Chapter 9: Other Topics in Phase Equilibria

This chapter deals with relations that derive in cases of equilibrium between combinations of two co-existing phases other than vapour and liquid, i.e., liquid-liquid, solid-liquid, and solid-vapour. Each of these phase equilibria may be employed to overcome difficulties encountered in purification processes that exploit the difference in the volatilities of the components of a mixture, i.e., by vapour-liquid equilibria. As with the case of vapour-liquid equilibria, the objective is to derive relations that connect the compositions of the two co-existing phases as functions of temperature and pressure.

9.1 Liquid-liquid Equilibria (LLE)

9.1.1 LLE Phase Diagrams

Unlike gases which are miscible in all proportions at low pressures, liquid solutions (binary or higher order) often display partial immiscibility at least over certain range of temperature, and composition. If one attempts to form a solution within that certain composition range the system splits spontaneously into two liquid phases each comprising a solution of different composition. Thus, in such situations the equilibrium state of the system is two phases of a fixed composition corresponding to a temperature. The compositions of two such phases, however, change with temperature. This typical phase behavior of such binary liquid-liquid systems is depicted in fig. 9.1a. The closed curve represents the region where the system exists
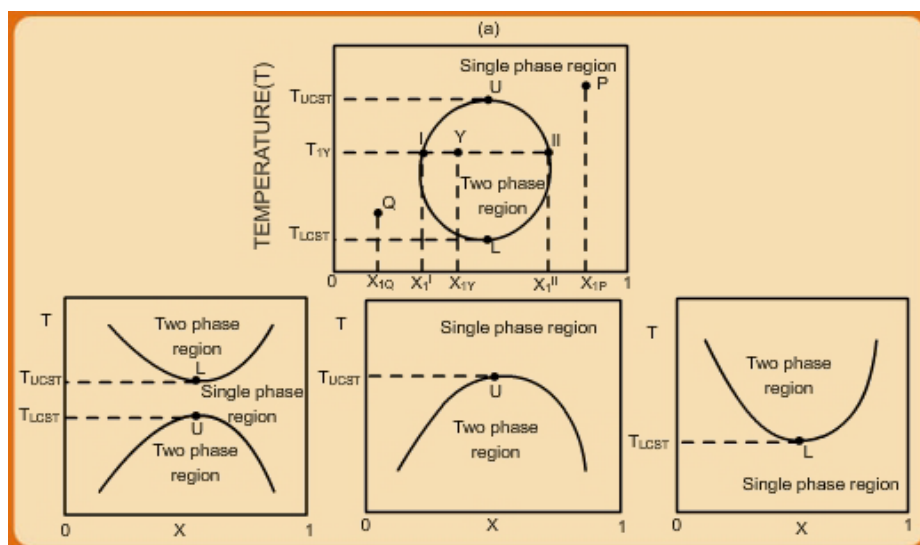

Fig. 9.1 Phase diagrams for a binary liquid system showing partial immiscibility

in two phases, while outside it the state is a homogenous single liquid phase. Take for example, the point P (or Q). This point defines a state where a homogeneous liquid solution exists at a temperature T_P (or T_Q) with a composition x_{1P} (or x_{1Q}). However, if one tries to form a solution of composition x_{1Y} (at a temperature T_Y) the system automatically splits into two liquid phases (I and II) with compositions given by x_1^I and x_1^{II}. The straight line MYN represents a tie-line, one that connects the compositions of the two liquid phases that co-exist in equilibrium. Any attempt to form a solution at T_Y with a composition corresponding to any point within MYN always results in two phases of fixed compositions given by x_1^I and x_1^{II}. The total mass (or moles) of the original solution is distributed between the two phases accordingly. Note, however, that the compositions at the end tie lines (horizontal and parallel to MYN) change as the temperature changes. Indeed as one approaches either point U or L, the tie line reduces to a point, and beyond either point the system exists as a single homogeneous solution. The temperatures corresponding to points U and L, i.e., T_{UCST} and T_{LCST} are called the *Upper Consolute Solution Temperature* (UCST) and *Lower Consolute Solution Temperature* (LCST) respectively. They define the limit of miscibility of the components of the binary solution. Not all liquid-liquid systems, however, depict the behaviour described by fig. 9.1a. Other variants of phase behaviour are shown in figs. 9.1b – 9.1c. In each case there is at least one consolute temperature.

9.1.2 Phase Stability Criteria

The passage of a liquid solution from a state of a single, homogeneous phase to a biphasic LLE state occurs when a single phase is no longer thermodynamically stable. It is instructive to derive the conditions under which this may take place. Let us consider a binary liquid mixture for example for which the molar Gibbs free energy of mixing (ΔG_{mix}) is plotted as function of mole fraction (x_1) of component 1 for two temperatures T_1 and T_2 (fig. 9.2). At temperature T_1 the value of ΔG_{mix} is always less than zero and also goes through a *minimum*. This signifies that the mixture forms a single liquid phase at all compositions at the given temperature. The mathematical description of this condition is given by the two following equations:

$$\left(\frac{\partial G_{mix}}{\partial x_1} \right)_{T,P} = 0 \qquad\qquad ..(9.1)$$

And:

$$\left(\frac{\partial^2 G_{mix}}{\partial x_1^2}\right)_{T,P} > 0 \qquad\qquad ..(9.2)$$

Alternately:

$$\left(\frac{\partial \Delta G_{mix}}{\partial x_1}\right)_{T,P} = 0 \qquad\qquad ..(9.3)$$

And:

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2}\right)_{T,P} > 0 \qquad\qquad ..(9.4)$$

However, at certain other temperature T_2 the value of ΔG_{mix}, while being always less than zero, passes through a region where it is concave to the composition axis. Consider a solution with a composition given by the point 'A'. At this composition the Gibbs free energy of the mixture is given by:

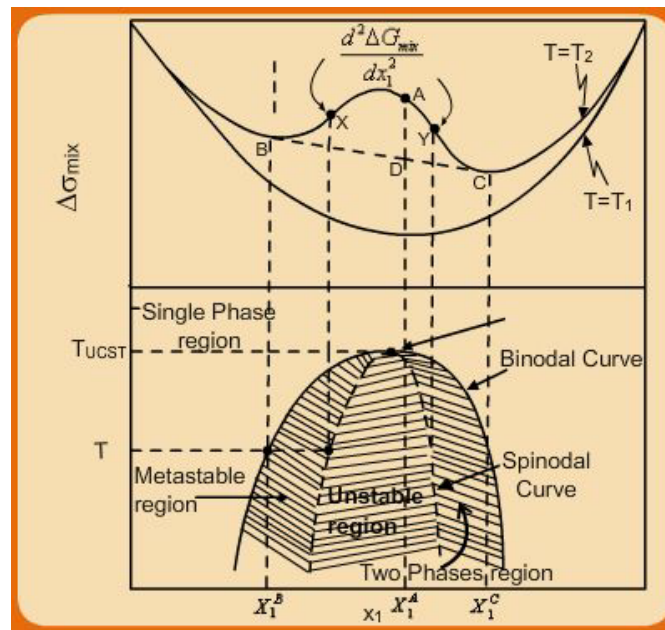$$G_{mix}^A = x_1^A G_1 + x_2^A G_2 + \Delta G_{mix}^A \qquad\qquad ..(9.5)$$

Fig. 9.2 Molar Gibbs free energy mixing vs. mole fraction x_1 for a binary solution

Let the points 'B' and 'C' denote the points of at which a tangent BC is drawn on the ΔG_{mix} curve for the isotherm T_2, and 'D' the point vertically below 'A' on the straight line BC (which is a tangent to the ΔG_{mix} curve at points B and C). If the solution at 'A' splits into two

phases with compositions characterized by x_1^B and x_1^C then its molar Gibbs free energy is given by:

$$G_{mix}^B = x_1^A G_1 + x_2^A G_2 + \Delta G_{mix}^D \qquad \qquad ..(9.6)$$

Clearly, since $\Delta G_{mix}^D < \Delta G_{mix}^A$, $(or\ G_{mix}^D < G_{mix}^A)$ a phase splitting is thermodynamically favoured over a single phase solution of composition x_1^A. Point 'D' represents the *lowest* Gibbs free energy that the mixture with an overall composition x_1^A can have at the temperature T_2. In other words, at the temperature T_2 a solution with an *overall* composition x_1^A exists in two phases characterized by compositions x_1^B and x_1^C. If n_B and n_C represent the quantities of solution in each phase then the following equation connects x_1^A to x_1^B and x_1^C :

$$x_1^A = \left(n_B x_1^B + n_C x_1^C \right) / \left(n_B + n_C \right) \qquad \qquad ..(9.7)$$

The above considerations allow one to formulate a phase separation criteria for liquid solutions. Essentially, for phase splitting to occur, the ΔG_{mix} curve must *in part* be concave to the composition axis. Thus in general mathematical terms a homogeneous liquid solution becomes *unstable* if:

$$\left(\partial^2 G_{mix} / \partial x^2 \right)_{T,P} < 0; \quad (where,\ x \equiv x_i) \qquad \qquad ..(9.8)$$

It follows that the alternate criterion for *instability* of a single phase liquid mixture is:

$$\left(\partial^2 \Delta G_{mix} / \partial x^2 \right)_{T,P} < 0 \qquad \qquad ..(9.9)$$

It may be evident that at T_2 the above conditions hold over the composition range $x_1^B < x_1 < x_1^C$. Conversely, a homogeneous liquid phase obtains for compositions over the ranges $0 < x_1 < x_1^B$ and $x_1^C < x_1 < 1$. In these ranges, therefore, the following mathematical condition applies:

$$\left(\partial^2 G_{mix} / \partial x^2 \right)_{T,P} > 0 \qquad \qquad ..(9.10)$$

Or:

$$\left(\partial^2 \Delta G_{mix} / \partial x^2 \right)_{T,P} > 0 \qquad \qquad ..(9.11)$$

Referring again to fig. 9.2 it may be evident that at points 'X' and 'Y' the following mathematical condition holds:

$$\left(\partial^2 \Delta G_{mix} / \partial x^2 \right)_{T,P} = 0 \qquad \qquad ..(9.12)$$

A series of ΔG_{mix} curves at other temperatures (say between T_1 and T_2) may be drawn, each showing different ranges of unstable compositions. All such curves may be more concisely expressed by the $T-x$ plot in fig. 9.2. There is an absolute temperature T^C above which the mixture is stable at all compositions since the condition described by eqn. 9.11 applies at all compositions. The *binodal* curve in fig. 9.2 represents the boundary between the single phase region and the two phase regions. Within the two phase region the *spinodal* curve represents the locus of points at which $\left(\partial^2 \Delta G_{mix}/\partial x^2\right)_{T,P} = 0$. As may be evident from the $T-x$ plot in fig. 9.2, it is the boundary between the unstable $\left[\left(\partial^2 \Delta G_{mix}/\partial x^2\right)_{T,P} < 0\right]$ and *metastable* $\left[\left(\partial^2 \Delta G_{mix}/\partial x^2\right)_{T,P} > 0\right]$ regions.

The above mathematical conditions may be used to explain the phase behaviour depicted in fig. 9.1. Since the binary mixture displays both UCST and LCST, it follows that at $T > T_{UCST}$ and $T < T_{LCST}$ the mixture forms single phase at all compositions. Thus for such temperatures the ΔG_{mix} curve is described by eqn. 9.11, i.e., $\left(\partial^2 \Delta G_{mix}/\partial x^2\right)_{T,P} > 0$ for all compositions. Conversely for $T_{LCST} < T < T_{UCST}$ the ΔG_{mix} curve displays a form corresponding to that for temperature T_2 in fig. 9.2. That is, for $T_{LCST} < T < T_{UCST}$ there is partial immiscibility of the mixture. The mathematical conditions for the existence of the consolute temperatures may then be surmised by the following relations.

➢ For the existence of UCST:

$$\left\{\begin{array}{l} \dfrac{\partial^2 G}{\partial x_1^2} = 0 \text{ for some value of } x_1 \text{ at } T = T_{UCST} \\[2ex] \text{and} \\[2ex] \dfrac{\partial^2 G}{\partial x_1^2} > 0 \text{ for all values of } x_1 \text{ at } T > T_{UCST} \end{array}\right\}$$

➢ For the existence of UCST:

$$\left\{\begin{array}{l} \dfrac{\partial^2 G}{\partial x_1^2} = 0 \text{ for some value of } x_1 \text{ at } T = T_{LCST} \\[2ex] \text{and} \\[2ex] \dfrac{\partial^2 G}{\partial x_1^2} > 0 \text{ for all values of } x_1 \text{ at } T < T_{LCST} \end{array}\right\}$$

The foregoing mathematical relations are more conveniently expressed in terms of the excess molar Gibbs free energy function as follows:

$$G^E = G_{mix} - G_{mix}^{id} \qquad \qquad ..(9.13)$$

Or:

$$G^E = G_{mix} - \left[x_1 G_1 + x_2 G_2 + RT \left(x_1 \ln x_1 + x_2 \ln x_2 \right) \right] \qquad ..(9.14)$$

Thus:

$$G_{mix} = G^E + \left[x_1 G_1 + x_2 G_2 + RT \left(x_1 \ln x_1 + x_2 \ln x_2 \right) \right] \qquad ..(9.15)$$

On applying the criterion for instability given by eqn. 9.8, an equivalent criterion obtains as follows:

$$\left(\frac{\partial^2 G^E}{\partial x^2} \right)_{T,P} + RT \left(\frac{1}{x_1} + \frac{1}{x_2} \right) < 0$$

$$\left(\frac{\partial^2 G^E}{\partial x^2} \right)_{T,P} + \frac{RT}{x_1 x_2} < 0 \qquad \qquad ..(9.16)$$

For an ideal solution $G^E = 0$; hence the condition in eqn. 9.16 can never hold. Thus, and ideal solution can *never* display phase-splitting behaviour.

Consider now the case of a binary mixture described by the excess Gibbs free energy function: $G^E = \alpha x_1 x_2$. Thus:

$$\left(\frac{\partial^2 G^E}{\partial x^2} \right)_{T,P} = -2\alpha \qquad \qquad ..(9.17)$$

On applying the condition given by eqn. 9.16 one obtains the following relation:

$$-2\alpha + \frac{RT}{x_1 x_2} < 0 \qquad \qquad ..(9.18)$$

Or:

$$2\alpha > \frac{RT}{x_1 x_2} \qquad \qquad ..(9.19)$$

The maximum value of the term $x_1 x_2 = 0.25$; hence the values of α that satisfies the inequality 9.19 is given by:

$$\alpha \geq 2RT \qquad \qquad ..(9.20)$$

An equivalent criterion of instability may be derived using activity coefficient as a parameter in place of the excess Gibbs free energy function. For simplicity we consider a binary solution. Thus we have:

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad \qquad ..(9.21)$$

On differentiating eqn. 9.21 one obtains:

$$\frac{d\left(G^E / RT\right)}{dx_1} = \ln \gamma_1 - \ln \gamma_2 + x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} \qquad \text{..(9.22)}$$

By Gibbs-Duhem relation:

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \qquad \text{..(9.23)}$$

Hence:

$$\frac{d\left(G^E / RT\right)}{dx_1} = \ln \gamma_1 - \ln \gamma_2 \qquad \text{..(9.24)}$$

$$\frac{d^2\left(G^E / RT\right)}{dx_1^2} = \frac{d \ln \gamma_1}{dx_1} - \frac{d \ln \gamma_2}{dx_1} \qquad \text{..(9.25)}$$

Or, multiplying both sides by x_2:

$$x_2 \frac{d^2\left(G^E / RT\right)}{dx_1^2} = (1 - x_1)\frac{d \ln \gamma_1}{dx_1} - x_2 \frac{d \ln \gamma_2}{dx_1} \qquad \text{..(9.26)}$$

Applying the Gibbs-Duhem relation again and upon simplification eqn. 9.26 reduces to:

$$\frac{d^2\left(G^E / RT\right)}{dx_1^2} = \frac{1}{x_2} \frac{d \ln \gamma_1}{dx_1} \qquad \text{..(9.27)}$$

For stability of a solution using eqn. 9.16 we have:

$$\left(\frac{\partial^2 G^E}{\partial x^2}\right)_{T,P} + \frac{RT}{x_1 x_2} > 0 \qquad \text{..(9.28)}$$

Upon substituting eqn. 9.27 in 9.28 one obtains after due algebraic simplification:

$$\frac{d \ln(x_1 \gamma_1)}{dx_1} > 0 \qquad \text{..(9.28)}$$

The above relation provides a convenient starting point for determining if a certain activity coefficient model may predict phase instability. As an illustration we apply it to Wilson eqn. for a binary (see table 6.2) wherein:

$$\ln \gamma_1 = \ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right) \qquad \text{..(9.29)}$$

On using eqn. 9.29 in 9.28 and after algebraic simplification one obtains:

$$\frac{d \ln(x_1 \gamma_1)}{dx_1} = \frac{x_2 \Lambda_{12}^2}{x_1(x_1 + x_2 \Lambda_{12})^2} + \frac{\Lambda_{21}^2}{(x_2 + x_1 \Lambda_{21})^2} \qquad \text{..(9.30)}$$

It may be seen that the RHS of the above equation is always > 0, hence eqn. 9.28 is satisfied. Hence it follows that the Wilson equations *cannot* be used to predict instability of a liquid solution.

9.1.3 Solving the liquid-liquid phase equilibria problem

We now present the equations needed to obtain the phase compositions for a biphasic liquid-liquid equilibria condition. Consider two liquid phases *I* and *II*, in equilibrium with each other and each containing N species. One starts with the basic phase equilibria criterion:

$$\hat{f}_i^I = \hat{f}_i^{II}; \quad (i = 1, 2, ...N) \tag{9.31}$$

In practice the majority of liquid-liquid extraction operations are carried out at low to moderate pressures. Thus the fugacities may be expressed in terms of activity coefficients. On expanding each term in the above equation we get:

$$\hat{f}_i^I = (x_i \gamma_i f_i)^I \tag{9.32}$$

$$\hat{f}_i^{II} = (x_i \gamma_i f_i)^{II} \tag{9.33}$$

Where, x_i = mole fraction of ith species in a phase

Since both the phases are at the same temperature and pressure at equilibrium, the pure component fugacities are equal: $f_i^I = f_i^{II}$

Thus it follows that:

$$(x_i \gamma_i)^I = (x_i \gamma_i)^{II}$$

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II}; \quad (i = 1, 2, ...N) \tag{9.34}$$

Further by mole balance:

$$\sum x_i^I = 1 \tag{9.35}$$

$$\sum x_i^{II} = 1 \tag{9.36}$$

Equation 9.34 represents the generalized LLE criterion applicable to systems with any number of components distributed between two co-existing partially miscible liquid phases. Additionally, a suitable activity coefficient model needs to be assumed for solving the LLE problem. The phase compositions are derived by solving a set of *N* equations of the type 9.34 (one for each component), along with two constraining equations of the type 9.35 and 9.36.

Example 9.1

Use the van Laar activity coefficient expression to predict the compositions of co-existing liquid phases (I and II) comprised of two partially miscible liquids (1) and (2) at 50°C and 4 bar. At these conditions the van Laar equations are given by:

$$\ln \gamma_1 = \frac{A_{12}}{[1+\frac{A_{12}x_1}{A_{21}x_2}]^2}; \ln \gamma_2 = \frac{A_{21}}{[1+\frac{A_{21}x_2}{A_{12}x_1}]^2}; A_{12} = 2.5; A_{21} = 3.5$$

(Click for solution)

9.1.4 Ternary liquid-liquid equilibria

As may be evident from fig. 9.1a, under two-phase conditions, one of the liquid phases usually contains one of the components in a more concentrated form. This feature of liquid-liquid equilibria is exploited in the process industry, typically in the form of *ternary* liquid-liquid extraction. In many instances of practical interest a binary (or higher) liquid mixture cannot be adequately concentrated in one of the components by vapour-liquid separation processes; this, either because of inadequate difference in *volatility* of the components, or because there is an azeotrope formation. In such instances an alternate approach to purifying a species to the required extent from other components could be through the addition of a third liquid (solvent) that is *partially* miscible with the original solution. In such a case a second liquid phase results, where one of the components in the original mixture may become preferentially concentrated due to its higher affinity for the added solvent. As with binary systems one can solve this ternary LLE problem by application of eqns. 9.34 – 9.36. Such phase equilibria data (either experimental or computed) are typically plotted as a "triangular diagram". A very simple example of such a diagram is shown in fig. 9.3. More complex versions of such diagrams may be found elsewhere (see S.I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Edition, Wiley India, 2006).
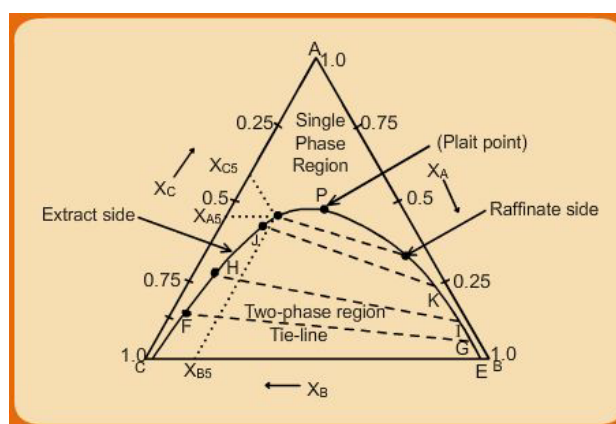

Fig. 9.3 Triangular diagram for ternary liquid-liquid phase equilibria

In this figure A and B comprise the original binary mixture to which a third, partially miscible solvent 'C' is added to preferentially extract A. Each apex of the triangle represents 100% mole (or mass) fraction of the species indicated at the apex. Each side of the triangle represents a mixture of two species that are indicated at the two ends of the side. The concentration of each species decreases linearly with distance along the perpendicular line that may be drawn from the apex to the opposite side of the triangle. The mass or mole fractions of each species corresponding to a point within the triangle is found by first drawing a line through the point parallel to the side opposite to the apex for that species. The point of intersection of the line with the appropriate side of the triangle provides the concentration fraction of the species. For example, for the point J the constituent compositions are shown as x_{AJ}, x_{BJ} and x_{CJ} respectively on the three sides of the triangle.

The dome shaped region DPE corresponds to the *two phase* region in the triangular diagram, while any point outside it represents either a binary or a ternary homogeneous mixture. The lines FG, HI, JK are typical tie lines across the two-phase region. The two end points of the line correspond to the two phases that co-exist in equilibrium. For example, the end point on the left side (here, F) of the dome DPE corresponds to the solvent-rich 'extract' phase where 'A' is preferentially concentrated, while the point G represents the raffinate phase that is rich in 'B'. Thus any point within the dome represents a biphasic system with the end points of the tie line through the point corresponding to the extract and raffinate phases. As may also be observed, the tie lines become shorter in length as one approaches the top part of the dome, until it reduces to a point at 'P'. This point is termed the 'plait point' and it signifies the condition at which the compositions of the two liquid phases in equilibrium become identical, and indeed transform to a single phase.

9.2 Solid-Liquid Equilibria

The prediction of solubility of a solid in a liquid is important for design of separation processes that utilize either preferential dissolution or crystallization as a route to purification of a species. The presence of a dissolved solid in a liquid also changes the *freezing* (as well as boiling) point of the latter, and its estimation is important for design of heat exchange equipments such as crystallizers (and evaporators). A wide variety of phase behaviour has been observed in systems which comprise mixtures of solids, mixture of a solid and a liquid and mixtures comprised of a liquid and more than a single solid (see R. T. DeHoff,

Thermodynamics in Materials Science, chaps. 9 and 10, McGraw-Hill, New York, 1993). This section is devoted to consideration of thermodynamic relations that allow computation of the solubility of solids in liquids as a function of temperature. Such relations may also be extended to estimate changes in freezing or boiling point of a liquid in presence of dissolved solids.

The phase equilibria relations developed here are limited to the simplest case of systems comprising a solid (1) and a liquid (2) (solvent). As with all other phase equilibria, one starts with the basis of equality of the species fugacity in the solid (*s*) and liquid (*l*) phases respectively.

$$\hat{f}_i^L = \hat{f}_i^S \qquad\qquad ..(9.37)$$

$$x_i \gamma_i^L f_i^L = z_i \gamma_i^S f_i^S \qquad\qquad ..(9.38)$$

Where, x_i and z_i are, respectively, the mole fractions of species 'i' in the liquid and solid solutions. Equivalently,

$$x_i \gamma_i^L = z_i \gamma_i^S \varsigma_i \qquad\qquad ..(9.39)$$

Where, $\varsigma_i \equiv f_i^S(T,P) / f_i^L(T,P)$ \qquad\qquad ..(9.40)

The right side of this equation, defines ψ_i as the ratio of fugacities at the temperature *T* and pressure *P* of the system. Note that for each pure species at its (say, normal) melting point $T_{m,i}$ we have: $f_i^S(T_{m,i}, P) = f_i^L(T_{m,i}, P)$ \qquad\qquad ..(9.41)

However at $T \neq T_{m,i}$; $f_i^S(T,P) \neq f_i^L(T,P)$

Thus, in general one needs to derive a suitable expression for ς_i defined by eqn. 9.40.

This may be done by through estimation of the enthalpy and entropy of fusion at the system temperature T, with values of the enthalpy and entropy at the melting point at the system pressure as datum. However, since the properties of solids are not dependent on pressure in a significant way, for convenience of computation one can assume the reference point as the *normal melting point $T_{m,i}$*. Accordingly, we may write for either the solid or the solvent species:

$$\Delta H_T^{fus} = \int_T^{T_m} C_P^L \, dT + \Delta H_{T_m}^{fus} + \int_{T_m}^T C_P^S \, dT \qquad\qquad ..(9.42)$$

Or: $\Delta H_T^{fus} = \Delta H_{T_m}^{fus} + \int\limits_{T_m}^{T} \left(C_P^S - C_P^L \right) dT$ ..(9.43)

In the same manner one may write:

$\Delta S_T^{fus} = \Delta S_{T_m}^{fus} + \int\limits_{T_m}^{T} \frac{\left(C_P^S - C_P^L \right)}{T} dT$ ..(9.44)

At temperature T_m, $\Delta G_{T_m}^{fus} = 0$, thus:

$\Delta H_{T_m}^{fus} - T_m \Delta S_{T_m}^{fus} = 0$ ..(9.45)

Or: $\Delta S_{T_m}^{fus} = \dfrac{\Delta H_{T_m}^{fus}}{T_m}$ ..(9.46)

Thus, using eqn. 9.46 in 9.44 we have:

$\Delta S_T^{fus} = \dfrac{\Delta H_{T_m}^{fus}}{T_m} + \int\limits_{T_m}^{T} \frac{\left(C_P^S - C_P^L \right)}{T} dT$ ..(9.47)

Further, at temperature T, we have:

$\Delta G_T^{fus} = \Delta H_T^{fus} - T \Delta S_T^{fus}$ ..(9.48)

Therefore, substituting eqns. 9.43 and 9.47 in 9.48 and re-arranging we have:

$\Delta G_T^{fus} = \Delta H_{T_m}^{fus} - T \dfrac{\Delta H_{T_m}^{fus}}{T_m} + \int\limits_{T_m}^{T} \left(C_P^S - C_P^L \right) dT - T \int\limits_{T_m}^{T} \frac{\left(C_P^S - C_P^L \right)}{T} dT$ ..(9.49)

If we further make the simplifying assumption that $\left(C_P^S - C_P^L \right)$ is constant over the temperature range T_m to T one obtains:

$\Delta G_T^{fus} = \Delta H_{T_m}^{fus} \left(1 - \dfrac{T}{T_m} \right) + \left(C_P^S - C_P^L \right)(T - T_m) - (C_P^S - C_P^L) T \ln\left(\dfrac{T}{T_m} \right)$ ..(9.50)

Now, $\int\limits_{L}^{S} dG_T = RT \int\limits_{f_L}^{f_S} d\ln f$

Or:

$\Delta G_T^{fus} = RT \ln \dfrac{f^S}{f^L}$ ..(9.51)

Thus, comparing eqn. 9.50 and 9.51:

$RT \ln \dfrac{f^S}{f^L} = \Delta H_{T_m}^{fu} \left(1 -^s \dfrac{T}{T_m} \right) + \left(C_P^S - C_P^L \right)(T - T_m) - (C_P^S - C_P^L) T \ln\left(\dfrac{T}{T_m} \right)$ ..(9.52)

Therefore using eqn. 9.52 in eqn. 9.40, we have:

$$RT \ln \varsigma = \Delta H_{T_m}^{fu} \left(1 - {}^s\frac{T}{T_m}\right) + \left(C_P^S - C_P^L\right)(T - T_m) - (C_P^S - C_P^L)T \ln\left(\frac{T}{T_m}\right)$$ ..(9.53)

Upon suitable rearrangement:

$$\ln \varsigma = \frac{\Delta H_{T_m}^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{(C_P^S - C_P^L)}{R}\left(1 - \frac{T_m}{T} - \ln\frac{T}{T_m}\right)$$ ..(9.54)

Now by eqn. 9.39:

$$x_i \gamma_i^L = z_i \gamma_i^S \varsigma_i$$ ..(9.39)

With ς_i given by the general expression as in eqn. 9.54, a suitable activity coefficient model may be chosen to represent the activity coefficients γ_i^S and γ_i^L in the solid and liquid phases, respectively and then eqn. 9.39 may be solved to yield the phase compositions. We illustrate the typical methodology of such calculations for a binary system.

Let us assume a solid (1) is to be solubilized in a liquid (2). The starting point is eqn. 9.39. However, in applying it we make the simplifying assumption that the liquid does not "dissolve" in the solid phase, and so the latter phase is a pure component solid. This is a reasonable approximation for many system of practical interest in the chemical industry. The liquid phase, however, will be a binary with the solid transforming to a "liquid" phase and then mixing with the liquid solvent. Thus, one may rewrite the phase equilibrium as:

$$f_1^S(T,P) = \hat{f}_1^L(T,P,x_1)$$ ..(9.55)

Now $\hat{f}_1^L(T,P,x_1) = x_1 \gamma_1(T,P,x_1) f_1^L$ ..(9.56)

Thus from the last two equations, the equilibrium solubility of the solid (x_1) in the liquid is given by:

$$x_1 = (\frac{f_1^S}{f_1^L})(\frac{1}{\gamma_1(T,P,x_1)})$$ ..(9.57)

Since activity coefficients are functions of temperature and composition only:

$$x_1 = \left(\frac{f_1^S}{f_1^L}\right)\left(\frac{1}{\gamma_1(T,x_1)}\right)$$ ..(9.58)

It follows that if the temperature at which the solubility is desired is the melting point T_m of the solid, then $f_1^S(T_m) = f_1^L(T_m)$.

Therefore, we have:

$$x_1 = \frac{1}{\gamma_1(T_m, x_1)} \qquad \qquad ..(9.59)$$

However, for any temperature T (other than T_m) eqn. 9.58 needs to be employed. Thus, we have:

$$\ln x_1 = -\ln \gamma_1 - \ln\left(\frac{f_1^S}{f_1^L}\right) \qquad \qquad ..(9.60)$$

Or using eqns. 9.40 and 9.52 (or 9.53) we have:

$$\ln x_1 = -\ln \gamma_1 - \left[\frac{\Delta H_{T_m}^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{(C_P^S - C_P^L)}{R}\left(1 - \frac{T_m}{T} - \ln\frac{T}{T_m}\right)\right] \qquad ..(9.61)$$

One may solve eqn. 9.61 (iteratively) for the solubility x_1, by assuming a suitable activity coefficient model for the liquid phase (for ex: van Laar, Regular Solution, NRTL, etc). In the special case where the temperature of interest T is close to the melting point T_m so that one can make the approximation $T/T_m \approx 1$ eqn. 9.61 reduces to:

$$\ln x_1 = -\ln \gamma_1 - \left[\frac{\Delta H_{T_m}^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad \qquad ..(9.62)$$

Example 9.2

Estimate solubility of a solid A in a liquid B at 300^oK, using (i) ideal solution assumption, (ii) regular solution model for liquid phase. The following data are available: $V_A^L = 100 cm^3/mol$; $V_B^L = 125 cm^3/mol$; $\delta_A = 9.5(cal/cc)^{1/2}$; $\delta_B = 7.5(cal/cc)^{1/2}$. Heat of fusion for A: 17.5 kJ/mol. Melting point for A = 350^oK.

(Click for solution)

For the purpose of further illustration of the results that typically obtain from application of the foregoing phase equilibria relations, we consider two limiting or special cases for a binary system assuming that eqn. 9.62 applies. It may be noted, however, that this assumption is not essential to the considerations below. Using eqn. 9.54 we write:

$$\ln \varsigma = \frac{\Delta H_{T_m}^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad \qquad ..(9.63)$$

Or, for any of the species:

$$\varsigma_i = \exp\left[\frac{\Delta H_i^{fus}}{RT_{m,i}}\left(\frac{T-T_{m,i}}{T}\right)\right] \qquad\qquad ..(9.64)$$

The limiting cases are:

1. Both phases form ideal solutions, i.e., $\gamma_i^L = 1$ and $\gamma_i^S = 1$ for all temperature and compositions.

2. The liquid phase behaves as an ideal solution ($\gamma_i^L = 1$), and all species in the solid state are completely immiscible, i.e., ($z_i\gamma_i^S = 1$)

Case 1

Writing eqn. 9.39 for both species, we have:

$$x_1 = z_1\varsigma_1 \qquad\qquad ..(9.65)$$

$$x_2 = z_2\varsigma_2 \qquad\qquad ..(9.66)$$

Further:

$$x_1 + x_2 = 1 \qquad\qquad ..(9.67)$$

$$z_1 + z_2 = 1 \qquad\qquad ..(9.68)$$

Using eqns. 9.57 – 9.60, one obtains:

$$x_1 = \frac{\varsigma_1(1-\varsigma_2)}{\varsigma_1-\varsigma_2} \qquad\qquad ..(9.69)$$

$$z_1 = \frac{1-\varsigma_2}{\varsigma_1-\varsigma_2} \qquad\qquad ..(9.70)$$

If one uses the simplified form for ς, then by eqn. 9.64:

$$\varsigma_1 = \exp\left[\frac{\Delta H_1^{fus}}{RT_{m,1}}\left(\frac{T-T_{m,1}}{T}\right)\right] \qquad\qquad ..(9.71)$$

$$\varsigma_2 = \exp\left[\frac{\Delta H_2^{fus}}{RT_{m,2}}\left(\frac{T-T_{m,2}}{T}\right)\right] \qquad\qquad ..(9.72)$$

On putting $x_1 = z_1 = 1$ it follows that $\varsigma_1 = 1$; thus, by eqn. 9.71, $T = T_{m,1}$. In the same manner if we put $x_2 = z_2 = 1$ then $\varsigma_2 = 1$; and $T = T_{m,2}$. On choosing a series of temperature T between $T_{m,1}$ *and* $T_{m,2}$ and for each case solving for x_i and z_i one obtains a $T-x-z$ plot that is shown schematically in fig. 9.4. The upper curve in fig. 9.4 is the *freezing* curve and the

lower curve is the *melting* curve. Any $T - x$ point within the lens-shaped region between the two curves corresponds to a two phase situation, while points outside the region depict a single phase. If a point is above the upper curve the state of the system is a homogeneous binary liquid mixture, whereas if the point lies beneath the melting curve, the state of the system is binary solid mixture. Any straight line parallel to the composition axis depicts a tie line (for example XY), the compositions at the two ends signifying the liquid and solid phase compositions. This behaviour is analogous to that of Raoult's law $T - x - y$ plot shown in fig.7.7.
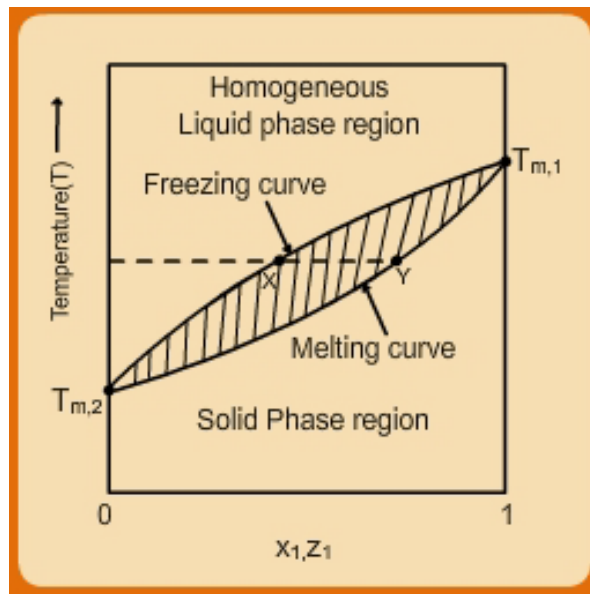

Figure 9.4 Case I, ideal liquid and solid solutions

An example of a system exhibiting a phase diagram of this type is a binary mixture of nitrogen/carbon monoxide at low temperatures. However, as may be evident, this phase behaviour is necessarily an idealized one. Its utility lies in that it can provide a reference system for interpreting the behviour of more complex, real systems.

Case 2

For this case the liquid phase forms ideal solution ($\gamma_i^l = 1$), and there is complete immiscibility for all species in the solid state ($z_i \gamma_i^s = 1$). Thus the governing phase equilibria relations are:

$$x_1 = \varsigma_1 \qquad\qquad\qquad\qquad\qquad ..(9.73)$$

$$x_2 = \varsigma_2 \qquad\qquad\qquad\qquad\qquad ..(9.74)$$

Since, ς_1 and ς_2 are functions of temperature alone (by eqns.9.71 and 9.72), it follows that x_1 and x_2 likewise are functions of temperature only. Thus eqns. 9.73 and 9.74 may be solved *independently* upon which one obtains two distinct plots on the $T - x_1$ diagram as shown in fig. 9.5. However, if eqns. 9.64 and 9.65 apply *simultaneously*, then we have: $\varsigma_1 + \varsigma_2 = 1$ and hence $x_1 + x_2 = 1$. Thus, it follows that under this condition the following relation holds:
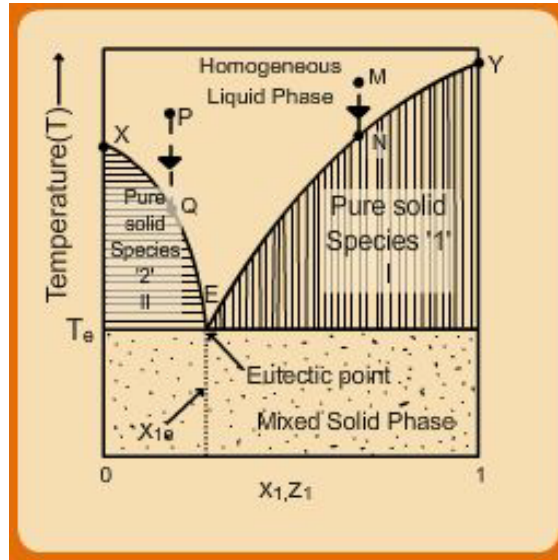

Fig. 9.5 T-x-z plot for Case II

$$\exp\left[\frac{\Delta H_1^{fus}}{RT_{m,1}}\left(\frac{T - T_{m,1}}{T}\right)\right] + \exp\left[\frac{\Delta H_2^{fus}}{RT_{m,2}}\left(\frac{T - T_{m,2}}{T}\right)\right] = 1 \tag{9.75}$$

On solving the above equation one obtains the *Eutectic temperature* T_e shown in fig. 9.5. This particular phase diagram is to be interpreted as follows. When eqn. 9.73 applies one has:

$$x_1 = \exp\left[\frac{\Delta H_1^{fus}}{RT_{m_1}}\left(\frac{T - T_{m_1}}{T}\right)\right] \tag{9.76}$$

This equation is valid over the temperature range $T = T_{m1}$, and the corresponding composition range $x_1^e < x < 1$, where $x_1 = x_{1e}$ the eutectic composition. Thus in this region (I) of the phase diagram a liquid solution can be in equilibrium with *only* pure species 1 as a solid phase. This is represented by region I on fig. 9.5 where liquid solutions with compositions x_1 given by line YE are in equilibrium with pure solid 1. Consider the system to be initially at a state

defined by point 'M'. If one cools the system it eventually reaches the point 'N' on the $T - x_1$ plot, at which condition only the component '1' just begins to freeze. This happens till one reaches the eutectic temperature T_e at which point component '2' begins to co-precipitate. In the same manner region II obtains by solving eqn. 9.74, i.e.,

$$x_2 = \exp\left[\frac{\Delta H_2^{sl}}{RT_{m_2}}\left(\frac{T - T_{m_2}}{T}\right)\right] \equiv 1 - x_1 \qquad\qquad ..(9.77)$$

This equation is valid only from $T = T_{m2}$, where, $x_1 = 0$, to $T = T_e$, where $x_1 = x_{1e}$, the eutectic composition. Equation 9.77 therefore applies where a liquid solution is in equilibrium with pure species 2 as a solid phase. This is represented by region II on fig. 9.5 where liquid solutions with compositions x_1 given by line XE are in equilibrium with pure solid 2. Consider an initial system state defined by point 'P' which is a binary solution. On cooling, the system eventually reaches the point 'Q' where only pure solid '2' begins to crystallize. On continued cooling, the eutectic temperature is reached, whereupon component '1' also precipitates simultaneously.

Finally, if one commences cooling from the point R with a solution composition given by $x_1 = x_{1e}$, no precipitation of any solid occurs till the temperature T_e (or point 'E') is reached; at which state, as mentioned above, eqn. 9.75 holds. This is a state where two solids are in equilibrium with the solution. Further cooling below T_e results in co-precipitation of both species, and the system enters a state where two immiscible solids are present.

Example 9.3

Compute the eutectic composition and temperature for a mixture of two substances A and B using the following data:

Property	A	B
Normal T_m (°K)	180	181
ΔH^{fus} (J/mol)	6600	9075

(Click for solution)

9.3 Solid-Vapour Equilibrium

This section deals with the solubility of solids in gases. The phase equilibria consideration here are relatively straightforward as the solubility of gases in solids is usually negligible. Therefore, the solid phase may be considered as pure; all non-ideality in the system therefore, derives from that of the gas phase. In the following analysis we, thus, consider that a pure solid phase (1) co-exists in equilibrium with a vapour-phase mixture of the gas (or solvent, 2) and the solute (i.e., 1). The phase equilibria relation for the component 1 may be written as:

$$f_1^S = \hat{f}_1^V \qquad\qquad ..(9.78)$$

A relation of the form of eqn. 6.119 used for pure liquid phase fugacity calculation may be employed to compute the fugacity of a pure solid at the temperature T and pressure P of the system.

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

For a pure solid the corresponding equation is:

$$f_1^S = P_1^{sat} \phi_1^{sat} \exp\left[\frac{V_1^S \left(P - P_1^{sat}\right)}{RT} \right] \qquad\qquad ..(9.79)$$

Here V_1^S is the molar volume of the solid, and P_1^{sat} is the vapour-phase saturation pressure for the solid solute at the given temperature. Now for the vapour phase fugacity of the solute on has:

$$\hat{f}_1^V = y_1 \hat{\phi}_1 P \qquad\qquad ..(9.80)$$

Thus using eqns. 9.78 – 9.80 one obtains:

$$P_1^{sat} \phi_1^{sat} \exp\left[\frac{V_1^S \left(P - P_1^{sat}\right)}{RT} \right] = y_1 \hat{\phi}_1 P \qquad\qquad ..(9.81)$$

The above equation may be written in a compressed form as follows:

$$y_1 = \left(\frac{P_1^{sat}}{P} \right) E \qquad\qquad ..(9.82)$$

Where,

$$E = \frac{\phi_1^{sat}}{\hat{\phi}_1} \exp\left[\frac{V_1^S \left(P - P_1^{sat}\right)}{RT} \right] \qquad\qquad ..(9.83)$$

The term E is called the *enhancement factor*. The vapour pressure P_1^{sat} of solids is typically very low ($\sim 10^{-5} - 10^{-3}$ bar), hence $\phi_1^{sat} \approx 1.0$. Further if the system pressure is also low or as $P \rightarrow P_1^{sat}$, $\hat{\phi}_1 \rightarrow 1$. Thus, on inspecting eqn. 9.82, it is evident that under such a condition

$E = 1.$ The corresponding solubility y_1 is termed the *ideal solubility*. At high pressures (with $P \gg P_1^{sat}$), the exponential Poynting factor tends to be greater than one, and the values of $\hat{\phi}_1$ are lower than unity. As a result, the factor E typically is higher than one. The enhancement factor, therefore, provides a measure of the degree to which pressure augments the solubility of the solid in the gas phase.

Example 9.4

A certain solid A has a vapour pressure of 0.01 bar at 300^0K. Compute its solubility at the same temperature in a gas B at a pressure of 1.0bar. The molar volume of the solid is 125cc/mol.

(Click for solution)

Assignment- Chapter 9