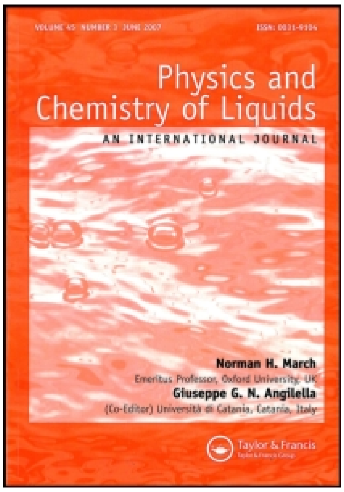

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TWO-COMPOUND FORMATION IN LIQUID BINARY ALLOYS: TEMPERATURE DEPENDENCE OF THERMODYNAMIC FUNCTIONS IN MERCURY INDIUM ALLOY

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A theory of the alloying behavior of compound forming liquid alloys, in which the formation of two types of compounds simultaneously is assumed in a quaternary mixture is presented within the framework of Bhatia *et al.*[1] and applied to study the thermodynamic properties of HgIn liquid alloy in the whole temperature range as suggested by the phase diagram. At 258 K $S_{CC}(0)$ and $S_{NC}(0)$ matches nicely with experimental results when interaction energies are included and it is concluded that HgIn complex is more stable than $HgIn_6$.

KEY WORDS: Binary alloys, compound formation.

1 INTRODUCTION

Conformal solution model[1,2,3] has been used to study thermodynamic properties of a large number of liquid binary alloys. In this model they proposed the idea of formation of more than one complexes at a time in the alloy. Their studies were limited to the formation of a single compound only. Lately experimental evidence has been coming for the simultaneous presence of two or more than two compounds in the liquid alloys. Tamaki *et al.*[4] were first to report experimental results for the thermodynamic properties of the liquid NaSn alloy, they found that the two types of compounds NaSn and Na_3Sn are formed in the alloy, which strongly suggested the formation of two types of compounds simultaneously in the liquid alloys.

Hoshino[5] calculated the entropy of mixing in NaSn system within a scheme that allowed complex formation of two types, assuming that there are no interaction energies and compared his calculations with the experimental results due to Tamaki *et al*[4]. But no study was undertaken for the calculations of thermodynamic properties such as $S_{CC}(0)$, $S_{NN}(0)$, $S_{NC}(0)$, activity and free energy of mixing which are more reliable indicators of stability of compounds.

Since very small amount of interaction energies can play crucial role in the compound formation tendency, it is desirable to include these. In this paper, we have included explicitly the interaction energies. This serves our objective to look at the simultaneous formation of two compounds and comparison of their stabilities.

Furthermore, to understand the thermodynamics of liquid alloys, it is necessary to understand the behavior of thermodynamic properties well above and well below the melting temperature, since temperature can play a crucial role in the formation of compounds in an alloy. At one temperature one compound may be more stable as compared to the other. $HgIn_6$ is likely to be formed in an indium rich region. The study of these thermodynamic properties at various temperatures is guided by the phase diagram[8]. The phase diagram of HgIn system exhibits for $T = 258$ K a liquid phase in the range of indium concentration $0 \leqslant C_{In} \leqslant 0.65$. However, for $C_{In} \geqslant 0.65$ the temperature of the liquid phase increases almost monotonically upto a value of $T = 429.8$ K corresponding to pure In. Therefore it is worth analysing the formation of compounds over a whole range of temperature from 240 K to 450 K.

In this paper we look at free energy of mixing, activity, correlation functions ($S_{CC}(0)$, $S_{NN}(0)$, $S_{NC}(0)$) for mercury indium liquid alloy treated as a quaternary mixture with four components Hg, In, HgIn and $HgIn_6$ in which two types of compounds are formed at a time.

2 THEORETICAL FORMALISM

In the conformal solution model Bhatia and Hargrove[6] assumed the formation of chemical complexes A_xB_y, x and y being small integers and considered that only one type of complex is formed at a time. Their model was a generalised one in the sense that it does not exclude the formation of more than one complex at a time. In the present formalism we assumed the formation of two complexes $A_\alpha B_\beta$ and $A_\mu B_\nu$ at a time. Following the formalism of Bhatia and Hargrove[6] but setting their $N = 1$, the binary alloy $A_C B_{1-C}$ is allowed to contain in all C gm atoms of A and $(1-C)$ gm atoms of B. In the liquid state assume that there are n_1 gm atoms of A, n_2 gm atoms of B, n_3 gm moles of $A_\alpha B_\beta$ (α, β being small integers) and n_4 gm moles of $A_\mu B_\nu$ (μ, ν being small integers) coexisting in the quaternary mixture, that is

$$CA + (1 - C)\, B \rightarrow n_1 A + n_2 B + n_3 A_\alpha B_\beta + n_4 A_\mu B_\nu$$

We have from the conservation of atoms

$$n_1 = C - \alpha n_3 - \mu n_4 \tag{1}$$

$$n_2 = (1 - C) - \beta n_3 - \nu n_4 \tag{2}$$

and

$$n = n_1 + n_2 + n_3 + n_4 = 1 - (\alpha + \beta - 1)\, n_3 - (\mu + \nu - 1)\, n_4 \tag{3}$$

The free energy of mixing for a quaternary mixture may be written as

$$G_M = G - C\, G_1^{(0)} - (1 - C)\, G_2^{(0)} = -n_3\, g_1 - n_4\, g_2 + G' \tag{4}$$

with

$$g_1 = \alpha G_1^{(0)} + \beta G_2^{(0)} - G_3^{(0)} \tag{5}$$

$$g_2 = \mu G_1^{(0)} + \nu G_2^{(0)} - G_4^{(0)} \tag{6}$$

and

$$G' = G - [n_1 G_1^{(0)} + n_2 G_2^{(0)} + n_3 G_3^{(0)} + n_4 G_4^{(0)}] \tag{7}$$

where $G_i^{(0)}$ ($i = 1, 2, 3, 4$) is the chemical potential for the pure species i in the solution. In Eqn. (4) first term ($-n_3 g_1$) represents the lowering of free energy due to formation of chemical complex $A_\alpha B_\beta$, the second term ($-n_4 g_2$) represents the lowering of free energy due to formation of chemical complex $A_\mu B_\nu$ and G' represents the free energy of mixing of the quaternary mixture of A, B, $A_\alpha B_\beta$ and $A_\mu B_\nu$. These constituents interact weakly with one another and the strong interactions are accomadated via the formation of chemical complexes $A_\alpha B_\beta$ and $A_\mu B_\nu$. Hence for G' we consider the conformal solution approximation. This enables one to express G_M as

$$G_M = -n_3 g_1 - n_4 g_2 + RT \sum_{i=1}^{4} n_i \ln\left(\frac{n_i}{n}\right) + \sum_{i<j}\sum \frac{n_i n_j}{n} w_{ij} \tag{8}$$

where w_{ij} ($i, j = 1, 2, 3, 4$) are the mutual interaction energies between four constituent species of the mixture. In this formalism we assumed that the interaction between two complexes (w_{34}) is small enough to be ignored.

The equilibrium values of n_3 and n_4 at a given temperature and pressure are given by

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0 \tag{9}$$

and

$$\left(\frac{\partial G_M}{\partial n_4}\right)_{T,P,C} = 0 \tag{10}$$

Using Eqn. (8) alongwith Eqns. (9) and (10), the equilibrium values of n_3 and n_4 are given by

$$\frac{n_1^\alpha n_2^\beta}{n_3 n^{\alpha+\beta-1}} = K_1 e^{Y_1} \tag{11}$$

$$\frac{n_1^{\mu} n_2^{\nu}}{n_4 n^{\mu+\nu-1}} = K_2 e^{Y_2} \tag{12}$$

where

$$K_1 = e^{-g_1/RT} \tag{13}$$

$$K_2 = e^{-g_2/RT} \tag{14}$$

$$\begin{aligned} Y_1 = {} & \frac{w_{12}}{RT}\left[(\alpha+\beta-1)\frac{n_1n_2}{n^2} - \alpha\frac{n_2}{n} - \beta\frac{n_1}{n}\right] + \frac{w_{13}}{RT}\left[(\alpha+\beta-1)\frac{n_1n_3}{n^2} - \alpha\frac{n_3}{n} + \frac{n_1}{n}\right] \\ & + \frac{w_{23}}{RT}\left[(\alpha+\beta-1)\frac{n_2n_3}{n^2} - \beta\frac{n_3}{n} + \frac{n_2}{n}\right] \end{aligned} \tag{15}$$

$$\begin{aligned} Y_2 = {} & \frac{w_{12}}{RT}\left[(\mu+\nu-1)\frac{n_1n_2}{n^2} - \mu\frac{n_2}{n} - \nu\frac{n_1}{n}\right] + \frac{w_{14}}{RT}\left[(\mu+\nu-1)\frac{n_1n_4}{n^2} - \mu\frac{n_4}{n} + \frac{n_1}{n}\right] \\ & + \frac{w_{24}}{RT}\left[(\mu+\nu-1)\frac{n_2n_4}{n^2} - \nu\frac{n_4}{n} + \frac{n_2}{n}\right] \end{aligned} \tag{16}$$

Equations (11) and (12) can be solved numerically to obtain the equilibrium values of n_3 and n_4 via Eqns. (1),(2),(15) and (16). Equation (8) for free energy of mixing can also be used to obtain the expression for the activity a_A as

$$RT \ \ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = G_M + (1-C)\left(\frac{\partial G_M}{\partial C}\right)_{T,P,C} \tag{17}$$

Eqns. (8) and (17) yields

$$\begin{aligned} RT \ \ln a_A = RT \ & \ln\left(\frac{n_1}{n}\right) + \left(\frac{n_2}{n}\right)w_{12} + \left(\frac{n_3}{n}\right)w_{13} + \left(\frac{n_4}{n}\right)w_{14} \\ & - \frac{1}{n^2}\sum_{i<j}\sum n_in_j w_{ij} \end{aligned} \tag{18}$$

Equations (8) and (18) are used in the following sections to investigate the behavior of G_M and activity.

3 EQUILIBRIUM INTERACTION ENERGY PARAMETERS, FREE ENERGY OF MIXING AND ACTIVITY

In order to calculate the values of disposable parameters and interaction energies w_{ij}'s, we find out the compound forming concentration for the two types of complexes. For the first complex $A_\alpha B_\beta$, $C_{C1} = \alpha/(\alpha + \beta)$ and for the second complex $A_\mu B_\nu$, $C_{C2} = \mu/(\mu + \nu)$. For the first complex whole of the concentration region is divided into two parts, $0 < C < C_{C1}$ and $C_{C1} < C < 1$. Then at the chemical composition $C_{C1} = \alpha/(\alpha + \beta)$, $G_M = -n_3 g_1/RT$, which gives a starting value for g_1/RT or K_1. With n_3 still given by $n_3 \rightarrow C/\alpha$, $0 < C < C_{C1}$ and $n_3 \rightarrow (1 - C)/\beta$, $C_{C1} < C < 1$ and g_1 determined above, the expression for G_M for $C < C_{C1}$ contains the single unknown parameter w_{23} (since $n_1 \simeq 0$). This value of w_{23} was determined from the observed data on G_M at an intermediate concentration between 0.1 and C_{C1}. Similarly a value of w_{13} is thus determined from the observed value of G_M at a concentration intermediate between C_{C1} and 0.9. Now by considering any intermediate concentration between 0.1 and C_{C1} or C_{C1} and 0.9 and using the above calculated values of w_{13}, w_{23} and g_1/RT, expression (11) gives the value of w_{12}. Similarly for the second complex $HgIn_6$ we can calculate the values of g_2/RT or K_2, w_{12}, w_{14} and w_{24}.

The numerically calculated values of n_3 and n_4 at different concentrations are used to calculate n_1, n_2 and n, which can in turn be further used to calculate numerically the best fit interaction energies w_{ij} and reaction constants g_1 and g_2. The best fit interaction energy parameters for different temperatures are given in Table 1.

The numerically calculated values of n_3 and n_4 alongwith n at various temperatures are plotted both with and without interaction energies in Figures 1, 2 and 3. Above calculated values of interaction energy parameters and the values of n_1, n_2, n_3, n_4 and n when used in Eqn. (8) gives the value of G_M at various temperatures and are plotted in Figures 4 and 5 along with experimental values[8]. The theoretical behavior of ln a_A vs C for various temperatures are plotted in Figures 6 and 7 along with experimental values[8].

4 LONG WAVELENGTH CORRELATION FUNCTIONS

The long wavelength correlation functions of Bhatia and Thornton[7], namely concentration-concentration correlation function, $S_{CC}(0)$, the number-number correlation function, $S_{NN}(0)$ and number-concentration correlation function, $S_{NC}(0)$ have been widely used to understand the stability of binary mixtures. These correlation functions are correlated with the thermodynamic functions,

$$S_{CC}(0) = RT\left(\frac{\partial^2 G_M}{\partial C^2}\right)^{-1}_{T,P,N} = (1 - C)\, a_A\left(\frac{\partial a_A}{\partial C}\right)^{-1}_{T,P,N} = C\, a_B\left(\frac{\partial a_B}{\partial(1 - C)}\right)^{-1}_{T,P,N} \tag{19}$$

Table 1

Temp.	g_1/RT	g_2/RT	w_{12}/RT	w_{13}/RT	w_{23}/RT	w_{14}/RT	w_{24}/RT
240 K	2.47	3.23	−0.43	1.61	0.32	0.054	4.09
258 K	2.30	3.0	−0.40	1.50	0.30	0.05	3.80
300 K	1.98	2.58	−0.34	1.29	0.26	0.043	3.27
400 K	1.48	1.94	−0.26	0.98	0.19	0.032	2.45

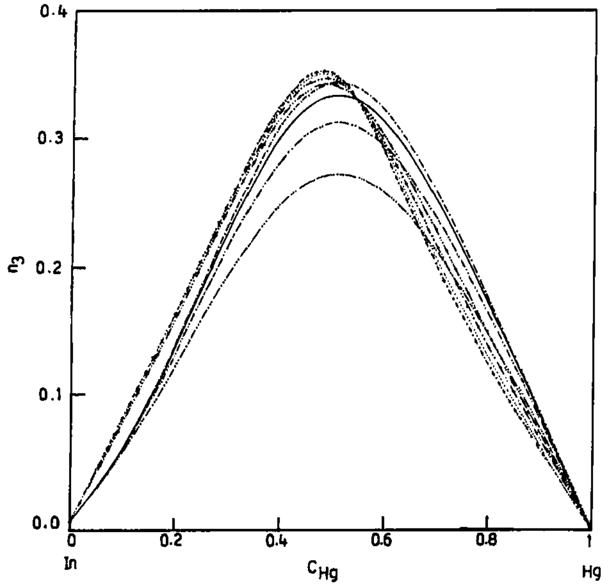

Figure 1 Concentration dependence of n_3 for mercury indium liquid alloy at $T = 240$ K (— · —), 258 K (——), 300 K(— ·· —), 400 K(— ··· —) when interaction energies are not included and at $T = 240$ K(●· ·●), 258 K(······), 300 K(●·· ●), 400 K(●· · · ●) when interaction energies are included.

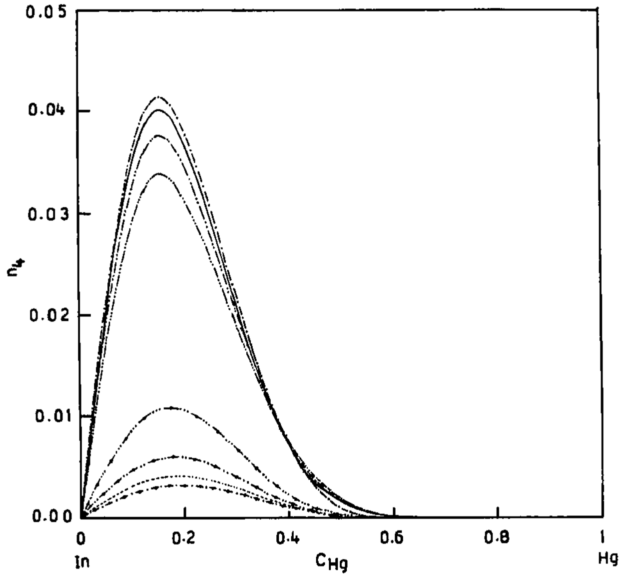

Figure 2 Concentration dependence of n_4 (Curves have the same meaning as in Figure 1).

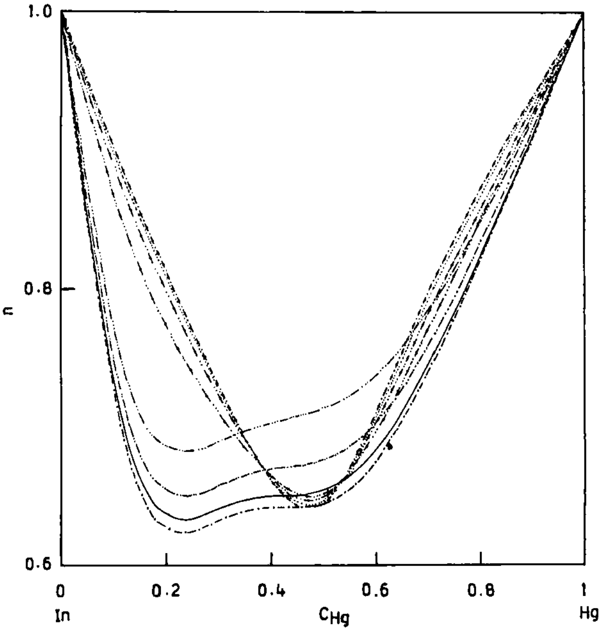

Figure 3 Concentration dependence of n (Curves have the same meaning as in Fig. 1).

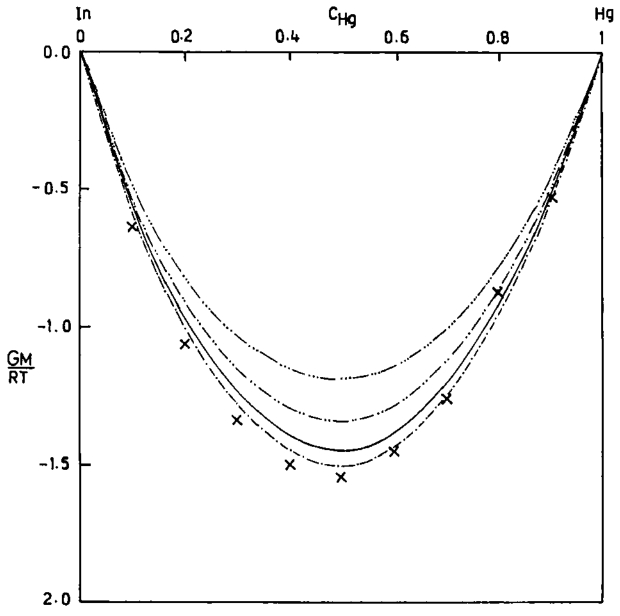

Figure 4 Free energy of mixing G_M/RT of mercury indium liquid alloy at different temperatures without including interaction energies (Curves have same the meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973)).

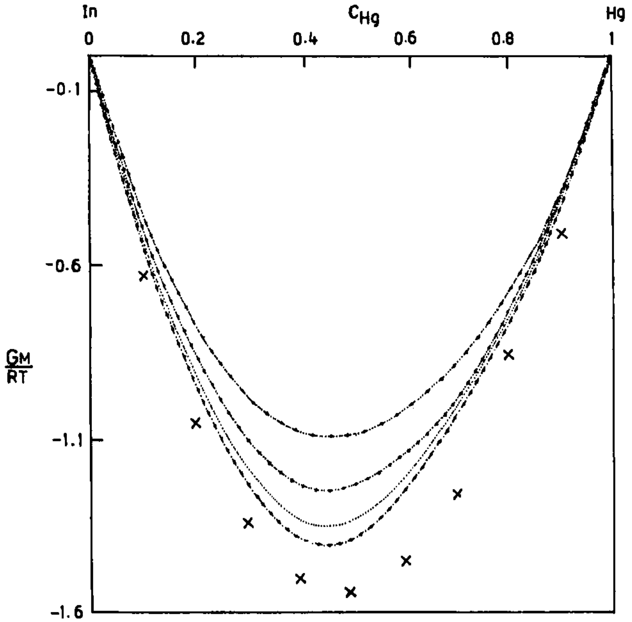

Figure 5 Free energy of mixing G_M/RT of mercury indium liquid alloy at different temperatures including interaction energies (Curves have same the meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973)).

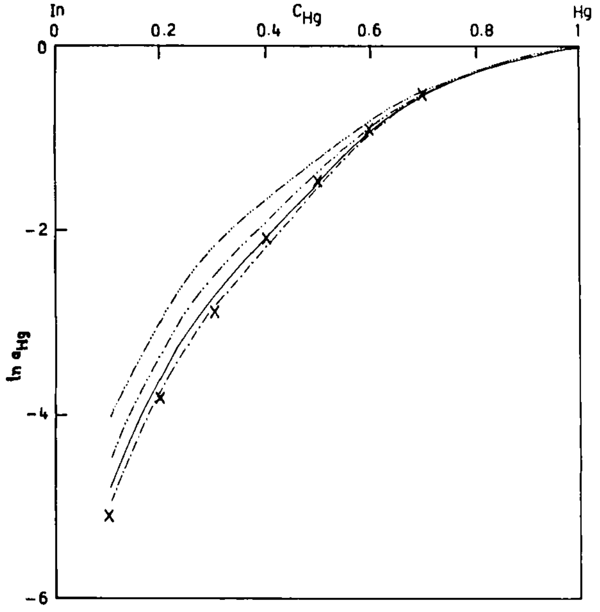

Figure 6 Activity (ln a_{Hg}) of Hg in mercury indium liquid alloy at different temperatures without including interaction energies (Curves have the same meaning as in Fig. 1 (x x x) experiment (Hultgren *et al.* 1973)).

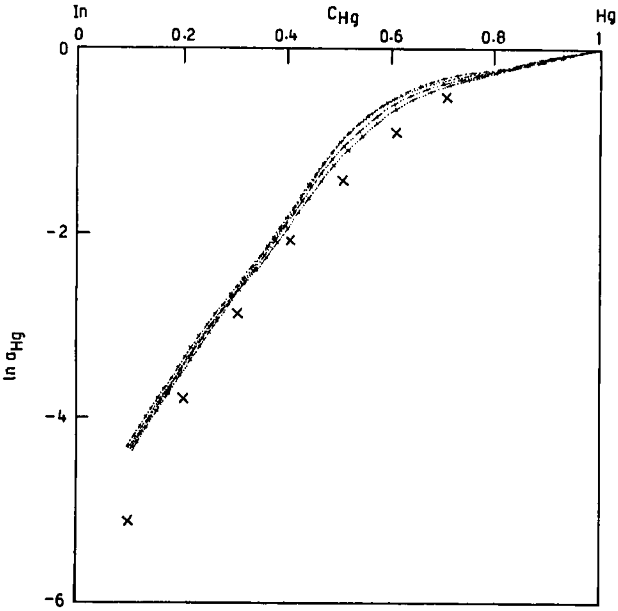

Figure 7 Activity ($\ln a_{Hg}$) of Hg in mercury indium liquid alloy at different temperatures including interaction energies (Curves have the same meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973)).

$$S_{NN}(0) = \rho\, k_B T k_T + \delta^2 S_{CC}(0) \tag{20}$$

$$S_{NC}(0) = -\delta\, S_{CC}(0) \tag{21}$$

and

$$\delta = (V_1 - V_2)/(C\, V_1 + (1 - C)\, V_2) \tag{22}$$

where V_1 and V_2 are the partial molar volumes of the two species, ρ is the number density, k_T is the isothermal compressibility and δ stands for dilatation factor.

The concentration-concentration correlation function $S_{CC}(0)$ in the long wavelength limit can be obtained with the help of Eqns. (8) and (19) and can be written as

$$S_{CC}(0) = \left[\sum_{i=1}^{4} \frac{(n_i')^2}{n_i} - \frac{(n')^2}{n} + \frac{2n}{RT}\sum_{i<j}\sum \left(\frac{n_i}{n}\right)' \left(\frac{n_j}{n}\right)' w_{ij}\right]^{-1} \tag{23}$$

This equation gives the theoretical behavior of $S_{CC}(0)$ and it is compared to the experimental values obtained directly from the activity data[8] using the last two identities of Eqn. (19) and are plotted in Figures 8 and 9 at various temperatures. Ideal $S_{CC}(0)$ ($= C(1 - C)$) is also plotted in these figures.

The $S_{CC}(0)$ as computed from Eqn. (23) have been used to obtain $S_{NN}(0)$ and $S_{NC}(0)$ as a function of concentration. Because of lack of experimental data on k_T

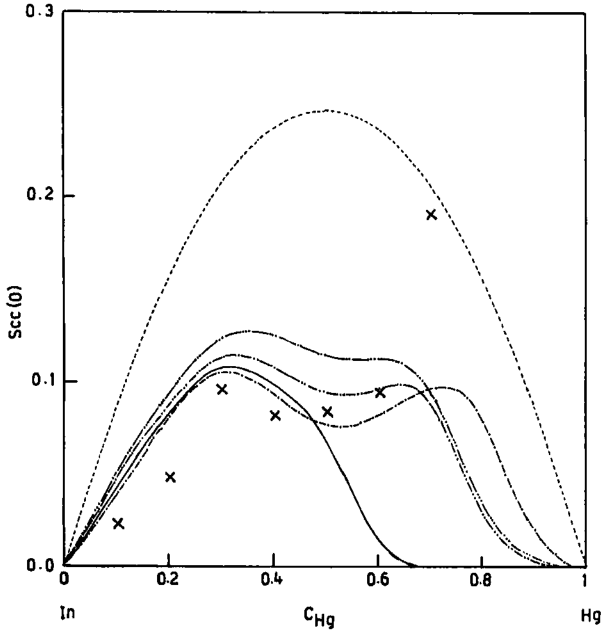

Figure 8 Concentration fluctuation ($S_{cc}(0)$) of mercury indium liquid alloy at different temperatures without interaction energies (Curves have the same meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973) and (- - -) corresponds to ideal values (i.e. $C(1 - C)$).

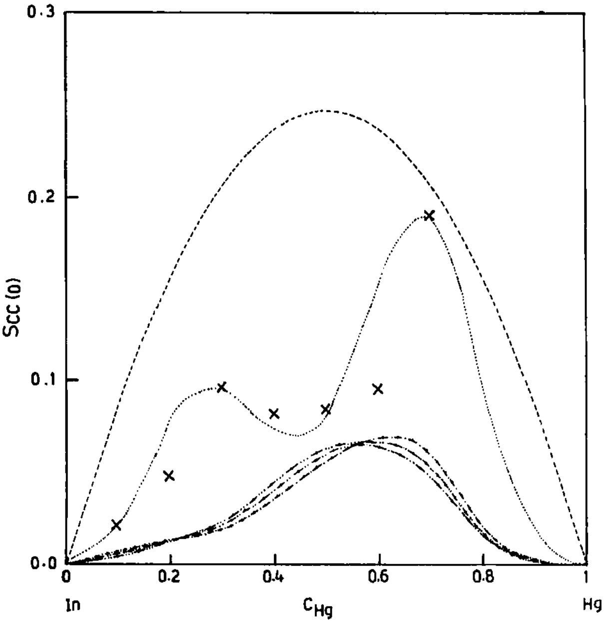

Figure 9 Concentration fluctuation ($S_{cc}(0)$) of mercury indium liquid alloy at different temperatures including interaction energies (Curves have the same meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973) and (- - -) corresponds to ideal values (i.e. $C(1 - C)$).

with C, for the binary alloy a linear variation of isothermal compressibility with concentration is used as

$$k_T = C^{\mathrm{Hg}}k_T + (1 - C)^{\mathrm{In}}k_T \tag{24}$$

corresponding to known isothermal compressibility of pure metals. The computed values of $S_{\mathrm{NN}}(0)$ and $S_{\mathrm{NC}}(0)$ for mercury indium system are given in Figures 10, 11, 12 and 13.

5 RESULTS AND DISCUSSION

In this paper we have used the theory of Bhatia *et al.*[1] that considers multi complex formation and have presented the calculations of free energy of mixing, activity, $S_{\mathrm{CC}}(0)$, $S_{\mathrm{NN}}(0)$ and $S_{\mathrm{NC}}(0)$ for various temperatures in two cases (i) without interaction energies and (ii) by including the interaction energies.

From the plot of n_3 vs C (Fig. 1), it is clear that when interaction energies are not included the complex formation tendency is less but by including interaction energies the height of the peaks rises. The maximum value of n_3 in both the cases i.e. when interaction energies are not included and when interaction energies are

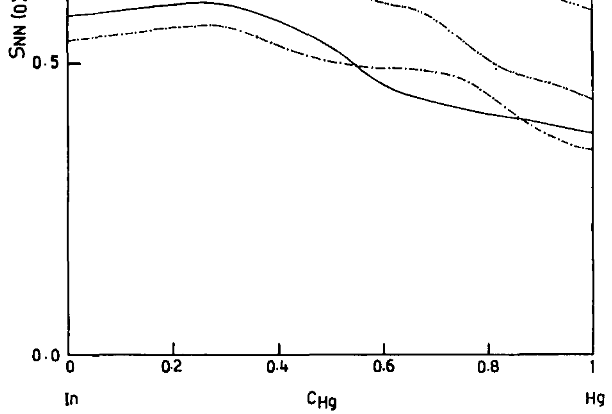

Figure 10 Number-Number correlation function ($S_{\mathrm{NN}}(0)$) of mercury indium liquid alloy at different temperatures without interaction energies (Curves have the same meaning as in Fig. 1).

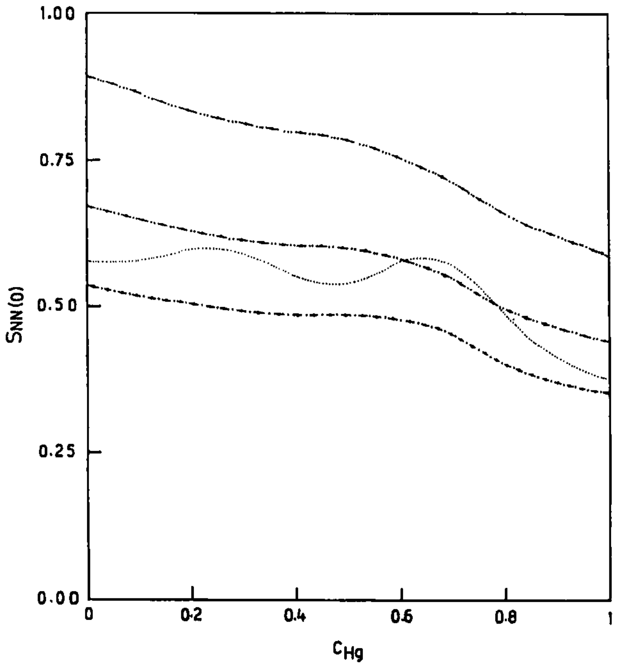

Figure 11 Number-number correlation function ($S_{NN}(0)$) of mercury indium alloy liquid at different temperatures including interaction energies (Curves have the same meaning as in Fig. 1).

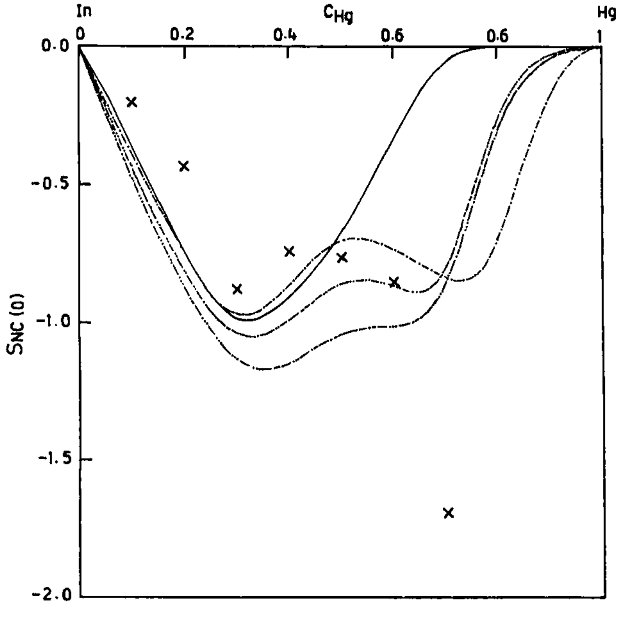

Figure 12 Number-concentration correlation function ($S_{NC}(0)$) of mercury indium liquid alloy at different temperatures without interaction energies (Curves have the same meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973)).

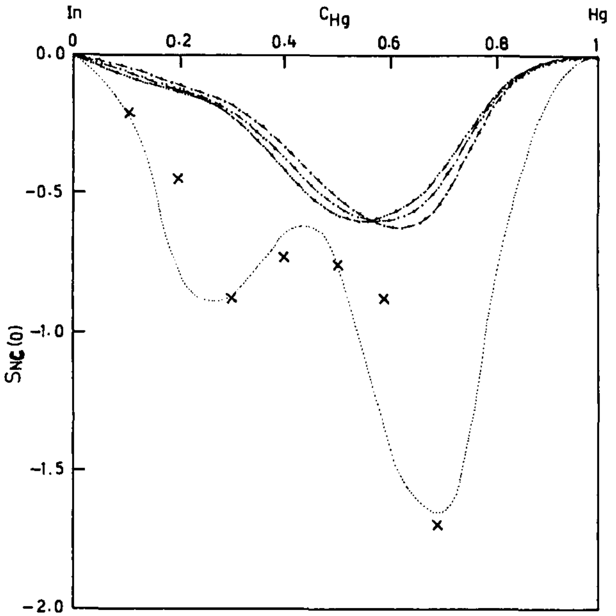

Figure 13 Number-concentration correlation function ($S_{NN}(0)$) of mercury indium liquid alloy at different temperature including interaction energies (Curves have the same meaning as in Fig. 1, (x x x) experiment (Hultgren *et al.* 1973)).

included lies around stoichiometric composition i.e. at $C_{Hg} = 0.5$. However, as the temperature rises the complex formation tendency decreases in both the cases.

Plot of n_4 vs C (Fig. 2) shows that as the temperature rises the value of n_4 goes on decreasing when interaction energies are not included, but when interaction energies are included then values of n_4 increases. Again in this case the maximum value of n_4 is around stoichiometric composition.

In case of n vs C (Fig. 3), the minima is at the stoichiometric composition corresponding to complex HgIn. Values of n_3 are greater than the values of n_4 at all concentrations which shows that complex HgIn is more stable than $HgIn_6$.

Without including interaction energy $S_{CC}(0)$ is not able to tell at which temperature HgIn is more stable. Also, there is a shift in peaks at higher temperatures and there is only one temperature where the compound is stable. This underlines the importance of inclusion of interaction energy and studying the thermodynamic properties in the whole concentration range suggested by the phase diagram. Furthermore though HgIn is more stable compound its stability decreases at higher temperatures. This also follows from the graph of $S_{CC}(0)$.

Towards the In rich region long wavelength fluctuations are maximum, as is evident from the plot of $S_{NN}(0)$ in Figures 10 and 11. This is true both in the case of with and without inclusion of interaction energies.

At 258 K $S_{NC}(0)$ (Fig. 13) matches very well with the experimental results when the interaction energy is included.

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