Chapter 6: Solution Thermodynamics and Principles of Phase Equilibria

In all the preceding chapters we have focused primarily on thermodynamic systems comprising pure substances. However, in all of nature, mixtures are ubiquitous. In chemical process plants – the ultimate domain of application of the principles of chemical engineering thermodynamics – matter is dominantly processed in the form of mixtures. Process streams are typically comprised of multiple components, very often distributed over multiple phases. Separation or mixing processes necessitate the use of multiple phases in order to *preferentially* concentrate the desired materials in one of the phases. Reactors very often bring together various reactants that exist in different phases. It follows that during mixing, separation, inter-phase transfer, and reaction processes occurring in chemical plants multi-component gases or liquids undergo composition changes. Thus, in the thermodynamic description of such systems, in addition to pressure and temperature, *composition* plays a key role.

Further, whenever multiple phases are present in a system, material and energy transfer occurs between till the phases are in *equilibrium* with each other, i.e., the system tends to a state wherein the all thermal, mechanical and *chemical potential* (introduced earlier in section 1.4) gradients *within* and *across* all phases cease to exist.

The present chapter constitutes a systematic development of the concept of a new class of properties essential to description of real mixtures, as well of the idea of the chemical potential necessary for deriving the *criterion* of phase and chemical reaction equilibrium. Such properties facilitate the application of the first and second law principles to quantitatively describe changes of internal, energy, enthalpy and entropy of multi-component and multiphase systems.

Of the separate class of properties relevant to multi-component and multi-phase systems, the *partial molar property* and the *chemical potential* are particularly important. The former is used for describing behaviour of homogeneous multi-component systems, while the latter forms the fundament to description equilibrium in multi-phase, as well as reactive systems.

As in the case of pure gases, the ideal gas mixture acts as a datum for estimating the properties of real gas mixtures. The comparison of the properties of the real and ideal gas mixtures leads to the introduction of the concept of *fugacity*, a property that is further related to the chemical potential. Fugacity may also be expressed as a function of volumetric properties of fluids. As we will see, the *functional* equivalence of fugacity and the chemical potential provides a convenient pathway for relating the temperature, pressure and phase composition of a system under equilibrium.

In the last chapter it was demonstrated that residual properties provide very suitable means of estimating real gas properties. But as pointed out its usage for description of liquid states is not convenient. This difficulty is overcome by the formulation of a concept of *ideal solution* behaviour, which serves as a datum for estimating properties of *real liquid solutions*. The departure of the property of a real solution from that of an ideal one is termed as *excess property*. In other words, the excess property plays a role similar to that of residual property. In the description of solution behaviour at low to moderate pressures, we employ yet another property, the *activity coefficient;* which originates from the concept of fugacity. The activity coefficient may also be related to the excess Gibbs energy. It is useful not only as a measure of the extent of non-ideality of a real solution but also, more significantly in describing phase equilibria at low to moderate pressures.

6.1 Partial Molar Property

We consider first the case of a homogenous (single-phase), open system that can interchange matter with its surroundings and hence undergo a change of composition. Therefore, the total value of any extensive property M^t $(M \equiv V, U, H, S, A, G)$ is not only a function of T and P, but also of the actual number of moles of each species present in the system. Thus, we may write the following general property relation:

$$M^t = nM = M\left(T, P,\ n_1, n_2 \ldots n_i \ldots n_N\right) \qquad \qquad ..(6.1)$$

Where $N \equiv$ total number of chemical species in the system

$$n = \text{total number of moles in the system} = \sum_i^N n_i \qquad \qquad ..(6.2)$$

Taking the total derivative for both sides of eqn. 6.1:

$$d\left(nM\right) = \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_{j \neq i}} dn_i \qquad ..(6.2)$$

Where, subscript n indicates that all mole numbers are held constant and subscript $n_{j \neq i}$ that all mole numbers except n_i are held constant. This equation has the simpler form:

$$d\left(nM\right) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i dn_i \qquad \qquad ..(6.3)$$

(the subscript x denotes differential at constant composition)

Where: $\bar{M}_i = \left[\dfrac{\partial(nM)}{\partial n_i} \right]_{P,T,n_{j \neq i}}$ ..(6.4)

Eqn. 6.4 defines the *partial molar property* $\bar{M}_i$ of species *i* in solution. It represents the change of total property '*nM*' of a mixture resulting from addition at constant T and P of a differential amount of species '*i*' to a finite amount of solution. In other words it also signifies the value of the property per mole of the specific species when it exists in solution. In general, the partial molar property of a substance differs from the molar property of the same substance in a pure state at the same temperature and pressure as the mixture or solution. This owing to the fact that while in a pure state the molecules interact with its own species, in a solution it may be subjected to different interaction potential with dissimilar molecules. This may render the value of a molar property different in mixed and pure states.

Now, $n_i = x_i n$; $dn_i = x_i dn + n\, dx_i$

Or : $dn_i = x_i dn + n\, dx_i$ ..(6.5)

Also: $d(nM) = ndM + Mdn$ ..(6.6)

Substituting eqns. 6.5 and 6.6 in eqn. 6.3 leads to:

$$ndM + Mdn = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i (x_i dn + n\, dx_i)$$ ..(6.7)

On re-arranging:

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i dx_i \right] n + \left[M - \sum_i \bar{M}_i x_i \right] dn = 0$$ ..(6.8)

While deriving eqn. 6.8 no specific constraints on the values of either *n* or *dn* have been applied. This suggests that the equation is valid for any arbitrary values of these two variables. Thus *n* and *dn* are independent of each other. Therefore, eqn. 6.8 can only be valid if the coefficients of these two variables are identically zero. On putting the coefficients to zero the following equations obtain:

$$dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i dx_i$$ ..(6.9)

$$M = \sum_i \bar{M}_i x_i \quad (at\ constant\ T\ \&\ P)$$ ..(6.10)

From eqn. 6.10, it follows, that $nM = n\sum_i x_i \bar{M}_i$ ...(6.11)

And also: $dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$ ...(6.12)

Equating (6.19) and (6.21) yields the well-known *Gibbs-Duhem* equation (*GDE*):

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{T,x} dT - \sum_i x_i d\bar{M}_i = 0$$

..(6.13)

The GDE must be satisfied for all changes in P, T, and in $\overline{M}_i$ caused by changes of state in a homogeneous phase. For the important special case of changes at constant T and P, it simplifies to:

$$\sum_i x_i d\bar{M}_i = 0$$

..(6.14)

Or, taking any arbitrary species '*j*': $\sum_i x_i \frac{d\bar{M}_i}{dx_j} = 0$ (*at const T, P*) ..(6.15)

Equations (6.14 and 6.15) implies that the partial molar properties of the various species ($\bar{M}_i$'s are not independent. Some key properties of partial molar properties are defined as follows:

$$\lim_{x_i \to o} \bar{M}_i = \bar{M}_i^{\infty}$$

$$\lim_{x_i \to 1} \bar{M}_i = M_i$$

$$\lim_{x_i \to 1} M = M_i$$

Select additional relations among partial properties are demonstrated in the Appendix 6.1.

Based on the foregoing considerations one may define an *isothermal molar property change of mixing* ΔM_{mix} as follows:

$$\Delta M_{mix}(T,P) = M(T,P) - \Sigma x_i M_i(T,P)$$

..(6.16)

Or: $\Delta M_{mix} = M - \Sigma x_i M_i = \Sigma x_i \bar{M}_i - \Sigma x_i M_i = \Sigma x_i (\bar{M}_i - M_i)$ ..(6.17)

(*M can be = V, U, H, S, A, G*)

Typical examples of molar volume change of mixing for a number of binary solutions are shown in figs. 6.1 and 6.2. Clearly then there can be substantial variation of this property depending upon the nature of the constituent molecules.
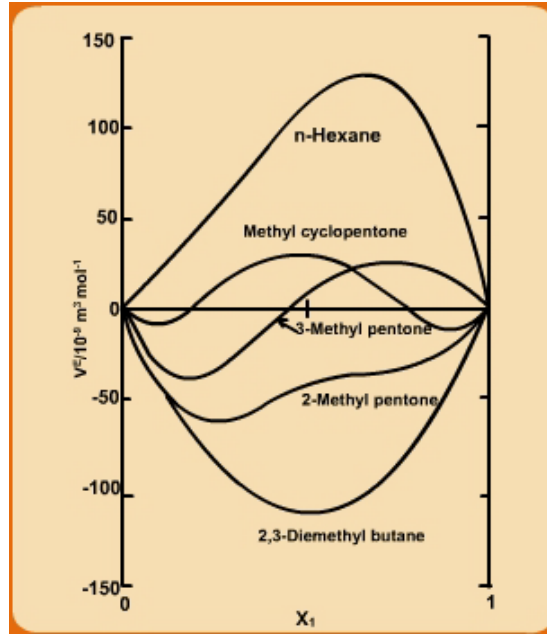
Fig. 6.1 Molar volume change of mixing for solutions of cyclohexane (1) with some other C_6 hydrocarbons (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

Example 6.1

Consider a solution of two species S1/S2 at 25°C such that $x_1 = 0.4$. If $\overline{V_1} = 40 \times 10^{-6}$ m^3/mol, find $\overline{V_2}$. The solution specific gravity is $= 0.90$, and the molecular weights of the species are 32 and 18 respectively.

(Click for solution)

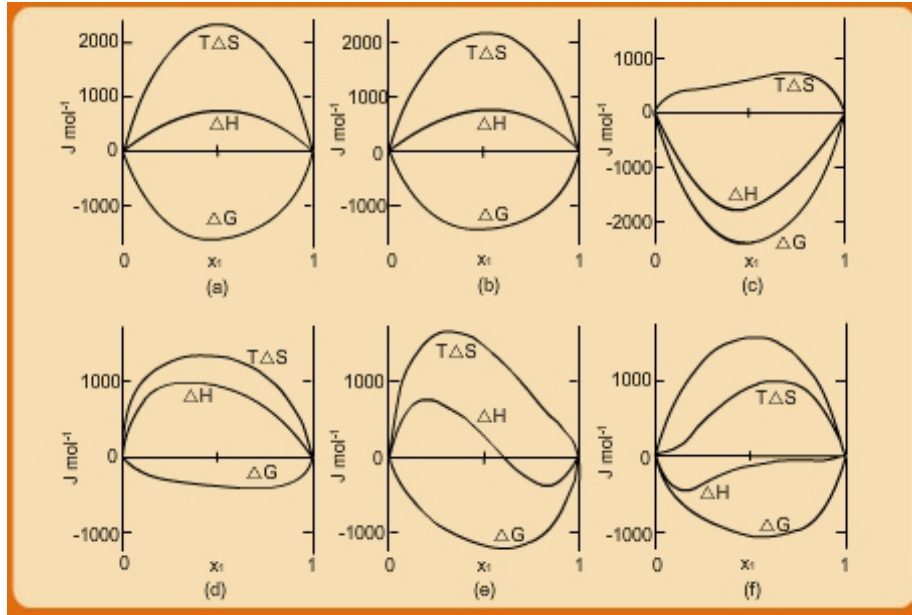
Fig. 6.2 Property changes of mixing at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2). (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

6.2 Partial Properties for Binary Solutions

The partial property is generally not amenable to *ab initio* computation from theory, but may be conveniently determined by suitably designed experiments that help obtain isothermal molar property of mixing (eqn. 6.17). Here we illustrate a set of results that derive for a binary mixture, and which may be applied to compute the relevant partial molar properties at any composition. Applying eqn. 6.10:

$$M = \bar{M}_1 x_1 + \bar{M}_2 x_2 \quad \left(at\ constant\ T\ \&\ P \right) \qquad ..(6.18)$$

$$\text{Or: } dM = (x_1 d\bar{M}_1 + \bar{M}_1 dx_1) + (x_2 d\bar{M}_2 + \bar{M}_2 dx_2) \qquad ..(6.19)$$

Applying the Gibbs-Duhem equation (6.14) gives:

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \qquad ..(6.20)$$

Now, since $x_1 + x_2 = 1, \ dx_1 = -dx_2$ $\qquad ..(6.21)$

Using Eqns. 6.19 – 6.21:

$$dM = \bar{M}_1 dx_1 - \bar{M}_2 dx_1 \qquad ..(6.22)$$

$$\text{Or: } \frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2 \qquad ..(6.23)$$

On solving eqns. 6.22 and 6.23 simultaneously:

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

..(6.24)

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

..(6.25)

If the molar property of the mixture M is available either from experiments or in analytical form, the partial molar properties may be estimated by applying the last two equations. Alternately, the experimental values of the mixture molar property (at a given T & P) may be plotted as a function of x_1 as shown in fig.6.3.
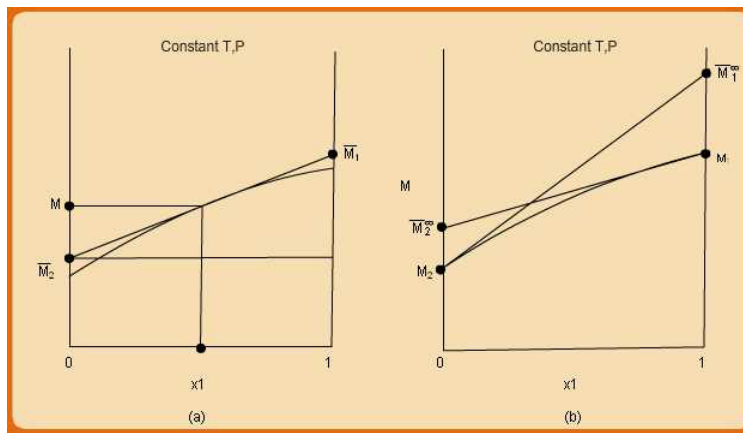

Fig. 6.3. Graphical method of determination of partial molar properties for a binary solution

For determining the partial molar properties at a given concentration one may draw a tangent to the M vs. x_1 curve, and $\bar{M}_1$ and $\bar{M}_2$ obtain as the right and left intercepts on the y-axis. This may be evident on comparing with the equations 6.24 and 6.25.

Using eqn. 6.17, the molar property M of a mixture is also written as:

$$M = \sum x_i M_i + \Delta M_{mix}$$

..(6.26)

In general the most common form of analytical relation (obtained by fitting a polynomial to the experimentally determined values of isothermal ΔM_{mix} as a function of composition) is the well-known Redlich-Kister equation, which for a binary solution is given by:

$$\Delta M_{mix} = x_1 x_2 [A + B(x_2 - x_1) + C(x_2 - x_1)^2 + ...]$$

..(6.27)

Where, *A, B, C* are temperature dependent and are determined from experimental measurements of ΔM_{mix}. For many practical applications the above equation is usually truncated to include only the terms corresponding to the parameters A and B. Fig. 6.4 shows the relation between the mixture enthalpy, the enthalpy change of mixing, the pure component and the partial molar enthalpies for a representative binary system.
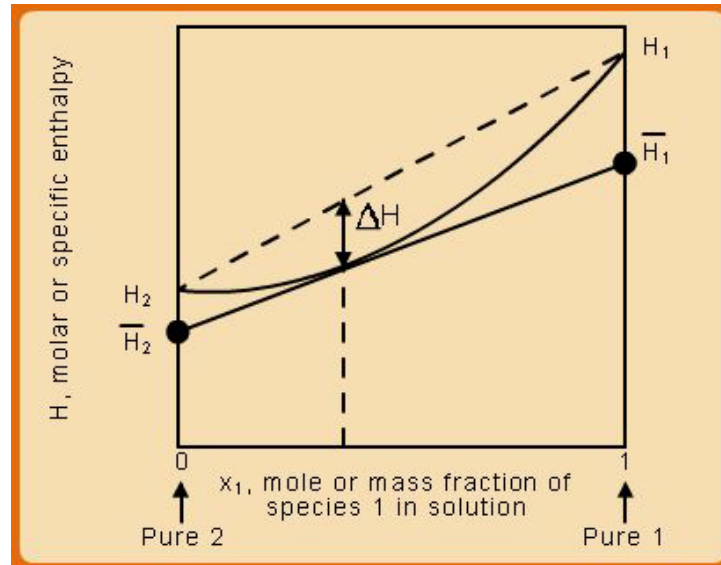

Fig. 6.4. Schematic showing pure component and partial molar enthalpies for a binary solution

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Example 6.2

The molar enthalpy of a binary solution is given by:

$V = 500\ x_1 + 1000\ x_2 + x_1 x_2\ (50\ x_1 + 40 x_2)$ cm^3/mol. Find the expressions for: $\overline{V}_1$, and $\overline{V}_1^{\infty}$.

(Click for solution)

6.3 Criteria of Thermodynamic Equilibrium

The nature of thermodynamic equilibrium has been introduced in section 1.4. As we know, it involves simultaneous thermal and mechanical equilibrium within a system. Apart from these constraints, the system must also be in a state of *chemical equilibrium*. In the most general sense, chemical equilibrium subsumes the following restrictions: (i) the various phases that may exist within the system are in equilibrium with each other in that there is no mass transfer of any chemical species between the phases; (ii) all reactions occurring in the system are also equilibrated, i.e., there is no further progress of the reaction in terms of conversion of the reactants to products. The last two criteria are better

understood in terms of the property called *chemical potential*, which we shall introduce in the following section. Here we focus on the overall, general criterion that must be in obeyed for any chemical system in equilibrium regardless of whatever species, phases or reactions that defines it.

Consider a closed system, which can be either homogeneous or heterogeneous, and which exists in a state of thermal and mechanical equilibrium with its surroundings. However, we assume that it is not under equilibrium with respect to possible inter-phase transfer of the chemical species or reactions between them. If the latter conditions prevail, all inter-phase transfer processes or reactive transformation of species must continue to occur till the point when the system is also at chemical equilibrium. In all real systems such changes are induced by finite gradients and are therefore are irreversible in nature. Applying the first law equation for all such changes for the system:

$$dU^t = dQ + dW \qquad\qquad ..(6.28)$$

We next consider that the system is under thermal and mechanical equilibrium with the surroundings (surr). Under such a situation:

$$dW = -PdV^t \qquad\qquad ..(6.29)$$

And also: $dS_{surr} = \dfrac{dQ_{surr}}{T_{surr}} = -\dfrac{dQ^t}{T}$ (note that $dQ_{surr} = -dQ^t$ for system) $\qquad\qquad ..(6.30)$

But by the second law: $dS_{surr} + dS^t \geq 0$ $\qquad\qquad ..(6.31)$

On combining eqns. 6.30 and 6.31 we get:

$$dQ^t \leq TdS^t \qquad\qquad ..(6.32)$$

Combining eqns. 6.28, 6.29 and 6.32:

$$dU^t + PdV^t - TdS^t \leq 0 \qquad\qquad ..(6.33)$$

It follows that for all incremental changes within the system, which take it closer to the final thermodynamic equilibrium, the property changes must satisfy the constraint imposed by eqn. 6.33. If the changes internal to the system occur under reversible conditions, the *equality* sign is valid; on the other hand, for irreversible processes the inequality condition holds.

Equation 6.33 can be used to generate alternate criteria of thermodynamic equilibrium, namely:

$$(dU^t)_{V^t,S^t} \leq 0 \qquad\qquad ..(6.34)$$

$$(dS^t)_{U^t,V^t} \leq 0 \qquad\qquad ..(6.35)$$

The other two criteria which are most apt in relation to thermodynamics of phase equilibria involve the use of Helmholtz and Gibbs free energy. If a process takes place under the constraints of constant temperature and volume then:

$$\left[dU^t - d(TS^t) \right]_{T,V^t} \leq 0$$

Or:

$$\left[d(U^t - TS^t) \right]_{T,V^t} \leq 0$$

$$(dA^t)_{T,V^t} \leq 0 \qquad ..(6.36a)$$

And, if the process occurs under constant temperature and pressure one may write:

$$\left[dU^t + d(PV^t) - d(TS^t) \right]_{T,P} \leq 0$$

Or: $\left[dG^t \right]_{T,P} \leq 0$ ..(6.36b)

Equation 6.36b provides the most practical of the three versions of general criteria of approach to equilibrium, as temperature and pressure are the most easily measurable of all the thermodynamic properties. As we have argued at the early part of this section at total thermodynamic equilibrium not only are thermal and mechanical gradients non-existent, there can be no further change in either the composition of any of the phases, or that of the reactive species. If there are any such incremental, *infinitesimal* changes of composition variables at the state of complete equilibrium the system once again must return to its stable state. This is exactly akin to the concept of equilibrium for mechanical systems presented in section 1.4. Therefore one may write the following equation to characterize thermodynamic equilibrium:

$$\left[dG^t \right]_{T,P} = 0 \qquad ..(6.37)$$

In summary, therefore, eqn. 6.37 constitutes a generalized description of thermodynamic equilibrium, which may be stated as follows:

"*The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at the given T and P*".

This criterion of equilibrium can be employed for determination of equilibrium states of a system in terms of its T, P and compositions. In principle, one first expresses G^t (at a given temperature and

pressure) as a function of the numbers of moles of each chemical species present in the various phases. Next one makes a partial differential operation on G^t with respect to moles of each species in the phases, and sets each such differential to zero to obtain the set of values for the mole numbers that *minimizes* G^t, subject to the constraints of conservation of mass. This procedure can be applied to problems of phase, chemical-reaction equilibria; and, of course, the most complex of chemical thermodynamic problems, where the criteria of phase and chemical-reaction equilibrium are valid simultaneously. As we will see, eqn. 6.37 forms the foundation for developing more *specific* criteria that can help describe both phase (section 6.3) and chemical reaction equilibria (section 8.3).

6.3 The Chemical Potential

In this section we focus on the properties of partial molar Gibbs free energy, which as we observed at the beginning of the chapter, is used for the description of phase and chemical reaction equlibria. The application of eqn. 6.3 to the molar Gibbs free energy of a mixture gives:

$$d\left(nG\right) = n\left(\frac{\partial G}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial G}{\partial T}\right)_{T,x} dT + \sum_i \bar{G}_i dn_i \qquad ..(6.38)$$

By definition the partial molar Gibbs free energy is termed the **chemical potential** of species i in the mixture, i.e.,:

$$\mu_i = \frac{\partial(nG)}{\partial n_i}\bigg|_{T,P,n_{j\neq i}} \qquad\qquad ..(6.39)$$

Or: $\mu_i = \bar{G}_i$ \qquad\qquad ..(6.40)

Using the result in eqn. 5.7 the first two partial derivatives in eqn. 6.28, may be replaced by $\left(nV\right)$ and $-\left(nS\right)$. Eqn. 6.38 then becomes:

$$d\left(nG\right) = \left(nV\right)dP - \left(nS\right)dT + \sum_i \mu_i dn_i \qquad ..(6.41)$$

With $n = 1$, and so $n_i = x_i$, eqn. 6.41 becomes:

$$dG = VdP - SdT + \sum_i \mu_i dx_i \qquad ..(6.42)$$

We next consider the use of chemical potential for obtaining a general criterion of thermodynamic equilibrium. Consider a closed system consisting of two phases α and β which are in equilibrium with each other. These phases could be vapour and liquid, solid and liquid, solid and vapour etc. Each phase

in the system may be treated as an open system, the interface between the two phases acting as the boundary across which material may be transferred. Thus we can apply 6.41 to both phases *individually*:

$$d\left(nG\right)^{\beta} = \left(nV\right)^{\beta} dP - \left(nS\right)^{\beta} dT + \sum_i \mu_i^{\beta} dn_i^{\beta} \qquad \text{..(6.43)}$$

$$d\left(nG\right)^{\alpha} = \left(nV\right)^{\alpha} dP - \left(nS\right)^{\alpha} dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} \qquad \text{..(6.44)}$$

In general we should denote the temperature and pressure of each phase also with the superscript in order to distinguish them. However, for the present purpose we assume thermal and mechanical equilibrium to prevail, i.e.

$$T^{\alpha} = T^{\beta}$$

$$P^{\alpha} = P^{\beta}$$

The total Gibbs free energy of the system changes with mass transfer between the two phases. The change in the total Gibbs energy of the two-phase system is the sum of the changes in each phase. The total volume and entropy of each phase is expressed by the following equations.

$$nV = \left(nV\right)^{\alpha} + \left(nV\right)^{\beta} \qquad \text{..(6.45)}$$

And $nS = \left(nS\right)^{\alpha} + \left(nS\right)^{\beta}$ ..(6.46)

Summing eqns. 6.43 and 6.44 and using eqns. 6.55 and 6.46 we get:

$$d\left(nG\right) = \left(nV\right) dP - \left(nS\right) dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta} = 0 \qquad \text{..(6.47)}$$

Since the mass transfer of each species takes place between the two phases in question, their change of mass in each phase must be equal and opposite: $dn_i^{\alpha} = -dn_i^{\beta}$

In which case eqn. 6.47 becomes:

$$d\left(nG\right) = \left(nV\right) dP - \left(nS\right) dT + \sum_i (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0 \qquad \text{..(6.48)}$$

If the system is considered to be already under thermal and mechanical equilibrium no changes in temperature and pressure may occur, then the last equation simplifies to:

$$\sum_i (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0 \qquad \text{..(6.49)}$$

We note that in the above sequence of equations no explicit constraint has been placed on the individual dn_i^α, which then are independent of each other. Thus for eqn. 6.49 to have general validity the coefficient of each dn_i^α has to be identically zero. Thus:

$$\mu_i^\alpha = \mu_i^\beta \qquad (i = 1, 2, \ldots N). \qquad\qquad ..(6.50)$$

The above proof has been simplified by assuming identical temperature and pressure for each phase. However, a more rigorous mathematical derivation of the phase equilibrium criterion leads to the result that if a system is under thermodynamic equilibrium, the temperature and pressures of all the phases are the same. If there is third phase ψ in the system we have considered, a second equation of the type (6.50) obtains:

$$\mu_i^\alpha = \mu_i^\psi \qquad\qquad ..(6.51)$$

Thus, if there are a total of δ phases in the system, one can generalize the result as follows:

By considering successive pairs of phases, we may readily generalize to more than two phases the equality of chemical potentials; thus for δ phases:

$$\mu_i^\alpha = \mu_i^\psi = \ldots = \mu_i^\delta \qquad (i = 1, 2, ..N) \qquad\qquad ..(6.52)$$

The above result allows us to advance a more general statement of the phase equilibrium criterion:

For a system under thermodynamic equilibrium, along with equality of the temperature and pressures of all phases, the chemical potential of each species is identical across all the phases.

6.4 Ideal Gas Mixtures and Liquid Solutions

We next explore the development of a quantitative definition of the chemical potential in terms of the volumetric properties and composition of mixtures. We have observed earlier that just as ideal gas state is a reference for real gas properties, ideal gas mixtures play the same role with respect to real gas mixtures. Therefore, it is instructive to establish the property relations for ideal gas mixture first.

Consider the constitution of an ideal gas mixture (containing N species) at a given temperature (T) and pressure (P). To obtain n moles of the total mixture we need to bring together n_i moles of each species $(n = \sum_i^N n_i)$ at temperature T but at a pressure p_i which corresponds to the *partial pressure* that each species would exert in the final mixture. If V^t is the total volume of the mixture, the following set of relations hold.

$P = nRT/V^t \Rightarrow p_i = n_i RT/V^t$

$Or \Rightarrow p_i/P = n_i/n = y_i$

$n = n_i + \sum_j n_j \quad \Rightarrow \quad Hence: \left[\dfrac{\partial n}{\partial n_i}\right]_{T,P,n_{j \neq i}} = 1$

$$\overline{V}_i^{ig} = \left[\dfrac{\partial(nV^{ig})}{\partial n_i}\right]_{T,P,n_{j \neq i}} = \left[\dfrac{\partial(nRT/P)}{\partial n_i}\right]_{T,P,n_{j \neq i}} = (RT/P)\left[\dfrac{\partial n}{\partial n_i}\right]_{T,P,n_{j \neq i}} = RT/P \qquad ..(6.53)$$

But the molar volume of the ith species $V^{ig} = RT/P$

Hence it follows:

$\overline{V}_i^{ig} = V^{ig}$ ..(6.54)

The last result indicates that the molar volume for a species does not change between its pure state and in an ideal gas mixture at the same T & P. It may then be concluded that for an ideal gas mixture the properties of each species are independent of that of the other ones. This may be easy to appreciate as the concept of an ideal gas is premised on the idea that the intermolecular interaction is non-existent in such a state. This conclusion leads to the well-known *Gibbs theorem*:

"Except for volume all other partial molar property of a species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at a temperature same as that of the mixture, but at a pressure equal to its partial pressure in the mixture."

In mathematical terms: $\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i)$ ..(6.55)

As an example let us consider the case of enthalpy of an ideal gas mixture. By Gibbs theorem:

$\overline{H}_i^{ig}(T,P) = H_i^{ig}(T,p_i)$ ..(6.56)

But, as the enthalpy of an ideal gas is independent of pressure it follows that:

$H_i^{ig}(T,p_i) = H_i^{ig}(T,P)$ ..(6.57)

It follows: $\overline{H}_i^{ig}(T,P) = H_i^{ig}(T,P)$ ..(6.58)

By the standard definition, the enthalpy of the mixture is:

$H_{mix}^{ig}(T,P) = \sum_i y_i \overline{H}_i^{ig}(T,P)$ ..(6.59)

Thus, using eqns. 6.56 – 6.59 we get:

$$H_{mix}^{ig}(T,P) = \sum_i y_i H_i^{ig}(T,P) \quad\quad ..(6.60)$$

It follows: $\Delta H_{mix}^{ig} = H_{mix}^{ig} - \Sigma y_i H_i^{ig} = 0 \quad\quad ..(6.61)$

Employing the same reasoning: $\Delta U_{mix}^{ig} = U_{mix}^{ig} - \Sigma y_i U_i^{ig} \quad\quad ..(6.62)$

The molar entropy of mixing of ideal gas mixture, however, is not zero. As stated above, the formation of 1 mole of mixture results from bringing together y_i moles each species at T and partial pressure p_i to form a mixture at T and P, Hence for isothermal mixing, y_i moles of each species goes from (T, p_i) to (T, P). Therefore:

$$S_i^{ig}(T,P) - S_i^{ig}(T,p_i) = -R\ln(P/p_i) = R\ln y_i \quad\quad ..(6.63)$$

On transposing: $S_i^{ig}(T,p_i) = S_i^{ig}(T,P) - R\ln y_i \quad\quad ..(6.64)$

But: $S^{ig}(T,P) = \sum_i y_i \overline{S}_i^{ig}(T,P) \quad\quad ..(6.65)$

So: $S^{ig}(T,P) = \sum_i y_i S_i^{ig}(T,p_i) \quad\quad ..(6.66)$

Using eqns. 6.63 - 6.67, one obtains:

$$S^{ig}(T,P) = \sum_i y_i S_i^{ig}(T,P) - R\sum_i y_i \ln y_i \quad\quad ..(6.67)$$

On applying the partial molar property operation (as given by eqn. 6.4) on 6.58, it may be shown that:

$$\overline{S}_i^{ig}(T,P) = S_i^{ig}(T,P) - R\ln y_i \quad\quad ..(6.68)$$

It further follows: $\Delta S_{mix}^{ig} = S^{ig}(T,P) - \Sigma y_i S_i^{ig}(T,P) = R\sum_i y_i \ln y_i \quad\quad ..(6.69)$

For Gibbs free energy relation we start from: $G = H - TS$

For an ideal gas mixture: $G^{ig} = H^{ig} - TS^{ig} \quad\quad ..(6.70)$

Taking the partial molar property derivative: $\overline{G}_i^{ig} = \overline{H}_i^{ig} - T\overline{S}_i^{ig} \quad\quad ..(6.71)$

On putting eqns. 6.58 and 6.59 into 6.71 we get the following relation for the chemical potential of each species in an ideal gas mixture:

$$\overline{G}_i^{ig} = \mu_i^{ig} \equiv G_i^{ig} + RT\ln y_i \quad\quad ..(6.72)$$

Using eqns. 6.51 and 6.58, it may be also shown that:

$$G_{mix}^{ig} = \sum_i y_i G_i^{ig} + RT\sum_i y_i \ln y_i \quad\quad ..(6.73)$$

Example 6.3

What is the change in entropy when $0.6\ \text{m}^3$ of CO_2 and $0.4\ \text{m}^3$ of N_2, each at 1 bar and 25°C blend to form a gas mixture at the same conditions? Assume ideal gases.

(Click for solution)

The Ideal Solution:

We have already seen that owing to the fact that pure ideal gases and mixtures are not subject to intermolecular interactions the partial molar properties (apart from volume) of each species is the same as that of the pure species at the same temperature and pressure. In other words each species "sees" no difference in their environment in pure or mixed state. One can conceptually extend this idea to posit an ideal solution behaviour which may serve as a model to which real-solution behavior can be compared. Consider a solution of two liquids, say A and B. If the intermolecular interaction in the pure species, (i.e., A-A and B-B) is equal to the *cross-species* interaction A-B, neither A nor B type molecules will "see" any difference in their environment before and after mixing. This is in a sense the same condition as one obtains with idea gas mixtures. Hence an *identical* set of ideal solution property relations may be constructed based on the model of ideal gas mixture. By convention while describing properties of liquid solutions mole fractions y_i are replaced by x_i. The following relations therefore, derive for ideal (liquid) solution properties (denoted by a superscript '*id*'):

$$H^{id} = \sum_i x_i H_i \text{ and, } V^{id} = \sum_i x_i V_i \qquad\qquad ..(6.74)$$

$$S^{id} = \sum_i x_i S_i - R\sum_i x_i \ln x_i \qquad\qquad ..(6.75)$$

Hence $G^{id} = \sum_i x_i G_i + RT\sum_i x_i \ln x_i \qquad\qquad ..(6.76)$

Lastly, $\mu_i^{id} = \bar{G}_i^{id} = G_i + RT \ln x_i \qquad\qquad ..(6.77)$

As we will see later the ideal solution model can also serve to describe the behaviour of mixtures of real gases or solids.

6.5 Excess Properties

Unlike for real gases (pure or mixtures) the EOS based approach to calculation of thermodynamic properties of real liquid solutions have not proved very successful. However, as molar *residual property* is defined for real gases, for *real* liquid solutions one may formulate a different departure

function called the molar *excess property* that quantify the deviation from ideal solution property. The mathematical formalism of excess properties is, therefore, analogous to that of the residual properties.

If *M* represents the molar (or unit-mass) value of any extensive thermodynamic property(e.g., *V,U, H, S, G,* etc.), then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. Thus:

$$M^E \equiv M - M^{id} \qquad\qquad ..(6.78)$$

The excess property bear a relationship to the property change of mixing. One may take the example of excess Gibbs free energy to illustrate the point. Thus:

$$G^E = G - G^{id} \qquad\qquad ..(6.79)$$

Or: $G^E = G - \left(\sum_i x_i G_i + RT \sum_i x_i \ln x_i \right) \qquad\qquad ..(6.80)$

Thus: $G^E = \Delta G_{mix} - RT \sum_i x_i \ln x_i \qquad\qquad ..(6.81)$

Other relations include:

$$H^E = H - H^{id} = \Delta H_{mix} \qquad\qquad ..(6.82)$$

$$S^E = \Delta S_{mix} + R \sum_i y_i \ln y_i \qquad\qquad ..(6.83)$$

Also: $G^E = H - TS^E$

The non-ideality of real liquid solutions are depicted well by use of excess properties, especially through the behaviour of G^E, H^E and S^E. The excess Gibbs energy is typically obtained from low pressure vapour-liquid equilibrium data, while H^E is obtained by measuring isothermal enthalpy change of mixing. Lastly S^E is derived using the following relation:

$$S^E = \frac{H_E - G^E}{T} \qquad\qquad ..(6.84)$$

Fig. 6.5 shows the variation of each of the excess property as a function of liquid mole fraction for a number of binary solutions.
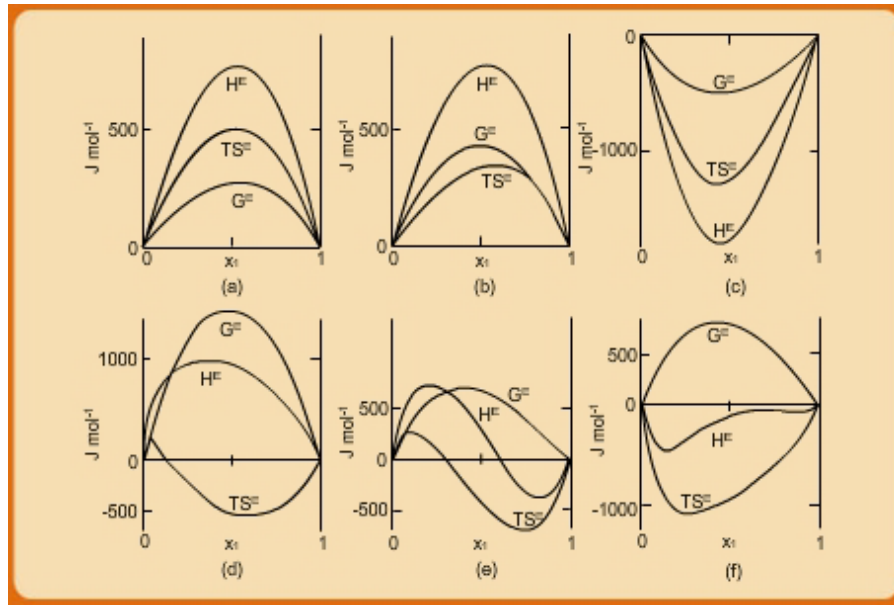
Fig. 6.5 Excess properties at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2);(*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2). (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

6.6 Fugacity of pure substances

It has been shown in section 6.3 that the chemical potential provides a fundamental description of phase equilibria. As we shall further see in chapter 8, it also proves an effective tool for depicting chemical reaction equilibria. Nevertheless, its direct usage is restricted, as it is not easy to directly relate the chemical potential to thermodynamic properties amenable to easy experimental determination, such as the volumetric properties. The definition of a new function called fugacity, itself related to the chemical potential, helps bridge the gap.

The concept of fugacity is advanced based on the following thermodynamic relation for an ideal gas. For a single component closed system containing an ideal gas we have (from eqn. 5.7):

$$dG = VdP - SdT$$

At constant temperature, for a pure ideal gas 'i' the above equation reduces to:

$$dG_i^{ig} = V_i^{ig} dP = RTdP/P = RTd\ln P \qquad\qquad ..(6.85)$$

$$G_i^{ig} = \Gamma_i(T) + RTd\ln P \qquad\qquad [\text{Where, } \Gamma_i(T) \text{ is the constant of integration}]$$

Utilizing the essential simplicity of eqn. 6.85 we apply it a real fluid but by replacing pressure with fugacity (since it is not valid for a real fluid):

$dG_i = V_i dP$ (At const. T)

Thus, $dG_i = RTd \ln f_i$

Hence, $G_i = \Gamma_i(T) + RTd \ln f_i$ ..(6.86)

Since f_i has the units of pressure, it is often described as a "fictitious pressure". It may be noted that the definition of fugacity as provided by eqn. 6.86 is completely general in nature, and so can be extended to liquids and solids as well. However, the calculation of fugacity for the latter will differ from that for gases. This equation provides a partial definition of f_i, the fugacity of pure species 'i'. Subtracting eqn. 6.85 form 6.86 gives:

$$G - G^{ig} = G_i^R = RT \ln \frac{f_i}{P}$$ ..(6.87)

The dimensionless ratio f_i / P is termed *fugacity coefficient* (ϕ).

Thus: $G_i^R = RT \ln \phi_i$ ..(6.88)

Where, $\phi_i \equiv f_i / P$ ..(6.89)

Clearly for an ideal gas the following relations hold: $G_i^R = 0$; $f_i^{ig} = P$; accordingly, $\phi_i = 1$.

However, by eqn. 5.38: $\dfrac{G^R}{RT} = \int_0^P (Z - 1) \dfrac{dP}{P}$

Thus, using the last relation in eqn. 6.78:

$$\ln \phi_i = \int_0^P (Z_i - 1) \frac{dP}{P} \qquad \text{(At const. T)}$$ ..(6.90)

6.7 Fugacity-based phase equilibrium criterion for pure component system

The general criterion of thermodynamic equilibrium has been defined by eqn. 6.38. Applying it to, for example, a vapour (V) and liquid (L) system of a pure component 'i' we have:

$\mu_i^V = \mu_i^L$ ..(6.91)

However, for a pure component system: $\lim_{x_i \to 1} \overline{M}_i = M_i$.

Thus: $\mu_i^V \equiv \overline{G}_i^V = G_i^V$ and $\mu_i^L \equiv \overline{G}_i^L = G_i^L$ ..(6.92)

Thus, using eqn. 6.91 and 6.92 we have:

$G_i^V = G_i^L$ ..(6.93)

The above equation may be generalized for any other types of phases. However, the eqn. 6.93 is rendered more easily applicable if the chemical potential is replaced by fugacity. Thus integrating eqn. 6.86 between vapour and liquid states of a pure component:

$$\int_L^V dG_i = RT \int_L^V d \ln f_i \qquad\qquad ..(6.94)$$

$$G_i^V - G_i^L = RT \ln(f_i^V / f_i^L) \qquad\qquad ..(6.95)$$

Now applying eqn. 6.93 to 6.95 it follows $\quad RT \ln(f_i^V / f_i^L) = 0$

Or:

$$f_i^V = f_i^L = f_i^{sat} \qquad\qquad ..(6.96)$$

In eqn. 6.86 f_i^{sat} indicates the value for either saturated liquid or saturated vapor, this is because the coexisting phases of saturated liquid and saturated vapor are in equilibrium. Since under such condition the pressure is P_i^{sat}, we can write:

$$\varphi_i^V = \frac{f_i^V}{P_i^{sat}}$$

$$\phi_i^L = \frac{f_i^L}{P_i^{sat}}$$

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}}$$

Thus, employing eqn. 6.86 again, it follows:

$$\phi_i^V = \phi_i^L = \phi_i^{sat} \qquad\qquad ..(6.97)$$

Both eqns. 6.93, 6.96 and 6.97 represent *equivalent* criterion of vapor/liquid equilibrium for pure species.

6.8 Fugacity expressions for pure gases

Fugacity coefficient (and hence fugacity) of pure gases may be conveniently evaluated by applying eqn. 6.80 to a *volume-explicit* equation of state. The truncated virial EOS is an example of the latter type, for which the compressibility factor of pure species (*i*) is given by:

$$Z_i = 1 + \frac{B_{ii}P}{RT}$$

Or $Z_i - 1 = \dfrac{B_{ii}P}{RT}$

Thus, on using eqn. 6.80: $\ln \phi_i = \dfrac{B_{ii}}{RT} \displaystyle\int_0^P dP$ (at const T)

Hence, $\ln \phi_i = \dfrac{B_{ii}P}{RT}$ ..(6.98)

Eqn. 6.80 is, however, not amenable to use for obtaining expressions using cubic EOSs. The general equation for such purposes is relatively more involved and we derive it below.

Example 6.4

Estimate the fugacity of ethane at 122.2 K and 5 bar using the truncated virial EOS. For ethane $T_c = 305.4K$, $P_c = 48.84$ bar, $\omega = 0.099$

(Click for solution)

==

Derivation of fugacity coefficient expression for cubic EOS:

Starting from eqn. 5.38:

$$\dfrac{G^R}{RT} = \ln \phi = \ln\left(\dfrac{f}{P}\right) = \dfrac{1}{RT}\int_0^P \left(V - \dfrac{RT}{P}\right)dP$$ ..(6.99)

Now: $\displaystyle\int VdP = \int d(PV) - \int PdV$ ..(6.100)

Using Eqn. 6.100 in 6.99:

$$\ln \phi = \dfrac{1}{RT}(PV - RT) - \int_{V=\infty}^{V} \dfrac{P}{RT}dV - \int_{PV=RT}^{PV} \dfrac{d(PV)}{PV} + \int_{V=\infty}^{V} \dfrac{dV}{V}$$

$$= (Z-1) - \int_{PV=RT}^{PV} d\ln(PV) + \int_{V=\infty}^{V} \dfrac{dV}{V} - \int_{V=\infty}^{V} \dfrac{P}{RT}dV$$

On simplifying:

$$\ln \phi = (Z-1) - \ln Z + \ln \dfrac{V}{V_\infty} - \dfrac{1}{RT}\int_{V=\infty}^{V} PdV$$ ..(6.101)

Here: V_∞ = molar volume at $P \to 0$, or V_∞ = ideal gas volume

Therefore: $V / V_\infty = Z$ ..(6.102)

Using eqn. 6.102 in 6.101 one arrives at:

$$\ln \phi = (Z-1) - \dfrac{1}{RT}\int_{V=\infty}^{V} PdV$$ ..(6.103)

==

Equation 6.103 is a generalized expression for obtaining pure component fugacity from a pressure explicit EOS. We show below the expressions for fugacity coefficients that derive on application of the above equation to various cubic EOSs. (The reader may refer to section 2.3.3 for various forms of cubic EOS).

VdW EOS:

$$\ln \phi = Z - 1 - \ln \frac{P(V - b)}{RT} - \frac{a}{RTV}$$

..(6.104)

RK-EOS:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{a}{bRT} \ln\left(\frac{Z + B}{Z}\right); B = \frac{bP}{RT}$$

..(6.105)

SRK EOS:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{a}{bRT} \ln\left(\frac{Z + B}{Z}\right); B = \frac{bP}{RT}$$

..(6.106)

PR-EOS:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT} \ln\left[\frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})}\right]; B = \frac{bP}{RT}$$

..(6.107)

Example 6.5

Estimate the fugacity of ammonia vapor at 4.0 MPa and 321K assuming that it obeys the RK equation of state.

(Click for solution)

6.9 Generalized Correlations for the Fugacity Coefficient

The generalized correlation approach which has been presented earlier for calculation compressibility factor Z (section 2.3), and the residual enthalpy and entropy of gases (section 5.7), can also be applied for computing fugacity coefficients for pure gases and gaseous mixtures. Equation (6.90) can be rewritten in a generalized form as follows:

$$P = P_C P_r; \text{hence, } dP = P_c dP_r$$

Hence, an alternately, $\ln \phi = \int_{O}^{P_r} (Z-1)\dfrac{d\,P_r}{P_r}$ (at const. T_r)   ..(6.109)

Substitution for $Z = Z_0 + \omega Z_1$, gives:

$$\ln \phi = \int_{O}^{Pr} (Z^O - 1)\dfrac{d\,P_r}{P_r} + \omega \int_{O}^{Pr} Z^1 \dfrac{d\,P_r}{P_r}$$ ..(6.110)

The last equation may be written in alternative form:

$$\ln \phi = \ln \phi^0 + \omega \ln \phi^1$$ ..(6.111)

Or: $\phi = (\phi^0)(\phi^1)^\omega$ ..(6.112)

Where, $\ln \phi^0 = \int_{O}^{P_r} (Z^O - 1)\dfrac{d\,P_r}{P_r}$ ..(6.113)

$$\ln \phi^1 = \int_{O}^{P_r} Z^1 \dfrac{d\,P_r}{P_r}$$ ..(6.114)

For obtaining the values of the integrals in the last two equations, the tabulated data for Z^0 and Z^1 for various values of T_r and P_r may be used for numerical or graphical computations. Yet another approach is due to Lee-Kesler which employsa variant of the BWR-EOS (eqn. 2.17) to evaluate the expressions for $\ln \phi^0$ and $\ln \phi^1$ for a wide range of values of T_r and P_r and are available in the form of extended tables. In either case the fugacity coefficient is finally computed using eqn. 6.112. (see figs 6.6 and 6.7).

Example 6.6

Estimate the fugacity of methane at 32C and 9.28 bar. Use the generalized correlation approach.

(Click for solution)

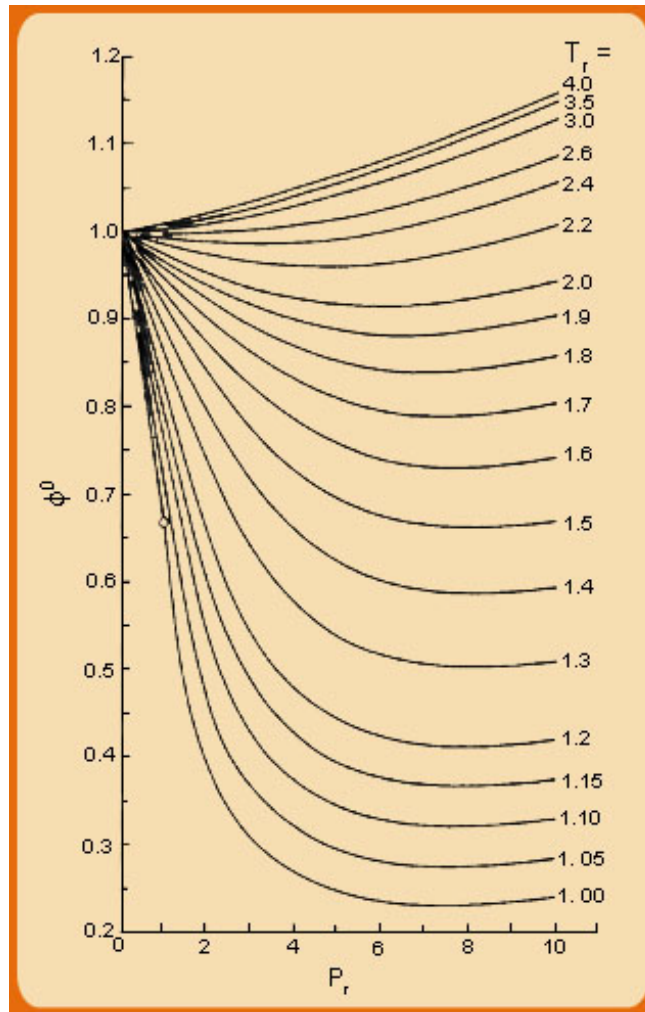---

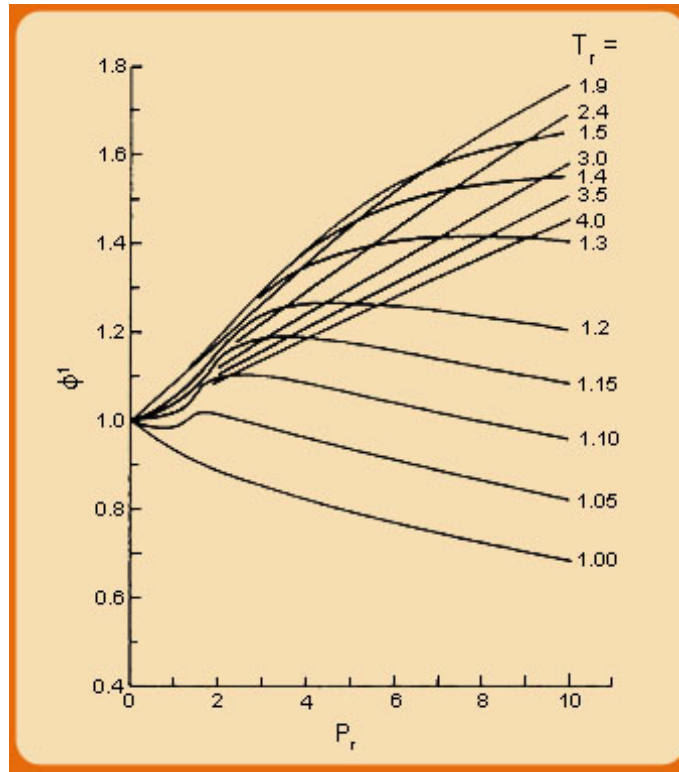Fig. 6.6 Correlation of ϕ^0 drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

FIG 6.7 Correlation of ϕ^1 drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

The above set of equations may well be used for estimating the *overall* fugacity coefficient of a gaseous mixture. As in earlier instance (sections, 2.3 and 5.7) one makes use of pseudo-critical properties that are estimated from the following set of linear relations:

$$T_{C,m} = \sum_i y_i T_{C,i} \; ; \qquad\qquad P_{C,m} = \sum_i y_i P_{C,i} \qquad\qquad\qquad \omega_m = \sum_i y_i \omega_i \qquad\qquad ..(2.32)$$

The subscript '*i*' runs over all the species present in the mixture '*m*'. The above relations allow the mixture to be treated as *single* substance; the methodology outlined above for pure species may then be used to compute the fugacity coefficient of the mixture.

6.10 Expression for Fugacity of a Pure Liquid

Since the representation of liquid state by EOS is generally difficult, the calculation of fugacity of a compressed (or sub-cooled) liquid is based on the *saturated liquid* state as a reference state. One starts with the two generic relations (that apply to any pure real fluid '*i*') already introduced in the section 6.7, namely:

$$dG_i = V_i dP \text{ (at const. T)}$$

$$dG_i = RTd \ln f_i$$

The two equations above may be combined to yield:

$$V_i dP = RTd \ln f_i \qquad ..(6.115)$$

As shown (eqn. 6.96) at the saturation condition for co-existing vapour and liquid phases:

$$f_i^V = f_i^L = f_i^{sat}$$

Thus for a compressed liquid state at a given pressure one can write for an isothermal change of pressure from P_i^{sat} to the compressed liquid pressure P:

$$G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i dP \qquad ..(6.116)$$

Alternately, $G_i - G_i^{sat} = RT \dfrac{f_i}{f_i^{sat}}$ $\qquad ..(6.117)$

On equating the last two equations:

$$\ln \frac{f_i}{f_i^{sat}} = \frac{1}{RT} \int_{P_i^{sat}}^{P} V_i dP \qquad ..(6.118)$$

Since V_i, the liquid–phase molar volume, is a relatively weak function of pressure at temperatures well below the critical temperature, one may approximate $V_i \cong V_i^l$, where, V_i^l is the molar volume of the saturated liquid at the temperature of interest.

Using $f_i^{sat} = \phi_i^{sat} P_i^{sat}$ in the integrated form of eqn. 6.108 gives:

$$f_i(T,P) = \phi_i^{sat} P_i^{sat} \exp[\frac{V_i^l (P - P_i^{sat})}{RT}] \qquad ..(6.119)$$

The exponential term on the left side of the last equation is known as a *Poynting factor.* It may be noted that the calculation of the term ϕ_i^{sat} can be made based on any EOS suitable for gases at the given temperature T and pressure P_i^{sat}.

Example 6.7

Estimate the fugacity of cyclopentane at 110 C and 275 bar. At 110 C the vapor pressure of cyclopentane is 5.267 bar.

(Click for solution)

6.11 Fugacity and Fugacity Coefficient of Species in Mixture

The definition of the fugacity of a species in a mixture is similar to the definition of the pure species fugacity. For an ideal gas mixture the chemical potential is given by eqn. (6.63):

$$\mu_i^{ig} \equiv G_i^{ig} + RT \ln y_i \qquad ..(6.63)$$

Or: $d\mu_i^{ig} = dG_i^{ig} + RTd \ln y_i$ (at const. T) $\qquad ..(6.120)$

But $dG_i^{ig} = V_i dP = RTd \ln P$ (at const. T)

Thus: $d\mu_i^{ig} = RTd \ln P + RTd \ln y_i = RTd \ln(y_i P)$ $\qquad ..(6.121)$

Or: $d\mu_i^{ig} = RTd \ln p_i$ (where $p_i =$ partial pressure of ith species) $\qquad ..(6.122)$

Using the same idea implicit in eqn. 6.86, we extend eqn. 6.122 to define a similar expression for fugacity of species in a *real* mixture:

$$d\mu_i = RTd \ln \hat{f}_i \qquad ..(6.123)$$

Here, $\hat{f}_i$ is the fugacity of species i in the mixture, which replaces the partial pressure p_i of eqn. 6.122. As we will demonstrate later, $\hat{f}_i$ is not a partial molar property, and is therefore denoted by a *circumflex* rather than by an *overbar*, as are partial properties. On integrating eqn. 6.123 between the any two multi-component phases α and ψ in equilibrium with each other:

$$\int_{\mu_i^{\psi}}^{\mu_i^{\alpha}} d\mu_i = RT \int_{\hat{f}_i^{\psi}}^{\hat{f}_i^{\alpha}} d \ln \hat{f}_i \qquad ..(6.124)$$

Hence, $\mu_i^{\alpha} - \mu_i^{\beta} = RT \ln\left(\hat{f}_i^{\alpha} / \hat{f}_i^{\beta} \right)$ $\qquad ..(6.125)$

But by eqn. 6.42, for equilibrium: $\mu_i^{\alpha} = \mu_i^{\psi}$

It follows, therefore, $\mu_i^{\alpha} - \mu_i^{\psi} = RT \ln\left(\hat{f}_i^{\alpha} / \hat{f}_i^{\psi} \right) = 0$

Or: $\hat{f}_i^{\alpha} / \hat{f}_i^{\psi} = 1$

That is: $\hat{f}_i^{\alpha} = \hat{f}_i^{\psi}$ $\qquad ..(6.126)$

Therefore, for an arbitrary number of phases in equilibrium with each other:

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\psi} = ... = \hat{f}_i^{\delta} \ (i = 1,2,..N) \qquad ..(6.127)$$

Thus, eqn. 6.126 offers a criterion of equilibrium corresponding to that provided by eqn. 6.42. The great advantage this equivalence offers is that, the fugacity coefficients of species in a mixture can be related to the volumetric properties of the mixtures, which facilitates the solution of phase and chemical reaction equilibria problems.

On comparing eqns. 6.122 and 6.123, the following limiting condition obtains:

$$\lim_{P \to 0} \hat{f}_i = y_i P \qquad ..(6.128)$$

It follows that a *fugacity coefficient* $\hat{\phi}_i$ (dimensionless) of a species in a real gas mixture may be defined as:

$$\hat{\phi}_i^V \equiv \frac{\hat{f}_i^V}{y_i P} \qquad ..(6.129)$$

Although the derivation above defines the fugacity coefficient with respect to gaseous mixture the definition may be extended to represent fugacity coefficient of a species in a real liquid solution as well. Accordingly, in that case it is defined in the following manner:

$$\hat{\phi}_i^L \equiv \frac{\hat{f}_i^L}{x_i P} \qquad ..(6.130)$$

6.12 Relation between residual property and species fugacity coefficients in mixtures

As we know, for any molar property (M), the definition of residual property M^R is given by:

$$M^R = M - M^{ig} \quad \Rightarrow \quad nM^R = nM - nM^{ig}$$

It follows that:

$$\left[\frac{\partial (nM^R)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = \left[\frac{\partial (nM)}{\partial n_i} \right]_{T,P,n_{j \neq i}} - \left[\frac{\partial (nM^{ig})}{\partial n_i} \right]_{T,P,n_{j \neq i}} \qquad ..(6.131)$$

Or: $\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig} \qquad ..(6.132)$

For the specific case of molar Gibbs free energy:

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig} = \mu_i - \mu_i^{ig} \qquad ..(6.133)$$

From eqns. 6.122 and 6.123 $d\mu_i^{ig} = RTd \ln p_i;$ and $d\mu_i = RTd \ln \hat{f}_i$

On integrating between the real and ideal states:

$$\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{p_i} = RT \ln \frac{\hat{f}_i}{y_i P} = RT \ln \hat{\phi}_i$$ ..(6.134)

On comparing eqns. 6.131 and 6.122:

$$\overline{G}_i^R = RT \ln \hat{\phi}_i$$ ..(6.135)

But by definition: $G^R = \sum_i y_i \overline{G}_i^R$ ..(6.136)

Thus, on inspecting 6.133 and 6.135:

$$\ln \hat{\phi}_i = \left[\frac{\partial (nG^R / RT)}{\partial n_i} \right]_{T,P,n_{j\neq i}}$$ ..(6.137)

It follows that:

$$\frac{G^R}{RT} = \sum_i y_i \ln \hat{\phi}_i$$ ..(6.138)

Since $\ln \hat{\phi}_i$ is a partial molar property, the Gibbs-Duhem relation (eqn. 6.14) applies, that is:

$$\sum_i x_i d \ln \hat{\phi}_i = 0 \quad \text{(at const. T and P)}$$ ..(6.139)

6.13 Expressions for gas phase $\hat{\phi}_i$ using EOS

In this section we derive the expressions for computing the fugacity coefficients for individual species in a real gas mixture. As in the case of pure real gases (section 6.8) we consider the truncated virial EOS and the various cubic EOSs. From eqn. (6.90):

$$\ln \phi = \int_0^P (Z-1) \frac{dP}{P}$$

Further by eqn. (6.137):

$$\ln \hat{\phi}_i = \left[\frac{\partial (nG^R / RT)}{\partial n_i} \right]_{T,P,n_{j\neq i}}$$.

From these two relations we obtain the following equations:

$$\frac{nG^R}{RT} = \int_0^P (nZ - n)\frac{dP}{P} \qquad ..(6.140)$$

$$\ln\hat{\phi}_i = \int_0^P \left[\frac{\partial(nZ - n)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \frac{dP}{P} \qquad ..(6.141)$$

Now, $\dfrac{\partial(nZ)}{\partial n_i} = \bar{Z}_i$; and $\dfrac{\partial n}{\partial n_i} = 1$

Hence: $\ln\hat{\phi}_i = \int_0^P \left(\bar{Z}_i - 1\right)\dfrac{dP}{P}$ \qquad ..(6.142)

Species Fugacity Coefficients (in a gas mixture) from the Virial EOS:

The expression for computing the mixture virial coefficient corresponds to eqn. 2.25. One may rewrite the expression for a binary mixture as follows:

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12} \qquad ..(6.143)$$

Where, $\delta_{12} = 2B_{12} - B_{11} - B_{22}$ \qquad ..(6.144)

Using (6.140 / 6.141): $nZ = n + \dfrac{nBP}{RT}$

Or: $nZ - n = \dfrac{nBP}{RT}$ \qquad ..(6.145)

Therefore:

$$\bar{Z}_1 \equiv \left[\frac{\partial(nZ)}{\partial n_1}\right]_{T.P,n_2} = \left[\frac{\partial\left(n + \dfrac{nBP}{RT}\right)}{\partial n_1}\right]_{T.P,n_2} = 1 + \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} \qquad ..(6.146)$$

Using (6.148) in (6.142):

$$\ln\hat{\phi}_1 = \int_0^P \left(\bar{Z}_1 - 1\right)\frac{dP}{P} = \frac{1}{RT}\int_0^P \left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} dP = \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} \qquad ..(6.147)$$

Now putting (6.133) it may be shown that:

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + y_2^2 \delta_{12} \qquad ..(6.148)$$

Therefore putting (6.148) in (6.147), one obtains:

$$\ln \hat{\phi_1} = \frac{P}{RT}(B_{11} + y_2^2 \delta_{12}) \hspace{4cm} ..(6.149)$$

In a similar manner, one may show that:

$$\ln \hat{\phi_2} = \frac{P}{RT}(B_{22} + y_1^2 \delta_{12}) \hspace{4cm} ..(6.150)$$

Example 6.8

For the following system compute the species fugacity coefficients for an equimolar mixture at 20 bar and 500K.

	T_c (K)	P_c (bar)	V_c X 10^3 (m^3/mol)	Z_c	ω	y_i
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.4
Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.6

(Click for solution)

Fugacity coefficient expression for species in a mixture by pressure explicit EOS:

The eqn. 6.130 is useful for application to volume explicit EOSs only. For pressure explicit EOS (cubic EOSs) the expression for obtaining the species fugacity coefficient in a mixture is relatively complex. For the present purpose we provide below the generic equation used for pressure explicit EOS, while its proof is provided at the end of the present chapter.

$$RT \ln \hat{\phi_i} = -\int_{V=\infty}^{V} \left\{ \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right\} dV - RT \ln Z \hspace{2cm} ..(6.153)$$

We enlist below the resultant final expressions that obtain for species fugacity in a gaseous mixture corresponding to various forms of cubic EOSs.

For illustration we take the RK-EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \hspace{4cm} ..(6.154)$$

Next one writes the parameters 'a' and 'b' for the mixture using typical mixing rules described by eqns. 2.29 to 2.31:

$$a = \sum_i \sum_j y_i y_j \sqrt{a_i a_j} (1 - k_{ij})$$

k_{ij} = binary interaction parameter

where, $k_{ii} = k_{jj} = 0$; $k_{ij(i \neq j)}$ is very often also put to zero, as it is difficult to obtain.

$$b = \sum_i y_i b_i$$

$$\omega = \sum_i y_i \omega_i$$

Thus the RK-EOS may be written as:

$$P = \frac{RT}{V - \sum_i (n_i / n) b_i} - \frac{\sum_i \sum_j (n_i n_j / n^2) \sqrt{a_i a_j} (1 - k_{ij})}{V(V + \sum_i (n_i / n) b_i)}$$

Using the last expression one can derive the expression for $\left(\dfrac{\partial P}{\partial n_i} \right)_{T,V,n_j}$ and use it in (6.153) to obtain:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{b_m RT}\left[(\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}}\right] \ln(\frac{Z + B}{Z}); B = \frac{b_m P}{RT}$$

..(6.155)

Similarly for *SRK EOS:*

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{b_m RT}\left[(\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}}\right] \ln(\frac{Z + B}{Z}); B = \frac{b_m P}{RT}$$

..(6.156)

For PR EOS:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{2\sqrt{2}b_m RT}\left[\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}}\right] \ln\left[\frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})}\right]; B = \frac{b_m P}{RT}$$

..(6.157)

Example 6.9

Calculate the fugacities of ethylene and propylene in a mixture of 70 mole percent ethylene and 30 mole percent propylene at 600 K and 60 bar. Assume that the mixture follows the Redlich-Kwong equation of state.

	T_c (K)	P_c (bar)
Ethylene (1)	283.1	51.17
Propylene (2)	365.1	46.0

(Click for solution)

6.14 The Lewis/Randall Rule:

A simple equation for the fugacity of a species in an ideal solution follows from the following equations. In general, for any solution: $\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$ ..(6.158)

Applying to ideal solution, $\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}$ ..(6.159)

However we know (eqn. 6.77) that: $\mu_i^{id} = \bar{G}_i^{id} = G_i + RT \ln x_i$ ..(6.160)

Also, from eqn. 6.86: $G_i = \Gamma_i(T) + RT \ln f_i$

Thus, $\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$ ..(6.161)

on comparing eqns. 6.158&6.160: $\hat{f}_i^{id} = x_i f_i$ ..(6.162)

The last relation is known as the *Lewis/Randall rule*, and applies to each species in an ideal solution at all conditions of temperature, pressure, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant being the fugacity of pure species *i* in the same physical state as the solution and at the same T and P.

6.15 Dependence of G^E on temperature and pressure

The idea of the molar excess property has been introduced in section 6.5 with the following definition:

$$M^E = M - M^{id}$$ ..(6.163)

Typically the property M can be an intensive property such as: V, U, H, S, G, A, etc. The relations between the molar excess properties of V, H and G is particular significant for description of non-ideal

solution thermodynamics. One may start from the generic total derivative of the Gibbs free energy for

a real solution and an ideal solution in the same way as eqns. 5.27 and 5.28:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \qquad ..(6.164)$$

One may write the same equation specifically for an ideal solution, whence:

$$d\left(\frac{G^{id}}{RT}\right) = \frac{V^{id}}{RT}dP - \frac{H^{id}}{RT^2}dT \qquad ..(6.165)$$

Thus subtracting eqn. 6.165 from 6.164:

$$d\left(\frac{G^E}{RT}\right) = \frac{V^E}{RT}dP - \frac{H^E}{RT^2}dT \qquad ..(6.166)$$

Thus we may write the following further *generative* relations:

$$\frac{V^E}{RT} = \left[\frac{\partial(G^E/RT)}{\partial P}\right]_T \qquad ..(6.167)$$

$$\frac{H^E}{RT} = -T\left[\frac{\partial(G^E/RT)}{\partial T}\right]_P \qquad ..(6.168)$$

And further: $\dfrac{S^E}{RT} = \dfrac{H^E}{RT} - \dfrac{G^E}{RT}$ ..(6.169)

The sensitivity of the excess Gibbs free energy to changes in temperature and pressure may be estimated to show the effect of pressure and temperature on liquid phase properties. For example, for an equimolar mixture of benzene and cyclohexane at 298K and 1 bar are (source: J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001):

$$V^E = 0.65 cm^3/mol$$
$$H^E = 800 cm^3/mol$$

Thus it follows:

$$\left[\frac{\partial(G^E/RT)}{\partial P}\right]_{T,x} = \frac{V^E}{RT} = \frac{0.65}{83.14 x 298} = 2.62 x 10^{-5} bar^{-1}$$

$$\left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x} = -\frac{H^E}{RT^2} = -\frac{800}{83.14 x 298^2} = -1.08 x 10^{-3} K^{-1}$$

$$\Delta G^E (for \Delta T = 1\ K) \approx \Delta G^E (for\ \Delta P = 40\ bar)$$

The above calculations suggest that to effect the same change in excess Gibbs free energy brought about a change of 1K, one needs to change the pressure to change by about 40bar. Hence the excess Gibbs free energy exhibits a relatively weak dependence on pressure.

6.16 The Activity Coefficient

While we have defined fugacity coefficients of individual species in a liquid solution by 6.153, we may define yet another parameter called *activity coefficient* in order to describe the non-ideality of a liquid solution, especially at low to moderate system pressure.

We have by eqn. 6.155: $\overline{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$

And from eqn. 6.158: $\overline{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$

Using the above equations: $\overline{G}_i - \overline{G}_i^{id} = \overline{G}_i^E = RT \ln \dfrac{\hat{f}_i}{x_i f_i}$ ..(6.170)

The left side of this equation is the partial excess Gibbs energy $\overline{G}_i^E$; the dimensionless ratio $\hat{f}_i / x_i f_i$ appearing on the right is the *activity coefficient* of species i in solution, represented by the symbol γ_i. Thus, by definition:

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}$$

$$\hat{f}_i = x_i \gamma_i f_i \qquad \qquad ..(6.171)$$

Whence, $\overline{G}_i^E / RT = \ln \gamma_i$ ..(6.172)

But $G^E = \sum_i x_i \overline{G}_i^E$ ..(6.173)

On comparing the last two equations we conclude that γ_i is a partial molar property with respect to G^E. Thus, we have:

$$\ln \gamma_i = \frac{\partial (nG^E / RT)}{\partial n_i}\bigg|_{T,P,n_{j \neq 1}} \qquad ..(6.174)$$

It follows from the definition of activity coefficient (eqn. 6.163) that for an ideal solution its value is unity for all species as $G^E = 0$. For a non-ideal solution, however, it may be either greater or less than unity, the larger the departure from unity the greater the non-ideality of the solution. The

derivatives of the activity coefficient with respect to pressure and temperature can be correlated to the partial molar excess volume and enthalpy respectively.

Using eqn. 6.167 and 6.168 in conjunction with 6.173/6.174 the following results are obtained:

$$\frac{\overline{V}_i^E}{RT} = \left[\frac{\partial \ln \gamma_i}{\partial P}\right]_{T,x} \qquad \text{..(6.175)}$$

$$\frac{\overline{H}_i^E}{RT^2} = \left[\frac{\partial \ln \gamma_i}{\partial T}\right]_{P,x} \qquad \text{..(6.176)}$$

As we have seen in the last section that the value of the function $\left[\dfrac{\partial(G^E/RT)}{\partial T}\right]_{P,x}$ is relatively larger

compared to $\left[\dfrac{\partial(G^E/RT)}{\partial P}\right]_{T,x}$; thus comparing eqns. 6.167 and 6.168 with 6.175 and 6.176

respectively, one may conclude that the activity coefficients are far *more* sensitive to changes in temperature than to changes in pressure. For this reason for phase equilibria computations at low to moderate pressures, the activity coefficients are assumed invariant with respect to pressure.

Since the activity coefficients are partial molar properties, they are related by the Gibbs Duhem equation (at constant temperature and pressure) as follows:

$$\sum_i x_i d \ln \gamma_i = 0 \qquad \text{..(6.177)}$$

The above equation may be used to validate or check the consistency of experimental data on isothermal activity coefficients for a binary system. The following equation may be derived from eqn. 6.177 for this purpose (by assuming negligible effect of pressure on the liquid phase properties):

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0 \qquad \text{..(6.178)}$$

Thus, if the function ln (γ_1/γ_2) is plotted over the entire range of x_1, (fig. 6.8) the two areas above and below the x-axis in the resulting curve must add up to zero, if the activity coefficients are consistent. Representative values and the

$$0 = \int_0^1 \ln(\gamma_1/\gamma_2)dx_1$$
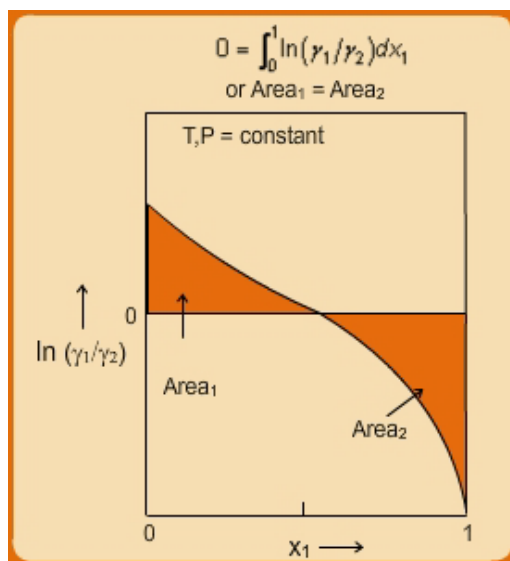or Area₁ = Area₂

T,P = constant

Figure 6.8 Thermodynamic consistency tests for activity coefficients in binary mixtures.

nature of variation in the magnitude of activity coefficients is shown in fig. 6.9; they correspond to the

same systems for which excess property variations were depicted in fig. 6.5.
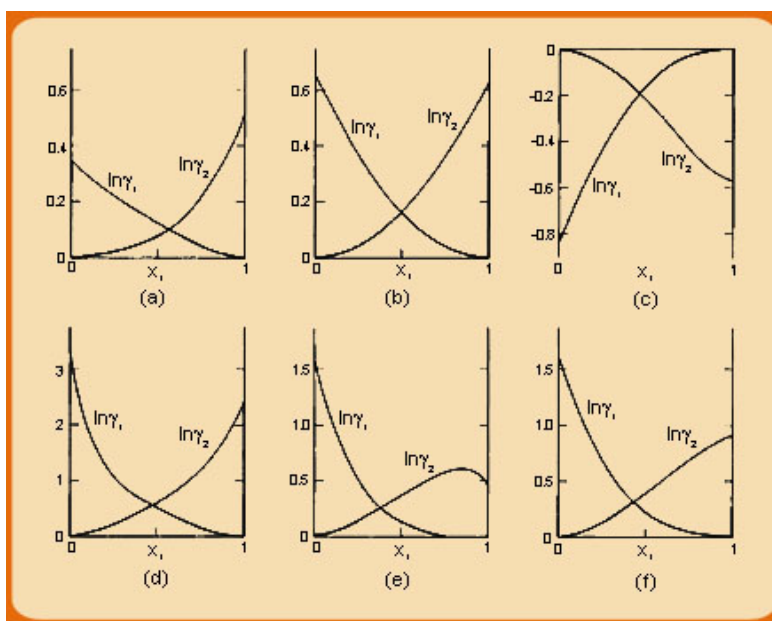

Fig. 6.9 Activity coefficients at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2). (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

6.17 Use of VLE data for generation of activity coefficient models

In general during the process design of chemical plants, especially for distillation and liquid-liquid separation systems, it is necessary to predict the values of activity coefficients for carrying out phase equilibrium calculations. However, experimental data on activity coefficients of various types of liquid solutions are often not available at conditions (of temperature and/or composition) of interest. In such cases activity coefficient models - which relate G^E to solution composition (at a given T&P) - are useful. Most of such models are based on semi-empirical considerations. These models are all characterized by a set of parameters that are temperature dependent. Vapour-liquid equilibrium (VLE) data at low pressures are readily used for computing the value of such parameters. The more general form of the VLE relationship is discussed in the next chapter. The VLE equation is essentially a relation that relates the equilibrium vapour and liquid phase compositions at a given temperature and pressure. For the purpose of demonstrating the method of generating the activity coefficient models, we state here without proof, the simple VLE relation that applies to low pressure systems containing an ideal gas phase, but a non-ideal liquid phase. At low pressures it is of the following form:

$$y_i P = x_i \gamma_i P_i^{sat} \qquad\qquad\qquad ..(6.179)$$

Where, $i = 1, 2...N$; y_i, x_i, P, $\& P_i^{sat}$ denote the vapour phase compos

$y_i \equiv$ equilibrium vapour phase mole fraction of ith species
$x_i \equiv$ equilibrium liquid phase mole fraction of ith species

$\gamma_i \equiv$ activity coefficeint of ith species in the liquid phase; i.e., at the given x_i
$P_i^{sat} =$ saturation vapour pressure of ith species at the equilibrium temperature

And $P =$ equilibrium pressure

It follows from eqn. 6.179 that: $\gamma_i = \dfrac{y_i P}{x_i P_i^{sat}}$ $\qquad\qquad\qquad ..(6.180)$

In a typical *isothermal* VLE data generation experiment, the equilibrium pressure and the corresponding vapour and liquid phase compositions are measured and the activity coefficients of each species estimated at each set of liquid phase composition using eqn. 6.180. For freezing ideas let us consider a binary system. Once the different sets of activity coefficient values for various liquid phase compositions, ideally ranging over $x_i = 0 \,to\, 1$, the excess molar Gibbs free energy is computed at each composition using the following equation (obtained by combining eqns. 6.172, and 6.173):

$$G^E / RT = \sum_i x_i \ln \gamma_i \text{ (At const. T)} \qquad\qquad ..(6.181)$$

The values of G^E/RT are in turn used to obtain a set of values of a new function: (G^E/x_1x_2RT) are generated which is then fitted using a polynomial function of the following form:

$$G^E / x_1 x_2 RT = A + Bx_1 + Cx_1^2 + ... \qquad\qquad ..(6.182)$$

The final form of the polynomial is generally dependent on the nature of the constituent species of the liquid phase as well as the temperature. Representative plots for this form of data reduction for generating the (G^E/x_1x_2RT) function are shown in figures 6.10 and 6.11.
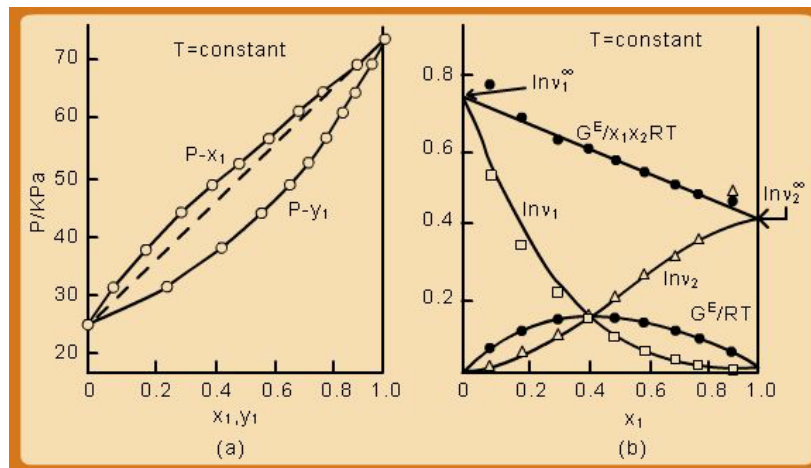

Fig. 6.10 Representative plot of experimental P-x-y, activity coefficient and molar excess Gibbs free energy data for systems exhibiting positive deviation from Raoult's Law
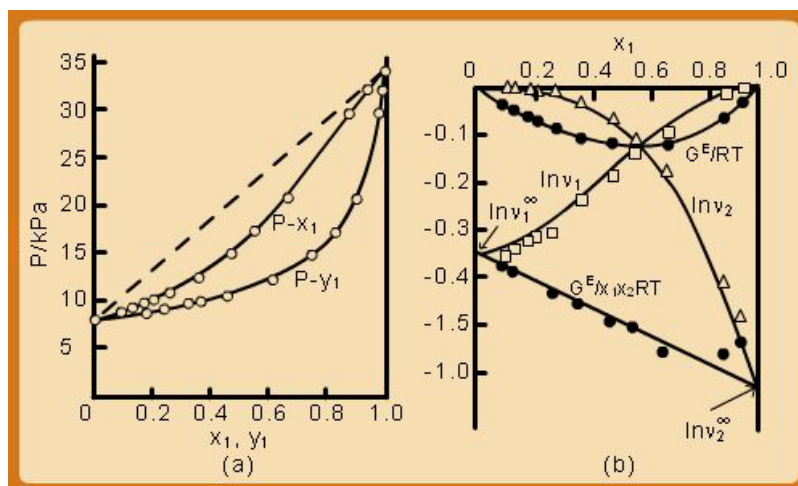

Fig. 6.11 Representative plot of experimental P-x-y, activity coefficient and molar excess Gibbs free energy data for systems exhibiting negative deviation from Raoult's Law

Once the values of the parameters A, B, C etc., have been calculated from an isothermal set of VLE data, the actual function for the activity coefficients may be derived by applying eqn. 6.174.

6.18 Activity Coefficient Models

In this section we present the forms of the various activity coefficient models commonly used for VLE calculations. Such models may be divided into two major groups depending upon their applicability to various types of solutions:

1. Margules/Van Laar/Regular Solution Models
2. Wilson/NRTL (Non-Random Two Liquid)/UNIQUAC (Universal Quasi Chemical) Model.

The models in Group 1 are termed as "Homogeneous Mixture" models, while those in Group 2 are termed "Local Composition" models. The reason for such distinction is as follows. The non-ideal behaviour of liquid solutions derives from two sources: (i) difference in *molecular size/shape* of constituent (ii) and the difference between the *inter-species and intra-species molecular interaction energies*. The Group 1 models generally apply to systems in which the inter-species and intra-species molecular interaction energies differ from each other, but in a relatively moderate measure. On the other hand type 2 models are principally useful for describing systems where the constituent molecular species differ on account of both size/shape as well molecular interaction energies. Thus while group I models useful for moderate deviation from ideal solution behaviour, those in group 2 represent strongly non-ideal solutions.

In case the chemical species in the solution do not differ significantly in terms of size/shape, they tend to distribute uniformly across the entire solution volume. Accordingly Group 1 models are based on the premise that molecules are "homogeneously" distributed over the solution volume in that there is no difference between the overall *macroscopic* composition and *microscopic* (local) composition around a single central molecule. The Group 2 models, however, account for both types of differences: in the size of the molecules of the chemical species as well as in their interaction energies. It is reasonable to expect that owing to such differences molecular packing at the microscopic level to be non-homogeneous. As a result, the local composition around a central molecule is likely to differ from the average macroscopic composition.

All models used for predicting species activity coefficient contain about 2 – 3 parameters. Models which employ a larger number of parameters improve the accuracy of prediction but at the

same time are rendered computationally difficult. Additionally a larger number of experimentally determined values of activity coefficients are needed for fixing the values of the model parameters. In general, these parameters are much more sensitive to variations in temperature than pressure. This has already been highlighted while discussing the significance of eqns. 6.175 and 6.176. Thus, if computations of the activity coefficients occur over reasonably low range of pressures (typically about 10-20 bar) the model parameters may be assumed to remain invariant. The dependence of enthalpic quantities on temperature is usually strong. Thus, once again inspecting eqn. 6.176, we may conclude that, in general, the dependence of activity coefficients on temperature variations is relatively more significant. If the temperature variations over which activity coefficients are needed exceed $\sim 10^0$C, the effect of temperature on model parameters need to be considered. Table 6.1 presents the domain of applicability of the various commonly used activity coefficient models. For simplicity, we provide in the table 6.2 the model expressions for *binary solutions* and that of the corresponding activity coefficient formulas. In table 6.3 expressions of select models for higher order liquid mixtures are presented.

Table 6.1 Applicability of Activity Coefficient Models

System Type	Models
Species similar in size and shape	One-constant Margules
Moderately non-ideal mixtures	Two-constant Margules, Van Laar, Regular Solution
Strongly non-ideal mixtures (for example Alcohols+Hydrocarbons)	Wilson, NRTL, UNIQUAC
Solutions with miscibility gap	NRTL, UNIQUAC

Table 6.2: Select Models for the Excess Gibbs Energy and Activity Coefficients for Binary Systems

Model Name	G^E/RT	Binary parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Two-suffix Margules	$G^E/RT = Ax_1x_2$ (One-constant)	A	$\ln \gamma_1 = Ax_2^2$
			$\ln \gamma_2 = Ax_1^2$
Three-suffix Margules	$G^E/RT = x_1x_2(A_{21}x_1 -$ (Two-constant)	A_{21}, A_{12}	$\ln \gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$
			$\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$
Van Laar	$G^E/RT = \dfrac{A_{12}A_{21}x_1x_2}{A_{12}x_1 + A_{21}}$	A_{21}, A_{12}	$\ln \gamma_1 = A_{12}/(1 + \dfrac{A_{12}}{A_{21}}\dfrac{x_1}{x_2})^2 ;$ $\ln \gamma_2 = A_{21}/(1 + \dfrac{A_{21}}{A_{12}}\dfrac{x_2}{x_1})^2$ Conversely: $A_{12} = \ln \gamma_1 (1 + \dfrac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1})^2 ; A_{21} = \ln \gamma_2 (1$
Wilson	$\dfrac{G^E}{RT} = -x_1 \ln(x_1 + x_2\Lambda_{12})$	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_1 = \ln(x_1 + x_2\Lambda_{12}) + x_2\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}}\right.$
			$\ln \gamma_2 = \ln(x_2 + x_1\Lambda_{21}) + x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}}\right.$
NRTL	$G^E/RT = x_1x_2\left(\dfrac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \dfrac{\tau_{12}G_{12}}{x_2 + x_1G_1}\right.$		$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\dfrac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \dfrac{\tau_1}{(x_2 + }\right.$

Where,

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

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

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau}{\left(x_1 + \right.} \right.$$

Except for the NRTL model, all others are characterized by two parameters that are essentially *adjustable* with variations of temperature. For the Wilson equation in the above table the parameters are defined as follows:

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{a_{12}}{RT}\right); \Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{a_{21}}{RT}\right) \qquad\qquad\qquad ..(6.183)$$

Here V_1 and V_2 are the pure component molar volumes at the temperature of the system; and a_{12} and a_{21} are constants for a given pair of components. However, as the expressions in 6.183 indicate, the parameters Λ_{12} and Λ_{21} are temperature dependent. The parameters for NRTL are, α, τ_{12}, and τ_{21}, the latter two are temperature dependent.

Table 6.3 Expressions for the Molar Excess Gibbs Energy and Activity Coefficients of Multi-component Systems obeying Wilson & NRTL Models

Name	Molar excess Gibbs energy	Activity coefficient for component i
Wilson	$\dfrac{G^E}{RT} = -\sum_i^N x_i \ln\left(\sum_j^N x_j\Lambda_{ij}\right)$	$\ln\gamma_i = 1 - \ln\left(\sum_j^N x_j\Lambda_{ij}\right) - \sum_k \dfrac{x_k\Lambda_{ki}}{\sum_j x_j\Lambda_{kj}}$
NRTL	$\dfrac{G^E}{RT} = \sum_i^N x \dfrac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k G_{ki}x_k}$	$\ln\gamma_i = \dfrac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k} + \sum_k^N \dfrac{x_jG_{ij}}{\sum_k^N G_{kj}x_k}\left(\tau_{ij} - \dfrac{\sum_k^N x_k\tau_{kj}G_{kj}}{\sum_k^N G_{kj}x_k}\right)$

A common feature of all the models are that the parameters are basically related to the infinite dilute activity coefficients for each binary. Table 6.4 provides the relevant relations for each model.

Table 6.4 Relation between the model parameters and infinite dilute activity coefficients

Model	Relation between the model parameters and infinite dilute activity coefficients
Two-suffix Margules	$\ln\gamma_1^\infty = \ln\gamma_2^\infty = A$
Three-suffix Margules	$\ln\gamma_1^\infty = A_{12}$; $\ln\gamma_2^\infty = A_{21}$
Van Laar	$\ln\gamma_1^\infty = A_{12}$; $\ln\gamma_2^\infty = A_{21}$
Wilson	$\ln\gamma_1^\infty = 1 - \Lambda_{21} - \ln\Lambda_{12}$; $\ln\gamma_2^\infty = 1 - \Lambda_{12} - \ln\Lambda_{21}$
NRTL	$\ln\gamma_1^\infty = \tau_{21} + \tau_{12}\exp(-\alpha\tau_{12})$; $\ln\gamma_2^\infty = \tau_{12} + \tau_{21}\exp(-\alpha\tau_{21})$

Example 6.10

Methanol (1)-acetone (2) system is described by the Van Laar activity coefficient model. At 60^0C, the model parameters are $A_{12} = 0.47;\ A_{21} = 0.78$. Estimate the activity coefficients for a solution containing 10mole% of methanol.

Regular Solution (RS) Model

This activity coefficient model is derived for solutions that show moderate deviations from ideal solution behaviour, and for which V^E and S^E are both zero. The model was proposed by Scatchard and Hildebrand (J. H. Hildebrand & R. L Scott. *The Solubility of Non-electrolytes*, Dover, 1964) and constitutes one of few models that are derived from theory. Known as the *Regular Solution Model*, the molar excess Gibbs free energy function is given by:

$$G^E / RT = (x_1 V_1 + x_2 V_2) \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 \qquad \qquad ..(6.184)$$

It follows that:

$$\ln \gamma_1 = V_1 \Phi_2^2 (\delta_1 - \delta_2)^2 \qquad \qquad ..(6.185)$$

$$\ln \gamma_2 = V_2 \Phi_1^2 (\delta_1 - \delta_2)^2 \qquad \qquad ..(6.186)$$

where, Φ_i = volume fraction = $\dfrac{x_i V_i}{V_m}$; V_i = molar volume of pure ith species, and $V_m = \sum_i x_i V_i$

Further: δ_i = solubility parameter for i^{th} species, which is given by:

$$\delta_i = \sqrt{\frac{\left(\Delta U_i^{vap}\right)}{V_i}} \cong \sqrt{\frac{\left(\Delta H_i^{vap} - RT\right)}{V_i}} \qquad \qquad ..(6.187)$$

Where, ΔU_i^{vap}, ΔH_i^{vap} are molar internal energy, and enthalpy of vapourization of ith species at the temperature of interest.

The above relations may be extended to multi-component mixtures for which:

$$RT \ln \gamma_i = V_i \left(\delta_i - \bar{\delta}\right)^2 \qquad \qquad ..(6.188)$$

$$\bar{\delta} = \sum_j \Phi_j \delta_j \qquad \qquad ..(6.189)$$

$$\Phi_j = \frac{x_j V_j}{\sum_j x_j V_j} \; ; \; (\text{where, } j \to \text{runs over all the species}) \qquad \qquad ..(6.190)$$

The solubility parameters for a set of select substances are provided in Appendix IV.

Example 6.11

Use of Regular Solution Model to estimate activity coefficients for an equimolar benzene (1) / cyclohexane (2) solution 350°K. The solubility parameters are: $\delta_1 = 9.2 \; (\text{cal/cm}^3)^{1/2}$; $\delta_2 = 8.2 \; (\text{cal/cm}^3)^{1/2}$. The molar volumes: $V_1^L = 88 \; \text{cm}^3/\text{mol}$; $V_2^L = 107 \; \text{cm}^3/\text{mol}$

(Click for solution)

UNIQUAC: Group Contribution Method for Evaluation of Activity Coefficients

The acronym UNIQUAC stands for *Universal Quasi Chemical Equation*. The principle that the UNIQUAC method is founded on is that of *group contribution*. The methodology is based on the postulate that any thermo-physical property of a pure substance is a *weighted sum* of the chemical groups that constitute it. Since the number of functional groups (such as $-CH_3, -CH_2, -OH, -COOH$, etc.) are few (about 50 or so) in comparison to the vast number of chemical species they can form, the approach based on group contribution constitutes an universal, and indeed a versatile method of prediction of a wide variety of properties of a very large number of substances. Properties as diverse as normal boiling point, enthalpy of vapourization, molar volume, thermal conductivity, viscosity, surface tension, etc may be estimated when no direct experimental data are available.

While estimating any property, a molecule is decomposed into the functional groups that make it up. Intermolecular interactions (in a pure fluid or a mixture) are then considered to be approximately equal to the weighted sum of group-group interactions. Characteristic quantitative values representing group interactions have been obtained from regression of experimental data for binary systems. The use of this approach for predicting a wide variety of number of physic-chemical properties has been demonstrated comprehensively by Reid et. al. (J C. Reid, J. M. Prausnitz, and B. E. Polling, *The Properties of Gases and Liquids*, 4th ed. McGraw Hill, 1987). A group contribution method is, however, necessarily approximate as it is based on the simple additivity of contributions from each

group; further it assumes the contribution made by each group is independent of the nature of the adjacent group.

In extending the method to prediction of activity coefficients, the molar excess Gibbs free energy is divided into two parts: *combinatorial* and *residual*. The combinatorial part accounts for non-ideality of a mixture arising from *differences in size and shape* of constituent molecular species; whereas the residual part considers the *difference between inter-molecular and intra-molecular interaction energies.*

We provide there the final UNIQUAC activity coefficient relations for a binary. It is may be easily extended to represent ternary and higher order mixtures (J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1998). The function $g \equiv G^E / RT$ is comprised of the combinatorial and residual parts as follows:

$$g = g^C + g^R \qquad \qquad ..(6.191)$$

The combinatorial part represents pure species parameters, while the residual part contains two binary parameters for each pair of molecules. In general for a system comprised of N molecular species, we have the following relations:

$$g^C = \sum_i^N x_i \ln \frac{\Phi_i}{x_i} + 5 \sum_i^N q_i x_i \ln \frac{\theta_i}{\Phi_i} \qquad \qquad ..(6.192)$$

$$g^R = -\sum_i^N q_i x_i \ln \left(\sum_j \theta_i \tau_{ji} \right) \qquad \qquad ..(6.193)$$

Where:

$$\Phi_i = \frac{x_i r_i}{\sum_j^N x_j r_j} \qquad \qquad ..(6.194)$$

$$\theta_i = \frac{x_i q_i}{\sum_j^N x_j q_j} \qquad \qquad ..(6.195)$$

r_i = relative molecular volume; q_i = relative molecular surface area (both are pure species parameters)

The binary interaction parameters τ_{ji} and τ_{ij} which need to be regressed from binary VLE data are temperature dependent. They are the UNIQUAC *model parameters* and are provided by:

$$\tau_{ji} = \exp\left[-\left(\frac{u_{ji}-u_{ii}}{RT}\right)\right]; \text{ and, } \tau_{ij} = \exp\left[-\left(\frac{u_{ij}-u_{jj}}{RT}\right)\right] \qquad ..(6.196)$$

The activity coefficient is also divided into two parts:

$$\ln\gamma_i = \ln\gamma_i^C (combinatorial) + \ln\gamma_i^R (residual) \qquad ..(6.197)$$

$$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \qquad ..(6.198)$$

$$\ln\gamma_i^R = q_i\left(1 - \ln s_i - \sum_j^N \theta_j \frac{\tau_{ij}}{s_j}\right); \rightarrow (j \equiv \text{dummy variable}) \qquad ..(6.199)$$

$$J_i = \frac{r_i}{\sum_j^N r_j x_j} \qquad ..(6.200)$$

$$L_i = \frac{q_i}{\sum_j^N q_j x_j} \qquad ..(6.201)$$

$$s_i = \sum_l^N \theta_l \tau_{li}; (l \rightarrow \text{dummy index})$$

The computation of the parameters J_i, L_i and s_i is based on the UNIFAC (*Universal Functional Group Activity Coefficients*) method (see eqns. 6.202 and 6.203 below), which is an extension of the UNIQUAC model. The application of the UNIFAC method is premised on the idea that a solution is composed of the sub-groups rather than molecules themselves. The groups are essentially small, self-contained chemical units, each designated as *k*, for which the relative volume and surface areas are denoted as R_k and Q_k respectively. When a molecule may be constructed from more than a single set of subgroups, the one with the least number of different subgroups is assumed as the correct one. The values of R_k and Q_k for various common subgroups are shown in table 1 of *Appendix V*. More exhaustive tables may be found elsewhere (J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1998).

Apart from the dependence on pure species properties species R_k and Q_k, the activity coefficients are functions of interaction between the various subgroups. As shown in table 1 of Appendix V, a cluster of sub-groups are classified under a main group, which are primarily descriptive. All subgroups under a main group are identical with respect to group interactions. Accordingly the

interaction between group parameters is identified with pairs of main groups under which the former are classified. Parametric values of select pairs of main groups are provided in table 2 of *Appendix V*.

One of the distinct advantages of the UNIFAC model is that it is able to predict activity coefficients more effectively in mixtures where constituent molecules have large size differences, as in polymer solutions.

In the UNIFAC method the expression for the combinatorial part of the activity coefficient is the same as that in eqn. 6.196. However, the residual part takes a somewhat different form.

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right)$$

..(6.200)

$$\ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k} \right) \right] \rightarrow (k \equiv subgroup)$$

..(6.201)

The terms J_i *and* L_i are given by eqns. 6.198 and 6.199. However, the other parameters are defined as:

$$r_i = \sum_k v_k^{(i)} R_k$$

..(6.202)

$$q_i = \sum_k v_k^{(i)} Q_k$$

..(6.203)

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i}$$

..(6.204)

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk}$$

..(6.205)

$v_k^{(i)} \equiv$ number of kth subgroup in i^{th} molecular species

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j}$$

..(6.206)

$$s_k = \sum_m \theta_m \tau_{mk}$$

..(6.207)

$$\tau_{mk} = \exp\left(-\frac{a_{mk}}{T} \right)$$

..(6.208)

Thus, in summary the key UNIFAC parameters are R_K, Q_K and a_{mk}. Tables containing the values of these parameters are recorded more exhaustively elsewhere (H. K. Hansen, P. Rasmusen, Aa.

Fredenslund, M.Schiller, and J. Gmehling, *IEC Research*, Vol 30, pp 2352 – 2355, 1991; and R.C Reid, J, M., Prausnitz, and B.E. Poling, in Properties of Gases and Liquids, 4th ed., McGraw-Hill, 1987). All the parameters in the UNIFAC approach are essentially binary and there are effectively two parameters that need to be determined from experimental VLE data.

Example 6.12

Use UNIFAC model to estimate activity coefficients for an equimolar n-pentane (1) /acetone (2) solution 320°K.

(Click for solution)

Appendix 6.1

Some relations among partial properties

Every equation that provides a *linear* relation among thermodynamic properties of a *constant-composition* (single-phase) solution can be used to derive a corresponding equation relating the partial molar properties. As an example, this is demonstrated below for the property enthalpy.

One may write for a constant composition solution: $H = U + PV$

It follows that for the entire system: $nH = nU + P(nV)$

Applying the definition of partial molar properties:

$$\left[\frac{\partial(nH)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \left[\frac{\partial(nU)}{\partial n_i}\right]_{T,P,n_{j\neq i}} + P\left[\frac{\partial(nV)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \qquad ..(A.6.1.1)$$

Hence: $\bar{H}_i = \bar{U}_i + P\bar{V}_i$

Similar relations may be derived for other thermodynamic properties. Other forms of relationships are also derivable as is illustrated below, as an example, using Gibbs free energy relations.

For an open multi-component system: $d(nG) = (nV)dP - (nS)dT + \sum_i \bar{G}_i dn_i$ \qquad ..(A.6.1.2)

By Maxwell Relations: $\left(\frac{\partial V}{\partial T}\right)_{P,n} = -\left(\frac{\partial S}{\partial P}\right)_{T,n}$

Also for both P and n = constant, we have: $d(nG) = -(nS)dT$

Or $\left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -(nS)$ \qquad ..(A.6.1.3)

Thus:
$$\left[\frac{\partial}{\partial n_i}\left\{\frac{\partial(nG)}{\partial T}\right\}_{P,n}\right]_{T,P,n_{j\neq i}} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$$

Or:
$$\left[\frac{\partial}{\partial T}\left\{\frac{\partial(nG)}{\partial n_i}\right\}_{T,P,n_{j\neq i}}\right]_{P,n} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$$

Hence
$$\left[\frac{\partial \overline{G}_i}{\partial T}\right]_{P,n} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = -\overline{S}_i \qquad ..(A.6.1.4)$$

In the same manner, it may be shown that:
$$\left[\frac{\partial \overline{G}_i}{\partial P}\right]_{T,n} = -\left[\frac{\partial(nV)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \overline{V}_i \qquad ..(A.6.1.5)$$

So if one writes at const n, $\overline{G}_i = \overline{G}_i(T,P)$, it follows:

$$d\overline{G}_i = \left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial \overline{G}_i}{\partial T}\right)_{P,x_i} dT \qquad ..(A.6.1.6)$$

Using (A.6.1.4) and (A.6.1.5) in (A.6.1.6) one obtains:

$$d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT \qquad ..(A.6.1.7)$$

Equation A.6.1.7 is exploited in the derivation of relations for fugacity of individual species in real mixtures. As with the Gibbs free energy function; those given by eqns. 5.3 – 5.5 can be used as starting points for the corresponding relations of the form given by eqn. A.6.1.7.

Appendix 6.2

Derivation of the expression for species fugacity coefficient for pressure explicit EOS

$dG = VdP - SdT$

It may be shown that: $d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT$

At constant T: $d\overline{G}_i = \overline{V}_i dP$ $\qquad$ ..(A.6.2.1)

Using (A.6.2.1) and (A.6.2.2): $\overline{V}_i dP = RTd\ln \hat{f}_i$ $\qquad$ ..(A.6.2.3)

But by defintion: $d\overline{G}_i = RTd\ln \hat{f}_i$ $\qquad$ ..(A.6.2.2)

We may also write for the pure compoent: $dG_i^{ig} = V_i^{ig} dP$ $\qquad$ ..(A.6.2.4)

$$dG_i^{ig} = RT \ln \hat{f}_i^{ig} \qquad ..(A.6.2.5)$$

Using $(A.6.2.2)$ and $(A.6.2.5)$ and integrating: $\bar{G}_i - G_i^{ig} = RT \ln \left(\dfrac{\hat{f}_i}{\hat{f}_i^{ig}} \right)$

Or: $\bar{G}_i - G_i^{ig} = RT \ln \left(\dfrac{\hat{f}_i}{y_i P} \right) \qquad ..(A.6.2.6)$

Equivalently, using $(A.6.2.3)$ and $(A.6.2.4)$: $\bar{G}_i - G_i^{ig} = \dfrac{1}{RT} \int_0^P (\bar{V}_i - V_i^{ig}) dP$

Or: $\bar{G}_i - G_i^{ig} = \dfrac{1}{RT} \int_0^P \left(\bar{V}_i - \dfrac{RT}{P} \right) dP \qquad ..(A.6.2.7)$

Next we develop the expression for fugacity coefficient using the foregoing relations.

Using $(A.6.2.2)$ and $(A.6.2.3)$:

$$RT \left(\frac{\partial \ln \hat{f}_i}{\partial P} \right)_{T,n_i} = \bar{V}_i = \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,n_i} \qquad ..(A.6.2.8)$$

In the last eqn. $(\ )_{n_i}$ implies that all $n_i = $ constant

$$\text{Now:} \left(\frac{\partial \mu_i}{\partial P} \right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial V} \right)_{T,n_i} \left(\frac{\partial V}{\partial P} \right)_{T,n_i} \qquad ..(A.6.2.9)$$

Putting $(A.6.2.9)$ in $(A.6.2.8)$ and rearranging:

$$RT \left(\frac{\partial \ln \hat{f}_i}{\partial P} \right)_{T,n_i} \left[\frac{1}{\left(\dfrac{\partial V}{\partial P} \right)_{T,n_i}} \right] = \left(\frac{\partial \mu_i}{\partial V} \right)_{T,n_i}$$

$$RT \left(\frac{\partial \ln \hat{f}_i}{\partial P} \right)_{T,n_i} \left(\frac{\partial P}{\partial V} \right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial V} \right)_{T,n_i}$$

$$RT \left(\frac{\partial \ln \hat{f}_i}{\partial V} \right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial V} \right)_{T,n_i} \qquad ..(A.6.2.10)$$

For a multi-component mixture we may write the following expression for the total Helmholtz free energy:

$$A^t = A^t(T,V,n_1,n_2,...n_N)$$

One may write: $\left(\dfrac{\partial^2 A^t}{\partial V \partial n_i}\right) = \left(\dfrac{\partial^2 A^t}{\partial n_i \partial V}\right)$

Or: $\left[\dfrac{\partial}{\partial V}\left(\dfrac{\partial A^t}{\partial n_i}\right)_{T,V,n_j}\right]_{T,n_i} = \left[\dfrac{\partial}{\partial n_i}\left(\dfrac{\partial A^t}{\partial V}\right)_{T,n_i}\right]_{T,V,n_j}$ ..(A.6.2.11)

One can also prove that the chemical potential may be expressed in any of the following forms:

$$\mu_i = \left(\dfrac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\dfrac{\partial H^t}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\dfrac{\partial A^t}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\dfrac{\partial G^t}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Also, since $A^t = A^t(T,V^t,n_1,...,n_N); t = total$

$$dA^t = \left(\dfrac{\partial A^t}{\partial V^t}\right)_{T,n_i} dV + \left(\dfrac{\partial A^t}{\partial T}\right)_{V^t,n_i} dT + \sum_i \left(\dfrac{\partial A^t}{\partial n_i}\right)_{T,V^t,n_j} dn_i$$

By comparison to the coresponding closed system expression:

$$dA^t = -PdV^t - S^t dT + \sum_i \left(\dfrac{\partial A^t}{\partial n_i}\right)_{T,V,n_j} dn_i$$

Thus: $\left(\dfrac{\partial A^t}{\partial V^t}\right)_{T,n_i} = \left(\dfrac{\partial A}{\partial V}\right)_{T,n_i} = -P$

Therefore, eqn. (A.6.2.11) may be written as:

$$\left(\dfrac{\partial \mu_i}{\partial V}\right)_{T,n_i} = -\left(\dfrac{\partial P}{\partial n_i}\right)_{T,V,n_j} \tag{A.6.2.12}$$

Using $(A.6.2.10)$ and $(A.6.2.12)$:

$$RT\left(\dfrac{\partial \ln \hat{f}_i}{\partial V}\right)_{T,n_i} = -\left(\dfrac{\partial P}{\partial n_i}\right)_{T,V,n_j} \tag{A.6.2.13}$$

In general: $RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i} = RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i} + RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i}$

$$= RT\left(\dfrac{\partial \ln P}{\partial V}\right)_{T,n_i} + RT\left(\dfrac{\partial \ln V}{\partial V}\right)_{T,n_i} = RT\left(\dfrac{\partial \ln P}{\partial V}\right)_{T,n_i} + \dfrac{RT}{V}$$

Thus: $-RT\left(\dfrac{\partial \ln P}{\partial V}\right)_{T,n_i} = \dfrac{RT}{V} - RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i}$ ..(A.6.2.14)

Adding (13) and (14) one gets:

$$\int_{V=\infty}^{V} \left\{ RT \left(\frac{\partial \ln(\hat{f}_i / P)}{\partial V} \right)_{T,n_i} \right\} dV = \int_{V=\infty}^{V} \left\{ \frac{RT}{V} - \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - RT \left(\frac{\partial \ln PV}{\partial V} \right)_{T,n_i} \right\} dV$$

$$RT \ln \left(\frac{\hat{f}_i}{P} \right) - \left[RT \ln \left(\frac{\hat{f}_i}{P} \right) \right]_{V=\infty} = \int_{V=\infty}^{V} \left\{ \frac{RT}{V} - \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} \right\} dV - RT \ln PV + RT \ln RT$$

$$..(A.6.2.15)$$

But : $\left[RT \ln \left(\frac{\hat{f}_i}{P} \right) \right]_{V=\infty} = \left[RT \ln \left(\frac{y_i P}{P} \right) \right]_{V=\infty}$; since at $V = \infty$, i.e. ideal gas situation, $\hat{f}_i = y_i P$

Thus eqn.$(A.6.2.15)$ becomes:

$$RT \ln \left(\frac{\hat{f}_i}{y_i P} \right) = \int_{V=\infty}^{V} \left\{ \frac{RT}{V} - \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} \right\} dV - RT \ln(PV / RT)$$

$$RT \ln \hat{\phi}_i = -\int_{V=\infty}^{V} \left\{ \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right\} dV - RT \ln Z \qquad ..(A.6.2.16)$$

Equation (A.6.2.16) is useful for deriving the analytical expression for the fugacity coefficient of species in a mixture using typical pressure explicit cubic EOSs. However, for doing that the expression for $\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j}$ has to be obtained. This has been presented earlier in section 6.14.

Assignment- Chapter 6