

# Thermodynamics of Phase Equilibria and Phase Diagrams

Phase diagrams are generally represented in textbooks as mere geometrical intersections of lines. This geometrical emphasis makes the subject lifeless. Normally phase diagrams are presented as "horoscopes" where all the details of the system (i.e., melting points of the components, eutectic and triple point, etc.) are concisely presented. The elegance of the phase rule is lost when the phase diagrams are treated in the usual routine way. Phase diagrams have a thermodynamic basis and they can, under favorable conditions, be made to yield thermodynamic data. The purpose of this paper is to give a comprehensive account of phase equilibria from this point of view.

## Phase Equilibria in Multicomponent Mixtures (1)

We consider a phase having  $r$  components. We take the system under consideration to be an open one, i.e., a system which can gain or lose matter as well as heat and work. The Gibbs function for the system, an extensive property, will depend on temperature  $T$ , pressure  $P$ , and the amounts  $n_1, n_2, \dots, n_r$  (expressed in moles) of the various components of the system. We have for the most general variation

$$dG = -SdT + VdP + \sum_{i=1}^r \mu_i dn_i \quad (1)$$

where  $S$  and  $V$  are the entropy and volume and  $\mu_i$  is the chemical potential for the species  $i$ .

From the definition of the chemical potential, it follows that it is an intensive property of the phase in question. Expressed differently we can represent  $\mu_i$  as a function of  $T$ ,  $P$ , and mole fractions  $x_1, x_2, \dots, x_r$ .

Since  $\sum_{i=1}^r x_i = 1$ , the number of independent variables  $x_i$  would be  $r - 1$ . For the most general variation, the change in chemical potential of a component is given by

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P, x_1, \dots, x_{r-1}} dT + \frac{\partial \mu_i}{\partial P} \Big|_{T, x_1, \dots, x_{r-1}} dP + \sum_{i=r}^{i=r-1} \frac{\partial \mu_i}{\partial x_i} \Big|_{T, P, x_i} dx_i \quad (2)$$

where  $x_j$  represents all the quantities of the type  $x_i$  except  $x_i$  itself.

Using Maxwell's relations it follows that

$$\left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}\right]_{P, n_i, n_j} = \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial T}\right)_{P, n_i, n_j}\right]_{T, P, n_i} = -S_i \quad (3)$$

and

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}\right]_{T, n_i, n_j} = \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_{T, n_i, n_j}\right]_{T, P, n_i} = V_i \quad (4)$$

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where  $V_i$  and  $S_i$  are partial molar volume and partial molar entropy for the species  $i$  and respectively denote the increase in volume and entropy of the system due to unit increase in the number of moles of type  $i$ ; the pressure, temperature, and the amounts of other components remain unaltered. If the number of moles of the respective components is fixed, the mole fraction of the respective species is also automatically fixed and hence,

$$\begin{aligned} \left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_i, n_j} &= \left(\frac{\partial \mu_i}{\partial T}\right)_{P, x_i, x_j} = -S_i \\ \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_i, n_j} &= \left(\frac{\partial \mu_i}{\partial P}\right)_{T, x_i, x_j} = V_i \end{aligned} \quad (5)$$

Equation (2) can now be written for the phase  $\alpha$  in the following way,

$$d\mu_k^\alpha = -S_k^\alpha dT + V_k^\alpha dP + \sum_{i=1}^{r-1} \left(\frac{\partial \mu_k^\alpha}{\partial x_i^\alpha}\right)_{T, P, x_i^\beta} dx_i^\alpha \quad (6)$$

$(k = 1, 2, \dots, r)$

A similar expression can be written for the phase  $\beta$  and all others.

Now for equilibrium at a constant  $T$  and  $P$ ,

$$\mu_k^\alpha = \mu_k^\beta \quad (7)$$

Similarly, for equilibrium at temperature  $T + dT$  and pressure  $P + dP$  we have

$$\mu_k^\alpha + d\mu_k^\alpha = \mu_k^\beta + d\mu_k^\beta \quad (8)$$

From equations (7) and (8) it follows that

$$d\mu_k^\alpha = d\mu_k^\beta \quad (9)$$

On proper substitution, equation (9) yields the following set of  $r$  equations (for each component)

$$\begin{aligned} -S_k^\alpha dT + V_k^\alpha dP + \sum_{i=1}^{r-1} \left(\frac{\partial \mu_k^\alpha}{\partial x_i^\alpha}\right)_{T, P, x_i} dx_i^\alpha = \\ -S_k^\beta dT + V_k^\beta dP + \sum_{i=1}^{r-1} \left(\frac{\partial \mu_k^\beta}{\partial x_i^\beta}\right)_{T, P, x_i} dx_i^\beta \end{aligned} \quad (10)$$

The above equations give the relationship between variables  $T$ ,  $P$ , and  $x_i$ . One of the variables  $x_i^\alpha$  or  $x_i^\beta$  can be eliminated in the following way. If we multiply the set of  $r$  equations (10) by  $x_1^\alpha, x_2^\alpha, \dots, x_r^\alpha$  respectively and add and apply the Gibbs-Duhem relation, we get

$$\begin{aligned} x_1^\alpha \sum_{i=1}^{r-1} \left(\frac{\partial \mu_1^\alpha}{\partial x_i^\alpha}\right)_{T, P, x_i^\alpha} dx_i^\alpha + x_2^\alpha \sum_{i=1}^{r-1} \left(\frac{\partial \mu_2^\alpha}{\partial x_i^\alpha}\right)_{T, P, x_i^\alpha} dx_i^\alpha + \\ \dots + x_r^\alpha \sum_{i=1}^{r-1} \left(\frac{\partial \mu_r^\alpha}{\partial x_i^\alpha}\right)_{T, P, x_i^\alpha} dx_i^\alpha = 0 \end{aligned} \quad (11)$$

and recognizing that  $S = \Delta H/T$ , we get

$$\begin{aligned}
& - \sum_{i=1}^r \left( \frac{x_i^\alpha \Delta_{\alpha,\beta} H_i}{T} \right) dT + \sum_{i=1}^r (x_i^\alpha \Delta_{\alpha,\beta} V_i) dP = \\
& - \left\{ x_1^\alpha \sum_{i=1}^{r-1} \left( \frac{\partial \mu_i^\beta}{\partial x_i^\beta} \right)_{T,P,x_i^\beta} dx_i^\beta + \dots + x_r^\alpha \right. \\
& \quad \left. \sum_{i=1}^{r-1} \left( \frac{\partial \mu_i^\beta}{\partial x_i^\beta} \right)_{T,P,x_i^\beta} dx_i^\beta \right\} \quad (12)
\end{aligned}$$

Similarly when the set of equations (10) is multiplied by  $x_1^\beta, x_2^\beta, \dots, x_r^\beta$  and added we have

$$\begin{aligned}
& - \sum_{i=1}^r \left( \frac{x_i^\beta \Delta_{\alpha,\beta} H_i}{T} \right) dT + \sum_{i=1}^r (x_i^\beta \Delta_{\alpha,\beta} V_i) dP = \\
& x_1^\beta \sum_{i=1}^{r-1} \left( \frac{\partial \mu_i^\alpha}{\partial x_i^\alpha} \right)_{T,P,x_i^\alpha} dx_i^\alpha + \dots + x_r^\beta \\
& \quad \sum_{i=1}^{r-1} \left( \frac{\partial \mu_i^\alpha}{\partial x_i^\alpha} \right)_{T,P,x_i^\alpha} dx_i^\alpha \quad (13)
\end{aligned}$$

$\Delta_{\alpha,\beta} H_i$  may be defined as the increase in enthalpy during the transformation of one mole of the species  $i$  from the phase  $\alpha$  to phase  $\beta$ . ( $\Delta_{\alpha,\beta} H_i$  is equal to the latent heat of phase transformation only when the mixture is ideal.) Similarly  $\Delta_{\alpha,\beta} V_i$  is the corresponding volume change during the transformation of one mole of the species  $i$  from phase  $\alpha$  to phase  $\beta$ . Equations (12) and (13) can further be simplified provided it is assumed that the mixture is ideal. Under this condition,

$$\begin{aligned}
\sum_{i=1}^{r-1} \left( \frac{\partial \mu_k}{\partial x_i} \right)_{T,P,x_i} dx_i &= \frac{RT}{x_k} dx_k \quad (14) \\
(k &= 1, 2, \dots, r)
\end{aligned}$$

and hence equations (12) and (13) reduce to

$$\begin{aligned}
& - \sum_{i=1}^r \left( \frac{x_i^\alpha \Delta_{\alpha,\beta} H_i}{T} \right) dT + \sum_{i=1}^r (x_i^\alpha \Delta_{\alpha,\beta} V_i) dP = \\
& - \sum_{i=1}^{i=r} x_i^\alpha \frac{RT}{x_i^\beta} dx_i^\beta \quad (15)
\end{aligned}$$

and a corresponding equation for phase  $\beta$ .

$$\begin{aligned}
& - \sum_{i=1}^r \left( \frac{x_i^\beta \Delta_{\alpha,\beta} H_i}{T} \right) dT + \sum_{i=1}^r (x_i^\beta \Delta_{\alpha,\beta} V_i) dP = \\
& \sum_{i=1}^{i=r} x_i^\beta \frac{RT}{x_i^\alpha} dx_i^\alpha \quad (16)
\end{aligned}$$

Equation (15) cannot be integrated and it is not of much use beyond giving a general relationship for the way in which  $T, P$ , and  $x_i$  vary simultaneously. This has been used for analyzing ternary phase equilibrium data (2). For isobaric changes in the case of ideal ternary mixtures involving liquid-vapor equilibria

$$\begin{aligned}
\frac{x_1' \Delta_e H_1 + x_2' \Delta_e H_2 + x_3' \Delta_e H_3}{RT^2} &= \left( \frac{x_1'}{x_1} - \frac{x_3'}{x_3} \right) \left( \frac{\partial x_1}{\partial T} \right)_P + \\
& \left( \frac{x_2'}{x_2} - \frac{x_3'}{x_3} \right) \left( \frac{\partial x_2}{\partial T} \right)_P \quad (17)
\end{aligned}$$

where the primed quantities refer to the vapor phase and unprimed quantities refer to the liquid phase.  $\Delta_e H_i$  ( $i = 1, 2, 3$ ) is the latent heat of evaporation of the species  $i$ . Particularly useful results are obtained for isothermal-isobaric processes. Thus, we have

$$\left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} = - \left( \frac{x_2' - x_3'}{x_2 - x_3} \right) / \left( \frac{x_1' - x_3'}{x_1 - x_3} \right) \quad (18)$$

which reduces to

$$\left( \frac{\partial x_1}{\partial x_2} \right)_{T,P} = -(p_2^0 - p_3^0) / (p_1^0 - p_3^0) \quad (19)$$

where  $p_i^0$  ( $i = 1, 2, 3$ ) is the vapor pressure of pure component  $i$ . The phase equilibrium data (3, 4) for the carbon tetrachloride-toluene-ethylene dibromide system satisfies equation (17). In Figure 1 the mole percentage of toluene is plotted against the mole percentage of ethylene dibromide, at several temperatures. Straight lines are invariably obtained and the slope is found to be in reasonable agreement with equation (19).

We shall see below that equations (15) and (16) yield various well-known relations for ideal binary mixtures.

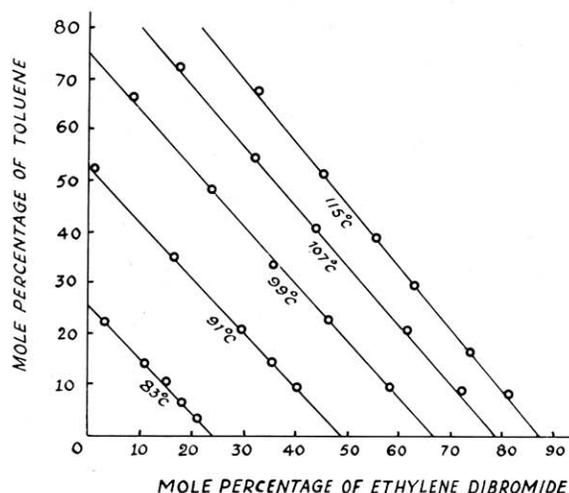


Figure 1. Test of equation (19) for carbon tetrachloride-toluene-ethylene dibromide system (2).

### Ideal Binary Mixtures

For ideal binary mixtures, equations (15) and (16) reduce to

$$\begin{aligned}
& - \frac{(x_1^\alpha \Delta_{\alpha,\beta} H_1 + x_2^\alpha \Delta_{\alpha,\beta} H_2)}{T} dT + \\
& \quad (x_1^\alpha \Delta_{\alpha,\beta} V_1 + x_2^\alpha \Delta_{\alpha,\beta} V_2) dP = \\
& - RT \left( \frac{x_1^\alpha}{x_1^\beta} - \frac{x_2^\alpha}{x_2^\beta} \right) dx_1^\beta \quad (20)
\end{aligned}$$

and

$$\begin{aligned}
& - \frac{(x_1^\beta \Delta_{\alpha,\beta} H_1 + x_2^\beta \Delta_{\alpha,\beta} H_2)}{T} dT + \\
& \quad (x_1^\beta \Delta_{\alpha,\beta} V_1 + x_2^\beta \Delta_{\alpha,\beta} V_2) dP = \\
& RT \left( \frac{x_1^\beta}{x_1^\alpha} - \frac{x_2^\beta}{x_2^\alpha} \right) dx_1^\alpha \quad (21)
\end{aligned}$$

since  $dx_1 + dx_2 = 0$ .

For isobaric changes we have,

$$\left( \frac{\partial x_1^\beta}{\partial T} \right)_P = \frac{x_1^\alpha \Delta_{\alpha,\beta} H_1^0 + x_2^\alpha \Delta_{\alpha,\beta} H_2^0}{RT^2} / \left( \frac{x_1^\alpha}{x_1^\beta} - \frac{x_2^\alpha}{x_2^\beta} \right) \quad (22)$$

and

$$- \left( \frac{\partial x_1^\alpha}{\partial T} \right)_P = \frac{x_1^\beta \Delta_{\alpha,\beta} H_1^0 + x_2^\beta \Delta_{\alpha,\beta} H_2^0}{RT^2} / \left( \frac{x_1^\beta}{x_1^\alpha} - \frac{x_2^\beta}{x_2^\alpha} \right) \quad (23)$$

where the superscript  $^0$  refers to the pure components.

When vapor-liquid equilibria are considered and  $\beta$  is the vapor phase,  $Px_1^\beta = x_1^\alpha p_1^0$ . These equations show how the boiling point of the mixture varies with composition in either phase. When the equilibrium between solid and liquid phases is involved, equations

(22) and (23) simply show the variation of melting point with the change in composition in either phase. These can be readily reduced to van't Hoff's relations for the depression of freezing point and the elevation of boiling point for the particular case where one of the components does not exist in a particular phase.

### Phase Equilibrium in Ideal Binary Condensed Systems

When the equilibrium between solid (s) and liquid (l) phases is involved, equations (20) and (21) reduce to

$$-\sum_{i=1}^2 \frac{x_i^l \Delta_f H_i^0}{RT^2} = \left( \frac{x_1^l}{x_1^s} - \frac{x_2^l}{x_2^s} \right) \frac{dx_1^s}{dT} \quad (24)$$

and

$$\sum_{i=1}^2 \frac{x_i^s \Delta_f H_i^0}{RT^2} = \left( \frac{x_1^s}{x_1^l} - \frac{x_2^s}{x_2^l} \right) \frac{dx_1^l}{dT} \quad (25)$$

where  $\Delta_f H_i^0$  is the latent heat of fusion of the component  $i$ . In a binary mixture the above equations give the slopes of the phase boundaries when melting point is plotted against composition. The maxima or minima in the melting point composition curve would occur when  $x_1^l = x_1^s$ .

From equation (25) a rule similar to that of Konovaloff for liquid-vapor systems can be deduced for the present case. Thus, if  $dx_1^l/dT$  is positive, the solid phase will become richer in the first component as the temperature is increased, showing thereby that fractional crystallization is possible.

If the solid phase consists exclusively of the solvent, i.e., component 1, we obtain from equation (25)

$$\frac{dx_1^l}{dT} = \frac{x_1^l \Delta_f H_1^0}{RT^2} \quad (26)$$

which on integration yields van't Hoff's law for the depression of freezing point. On the other hand, if the solid phase consists of only the solute, i.e., component 2, equation (25) yields

$$\frac{dx_2^l}{dT} = \frac{x_2^l \Delta_s H}{RT^2} \quad (27)$$

which shows how the solubility varies with temperature. Here  $\Delta_s H$  is the heat of solution.

From equations (26) and (25) it also follows that if both the phases are ideal,

$$\frac{dx_1^s}{dx_1^l} = \frac{x_1^l \Delta_f H_1^0 + x_2^l \Delta_f H_2^0 x_1^s x_2^s}{x_1^s \Delta_f H_1^0 + x_2^s \Delta_f H_2^0 x_1^l x_2^l} \quad (28)$$

On integration, we get the following relation between the composition of the two phases at any instant

$$\Delta_f H_2^0 \ln \frac{x_1^s}{x_1^l} = \Delta_f H_1^0 \cdot \ln \frac{x_2^s}{x_2^l} + \text{constant} \quad (29)$$

Thus, if  $\ln(x_1^s/x_1^l)$  is plotted against  $\ln(x_2^s/x_2^l)$ , a straight line should be obtained. This can be a convenient test for the ideality of a binary solid solution.

More useful conclusions can be drawn from equation (10) for solid-liquid equilibria. If  $\gamma_i$  is the activity coefficient of the component  $i$ , we have on integration (5),

$$-\ln \frac{x_i^l \gamma_i^l}{x_i^s \gamma_i^s} = \frac{\Delta_f H_i^0}{R} \left( \frac{1}{T} - \frac{1}{T_i^0} \right) + \frac{\Delta_f C_{p,i}^0}{R} \left( \ln \frac{T_i^0}{T} + 1 - \frac{T_i^0}{T} \right) \quad (30)$$

where

$$\Delta_f H_i = \Delta_f H_i^0 + \int_{T_i^0}^T (C_{p,i}^l - C_{p,i}^s) dT \quad (31)$$

and

$$\Delta_f C_{p,i}^0 = C_{p,i}^l - C_{p,i}^s \quad (32)$$

Here  $C_{p,i}^l$  is the molar heat capacity at constant pressure of the component  $i$  in the liquid state and  $C_{p,i}^s$  is that for the same component in the crystalline state. For the purpose of integration, it is assumed that the molar heat capacities are independent of temperature. The chemical potential of the component  $i$  is given by the following relation,

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i \quad (33)$$

where  $\gamma_i$  is the activity coefficient. Equations similar to (28) are also obtained for isobaric changes in the case of vapor-liquid equilibria.

We shall see below that the above considerations give a more meaningful interpretation to phase diagrams and phase boundaries. We shall illustrate this by confining our attention to solid-liquid equilibria.

### Eutectic Systems

Equation (10) would represent the two coexistence curves in a binary eutectic diagram. On integration one would obtain

$$-\ln x_i^l \gamma_i^l = \frac{\Delta_f H_i^0}{R} \left( \frac{1}{T} - \frac{1}{T_i^0} \right) + \frac{\Delta_f C_{p,i}^0}{R} \left( \ln \frac{T_i^0}{T} + 1 - \frac{T_i^0}{T} \right) \quad (34)$$

Ideal phase boundaries can be predicted by using the above equation from which the liquidus temperatures can be calculated for different mole fractions. If the temperature and concentration dependence of activity coefficients are known, this can be done even for non-ideal mixtures. Alternatively, activity coefficients can be determined from phase diagrams (6). But there is one limitation. It is not possible to evaluate activity coefficients for different compositions of mixtures at the same temperature. For a regular mixture,<sup>1</sup> the activity coefficients are given by

$$RT \ln \gamma_1 = \alpha' x_2^2$$

where  $\alpha'$  is a constant which may be supposed to be independent of temperature within a small temperature range. Actually,  $\alpha'$  is temperature dependent (7, 8). For testing whether an eutectic mixture is regular or not,  $\ln \gamma_1$  is plotted against  $x_2^2/T$  or  $\ln \gamma_2$  against  $x_1^2/T$ . For a regular mixture, a straight line passing through the origin should be obtained. For naphthalene-phenanthrene and naphthalene- $\alpha$ -naphthylamine mixtures, the two curves have practically the same slope and pass through the origin indicating only slight deviation from regular behavior (9).

If the mixture behaves ideally, it is possible to predict the eutectic composition and temperature from

<sup>1</sup> We define two types of regular solutions: symmetrical regular and unsymmetrical regular. Symmetrical regular solutions are defined as solutions for which the logarithms of the activity coefficients are expressible as symmetrical functions of the mole fractions. This is not the case for unsymmetrical regular solutions. Both types of solutions have ideal entropy of mixing. The activity coefficients of unsymmetrical regular mixtures are given by the following equations,

$$RT \ln \gamma_2 = x_2^2 [A + B(1 - 4x_1) + C(1 - 2x_1)(1 - 6x_1)]$$

$$RT \ln \gamma_1 = x_1^2 [A + B(3 - 4x_1) + C(1 - 2x_1)(5 - 6x_1)]$$

where  $A$ ,  $B$ , and  $C$  are constants.

equation (34) for the two components. If the subscript  $e$  denotes the corresponding quantities at the eutectic point, the following relations must be satisfied for ideal mixtures at the eutectic point.

$$-\ln(x_1^l)_e = \frac{\Delta_f H_1^0}{R} \left( \frac{1}{T_e} - \frac{1}{T_1^0} \right) \quad (35)$$

and

$$-\ln(x_2^l)_e = \frac{\Delta_f H_2^0}{R} \left( \frac{1}{T_e} - \frac{1}{T_2^0} \right) \quad (36)$$

For the sake of simplicity we assume that the latent heat of fusion is independent of temperature. Remembering that  $(x_1^l)_e + (x_2^l)_e = 1$ , we find, on solving equations (35) and (36)

$$\frac{(x_1^l)_e^{1/\Delta_f H_1^0}}{(x_2^l)_e^{1/\Delta_f H_2^0}} = e^{(1/R)(1/T_1^0 - 1/T_2^0)} \quad (37)$$

and

$$-(\Delta_f H_1^0/R)(1/T_e - 1/T_1^0) + e^{-(\Delta_f H_2^0/R)(1/T_e - 1/T_2^0)} = 1 \quad (38)$$

From these the eutectic temperature and the eutectic composition can be easily calculated.

### Systems Exhibiting Complete Miscibility in Solid and Liquid Phases

The slopes of the liquidus and solidus curves of phase diagrams for systems exhibiting complete miscibility in solid and liquid phases would be given by equations (24) and (25) so that

$$\frac{dx_1^s}{dT} = -\frac{(x_1^l \Delta_f H_1^0 + x_2^l \Delta_f H_2^0)}{RT^2(x_1^l/x_1^s - x_2^l/x_2^s)} \quad (39)$$

and

$$\frac{dx_1^l}{dT} = \frac{(x_1^s \Delta_f H_1^0 + x_2^s \Delta_f H_2^0)}{RT^2(x_1^s/x_1^l - x_2^s/x_2^l)} \quad (40)$$

Equations (39) and (40) hold only for ideal systems. What follows would apply to all systems in the category under discussion.

Equation (30) can be used for predicting phase boundaries (10, 11) in the following manner. Putting  $\lambda_i$  for the right hand side of equation (30) gives, for the coexistence curve for each component,

$$\ln \frac{x_1^l \gamma_1^l}{x_1^s \gamma_1^s} = -\lambda_1 \quad \text{and} \quad \ln \frac{x_2^l \gamma_2^l}{x_2^s \gamma_2^s} = \lambda_2 \quad (41)$$

These can be solved for  $x_2^l$  and  $x_2^s$ . Thus,

$$x_2^l = \frac{e^{\lambda_1 \gamma_1^l \gamma_2^s} - \gamma_2^s \gamma_1^s}{e^{\lambda_1 \gamma_1^l \gamma_2^s} - e^{-\lambda_2 \gamma_2^l \gamma_1^s}}; \quad x_2^s = \frac{e^{\lambda_1 \gamma_1^l \gamma_2^l} - \gamma_2^l \gamma_1^s}{e^{\lambda_1 + \lambda_2} \gamma_1^l \gamma_2^s - \gamma_2^l \gamma_1^s} \quad (42)$$

For ideal mixtures, equation (42) reduces to

$$x_2^l = \frac{e^{\lambda_1} - 1}{e^{\lambda_1} - e^{-\lambda_2}}; \quad x_2^s = \frac{e^{\lambda_1} - 1}{e^{\lambda_1 + \lambda_2} - 1} \quad (43)$$

This equation is due to Seltz. It gives a method of predicting the composition of liquid and solid phases in equilibrium at each temperature provided melting points and heats of fusion of the two components are known.<sup>2</sup>

Equally interesting results are obtained when we consider mixtures having maximum and minimum melting

points. From equations (39) and (40) it follows that by applying the condition of maxima or minima, viz.,  $dT/dx_1^l = 0$  and  $dT/dx_1^s = 0$  we obtain  $x_1^l = x_1^s$ . When we apply this result in equation (41), we find that the necessary and sufficient condition for its occurrence is

$$e^{\lambda_2} = \frac{\gamma_2^l}{\gamma_2^s} \quad (44)$$

and

$$e^{\lambda_1} = \frac{\gamma_1^s}{\gamma_1^l}$$

In other words, we have

$$\ln \frac{\gamma_i^l}{\gamma_i^s} = \frac{\Delta_f H_i^0}{R} \left( \frac{1}{T_m} - \frac{1}{T_i^0} \right) \quad (i = 1, 2) \quad (45)$$

where  $T_m$  is the maximum or minimum temperature.

Further, if  $RT \ln \gamma_1^s = \beta'(x_2^s)^2$  and  $RT \ln \gamma_1^l = \alpha'(x_2^l)^2$  where  $\alpha'$  and  $\beta'$  are constants for a mixture which is regular both in the solid and liquid phase, we have at the maxima or minima

$$(\beta' - \alpha') \frac{(x_2^l)_m^2}{RT_m} = \frac{\Delta_f H_1^0}{R} \left( \frac{1}{T_m} - \frac{1}{T_1^0} \right) \quad (46)$$

and

$$(\beta' - \alpha') \frac{(x_1^l)_m^2}{RT_m} = \frac{\Delta_f H_2^0}{R} \left( \frac{1}{T_m} - \frac{1}{T_2^0} \right) \quad (47)$$

where the subscript  $m$  refers to the maximum or minimum temperature and  $\beta'$  and  $\alpha'$  refer to solid and liquid phase respectively. Thus, if the mixture is regular in both the phases, the difference in the value of interchange energies in the two phases which is related to  $\alpha'$  and  $\beta'$  can be readily estimated.

From equation (45) it is clear that minima in such two-phase equilibria (temperature-concentration diagrams) occur when the solid is more positively deviating from the ideal than the liquid solution and when the solid solution is less negatively deviating from ideality than the liquid solution. For maxima, the converse is true.

Phase diagrams of the type under discussion are obtained in anthracene-acenaphthene (12), diphenylacetylene-diphenylethylene (12), and germanium-tin (13). The ideal and experimental phase boundaries for a typical case are shown in Figure 2. A mere visual comparison of experimental and ideal phase boundary does not give any definite idea about the extent of departure from ideality. For instance, the system diphenylacetylene-diphenylethylene gives evidence of considerable deviation from ideality when the solid-liquid equilibrium data are subjected to analysis which may not be otherwise obvious. For a regular solid and liquid mixture,

$$RT \ln \frac{\gamma_1^l}{\gamma_1^s} = \alpha'(x_2^l)^2 - \beta'(x_2^s)^2 \quad (48)$$

which can be written as,

$$\frac{(x_2^l)^2}{T \ln(\gamma_1^l/\gamma_1^s)} = \frac{\beta'}{\alpha'} \frac{(x_2^s)^2}{T \ln(\gamma_1^l/\gamma_1^s)} + \frac{R}{\alpha'} \quad (49)$$

The value of  $\ln \gamma_1^l/\gamma_1^s$  can be determined from equation (30) provided the necessary data are available. Equation (49) can be used for the test for regular behavior and for estimating the values of  $\alpha'$  and  $\beta'$  by simply plotting  $(x_2^l)^2/T \ln(\gamma_1^l/\gamma_1^s)$  against  $(x_2^s)^2/T \ln(\gamma_1^l/\gamma_1^s)$ .

<sup>2</sup> In a similar manner boiling and condensation curves for completely miscible liquids can be drawn (5, p. 351). When two components which are immiscible in the liquid state are considered, the coexistence curves resemble that obtained in the case of eutectic systems.

When such a plot is made for a diphenylacetylene-diphenylethylene system, a straight line is obtained showing that the system is regular (12).

A good recent example of a system having a minimum melting point for which accurate data are available is the nickel-manganese system (14) which appears to be unsymmetrical regular (15).

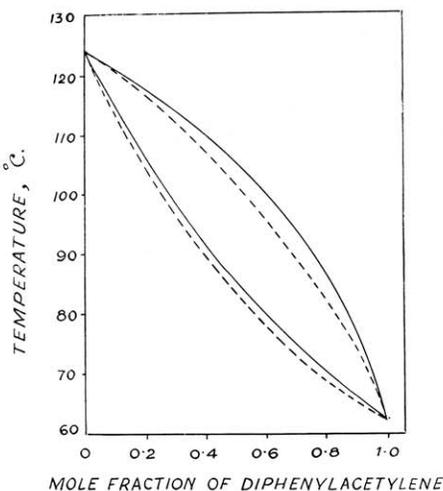


Figure 2. Phase diagram of diphenyl acetylene-diphenyl ethylene; ----, experimental curve; —, ideal curve.

When changes at constant composition are considered, i.e., when  $x_1^\alpha = x_1^\beta$ , and the equilibrium between liquid and vapor phases is involved, we have from equations (12) and (13)

$$\frac{d \ln P}{dT} = \frac{x_1 \Delta_e H_1^0 + x_2 \Delta_e H_2^0}{RT^2} \quad (50)$$

where  $\Delta_e H_1^0$  and  $\Delta_e H_2^0$  are the heat of evaporation of the two components 1 and 2. Equation (50) shows how the boiling point of an azeotropic mixture changes with total pressure  $P$ .

### Mixtures Having a Congruent Melting Point

The equilibrium diagram for a mixture having a congruent melting point is shown in Figure 3. A and B respectively represent the melting points of A and B, the two components, C and E are the eutectic points, and D is the congruent melting point. The composition of the addition compound can be read from the phase diagram. The coexistence curves AC and EB should be given by equations similar to (34). The equation for the phase boundary CDE can be obtained in the following way.

For the sake of simplicity we consider the case when compound AB alone is formed. On mixing the two components, the following reaction takes place,



Let us start with a mixture of  $x_1$  moles of A and  $x_2$  moles of B such that  $x_1 + x_2 = 1$ . We further suppose that  $x$  moles of AB are formed. Then

$$\begin{aligned} X_{AB}, \text{ the mole fraction of AB} &= x/(1-x) \\ X_A, \text{ the mole fraction of A} &= (x_1 - x)/(1-x) \\ X_B, \text{ the mole fraction of B} &= (x_2 - x)/(1-x) \end{aligned}$$

The equilibrium constant  $K$  of the first stage of the reaction is given by

$$K = \frac{x_{AB}}{x_A x_B} \quad (51)$$

for an ideal system. But

$$\frac{d \ln k}{dT} = \frac{\Delta H}{RT^2} \quad (52)$$

where  $\Delta H$  is the heat of formation of AB in the liquid phase. Combining equations (51) and (52), we have

$$\frac{d \ln x_{AB}}{dT} - \frac{d \ln x_A}{dT} - \frac{d \ln x_B}{dT} = \frac{\Delta H}{RT^2} \quad (53)$$

Since the sum of the mole fractions is unity, the condition for equilibrium for the overall reaction is

$$\mu_{AB}^s = \mu_{AB}^l = \mu_A^l + \mu_B^l \quad (54)$$

where  $\mu_{AB}^s$  is the chemical potential of the compound in the solid phase and  $\mu_{AB}^l$ ,  $\mu_A^l$ , and  $\mu_B^l$  are the chemical potentials of AB, A and B in the liquid phase.

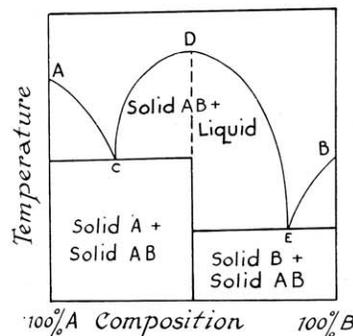


Figure 3. Phase diagram for a mixture having a congruent melting point.

Further

$$d\mu_{AB}^s = d\mu_{AB}^l = d\mu_A^l + d\mu_B^l \quad (55)$$

and since  $dP = 0$ , we have

$$\begin{aligned} -S_{AB}^s dT = & \left\{ -S_A^l dT + \sum \left( \frac{\partial \mu_A^l}{\partial x_i^l} \right)_{T,P,x_j^l} dx_i^l \right\} + \\ & \left\{ -S_B^l dT + \sum \left( \frac{\partial \mu_B^l}{\partial x_i^l} \right)_{T,P,x_j^l} dx_i^l \right\} \end{aligned} \quad (56)$$

If the mixture behaves ideally, we have

$$(S_{AB}^s - S_A^l - S_B^l) dT = -RT[d \ln x_A^l + d \ln x_B^l] \quad (57)$$

$(S_A^l + S_B^l - S_{AB}^s)$  would be equal to  $\Delta_f H/T$  where  $\Delta_f H$  is the heat of fusion. This would be equal to the hypothetical heat of fusion of AB if there were no dissociation. Equation (59) yields

$$\frac{d \ln x_A^l x_B^l}{dT} = \frac{\Delta_f H}{RT^2} \quad (58)$$

On integration we obtain,

$$\frac{\Delta_f H}{R} \left( \frac{1}{T} - \frac{1}{T_C} \right) = -\ln(x_A^l)(x_B^l) + \ln(x_A^l)_C(x_B^l)_C \quad (59)$$

where  $T_C$  denotes the congruent melting point and the quantities with the subscript C denote the mole fraction corresponding to that which would exist in molten addition compound. If the compound is completely dissociated,  $x_A^l$  and  $x_B^l$  may be put equal to the stoichiometric mole fraction  $\xi_A$  and  $\xi_B$ . If equation (60) is valid, the plot of  $(1/T - 1/T_C)$  against  $\ln(\xi_A)(\xi_B)$  should yield a straight line. Such straight line plots are

obtained for a number of systems (16), but nothing more can be safely inferred in the absence of any definite information regarding the complete dissociation of the compound.

If there is no dissociation of the complex, the congruent melting point would correspond to the hypothetical melting point  $T_0$ . In this case, the phase diagram would show a sharp maximum. However, when dissociation occurs in the molten state, the products of dissociation lower the effective mole fraction of the solute and the curve would be flattened. Thus, the flatness of the maximum is indicative of the extent of dissociation in the liquid state.

Similar consideration can be employed for interpreting the phase boundaries in the case of incongruent melting points.

### Partial Miscibility in the Solid Phase

So far we have discussed the cases in which the components were completely miscible in the solid and liquid phases. Cases occur where there is a region of limited solid solubility. Such phase diagrams are shown in Figure 4. The point C in Figure 4a is a eutectic and D in Figure 4b is a peritectic point. The solidus and liquidus curves would be described by equation (30).

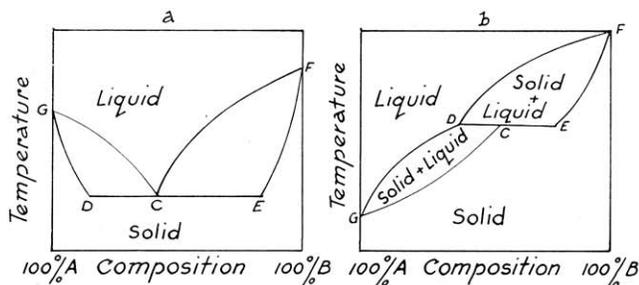


Figure 4. Phase diagram of a system showing a peritectic point.

One important characteristic of such phase diagrams is that for the particular liquid composition at a certain temperature one has two different compositions in the solid phase which can be in equilibrium with the liquid phase. Thus, from equation (30), it follows that

$$(x_1^*)_D(\gamma_1^*)_D = (x_1^*)_E(\gamma_1^*)_E \quad (60)$$

and

$$(x_2^*)_D(\gamma_2^*)_D = (x_2^*)_E(\gamma_2^*)_E \quad (61)$$

These considerations have been employed for checking the internal consistency of solid-liquid equilibrium data for carbon tetrachloride-cyclohexane system which appears to have a eutectic point (8).

### Critical Mixing Separation in Two Phases

We include the phenomenon of critical mixing for discussion here for the sake of completeness. There are certain liquid mixtures which are miscible in all proportions at ordinary pressure provided the temperature is above or below a certain temperature called the critical solution temperature.

A quantitative interpretation of the phenomenon can be given as follows. For a binary mixture to be stable and not to separate into two phases, the following conditions have to be satisfied.

$$\partial \mu_i / \partial x_i = \partial^2 \mu_i / \partial x_i^2 = 0 \quad (62)$$

These conditions can be used for predicting the critical solution temperature for a regular mixture. The chemical potential of component 1 for a binary regular mixture is given by

$$\mu_1 = \mu_1^0 + RT \ln x_1 + \alpha' x_2^2 \quad (63)$$

where  $\mu_1^0$  is a constant which depends only on temperature and pressure. Remembering that  $x_1 + x_2 = 1$ , we have

$$\left( \frac{\partial \mu_1}{\partial x_2} \right) = \frac{RT_{cr}}{1 - (x_2)_{cr}} + 2\alpha'(x_2)_{cr} = 0 \quad (64)$$

and

$$\left( \frac{\partial^2 \mu_1}{\partial x_2^2} \right) = - \frac{RT_{cr}}{\{1 - (x_2)_{cr}\}^2} + 2\alpha' = 0 \quad (65)$$

where  $(x_2)_{cr}$  denotes the mole fraction of second component at the critical solution temperature,  $T_{cr}$ . On solving equations (64) and (65), we have,

$$(x_2)_{cr} = 0.5 \quad (66)$$

and

$$T_{cr} = \frac{\alpha'}{2R} \quad (67)$$

Thus for a regular mixture the critical point occurs at the equimolar mixture.

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