

SOLID-LIQUID EQUILIBRIA IN BINARY AND MULTI-COMPONENT MIXTURES

by R. P. RASTOGI, *Department of Chemistry, Lucknow University*

(Communicated by B. N. Srivastava, F.N.I.)

(Received December 8, 1954; read March 4, 1955)

1. INTRODUCTION

Solid solutions are an important class of mixtures on account of their applicability to metallic solutions and alloys. Such solutions are amenable to theoretical treatment as most of statistical theories assume crystalline or quasi-crystalline model which is certainly true even for the liquid mixtures near the freezing-point. Significant progress has been made in recent years in interpreting the concept of superlattices and the order-disorder phenomenon in alloys (Guggenheim, 1952). Thermodynamic interpretation of solidus and liquidus curves has been previously attempted (Seltz, 1934; Scatchard and Hamer, 1935) but not to a satisfactory degree. In the present paper it is intended to discuss solid-liquid equilibria in greater detail in the light of newer thermodynamic theories.

It is generally believed that for two electrolytes to form a solid solution, the following conditions must be satisfied :—

- (1) The formulae of the two components must be similar.
- (2) There must be similar unit cells containing exactly the same number of positive and negative ions in geometrically similar positions.
- (3) The size of the ions should be approximately the same.
- (4) The polarization of the ions must not be different.

Similarly for non-electrolytes, the conditions for the formation of solid solutions are :—

- (1) The formulae and structure of the components must be similar.
- (2) The crystal structure of the components should be similar.
- (3) The molar volumes should not differ appreciably.

In this paper we shall consider only solid solutions of non-electrolytes. Such solutions may be ideal, regular or non-ideal. The conditions for ideal or regular solutions have been predicted from statistical mechanics (Rushbrooke, 1949) according to which an ideal solution must satisfy the following microscopic conditions :—

- (i) The systems of the assembly can be regarded as independent systems, the partition function of any one of them being entirely unaffected by the composition of the solution.
- (ii) The systems in the condensed phase are of approximately equal size and shape and pack in the same way and have the same number of nearest neighbours.
- (iii) There are no preferential interactions between different systems within the condensed phase so that all the atoms move in the potential field which is not sensibly affected by the composition of the solution. Further the potential energy can be regarded as the sum of contributions from pairs of nearest neighbours.
- (iv) The vapour phase behaves as a mixture of perfect gases.
- (v) The volume of the condensed phase is negligible compared to that of vapour.

Non-ideal but regular solutions are those in which all the above conditions are satisfied except condition (iii). The gaseous mixtures at low pressures may be expected to behave ideally as the molecules are far apart. The liquid mixtures, in general, may or may not be ideal. The solid solutions in most of the cases cannot be expected to behave ideally since the molecules are usually very close and the interactions cannot be neglected. These solutions may approximate to regular solutions in a few cases.

2. EQUILIBRIUM CONDITIONS IN A MULTI-COMPONENT SYSTEM

We now proceed to deduce the conditions of solid-liquid equilibrium in a multi-component non-ideal system consisting of r components capable of existing in liquid as well as solid phase. Following the procedure adopted previously (Srivastava and Rastogi, 1953) it can be shown that

$$\sum_{i=1}^r N_i (\bar{S}'_i - \bar{S}_i) = \left\{ N_1 \sum_{i=1}^{r-1} \left(\frac{\partial \mu'_1}{\partial N'_i} \right)_{T, P, N'_j} dN'_i + N_2 \sum_{i=1}^{r-1} \left(\frac{\partial \mu'_2}{\partial N'_i} \right)_{T, P, N'_j} dN'_i + \dots \text{up to } r \text{ terms} \right\} \quad \dots (1)$$

where \bar{S}'_i and \bar{S}_i are the partial molar entropy of the component i in the liquid and solid phase respectively. N_1, N_2, \dots are the mole-fractions in the solid phase while N'_1, N'_2, \dots are the mole-fractions in the liquid phase. μ_i represents the chemical potential of the component i . For condensed systems the pressure changes have insignificant effect and hence the term due to pressure changes does not occur in the above equations. Now, it can be easily seen

$$N_1 (\bar{S}'_1 - \bar{S}_1) + N_2 (\bar{S}'_2 - \bar{S}_2) + \dots \text{up to } r \text{ terms} = \sum_{i=1}^r \frac{N_i \lambda_i}{T} \cdot dT \quad \dots (2)$$

where $\sum N_i \lambda_i$ is the heat of melting of one mole containing N_1, N_2, \dots mole-fractions of the respective components in the solid phase without sensibly altering the composition of the liquid phase. λ_i is the heat of melting of the component i and includes the partial molar heat function for the component i . Using equation (2), equation (1) yields

$$\sum_{i=1}^r \frac{N_i \lambda_i}{T} \cdot dT = \left\{ N_1 \sum_{i=1}^{r-1} \left(\frac{\partial \mu'_1}{\partial N'_i} \right)_{T, P, N'_j} dN'_i + N_2 \sum_{i=1}^{r-1} \left(\frac{\partial \mu'_2}{\partial N'_i} \right)_{T, P, N'_j} dN'_i + \dots \text{up to } r \text{ terms} \right\} \quad \dots (3)$$

The above equation holds for any non-ideal multi-component system when the solid phase is in equilibrium with the liquid phase.

Similarly it is easy to show that

$$- \sum_{i=1}^r \frac{N'_i \lambda_i}{T} \cdot dT = \left\{ N'_1 \sum_{i=1}^{r-1} \left(\frac{\partial \mu_1}{\partial N_i} \right)_{T, P, N_j} dN_i + N'_2 \sum_{i=1}^{r-1} \left(\frac{\partial \mu_2}{\partial N_i} \right)_{T, P, N_j} dN_i + \dots \text{up to } r \text{ terms} \right\} \quad \dots (4)$$

3. IDEAL SOLUTIONS

For ideal solutions the chemical potential is given by

$$\mu_i = \mu_i^0 + RT \log N_i$$

where μ_i^0 depends on temperature and pressure. Accordingly we have

$$\left(\frac{\partial \mu_i}{\partial N_i}\right)_{T,P} = \frac{RT}{N_i}$$

Three cases may arise. Firstly the liquid phase may be alone ideal, the solid phase remaining non-ideal. Secondly the solid phase may be alone ideal. Thirdly both the phases may be ideal. Taking the first case we have from equation (3)

$$\sum_{i=1}^r \frac{N_i \lambda_i}{T} \cdot dT = RT \left[\frac{N_1}{N_1'} dN_1' + \frac{N_2}{N_2'} dN_2' + \dots + \frac{N_r}{N_r'} dN_r' \right]$$

which for a bicomponent system yields

$$\frac{N_1 \lambda_1^0 + N_2 \lambda_2^0 - H_M}{T} \cdot dT = RT \left(\frac{N_1}{N_1'} - \frac{N_2}{N_2'} \right) dN_1' \quad \dots \quad (5)$$

where λ_1^0 and λ_2^0 are the heat of fusion of pure components and H_M is the heat of mixing in the solid phase. The heat of mixing will be zero if the solid phase is also ideal. If we put $N_1/N_1' = \alpha$; $N_2/N_2' = \beta$ where α and β are the separation ratios of the respective components, the maxima or minima in the melting-point composition curve will occur when $\alpha = \beta$.

From equation (5) a rule similar to that of Konowaloff for liquid-vapour system can be deduced for the present case. Thus, if dN_1'/dT is positive the first component will get enriched in the solid phase as the temperature is increased showing thereby that fractional crystallization is possible. Again if the solid phase exclusively consists of the solvent, i.e., component 1, we obtain

$$\frac{dN_1'}{dT} = \frac{N_1 \lambda_1^0}{RT^2} \quad \dots \quad (6)$$

which on integration yields the van't Hoff's law for the depression of freezing-point. On the other hand, if the solid phase is constituted by only the solute, equation (5) readily yields an expression relating solubility with temperature

Taking the second case into consideration (when solid phase is alone ideal), we have from equation (4)

$$- \sum_{i=1}^{i=r} \frac{N_i' \lambda_i}{T} \cdot dT = RT \left\{ \frac{N_1'}{N_1} dN_1 + \frac{N_2'}{N_2} dN_2 + \dots + \frac{N_r'}{N_r} dN_r \right\} \quad \dots \quad (7)$$

which for a two-component system yields

$$\frac{dN_1}{dT} = \frac{-(N_1' \lambda_1^0 + N_2' \lambda_2^0 - H'_M)}{RT^2} \left/ \frac{N_1'}{N_1} - \frac{N_2'}{N_2} \right. \dots \quad (8)$$

where H'_M is the heat of mixing for the liquid phase. Again a similar condition for stationary melting point can be deduced from equation (8). It also follows from equation (8) that if dN_1/dT is positive $\alpha > \beta$. The heat of mixing would be zero if the liquid phase is ideal.

From equations (5) and (8) it follows that if both the phases are ideal

$$\frac{dN_1}{dN_1'} = \frac{N_1' \lambda_1^0 + N_2' \lambda_2^0}{N_1 \lambda_1^0 + N_2 \lambda_2^0} \cdot \frac{N_1 N_2}{N_1' N_2'} \quad \dots \quad (9)$$

On integrating the above equation we get the following relation between the composition of the two phases at any instant

$$\lambda_2^0 \log \frac{N_1}{N_1'} = \lambda_1^0 \log \frac{N_2}{N_2'} + \text{constant} \quad \dots \quad (10)$$

It follows that if $\log \frac{N_1}{N_1'}$ is plotted against $\log \frac{N_2}{N_2'}$, straight line would be obtained.

This can be a convenient test for testing the ideality of a binary solid solution.

Applying the above considerations to a simple binary eutectic system, the liquidus curve of the component 1 would be represented by equation (5) when $N_2 = 0$ while the liquidus curve for the component 2 will again be given by equation (5) when $N_1 = 0$. Thus the equation for the liquidus curve of component 1 is given by

$$\log N_1' = \frac{-\lambda_1^0}{RT} + \text{constant} \quad \dots \quad (11)$$

Similarly for the component 2 we have

$$\log N_2' = \frac{-\lambda_2^0}{RT} + \text{constant} \quad \dots \quad (12)$$

We suppose that T_1^0 and T_2^0 are respectively the freezing-points of the respective components. At the eutectic point the two curves meet. If N_1^e and T_e be the mole-fraction of the component 1 and the eutectic temperature, we have from equations (11) and (12)

$$\log N_1^e = \frac{-\lambda_1^0}{R} \left[\frac{1}{T_e} - \frac{1}{T_1^0} \right]; \quad \log (1-N_1^e) = \frac{-\lambda_2^0}{R} \left[\frac{1}{T_e} - \frac{1}{T_2^0} \right]$$

Eliminating T_e between the two equations, we have

$$\frac{\log N_1^e}{\lambda_1^0} - \frac{\log (1-N_1^e)}{\lambda_2^0} = \frac{1}{R} \left[\frac{1}{T_1^0} - \frac{1}{T_2^0} \right] \quad \dots \quad (13)$$

The above equation should hold at the eutectic point provided the mixture behaves ideally. On eliminating N_1^e we get the relation which gives the value of the eutectic temperature.

Let us examine the above relations for the system naphthalene-phenanthrene which appears to be ideal from considerations of solubility parameters as defined by Hildebrand (1950). The data for this system can be taken from International Critical Tables (1929). Taking the value of heat of fusion of naphthalene and phenanthrene as 19.07 and 18.1 kilojoules/gm. mol., the mole-fraction of naphthalene at the eutectic point is found to be 0.66 whereas the observed value is 0.62. The agreement is fairly satisfactory.

4. REGULAR MIXTURES

The ideal solutions are the simplest to deal with from the quantitative point of view, but they are only exceptions. After them regular solutions are the simplest to be amenable to theoretical analysis. The statistical theory predicts that any mixture of two kinds of molecules of similar size and shape should obey certain laws called the laws of strictly regular solution to which formula for regular solution

are a useful approximation. Hildebrand has experimentally demonstrated that a considerable number of binary mixtures follow exactly or approximately the laws of regular solutions. For deducing the laws of strictly regular solutions various procedures are adopted. The simplest of them assumes a completely random distribution of two kinds of molecules in spite of non-zero energy of mixing. This is called the zeroth approximation. The quasi-chemical treatment of 'strictly regular solution' (Guggenheim, 1935; Rushbrooke, 1938) is reasonably rigorous. The model used involves a quasi-lattice of co-ordination number z in which each molecule occupies a single lattice site. This situation is more nearly appropriate to solid solutions than to liquid solutions. The model would still be a reality for liquid solutions at the freezing point of the components. Various improvements have been made on this approximation. Bethe's method (Bethe, 1935; Rushbrooke, 1938) has been shown to be equivalent to quasi-chemical treatment. The essential basis of these approximations is 'the hypothesis of non-interference of pairs' which cannot hold in a closed-packed lattice and one must take into account triangular triplets or tetrahedral quadruplets instead of pairs. Expressions for partial pressures and chemical potentials have been deduced even for such a case but cannot be used in practice (Guggenheim, 1952). For practical purposes the zeroth approximation is much more helpful than the more refined approximations. Using zeroth approximation the chemical potential of the component i is given by

$$\begin{aligned}\mu_1 &= \mu_1^0 + RT \log N_1 + N_2^2 w \\ \mu_2 &= \mu_2^0 + RT \log N_2 + N_1^2 w \quad \dots \quad \dots \quad \dots \quad (14)\end{aligned}$$

where w , the interchange energy is defined as the decrease in potential energy on exchange of a single pair of molecules between the pure components. In terms of pair energies ϵ_{11} , ϵ_{12} and ϵ_{22}

$$w = \frac{1}{2}z(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}) \quad \dots \quad \dots \quad \dots \quad (15)$$

It can be shown that if solid phase is regular

$$\left(\frac{\partial \mu_i}{\partial N_i}\right)_{T,P} = \frac{RT}{N_i} - 2(1-N_i)w \quad (i = 1, 2) \quad \text{and} \quad H_M = N_1 N_2 w,$$

on the other hand, if liquid phase is regular

$$\left(\frac{\partial \mu'_i}{\partial N'_i}\right)_{T,P} = \frac{RT}{N'_i} - 2(1-N'_i)w' \quad (i = 1, 2) \quad \text{and} \quad H'_M = N'_1 N'_2 w',$$

where w and w' are the interchange energies in the solid and liquid phases respectively.

We shall consider the following cases:

A. *Liquid phase regular but solid phase ideal.*

Substituting relevant values in equations (3) and (4) we have

$$\frac{dN'_1}{dT} = \frac{N_1 \lambda_1^0 + N_2 \lambda_2^0}{T} \left/ RT \left(\frac{N_1}{N'_1} - \frac{N_2}{N'_2} \right) \right. + 2w' (N'_1 N_2 - N'_2 N_1) \quad \dots \quad (16)$$

and

$$- \frac{dN_1}{dT} = \frac{N'_1 \lambda_1^0 + N'_2 \lambda_2^0 - N'_1 N'_2 w'}{RT^2} \left/ \left(\frac{N'_1}{N_1} - \frac{N'_2}{N_2} \right) \right. \quad \dots \quad (17)$$

B. *Solid phase regular but liquid phase ideal.*

For this case equations (3) and (4) yield

$$\frac{dN'_1}{dT} = \frac{N_1\lambda_1^0 + N_2\lambda_2^0 - N_1N_2w}{RT^2} \bigg/ \left(\frac{N_1}{N'_1} - \frac{N_2}{N'_2} \right) \quad \dots \quad (18)$$

and

$$- \frac{dN_1}{dT} = \frac{N'_1\lambda_1^0 + N'_2\lambda_2^0}{RT^2} \bigg/ \left(\frac{N'_1}{N_1} - \frac{N'_2}{N_2} \right) \quad \dots \quad (19)$$

C. *Both phases regular.*

For this case we have the following equation for the liquidus curve

$$\frac{dN'_1}{dT} = \frac{N_1\lambda_1^0 + N_2\lambda_2^0 - N_1N_2w}{T} \bigg/ RT \left(\frac{N_1}{N'_1} - \frac{N_2}{N'_2} \right) + 2w'(N'_1N_2 - N'_2N_1) \quad \dots \quad (20)$$

The corresponding equation for solidus curve is given by

$$- \frac{dN_1}{dT} = \frac{N'_1\lambda_1^0 + N'_2\lambda_2^0 - N'_1N'_2w'}{T} \bigg/ RT \left(\frac{N'_1}{N_1} - \frac{N'_2}{N_2} \right) - 2w(N_2N'_1 - N_1N'_2) \quad (21)$$

For cases A and B, the necessary and sufficient condition of stationary melting point is

$$N_1/N_2 = N'_1/N'_2 \quad \dots \quad (22)$$

which is identical with the condition found for ideal mixtures. But for C, the maxima or minima in the solidus or liquidus curve will occur when

$$\begin{aligned} N_1/N_2 &= N'_1/N'_2 \\ 2w \cdot N_1N_2 &= RT \\ \text{or } 2w'N'_1N'_2 &= RT \end{aligned}$$

The condition $N_1/N_2 = N'_1/N'_2$ simply means that the solidus and liquidus should touch at the maxima or minima. However, if they do not touch and still have a maxima or minima, the other condition has to be satisfied. This means that in an ideal mixture if maxima or minima occurs the two curves must touch each other. The above equation also tells us that for maxima or minima the minimum value of interchange energy that is permissible is $4T$. If for any system the value of interchange energy is less than this amount, only the first condition will determine the existence of the stationary melting point.

Considering an eutectic system, the liquidus or the freezing point curves for the two components are given by the following equations :—

Case A.

$$\frac{dN'_1}{dT} = \frac{N'_1\lambda_1^0}{RT^2 - 2w'TN'_1N'_2}; \quad \frac{dN'_2}{dT} = \frac{N'_2\lambda_2^0}{RT^2 - 2w'TN'_1N'_2} \quad \dots \quad (23)$$

Case B.

$$\frac{dN'_1}{dT} = \frac{N'_1\lambda_1^0}{RT^2}; \quad \frac{dN'_2}{dT} = \frac{N'_2\lambda_2^0}{RT^2} \quad \dots \quad (24)$$

The relations are identical with those obtained for ideal mixtures.

For the Case C we obtain

$$\frac{dN'_1}{dT} = \frac{N'_1\lambda_1^0}{RT^2 - 2w'TN'_1N'_2}; \quad \frac{dN'_2}{dT} = \frac{N'_2\lambda_2^0}{RT^2 - 2w'TN'_1N'_2} \dots \dots (25)$$

5. ATHERMAL MIXTURES—SOLUTIONS OF MACROMOLECULES

It has been suggested that the departures from the laws of ideal solutions due to wide differences in size between the two species of molecules can be at least semi-quantitatively described by means of relatively simple formulae in which the only parameter is the ratio of the molar volumes (Guggenheim, 1952; Hildebrand, 1950).

The Gibbs function of a mixture containing n_1 moles of component 1 and n_2 moles of component 2 can be written as

$$G = n_1\mu_1^0 + n_2\mu_2^0 + RT \left\{ n_1 \log \frac{n_1}{n_1 + rn_2} + n_2 \log \frac{rn_2}{n_1 + rn_2} \right\} \dots (26)$$

where r denotes the ratio of the volumes of a molecule of type 2 to that of a molecule of type 1. From the above equation we obtain,

$$\begin{aligned} \mu_1 &= \mu_1^0 + RT \left\{ \log \frac{N_1}{1 + (r-1)N_2} + \frac{(r-1)N_2}{1 + (r-1)N_2} \right\} \\ \mu_2 &= \mu_2^0 + RT \left\{ \log \frac{rN_2}{1 + (r-1)N_2} - \frac{(r-1)N_1}{1 + (r-1)N_2} \right\} \dots \dots (27) \end{aligned}$$

These equations yield

$$\left(\frac{\partial \mu_1}{\partial N_1} \right)_{T, P} = RT \left\{ \frac{1}{N_1} - \frac{(r-1)^2 N_1}{1 + (r-1)N_2} \right\}$$

and

$$\left(\frac{\partial \mu_2}{\partial N_2} \right)_{T, P} = RT \left\{ \frac{1}{N_2} + \frac{(r-1)^2 N_1}{1 + (r-1)N_2} \right\} \dots \dots (28)$$

and similarly for the liquid phase.

Evidently the form of equations (26) and (27) implies that heat of mixing is zero. Using equations (3) and (4) and (28) we obtain

$$\frac{N_1\lambda_1^0 + N_2\lambda_2^0}{T} \cdot dT = RT \left\{ \left(\frac{N_1}{N'_1} - \frac{N_2}{N'_2} \right) - \frac{(r-1)^2(N_1N'_2 + N'_1N_2)}{1 + (r-1)N'_2} \right\} dN'_1 \quad (29)$$

$$- \frac{N'_1\lambda_1^0 + N'_2\lambda_2^0}{T} \cdot dT = RT \left\{ \left(\frac{N'_1}{N_1} - \frac{N'_2}{N_2} \right) - \frac{(r-1)^2(N'_1N_2 + N'_2N_1)}{1 + (r-1)N_2} \right\} dN_1 \quad (30)$$

These formulae will hold if the heat of mixing is zero and non-ideality mainly results due to differences in size. These conditions are favourable to solutions of macromolecules.

The strictly regular solution model has some serious limitations since, in order to fit in the regular lattice, molecules of the different species must be of nearly the same size, although the method has been extended to include molecules occupying a series of lattice sites. Thus for athermal mixtures of high polymers

$$\mu_1 = \mu_1^0 + RT \left[\log \frac{N_1}{1 + (r-1)N_2} + \frac{1}{2} z \cdot \frac{r - (r-1)N_1}{q - (q-1)N_1} \right]$$

The number q for a single chain or branched chain r -mer is related to r by the following relation

$$\frac{1}{2}z(r-q) = r-1$$

This follows because we consider a particular r -mer occupying a group of r -sites, each of these sites having z neighbouring sites some occupied by other elements of the same r -mer. Then zq is the number of pairs of neighbouring sites of which one is a member of the group occupied by the given r -mer and the other is not. Flory's approximation is usually obtained by making $z \rightarrow \infty$ (Flory, 1941). These and other more rigorous formulae can be used for yielding equations of solidus and liquidus for a solution of high polymer.

6. SOLID-LIQUID EQUILIBRIUM DATA FOR CHLORINE-BROMINE SYSTEM

In this section it is intended to apply the ideas developed in previous sections to interpret the available equilibrium data (International Critical Tables, 1929) for the system chlorine-bromine and test equations (5), (8), (16), (17), (18), (19), (20) and (21). For an ideal or regular system it is necessary to choose the components in such a way that the size and shape of the molecules are approximately the same. Moreover, the solutions have to conform to other restrictive conditions which are realized in practice with great difficulty. The system chosen for investigation is relatively simple. The crystals of chlorine and bromine are weakly bound crystals where the attraction is mainly due to Van der Waals' forces. The Van der Waals' interaction between two non-dipole molecules does not affect in first approximation their interaction with a third molecule and consequently there is no tendency towards the formation of bigger groups containing several molecules. For the sake of comparison the molar volumes of chlorine and bromine in solid as well as liquid phases are given below.

			Molar volume in the solid phase	Molar volume in the liquid phase
Chlorine	37.37 ml.	45.3 ml.
Bromine	47.04 ml.	51.3 ml.

In the crystal of chlorine there are 16 chlorine atoms in a tetragonal unit at -185°C . The molecules of chlorine are packed in such a way that each chlorine has its molecular partner 1.82 \AA away and neighbours in adjacent molecules as near as 2.52 \AA (Keesom and Taconis, 1936). Crystalline bromine has also been shown to be possessing definitely a molecular structure, the Br_2 molecule being easily recognised in the crystalline structure from the observed interatomic distances. In crystalline bromine each atom has one nearest neighbour at a distance 2.27 \AA , the other member of bromine molecule (Vonnegut and Warren, 1936). This agrees with the band spectrum value of 2.28 \AA and the electron diffraction value of 2.28 \AA . Each atom has three other close neighbours in the same reflection plane (plane of paper) at distances $3.30, 3.30, 3.75 \text{ \AA}$. Eight more neighbours in the planes above and below are at slightly larger distances $4.00, 4.00, 3.98$ and 4.10 . Thus it can be seen that the structure of orthorhombic bromine is apparently different from the crystal structure of chlorine. It may also be noted that the intramolecular distance for chlorine is 1.82 \AA while that for bromine is 2.27 \AA . Nevertheless complete series of solid solutions are formed between chlorine and bromine. From considerations of molar volume and crystal structure, the mixture of chlorine and bromine cannot be expected to behave rigorously as an ideal or regular mixture. The interchange of molecules in a lattice can only cause strain. The problem of packing may not be difficult in the liquid phase and hence we may reasonably expect the liquid phase to behave approximately as regular mixture owing to the

fact that the molar volumes of the two species differ by only 12% in the liquid phase.

The liquidus and solidus curves for the system have been drawn by using the experimental data given in I.C.T. and are shown in Fig. 1. The temperatures are correct to $\pm 2^\circ\text{C}$. and the mole-fractions are correct to $\pm 4\%$.

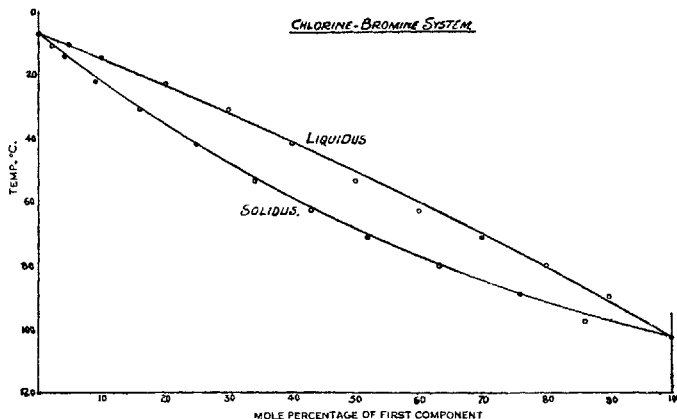


FIG. 1.

The quantities required for testing eqs. (5), (8), (16), (17), (18), (19), (20) and (21) can be easily found out. At any temperature a line drawn parallel to abscissa gives the composition of liquid and solid phase at equilibrium at the points of intersection of the liquidus and solidus curves, respectively. The latent heat of fusion are known at the freezing-point. The heat of fusion can be known at any other temperature by using the formula $\frac{d\lambda_i}{dT} = C_L - C_S + \frac{\lambda_i}{T}$ where C_S and C_L are the specific heat of solid and liquid species respectively. Inserting these values dN_1/dT and dN_1'/dT can be calculated from equations (5) and (8) and compared with the experimental slope determined from Fig. 1. The theoretical and experimental values are shown in Table I. The values show wide divergence and hence the mixture cannot be ideal.

The equations for regular solutions involve one or two adjustable parameters, i.e., w and w' , the interchange energy in the solid and liquid phase respectively. For the present purpose we may assume them to be temperature independent. Now, in order to test the equations of regular solutions w and w' may be calculated at a series of temperatures by employing the values of experimental slopes of liquids and solidus curves. If the equations hold for the system under consideration the values of w and w' should come out to be the same. The actual calculations for the present system reveal that this is not the case and consequently the two phases cannot be simultaneously regular nor any phase can behave as an ideal one, since in that case the interchange energy would have been zero. These conclusions agree with those previously deduced on the basis of considerations of molar volume, crystal structure and intra-molecular distances. However, we may assume the liquid phase to behave ideally, the solid phase remaining non-ideal.

The heat of mixing for non-ideal solutions is empirically represented as follows (Scatchard *et al.*, 1952; Barker, Brown and Smith, 1953)

$$H_M = N_1 N_2 [A + B(N_1 - N_2) + C(N_1 - N_2)^2 + D(N_1 - N_2)^3 + \dots] \quad (31)$$

where A , B , C , D are constants which are determined empirically. We suppose that they are practically independent of temperature. Assuming the liquid phase

to be regular and heat of mixing to be given by equation (31), we have the following equation for the liquidus curve

$$\frac{dN'_1}{dT} = \frac{N_1\lambda_1^0 + N_2\lambda_2^0 - N_1N_2[A + B(N_1 - N_2) + C(N_1 - N_2)^2 + \dots]}{RT} \left/ \left(\frac{N_1}{N'_1} - \frac{N_2}{N'_2} \right) \right. + \frac{2w'}{RT} (N'_1N_2 - N'_2N_1) \quad \dots \quad (32)$$

Accordingly we use equation (32) to fit the data. The observed experimental values of dN'_1/dT and those calculated from equation (32) are compared in the following table which also gives the values calculated from equation (5) which holds for ideal solutions. The observed values are in satisfactory agreement with those calculated by equation (32).

TABLE I

$$w' = -1080 \text{ cal./gm. mol.}, H_M = N_1N_2[+1236 + 13250(N_1 - N_2)^2]$$

N_1 (chlorine)	N'_1	$T^\circ \text{ K}$	λ_1^0 cal./gm. mol.	λ_2^0 cal./gm. mol.	$\left(\frac{dN'_1}{dT}\right)_{\text{obs.}}$	$\left(\frac{dN'_1}{dT}\right)_{\text{cal.}}$ from eq. (32)	$\left(\frac{dN'_1}{dT}\right)_{\text{cal.}}$ from eq. (5)
0.20	0.335	237	1,817	2,407	0.01000	0.00984	0.03363
0.30	0.46	225	1,782	2,355	0.01015	0.01015	0.03327
0.40	0.59	213	1,747	2,264	0.01054	0.01087	0.03047
0.50	0.70	203	1,718	2,204	0.01020	0.01000	0.02498
0.60	0.78	195	1,695	2,161	0.01020	0.01027	0.02357
0.76	0.90	183	1,660	2,085	0.00880	0.00620	0.01692

It is interesting to note that the heat of mixing in the solid phase is positive while that in the liquid phase is negative. The heat of mixing in the liquid phase can only be negative when $\epsilon_{12} > \epsilon_{11} + \epsilon_{22}$.

We take this opportunity to discuss the possibility of existence of bromine chloride in the condensed phase. Measurements of the transmission of chlorine-bromine light filters, containing an excess of liquid bromine demonstrate the existence of bromine chloride in mixtures of gaseous bromine and chlorine (Gray and Style, 1930). The freezing-point diagram of the system chlorine-bromine does not indicate the formation of stable bromine chloride molecule. However, it has been argued that it is 'compatible with the existence of a compound, if it is partly dissociated and in the solid forms a continuous series of solid solutions with both of its components'. (Sidgwick, 1933). It is obvious that if a stable type of molecule is formed in the condensed phase it would be a ternary system and the phase diagram would have been definitely complicated. Thus it seems that if at all bromine chloride is formed in the condensed phase it would be unstable as the complexes formed in a solution of alcohol and water are. Moreover, the formation of bromine chloride in the gaseous phase does not necessarily mean the formation in the condensed phase. The negative heat of mixing in the liquid phase does point to the fact that the interaction between unlike molecules is more prominent than between like molecules.

From the considerations of crystal structure, it can be conceived that since the size of chlorine molecules differ with bromine molecules by about 20% in the solid phase, the substitution of one molecule for the other would cause a considerable amount of strain or distortion in the crystal. This fact may be responsible for making the solid phase non-ideal. The amount of strain developed in the solid

solution of chlorine and bromine is probably insufficient to cause separation in two phases. Employing fairly arbitrary assumptions the strain energy in a binary solid solution of atoms of different sizes has been deduced (Lawson, 1947; Hildebrand and Scott, 1950). Using Scott's expression, i.e.,

$$\Delta E^D = \frac{2\delta_1\delta_2(V_1V_2)^{\frac{1}{2}}(V_1 - V_2)^2}{(N_1V_1^2 + N_2V_2^2)} N_1N_2 \dots \dots \dots (33)$$

where δ_1 and δ_2 are the solubility parameters of the two species and V_1 and V_2 are the molar volumes, ΔE^D , the strain energy for a equi-molar mixture of chlorine and bromine is found to be equal to 137 cal. which does not seem to be unreasonable.

The author is thankful to Prof. A. C. Chatterji for continued interest in the investigation.

This work forms part of the scheme supported by the Council of Scientific and Industrial Research.

SUMMARY

Thermodynamics of solid-liquid equilibria has been investigated. Equations of solidus and liquidus curves have been deduced for ideal, regular, athermal and non-ideal mixtures including solutions of high polymers. The conditions for stationary melting-point have also been deduced. Binary eutectic system has been discussed. The eutectic composition for naphthalene-phenanthrene system predicted from theory is in satisfactory accord with the observed value. The solid-liquid equilibrium data of chlorine-bromine system has been examined. It is found that the system is neither ideal nor regular but the equations assuming the liquid phase to be regular and solid phase to be non-ideal fit the data. Heat of mixing for the liquid phase is found to be negative while it is positive for the solid phase. The formation of bromine chloride molecules in the condensed phase is discussed. The interaction between chlorine and bromine molecules is more prominent than the interaction between the like molecules in the liquid phase, but it seems that the stable compound is not formed. The strain energy in the solid solution has been calculated and appears to be of the correct order of magnitude.

REFERENCES

- Barker, J. A., Brown, I., and Smith, F. (1953). Thermodynamics of alcohol solutions, the system ethanol and carbon tetrachloride. *Faraday Society Discussion on Equilibrium properties of solutions*, 142.
- Bothe, H. A. (1935). Statistical theory of superlattices. *Proc. Roy. Soc.*, **150**, 552.
- Flory, P. J. (1941). Thermodynamics of high polymer solutions. *J. Chem. Phys.*, **9**, 660.
- Gray, L. T. M., and Style, D. W. G. (1930). Absorption of light by chlorine, bromine and their gaseous mixtures. *Proc. Roy. Soc.*, **126**, 603.
- Guggenheim, E. A. (1935). The Statistical Mechanics of regular solutions. *Ibid.*, **148**, 304.
- (1952). *Mixtures*, Clarendon Press, Oxford.
- Hildebrand, J. H., and Scott, R. L. (1950). *Solubility of non-electrolytes*, Reinhold Publishing Corporation, New York.
- Keesom, W. H., and Taconis, K. W. (1936). Crystal Structure of chlorine. *Physica*, **3**, 237.
- (1936). *Proc. K. Acad. Wetensch Amsterdam*, **39**, 314.
- Lawson, A. W. (1947). Binary solid solutions. *J. Chem. Phys.*, **15**, 831.
- Rushbrooke, G. S. (1949). *Statistical Mechanics*, Oxford University Press.
- (1938). A note on Guggenheim's theory of strictly regular binary liquid mixtures. *Proc. Roy. Soc.*, **166**, 296.
- Scatchard, G., and Hamer, W. J. (1935). The application of equations for the chemical potential to equilibrium between solid solution and liquid solution. *J. Amer. Chem. Soc.*, **57**, 1809.
- Scatchard, G., Ticknor, L. B., Groat, J. R., and McCartney, E. R. (1952). Heats of mixing in some non-electrolyte solutions. *J. Amer. Chem. Soc.*, **74**, 3721.
- Seltz, H. (1934). Thermodynamics of solid solutions. I. Perfect Solutions. *J. Amer. Chem. Soc.*, **56**, 307.
- Sidgwick, N. V. (1933). Interhalogen Compounds. *Chem. Soc. Ann. Reports*.
- Srivastava, B. N., and Rastogi, R. P. (1953). Thermodynamics of systems of any number of components. *Proc. Nat. Inst. Sci. India*, **19**, 653.
- Vonnegut, B., and Warren, B. E. (1936). Structure of crystalline bromine. *J. Amer. Chem. Soc.*, **58**, 2461.