cases. For choice of an appropriate equation, a rule of thumb usually employed is this: When the ratio of molar volumes is close to unity, the Margules equation is preferred. When the ratio is quite different from unity, as is the case when water is one of the constituents, the van Laar equations are found to be satisfactory. For example, the chloroform–ethyl alcohol system, which shows a maximum and a minimum on the $\ln \gamma$ curves and whose ratio between pure component molar volumes is 1.38, is accurately represented by the Margules equation. For *n*-propanol–water system this ratio is 4.16 and the van Laar equations are found to represent the behaviour accurately.

It is to be remembered that in equations having only two constants, determination of γ_1 and γ_2 at a single known composition permits the evaluation of the constants and the complete γ curve. Equation (8.47) permits the evaluation of γ_1 and γ_2 when it is rearranged to the following form.

$$\gamma_i = \frac{y_i P}{x_i P_i^S} \tag{8.70}$$

The data required are a single set of equilibrium vapour–liquid composition values and the vapour pressures of the pure components. When an azeotrope is formed, only the azeotropic composition need be known, because it represents the composition of both the liquid and the vapour phases. The activity coefficients can be evaluated by putting $x = y$ in Eq. (8.70).

$$\gamma_i = \frac{P}{P_i^S} \tag{8.71}$$

Wilson equation. All the activity coefficient equations discussed so far can be deduced from the original Wohl's equation under proper simplifying assumptions. However, there are many equations that cannot be derived from the Wohl's general equation. Among such equations, the Wilson equation, the NRTL equation and the UNIQUAC equation are important from practical point of view. All these are based on the concept of local compositions, which are different from the overall mixture compositions. Based on molecular considerations, Wilson (1964) proposed the following equations for activity coefficients in a binary mixture.

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \tag{8.72}$$

Wilson equations have two adjustable positive parameters Λ_{12} and Λ_{21}. These are related to the pure component molar volumes and to the characteristic energy differences by

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT} \right] = \frac{V_2}{V_1} \exp\left[-\frac{a_{12}}{RT} \right]$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left[-\frac{\lambda_{12} - \lambda_{22}}{RT} \right] = \frac{V_1}{V_2} \exp\left[-\frac{a_{21}}{RT} \right] \tag{8.73}$$

where V_1 and V_2 are the molar volumes of pure liquids and λ's are the energies of interaction between the molecules designated in the subscripts. The differences in the characteristic energies (a_{ij}) are assumed to be temperature independent and this introduces no serious error in practical calculations. Wilson equation provides a good representation of VLE of a variety of miscible mixtures. It is particularly suitable for solutions of polar or associating components like alcohols in non-polar solvents for which the Margules and van Laar equations are generally inadequate.

Wilson equation suffers from two disadvantages, though not serious for many applications. Firstly, it is not suitable for systems showing maxima or minima on the ln γ versus x curves. Secondly, it is not useful for systems exhibiting limited miscibility. The use of Wilson equation is therefore recommended only for liquid systems that are completely miscible, or for partially miscible systems in the region where only one liquid phase exists.

Non-random two-liquid (NRTL) equation. The NRTL model, proposed by Renon and Prausnitz (1968), also is based on the local composition concept. The activity coefficients are

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{8.74}$$

In Eq. (8.74), the adjustable parameters are evaluated as

$$G_{12} = \exp(-\alpha_{12}\tau_{12}); \quad G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{8.75}$$

and

$$\tau_{12} = \frac{b_{12}}{RT}; \quad \tau_{21} = \frac{b_{21}}{RT} \tag{8.76}$$

The constants b_{12} and b_{21} are similar to the constants representing characteristic energy differences appearing in the Wilson equation. These, as well as the constant α_{12} are independent of composition and temperature. The parameter α_{12} is related to the non-randomness in the mixture. If α_{12} is zero, the mixture is completely random and the NRTL equation reduces to the Margules equation. It is found from fitting of experimental data that α_{12} varies from about 0.20 to 0.47. In the absence of the experimental data, the value of α_{12} is arbitrarily set, a typical choice being $\alpha_{12} = 0.3$. When α_{12} is arbitrarily fixed, NRTL equation becomes a two-parameter model.

NRTL equation is applicable to partially miscible as well as totally miscible systems. For moderately non-ideal systems, it offers no advantage over the van Laar and Margules equations. But, for strongly non-ideal solutions and especially partially miscible systems, the NRTL equations provide a good representation.

Universal quasi-chemical (UNIQUAC) equation. Abrams and Prausnitz (1975) extended the quasi-chemical theory of liquid mixtures to solutions containing molecules of different sizes. This extension is called the UNIQUAC theory. The UNIQUAC model consists of two parts—the combinatorial part, which describes the prominent entropic contribution and a residual part, which is due primarily to the intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined by the sizes and shape of the molecules and requires only pure-component data. The residual part depends on the intermolecular forces and involves two adjustable binary parameters.

The UNIQUAC equations for activity coefficients are

$$\ln \gamma_1 = \ln \frac{\phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1^*} + \phi_2^* \left(l_1 - \frac{r_1}{r_2} l_2 \right) - q_1' \ln (\theta_1' + \theta_2' \tau_{21}) + \theta_2' q_1' \left(\frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} \right) \tag{8.77}$$

$$\ln \gamma_2 = \ln \frac{\phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2^*} + \phi_1^* \left(l_2 - \frac{r_2}{r_1} l_1 \right) - q_2' \ln (\theta_2' + \theta_1' \tau_{12}) + \theta_1' q_2' \left(\frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right)$$

where

$$l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1), \qquad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \tag{8.78}$$

z is the coordination number, r, q and q' are pure-component molecular structure constants. The molecular size and surface area are given by r and q respectively. For fluids other than water or lower alcohols, $q = q'$. For alcohols, the surface of interaction q' is smaller than the geometric surface q. The adjustable binary parameters τ_{12} and τ_{21} are related to the characteristic energies Δu as follows.

$$\ln \gamma_1 = \ln \frac{\phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1^*} + \phi_2^* \left(l_1 - \frac{r_1}{r_2} l_2 \right) - q_1' \ln (\theta_1' + \theta_2' \tau_{21})$$

$$+ \theta_2' q_1' \left(\frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} \right)$$

$$\ln \gamma_2 = \ln \frac{\phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2^*} + \phi_1^* \left(l_2 - \frac{r_2}{r_1} l_1 \right) - q_2' \ln (\theta_2' + \theta_1' \tau_{12})$$

$$+ \theta_1' q_2' \left(\frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right)$$

$$l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1), \qquad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1)$$

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) = \exp\left(-\frac{a_{12}}{T}\right)$$
$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) = \exp\left(-\frac{a_{21}}{T}\right) \tag{8.79}$$

The segment fraction (φ^*) and the area fractions (θ and θ') are obtained as

$$\varphi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}, \qquad \varphi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}, \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$$

$$\theta_1' = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'}, \qquad \theta_2' = \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'}$$

The UNIQUAC equation satisfies a large number of non-electrolyte mixtures containing non-polar fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, etc., and water, including partially miscible mixtures. The main advantages of this equation are its wide applicability and simplicity arising primarily from the fact that there are only two adjustable parameters.

where C' is a constant of integration. Integrating and using the boundary condition that when $x_2 = 1$ (or $x_1 = 0$), $\gamma_2 = 1$ we get $C' = 0$. Therefore, we get the required expression:

$$\ln \gamma_2 = [a + (3/2)\, b + 2c]\, x_1^2 - [b + (8/3)\, c]\, x_1^3 + c x_1^4$$

The above example illustrates how the activity coefficient of one of the species in a binary mixture can be evaluated if the activity coefficient of the other is known as an analytical equation in x. Now, suppose that γ_1 is determined experimentally and is reported as a function of x in a tabular form. How is γ_2 evaluated? Rearrange Gibbs–Duhem equation, Eq. (7.101) in the form

$$d \ln \gamma_2 = -\frac{x_1}{x_2}\, d \ln \gamma_1 \tag{7.104}$$

Integrating the above equation, we obtain

$$\ln \gamma_2 = -\int \frac{x_1}{x_2}\, d(\ln \gamma_1) + C \tag{7.105}$$

When $x_1 = 0$, $\ln \gamma_2 = 0$ and hence, $C = 0$. As a result,

$$\ln \gamma_2 = -\int_{(\ln \gamma_1)\text{ at } x_1 = 0}^{(\ln \gamma_1)\text{ at } x_1} \frac{x_1}{x_2}\, d(\ln \gamma_1) \tag{7.106}$$

The integral in Eq. (7.106) is to be evaluated graphically. For this, plot a graph taking x_1/x_2 along the y-axis and $\ln \gamma_1$ on the x-axis. The area under the curve from $\ln \gamma_1$ at $x_1 = 0$ to the $\ln \gamma_1$ value at the desired concentration x_1 will give the integral in Eq. (7.106). The negative of this is the value of $\ln \gamma_2$ at x_1.

7.8 PROPERTY CHANGES OF MIXING

We know that the molar volume of an ideal solution is simply the average of the molar volumes of the pure components, each weighted according to its mole fraction. That is, $V = \sum x_i V_i$ for ideal solutions. If such a relation could be written for all extensive thermodynamic properties of a solution, then

$$M = \sum x_i M_i \tag{7.107}$$

where M is the molar property of the solution, M_i and x_i are the molar property of pure i and its mole fraction respectively. But Eq. (7.107) is not true even for ideal solutions when the property under consideration is entropy or entropy related functions like free energy. For non-ideal solutions, this equation cannot be used for the estimation of thermodynamic properties unless we apply a correction term ΔM, known as the *property change of mixing*. Thus, in general, when thermodynamic properties of a solution, whether ideal or real, are evaluated from the pure component properties the equation used should be

$$M = \sum x_i M_i + \Delta M \tag{7.108}$$

In Eq. (7.108), ΔM is the difference in the property of the solution M and sum of the properties of the pure components that make it up, all at the same temperature and pressure as the solution. Thus

$$\Delta M = M - \Sigma\, x_i M_i \tag{7.109}$$

Replacing M in Eq. (7.108) by the molar volume V,

$$V = \Sigma\, x_i V_i + \Delta V$$

where ΔV is the volume change on mixing. $\Delta V = 0$, for ideal solutions.

A more general definition of ΔM can be written as

$$\Delta M = M - \Sigma\, x_i M_i^0 \tag{7.110}$$

where M_i^0 is the molar property of pure i in a specified standard state. If the component exists in the pure form in the same state of aggregation as the solution and at the temperature and pressure as the solution, then $M_i^0 = M_i$. For example, if all components exist in the pure state as stable liquids at the temperature and pressure of the solution, $V_i^0 = V_i$ and $\Delta V = V - \Sigma\, x_i V_i$. Here, ΔV is the volume change of mixing when one mole of the solution is formed at constant temperature and pressure from the pure liquid constituents.

Property change of mixing is a function of temperature and pressure like any other thermodynamic property of solution and its value depends on the standard state specified for the components. Comparison of Eq. (7.14), which relates the properties of the solution to the partial molar properties of the constituent species, with Eq. (7.108) yields

$$\Delta M = \Sigma\, x_i(\overline{M}_i - M_i^0) \tag{7.111}$$

The quantity $\overline{M}_i - M_i^0$ can be treated as the change in the property of component i when one mole of pure i in its standard state is brought to the solution of given composition at the same temperature and pressure. Using Eq. (7.111), the volume change of mixing and free energy change of mixing can be written as

$$\Delta V = \Sigma\, x_i(\overline{V}_i - V_i^0) \tag{7.112}$$

$$\Delta G = \Sigma\, x_i(\overline{G}_i - G_i^0) \tag{7.113}$$

7.8.1 Activity and Property Change of Mixing

Free energy change of mixing, ΔG. Using the definition of fugacity, Eq. (6.118), the change in the free energy of a substance when it is brought from its standard state to the solution, can be written as

$$\overline{G}_i - G_i^0 = RT \ln \frac{\bar{f}_i}{f_i^0} = RT \ln a_i \tag{7.114}$$

Substitute this into Eq. (7.113). The result is

$$\frac{\Delta G}{RT} = \Sigma\, x_i \ln a_i \tag{7.115}$$

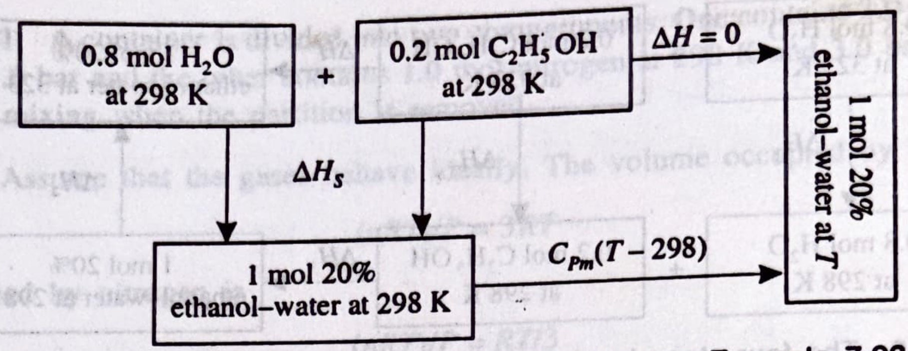

Fig. 7.10 Adiabatic mixing process described in Example 7.23.

7.10 EXCESS PROPERTIES

The difference between the property of a real solution and that of an ideal solution is important in chemical thermodynamics, especially in the treatment of phase equilibria. The *excess property*, M^E, is defined as the difference between an actual property and the property that would be calculated for the same temperature, pressure and composition by the equations for an ideal solution.

$$M^E = M - M^{id} \tag{7.131}$$

M is the molar property of the solution and M^{id} is the property of an ideal solution under the same conditions.

The excess property change of mixing is defined in a similar manner.

$$\Delta M^E = \Delta M - \Delta M^{id} \tag{7.132}$$

ΔM^E is the excess property change of mixing, ΔM and ΔM^{id} are the property changes of mixing for a real solution and an ideal solution respectively, both under the same conditions. As

$$\Delta M = M - \Sigma\, x_i M_i^0, \qquad \Delta M^{id} = M^{id} - \Sigma\, x_i M_i^0$$

Equation (7.132) can be written as

$$\Delta M^E = M - M^{id} \tag{7.133}$$

Compare Eq. (7.131) with Eq. (7.133). We see that

$$\Delta M^E = M^E \tag{7.134}$$

Equation (7.134) means that the excess property change of mixing and the excess property are the same.

Let us consider the excess volume V^E of a solution.

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

Since ideal solution involves no volume change of mixing, $\Delta V^{id} = 0$. Therefore, the excess volume of a solution and the volume change of mixing ΔV are the same. The same is true for some other extensive thermodynamic properties like enthalpy, internal energy, heat capacity, etc. Excess properties in these cases do not represent new thermodynamic properties. However, for entropy and entropy related functions, the excess properties are different from property changes of mixing and they represent new and useful quantities.

Excess functions indicate the deviations from ideal solution behaviour and are easily related to activity coefficients. Excess functions may be positive or negative; when the excess Gibbs free energy of a solution is positive the solution is said to exhibit positive deviation from ideality, whereas if it is less than zero, the deviation from ideality is negative.

The definition of partial molar excess functions is analogous to that of partial molar thermodynamic properties [see Eq. (7.1)].

$$\overline{M}_i^E = \left(\frac{\partial nM^E}{\partial n_i}\right)_{T,P,n_j} \tag{7.135}$$

$\overline{M}_i^E$ is the partial molar excess property of component i. Therefore, analogous to Eq. (7.132) we can write,

$$M^E = \Sigma x_i \overline{M}_i^E \tag{7.136}$$

Equation (7.136) says that the molar excess property M^E of a solution is the average of the partial molar excess property of each component weighted according to its mole fractions.

7.10.1 Excess Gibbs Free Energy

For phase equilibrium studies the most useful excess property is the partial molar excess Gibbs free energy which can be directly related to the activity coefficient. Excess Gibbs free energy is defined as

$$G^E = G - G^{\text{id}} \tag{7.137}$$

Using Eq. (7.136), we can write the excess Gibbs free energy as

$$G^E = \Sigma x_i \mu_i^E \tag{7.138}$$

where μ_i^E is the excess chemical potential or excess partial molar free energy of component i. But,

$$\mu_i^E = \mu_i - \mu_i^{\text{id}} = \Delta\mu_i - \Delta\mu_i^{\text{id}} \tag{7.139}$$

$\Delta\mu_i$, the change in chemical potential for component i when it is transferred from its standard state to the solution at the same temperature and pressure is related to its fugacity in the solution, as

$$\Delta\mu_i = RT \ln \frac{\bar{f}_i}{f_i^0} \tag{7.140}$$

$\bar{f}_i$ is the fugacity of component i in solution and f_i^0 is the fugacity in the standard state. Similarly, if the component becomes part of an ideal solution at the same conditions,

$$\Delta\mu_i^{\text{id}} = RT \ln \frac{\bar{f}_i^{\text{id}}}{f_i^0} \tag{7.141}$$

Since fugacity in an ideal solution is $\bar{f}_i^{\text{id}} = x_i f_i^0$, Eq. (7.141) can be written as

$$\Delta\mu_i^{\text{id}} = RT \ln x_i \tag{7.142}$$

In Eq. (7.140) the fugacity $\bar{f}_i$ is related to x_i, γ_i and f_i^0 as $\bar{f}_i = x_i \gamma_i f_i^0$, so that Eq. (7.140) becomes

$$\Delta\mu_i = RT \ln x_i\gamma_i \tag{7.143}$$

Substituting Eq. (7.142) and Eq. (7.143) into Eq. (7.139), the result is

$$\boxed{\mu_i^E = RT \ln \gamma_i} \tag{7.144}$$

Because of this simple relationship between activity coefficient and excess chemical potential it becomes possible to express the activity coefficient as a function of composition.

From Eq. (7.138), we see that the molar excess Gibbs free energy of a solution is simply,

$$G^E = RT \Sigma x_i \ln \gamma_i \tag{7.145}$$

Since $\mu_i^E = \overline{G}_i^E$, the partial molar free energy of a component i in the solution, the above equation can be put in the form of Eq. (7.135)

$$\boxed{\ln \gamma_i = \frac{\mu_i^E}{RT} = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{T,P,n_j}} \tag{7.146}$$

EXAMPLE 7.24 The two-suffix-Margules equation is the simplest expression for excess Gibbs free energy that is obeyed by chemically similar materials.

$$G^E = Ax_1x_2 \tag{7.147}$$

where A is an empirical constant independent of composition. Derive the expressions for the activity coefficients that result from this expression.

Solution Write Eq. (7.146) for components 1 and 2. Then

$$\ln \gamma_1 = \left[\frac{\partial(nG^E/RT)}{\partial n_1}\right]_{T,P,n_2}, \quad \ln \gamma_2 = \left[\frac{\partial(nG^E/RT)}{\partial n_2}\right]_{T,P,n_1}$$

Since $G^E = Ax_1x_2 = A(n_1/n)(n_2/n)$,

$$nG^E = A\frac{n_1n_2}{n} \tag{7.148}$$

Differentiating Eq. (7.148) with respect to n_1, keeping n_2 constant, we get

$$RT \ln \gamma_1 = An_2\left(\frac{n - n_1}{n^2}\right) = Ax_2^2$$

Differentiating Eq. (7.148) with respect to n_2, keeping n_1 constant, we get

$$RT \ln \gamma_2 = Ax_1^2$$

The desired expressions for activity coefficient are

$$\ln \gamma_1 = \frac{A}{RT}x_2^2, \quad \ln \gamma_2 = \frac{A}{RT}x_1^2$$

Figure 7.11 shows the plot of $\ln \gamma_1$, $\ln \gamma_2$ and G^E/RT against composition.