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PHASE DIAGRAM ANALYSIS USING A PARTIALLY ASSOCIATED SOLUTION MODEL FOR III–V BINARY SYSTEMS

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Abstract—Some of the physical and thermodynamic properties of III–V liquids can be explained by assuming that the liquids have a dual structure. The thermodynamic model which has been established for the present paper is a partially associated solution model. It was constructed on the assumption of the existence of associated complexes. The asymmetry of the liquidus curve and the amount of excess free energy determined from the phase diagram analysis can be explained by using the model. Some of the thermodynamic parameters obtained in this study are found to have important physical meanings. The interaction parameter between monoatomic species, $\omega_{A,B}$ is in a good agreement with the theoretical value proposed by Stringfellow. The heat of formation of associated complexes can be represented explicitly in terms of the spectroscopic ionicity and the dehybridization factor. The free energy of formation is empirically evaluated to be $20{\cdot}6(f_i - 0{\cdot}17)RT - 35{,}000 f_i D$ cal/mol for III–V binary liquids.

1. INTRODUCTION

The binary phase diagrams constituted by Group III and Group V elements are presently attracting attention for practical and theoretical reasons. The liquidus curves are of particular interest to those concerned with the growth and perfection of these semiconducting compounds and they have been examined theoretically by several investigators. These curves have been described as being parabolic with a relatively large curvature near the melting point[1], and seem to occur in some systems such as Ga–Sb, where the liquid solution is strictly regular. A close examination of the liquidus curves, however, reveals that they are asymmetric with respect to the stoichiometric composition as shown in Fig. 1. This tendency becomes appreciable in the III–V binary systems whose compounds have relatively larger ionicity. Previously, a thermodynamic analysis of these systems was attempted in terms of the simple regular solution model[2], sub-regular solution model[3] or quasi-chemical equilibrium model[4]. However, these models did not account for asymmetry of the thermodynamic properties. None of these models, even one with suitably chosen parameters, resulted in quantitatively reasonable agreement with experiment over the entire region of the diagram. Thus, for a better understanding of the thermodynamic properties of III–V systems, it seems vitally important to reconcile the departure from regularity in these solutions.

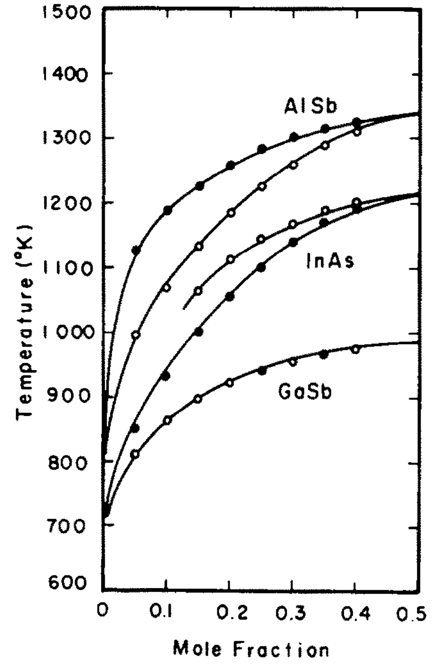

Fig. 1. Binary phase diagrams of Al–Sb[15, 7], In–As[16, 17] and Ga–Sb[18, 19] systems, where ● and ○ denote the experimental values on the Group III and V element rich sides, respectively, and the solid lines show the theoretical liquidus curves recalculated by the present PAS model.

Some of the physical properties of III–V liquids may be well explained by relating them to partly retained non-metallic bonding in the liquid state. Measurement of viscous flow in the arsenide[5] and antimonide[6] systems indicates that at temperatures slightly above the melting point of the stoichiometric composition almost always exhibits a positive excess viscosity. Also, their liquid state electric resistivities, which decrease by a factor of between 2 and 10 on fusion[7], appear to be much higher than those of silicon[8] and germanium[9], but lower than those of II–VI systems[10]. The resistivity/composition isotherm reaches a maximum at the stoichiometric composition, as does the viscosity, while the magnetic susceptibility reaches an equally sharp minimum[11]. These results suggest that some would-be conduction electrons are still in a bound state and that enough non-metallic bonding to cause these phenomena is retained after fusion. The bonding is probably due to a short-term localization of bound valence electrons in pairs or in groups of neighbouring atoms. The resulting structure may appear as small molecular complexes in a metallically bound matrix. The extent of stability and the concentration of complexes may be determined by the ionicity or the difference in electronegativities.

Phillips[12] estimated the ionicity of diatomic crystals with the formula $A^N B^{8-N}$ such as the zinc-blende, wurtzite, and rocksalt structures. In III–V compounds, the ionicity is relatively small, i.e. 0·426 for AlSb which is the largest in the group, compared with 0·546 for ZnTe which is the smallest of the II–VI compounds. It is well known that the II–VI liquids [13] and fused salt mixtures [14] have ionic properties which allow the presence of stable complexes in the liquid. Therefore the liquids in the III–V systems may be assumed to be partially ionic, but to a lesser extent than those in II–VI liquids or fused salt mixtures. The stable complexes present in the liquid have been known to affect both the liquidus curves and the thermodynamic behavior of inorganic systems [14]. To evaluate the thermodynamic properties of II–VI systems, Jordan [13] proposed a regular associated solution model. His model assumes symmetry with respect to the stoichiometric composition and could be valid for a strong degree of association. However, it cannot apply to III–V systems in which there is a relatively small amount of associated complexes and asymmetry in the liquidus curve. The present paper attempts to describe a thermodynamic model to account for the characteristics in the III–V systems which is consistent with the binary phase diagrams.

2. THEORY

In an A–B binary liquid constituted of Group III and Group V elements, let there be three species in equilibrium, that is, monomers A and B, and associated molecules AB in mole fractions of x_A, x_B and x_{AB}, respectively. The fraction of total A in both the combined state (AB) and uncombined state (A) is denoted by x_1, and the fraction of total B is denoted by x_2. The subscripts 1 and 2 refer to the true binary components. Prigogine and Defay[20] have shown that the chemical potential of 1 equals the chemical potential of A and similarly the chemical potential of 2 equals that of B. It is suggested as a first approximation that departures from a true associated solution due to short range nearest neighbour interactions can be simply taken into account by introducing activity coefficients γ_A, γ_B and γ_{AB} in a strictly regular ternary solution model. The excess free energy of mixing relative to the free energy of the ideal solution can be written as follows;

$$\Delta F^{xs} = x_A x_B \omega_{A,B} + x_A x_{AB} \omega_{A,AB} + x_B x_{AB} \omega_{B,AB} + x_{AB} \omega_R, \qquad (1)$$

where ω_R denotes the formation energy of associated complexes, $\omega_{A,AB}$ is the interaction energy between monomer A and molecule AB, and $\omega_{A,B}$ is the mutual interaction energy between monomers A and B. An equilibrium constant for an associated solution in the reaction $A(l) + B(l) = AB(l)$ can be expressed according to the mass reaction law,

$$a_{AB}/a_A a_B = c_o \exp(\omega_R/RT), \qquad (2)$$

where a_i is an activity of component i, and equal to $x_i \gamma_i$, and c_o is a constant related to the entropy of formation of associated complexes.

Further the activity coefficients, γ_A, γ_B and γ_{AB}, can be represented in the following form[5],

$$\begin{aligned} RT \ln\gamma_A &= x_B^2 \omega_{A,B} + x_{AB}^2 \omega_{A,AB} \\ &\quad + x_B x_{AB}(\omega_{A,B} - \omega_{B,AB} + \omega_{A,AB}) \\ RT \ln\gamma_B &= x_{AB}^2 \omega_{B,AB} + x_A^2 \omega_{A,B} \\ &\quad + x_A x_{AB}(\omega_{B,AB} - \omega_{A,AB} + \omega_{A,B}) \\ RT \ln\gamma_{AB} &= x_A^2 \omega_{A,AB} + x_B^2 \omega_{B,AB} \\ &\quad + x_A x_B(\omega_{A,AB} - \omega_{A,B} + \omega_{B,AB}). \qquad (3) \end{aligned}$$

In the present analysis, the concentration of associated complexes, x_{AB}, can be derived from eqn (2) and eqn (3) by assuming that the mole fraction of associated complexes, x_{AB}, in the liquid is small enough to set $(1 + x_{AB})^2 \cong 1$ and $x_A x_B \cong x_1 x_2$. By using the relations $x_A = x_1 - x_2 x_{AB}$ and $x_B = x_2 - x_1 x_{AB}$, we obtain

$$x_{AB} = x_1 x_2 P^{\cdot}_{AB}(1 + 2\Delta\omega^{-}_{AB}/RT), \qquad (4)$$

where $P^{\circ}_{AB} = c_o \exp[(\omega_R - \omega^{+}_{AB} + \omega_{A,B})/RT]$, $\Delta = 0{\cdot}5 - x_1$, and ω^{-}_{AB} and ω^{+}_{AB} are equal to $(\omega_{A,AB} \text{-} \omega_{B,AB})/2$ and $(\omega_{A,AB} + \omega_{B,AB})/2$, respectively. In eqn (4), the exponential term is expanded with respect to concentration, and it is terminated with the first power under the assumptions that the $\omega^{-}_{AB}(x_2 - x_1)/RT$ is very small within the present region of temperature and composition. The composition dependent term in $\omega_{A,B}(1 - x_1 x_2)$ is assumed to be negligible compared with $x_1\omega_{A,AB} + x_2\omega_{B,AB}$ through the derivation. Under the condition that $(\omega_R + \omega^{+}_{AB} - \omega_{A,B})$ is larger than ω^{-}_{AB}, substitution of eqn (4) into eqn (1) leads to the activity coefficients;

$$\begin{aligned} RT \ln\gamma_1 &= x_2^2 \omega_{A,B} + (\omega_R + \omega^{+}_{AB} - \omega_{A,B}) P^{\circ}_{AB} \\ &\quad [1 - (1 - 4\Delta)\omega^{-}_{AB}/RT], \\ RT \ln\gamma_2 &= x_1^2 \omega_{A,B} + (\omega_R + \omega^{+}_{AB} - \omega_{A,B}) P^{\circ}_{AB} \\ &\quad [1 + (1 + 4\Delta)\omega^{-}_{AB}/RT], \qquad (5) \end{aligned}$$

where the second term in the parenthesis expresses the contribution of the associated complexes. It is represented in a much simpler form than Jordan's expression. Therefore, from the above assumption on the nature of the associated complex, the present thermodynamic treatment may be called a partially associated solution model (PAS model).

In a more general thermodynamic analysis of the liquidus curves of binary systems with AB compound formation, Wagner[21] defined a parameter to be determined from the experimental liquidus curve;

$$\alpha = [T\varphi(x_1) - T^F]S^F/\Delta^2, \qquad (6)$$

where T^F and S^F are respectively the melting point and the entropy of fusion, and $\varphi(x_1) = 1 - (R/2S^F)\ln(1/4x_1x_2)$. The α given in eqn (6), which is equal to -1 times the integrand described by Wagner, is related to the activity coefficients as follows,

$$\alpha = (RT/2\Delta^2)\ln(\gamma_1\gamma_2/\gamma_1^{STC}\gamma_2^{STC}), \qquad (7)$$

where *STC* represents the stoichiometric composition. By putting eqn (5) into eqn (7), we obtain

$$\alpha = \omega_{A,B} + (\omega_R + \omega^{+}_{AB} - \omega_{A,B})P^{\circ}_{AB}(1 + 4\omega^{-}_{AB}\Delta/RT). \qquad (8)$$

It should be noted that the second term in eqn (8) involves a concentration dependent term. As the sign of Δ changes around $x_1 = 0{\cdot}5$, α is expected to behave in an asymmetric manner if $\omega^{-}_{AB} \gtrless 0$.

3. NUMERICAL ANALYSIS

The binary phase diagrams of III–V systems where the liquidus curve has been determined over the entire composition region, are available in five systems[15–21]. From these diagrams, the α-parameter along the liquidus curve has been calculated using eqn (6). The results are shown in Figs. 2 and 3, where the solid line shows the theoretical value. The values of the entropy of fusion and the melting point used in the calculation are listed in Table 1. As is seen in Figs. 2 and 3 the α-parameter is not constant and reaches a maximum value near the stoichiometric composition in all of III–V systems, and it is not symmetric with respect to $x_1 = 0{\cdot}5$. The maxima for In–As and In–Sb appear apparently in the In-rich side. In the Al–Sb system, it appears in Sb-rich side.

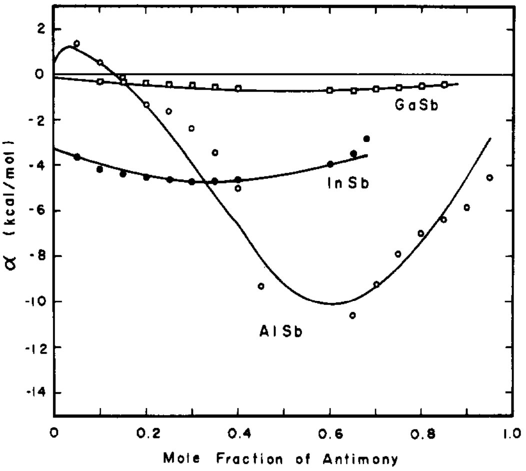

Fig. 2. α-parameter along with the liquidus curve as a function of antimony in the antimonides of Al, Ga and In, where solid curves were calculated by the present method. The phase diagram of the In–Sb system refers to [17] and [22].

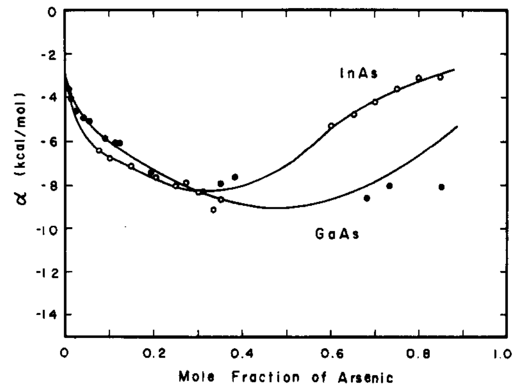

Fig. 3. α-parameter along with the liquidus curve as a function of arsenic in the arsenides of Ga and In, where the phase diagram of Ga–As system refers to [17] and [19].

Table 1. Values of properties of III-V compounds used in the calculation

Compound	T^F (°K)	S^F (e.u.)	f_i (12)
AlP	2823 (26)	17.12 (31)	0.307
AlAs	2043 (27)	16.83 (31)	0.274
AlSb	1338 (28)	14.74 (23)	0.426
GaP	1738 (25)	15.90 (24)	0.374
GaAs	1511 (18)	16.64 (30)	0.310
GaSb	985 (23)	15.80 (23)	0.261
InP	1343 (29)	14.12 (31)	0.421
InAs	1215 (16)	14.52 (30)	0.357
InSb	797 (23)	14.32 (23)	0.321

In the present PAS model, the α-parameter can be calculated in the following manner. For any two liquidus points selected at a given temperature on either side of and apart from the stoichiometric composition, eqn (8) holds and leads to the expression;

$$y \equiv RT(\alpha^{\mathrm{III}} - \alpha^{\mathrm{V}})/(\Delta^{\mathrm{III}} - \Delta^{\mathrm{V}})$$
$$= 4(\omega_R + \omega^{+}_{AB} - \omega_{A,B})\omega^{-}_{AB}c_0 \exp(U/RT), \qquad (9)$$

where U denotes $\omega_R + \omega_{A,B} - \omega^{+}_{AB}$, and the upper subscripts III and V indicate the III and V element rich side, respectively. Once log(y) vs I/T is plotted, as shown in Fig. 4 for the In–As system, the experimental points exhibit a fairly good linear relationship. Two sets of parameters, U and $4(\omega_R + \omega^{+}_{AB} - \omega_{A,B})\omega^{-}_{AB}c_0$, in eqn (9) can be determined from the slope and intersept of the line drawn in the figure. In order to evaluate the parameters in each term, two more sets of parameters will be determined. Thus eqn (8) is rewritten,

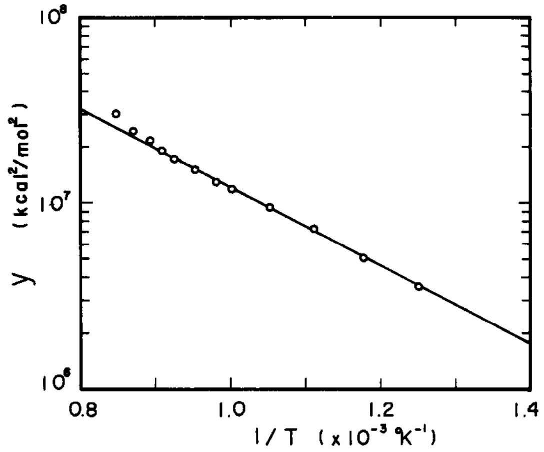

Fig. 4. The change of y as a function of $1/T$ in the In–As system.

$$z \equiv \alpha - y\Delta/RT = \omega_{A,B} + (\omega_R + \omega^{+}_{AB} - \omega_{A,B})c_0 \exp(U/RT). \qquad (10)$$

Now, two sets of parameters can be evaluated from the z vs exp (U/RT) plot, as is shown in Fig. 5. In such a

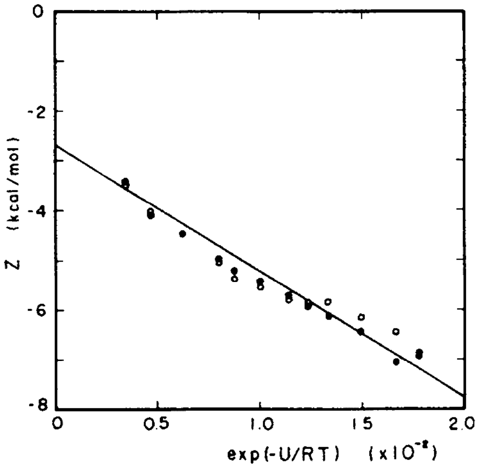

Fig. 5. The change of z as a function of $\exp(U/RT)$ in the In–As system, where ● and ○ denote the values at Group III and V element rich side of the phase diagram, respectively.

manner, four relationships have been obtained for the five unknowns; c_o, $\omega_{A,B}$, $\omega_{A,AB}$, $\omega_{B,AB}$ and ω_R. Obviously one more relation is necessary for evaluating these unknowns. In the association reaction, the most probable values of x_{AB} at a given temperature are calculated with the condition that the free energy of mixing, F^M, is a minimum with respect to x_{AB}, that is, $\delta F^M = 0$. The condition for the dissociation equilibrium between associated complexes and free monomers is given[32] by

$$\frac{\partial F^M}{\partial x_A} + \frac{\partial F^M}{\partial x_B} = \frac{\partial F^M}{\partial x_{AB}}. \tag{11}$$

As F^M is a sum of entropy of mixing and the excess free energy given by eqn (1), eqn (11) can be numerically solved for c_o with little difficulty. Hence we calculated the five unknowns from the above five relationships. For the In–As liquid, x_{AB} is found to be 0·11 at 1215°K, i.e. the melting point of the compound, and the other parameters are listed in Table 2.

Table 2. Values of thermodynamic parameters obtained from the phase diagram analysis by using the PAS model, where x_{AB} shows the value at the melting point

System	c_o	ω_R	$\omega_{A,AB}$	$\omega_{B,AB}$	$\omega_{A,B}$	x_{AB}
		(cal/mol)				
Al - Sb	330	-13600	1120	4170	400	0.21
In - As	23	-10200	-1780	-4850	-2700	0.11
In - Sb	47	- 7440	-590	-3300	-3300	0.04
Ga - As	16	-9850	-1150	-1450	-2000	0.14
Ga - Sb	6.8	-5170	1570	1420	400	0.04

Using this method, the other four systems have been analysed. The results are listed in Table 2. The recalculated α-parameter is illustrated with solid curves in Figs. 2 and 3. The calculated results are in excellent agreement with the experimental data. In particular this model successfully explains the asymmetry of the α-parameter in both the III and V element rich sides. The present analysis as shown in Table 2 clearly demonstrates that the value of $\omega_{A,AB}$ differs from that of $\omega_{B,AB}$ in all of the systems, even in the Ga–Sb system, and that $\omega_{A,AB}$ is smaller than $\omega_{B,AB}$ when the atomic radius of A is larger than that of atom B. It is this difference that essentially produces the asymmetric behavior in the liquidus curve.

As listed in Table 2, the concentration of associated complexes at the melting point has been estimated to be in the region of 0·04 to 0·21. To examine the accuracy of the approximations made in obtaining eqn (4), x_{AB} was compared with the exact x_{AB} calculated from eqns (2) and (3) using values of the parameters listed in Tables 1 and 2. The deviations were found to be 20–30 per cent. Also, the excess free energy approximated using eqn (5) deviated by 9 per cent or less from the exact value calculated from eqn (1). The value of x_{AB} becomes largest at their melting points and decreases drastically when the composition departs from stoichiometry along the liquidus curve. Clearly, the error involved in approximating the free energy in the present model is very small within the present region of composition and temperature. Therefore our PAS model is a reasonable description for the III–V binary liquids accompanying associated complexes.

4. DISCUSSION

It has been demonstrated that the excess quantities of the free energy used in the PAS model for the phase diagram analysis are very effective in describing associated complexes. Now we would like to extend out discussion to the physical meaning of the parameters obtained in the model.

As reported by Stringfellow[33], the liquid phase interaction parameters between monoatomic species can be calculated in terms of both the electronegativities and solubility parameters of the pure elements. When the molar volumes are nearly equal, the interaction parameter is represented by the form,

$$\omega_{A,B} = V(\delta_A - \delta_B)^2 - 3 \times 10^4(\chi_A - \chi_B)^2, \tag{12}$$

where V, δ and χ denote respectively the molar volume, the solubility parameter and the electronegativity. In binary systems of the type Ge–M and Si–M, the interaction parameters calculated from an equation similar to eqn (12) are generally in good agreement with the experimentally determined values[34]. This is illustrated in Fig. 6 by full circles. Interestingly, these binary systems do not contain any intermetallic compounds in solid state. The interaction parameters calculated by the PAS model for the III–V binary systems are always too small, compared with those obtained by the RS or QCE models. The discrepancy merely reflects the incompleteness of the latter thermodynamic models. As shown in Fig. 6, the present interaction parameters between monoatomic species are in good agreement with the theoretical values[33].

It seems evident that III–V liquids have a dual structure, consisting of associated complexes of AB in equilibrium with a matrix of more randomly arranged A and B atoms, but the structure of the complexes cannot be visualized at the present time. It can be said that the structure becomes more ionic and needs not be that of the solid compound, because the restriction of forming a

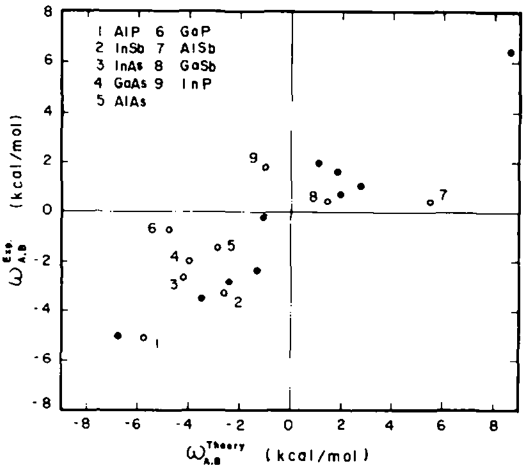

Fig. 6. Comparison of the experimental interaction parameters with the theoretical values calculated by Stringfellow[33], where the symboles, ● show the values for the Si–*M* and Ge–*M* systems directly extracted from the reference[34].

long-range lattice is now removed. The heat of formation of such associated complexes seems to originate from two important effects: ionicity, as implied in Pauling's thermochemical theory[35], and the tendency toward metallization, as discussed by Mooser and Pearson[36]. The former factor can be represented by the spectroscopic ionicity instead of the electronegativity term as pointed out by Phillips[12]. The latter factor is described by the dehybridization factor, D[37]. Dehybridization describes the decrease in energy of the homopolar covalent bond compared with the much less directional metallic bond. In the system in which the tendency of dehybridization is large, the homopolar covalent bonding is thoroughly destroyed on fusion. Therefore the heat of formation of associated complexes may be represented explicitly by the above two terms in the form,

$$\omega_R = \omega_R^{\circ} f_i D, \tag{13}$$

where ω_R° is the invariable constant and two values of f_i and D can be referred to the literatures[12, 37, 38]. As shown in Fig. 7, ω_R linearly depends on the factor f_iD, where ω_R° is -35 kcal/mol on the average. The quantity c_o is related to the entropy of formation of the associated complexes, that is, $c_o = \exp(-S/R)$[39]. As shown in Fig. 8, $\ln(c_o)$ is empirically related to the ionicity in a linear manner. Therefore, we now conclude that the free energy of formation of associated complexes in the liquid is given approximately as $20{\cdot}6(f_i - 0{\cdot}17)RT - 35{,}000 f_iD$ cal/mol for the III-V binary systems.

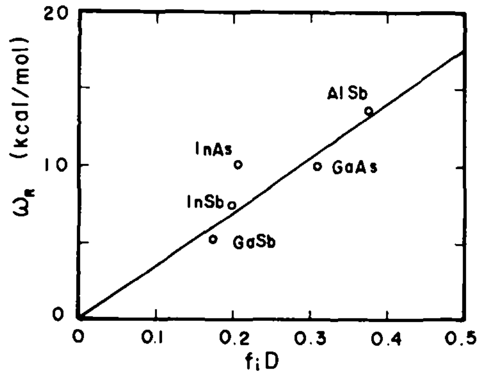

Fig. 7. Formation energy of associated complexes as a function of ionicity multiplyed by the dehybridization factor.

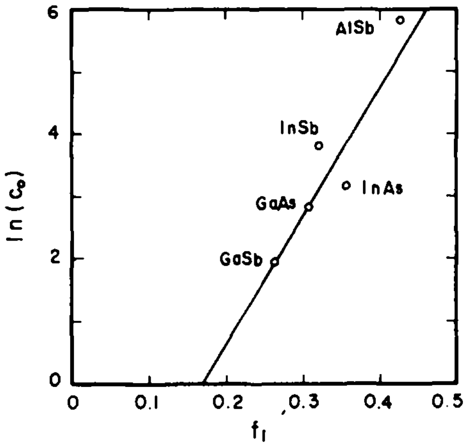

Fig. 8. The term related to the entropy of formation of associated complexes as a function of ionicity.

Finally we would like to demonstrate the feasibility of calculating all of the other III-V binary phase diagrams based upon the PAS model. Two parameters ω_R and c_o are easily determined from the above theoretical considerations. Two other parameters, $\omega_{A,AB}$ and $\omega_{B,AB}$, are estimated, (a) by assuming that ω_{AB}^{-} is a linear function of the difference between corresponding solubility parameters, and (b) by using the relation of eqn (11). The last parameter, $\omega_{A,B}$ has been determined from the actual binary phase diagram in the III-Group element rich side. From use of those values as listed in Table 3, the liquidus curves have been calculated for several binary systems. Results are shown in Fig. 9. It is found that the calculated curves are in fairly good agreement with the experimental data over all regions of composition and temperature.

Table 3. Estimated values of thermodynamic parameters of several III–V binary liquids by using the PAS model

System	c_o	ω_R	$\omega_{A,AB}$	$\omega_{B,AB}$	$\omega_{A,B}$
		(cal/mol)			
In - P	149	-11500	6379	3379	1820
Ga - P	61	-11350	4900	2300	-800
Al - P	15	-10150	-5100	-5100	-5100
Al - As	7.9	-8650	-1350	450	-1450

5. CONCLUSION

A model regarding the III–V binary phase diagrams has been established in this paper. The present PAS model is based on the assumption that associated complexes exist in the liquid. It has been found that the calculated liquidus curves are in excellent agreement with experimental data. In particular, the present model successfully explains the asymmetric behavior of the liquidus curve.

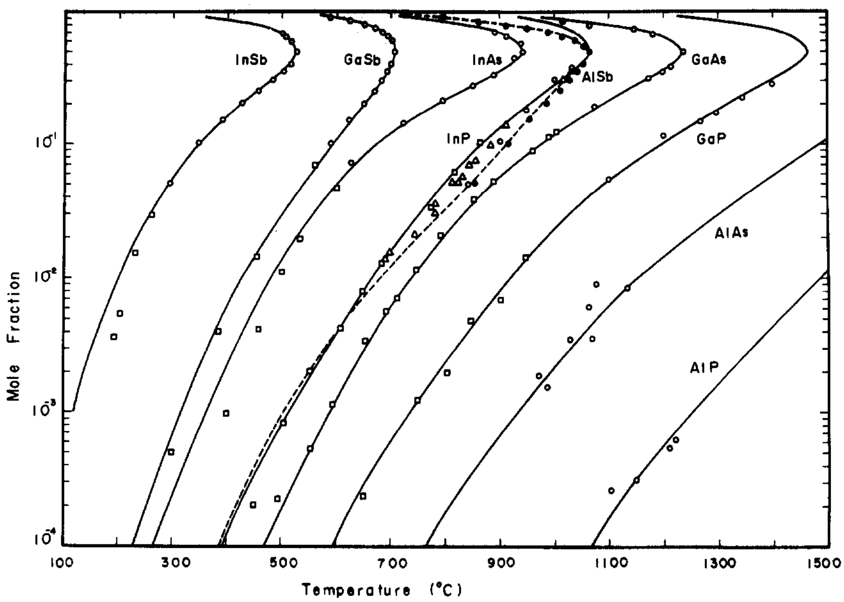

Fig. 9. Comparison of calculated phase diagrams with experimental data in III–V binary systems. The experimental data were extracted from the following references; InSb: [17] and [22], GaSb: [17], [18] and [19], InAs: [16] and [17], AlSb: [7] and [15], InP: [17] [40] and [43], GaAs: [17] and [19], GaP: [17] and [25], AlAs: [41], AlP: [42].

Some of the parameters obtained from the present analysis have been discussed and the following important results have been obtained. The interaction parameter between monoatomic species, ω_{AB} is in good agreement with the theoretical value proposed by Stringfellow. The heat of formation of associated complexes can be represented explicitly in terms of the spectroscopic ionicity and the dehybridization factor, and the free energy of formation has been empirically evaluated for the III–V binary liquids.

Therefore the PAS model has proven to be a useful tool to interpolate existing data and to predict unknown phase diagrams in III–V systems.

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