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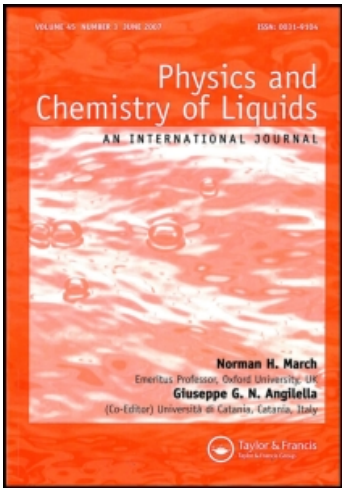

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NON ARRHENIUS BEHAVIOUR IN DEMIXING LIQUID ALLOYS

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A simple thermodynamic approach is considered to investigate the temperature dependence of the chemical diffusion coefficient in binary liquid alloys exhibiting miscibility gaps. Application is made to Bi-Zn, Cd-Ga and Al-In which show non Arrhenius behaviour which is significantly marked in the critical region.

KEY WORDS: Chemical diffusion coefficient, critical region.

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There are strong indications that the properties of demixing liquid alloys change anomalously as the composition and the temperature of the alloy tend to critical values $c \to c_c$ and $T \to T_c$. Sufficiently away from the critical region, their behaviour is more than a regular solution. Both experiment[1,2] and theory[3,4] suggest that the critical region is anomously dominated by large concentration fluctuation ($S_{cc}(0) \to \infty$). Singh and Sommer[3] observed that even a change of temperature of $\simeq 10^{-2}$ K in the vicinity of T_c may bring an increase in $S_{cc}(0)$ as large as $\simeq 10^2$. The X-ray and neutron scattering experiments reveal (for review see Chieux and Ruppersberg[5]) that the total structure factor, $S(q)$, of such systems is dominated by a strong small angle scattering which is likely to be produced by large concentration fluctuations. The temperature derivative of the resistivity of some immiscible liquid alloys[6] has a sharp peak at T_c.

The knowledge of the dynamic properties like diffusion coefficient and viscosity are equally useful to understand the microscopic scale mechanism of demixing of the two atomic species in binary liquid alloys. Here, we intend to pursue a thermodynamic approach to assess the temperature dependence of the diffusion coefficient in demixing liquid alloys over a wide range of temperature. Application is made to Bi-Zn, Cd-Ga and Al-In liquid alloys.

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Following Darken[7], the chemical diffusion coefficient, D, in a binary mixture consisting of Nc_A atoms of A and NC_B atoms of element B can be defined as

$$D = c_A D_B + c_B D_A = (c_A D_B^* + c_B D_A^*) \frac{d \ln a_A}{d \ln c_A} \tag{1}$$

where $D_i (i = A, B)$ are the intrinsic diffusion coefficients and D_i^* are the tracer diffusion coefficients of the components A and B. a_A is the activity of the component A. The inter-relationship between D and the concentration fluctuation in the long wavelength limit, $S_{cc}(0)$ can readily be established through a thermodynamic definition[8] of $S_{cc}(0)$.

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial c_A} \right)_{T,P,N} = c_B a_A \left(\frac{\partial a_A}{\partial c_A} \right)^{-1}_{T,P,N} = c_A a_B \left(\frac{\partial a_B}{\partial c_B} \right)^{-1}_{T,P,N}. \tag{2}$$

From (1) and (2), one readily obtains,

$$D = (c_A D_B^* + c_B D_A^*) \frac{S_{cc}^{id}(0)}{S_{cc}(0)}, \tag{3}$$

where $S_{cc}^{id}(0) = c_A c_B$. For ideal alloys, $S_{cc}(0) \to S_{cc}^{id}(0)$, then

$$D = c_A D_B + c_B D_A = c_A D_B^* + c_B D_A^* = D_{id}. \tag{4}$$

Therefore, we write

$$\frac{D}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{5}$$

In our analysis the quantity of central importance is $S_{cc}(0)$ which is strongly concentration and temperature dependent[3] for demixing liquid alloys. It is the temperature dependence of $S_{cc}(0)$ which allows us to investigate the temperature dependence of D. $S_{cc}(0)$ can be determined experimentally from Eq. (2) by measuing a_A as a function of c and T. But it is well known that the determination of thermodynamic functions of such systems in the vicinity of critical temperature is extremely difficult. Even above T_c, the different sets of data arising from various sources, say phase diagram, calorimetric, emf and vapour pressure measurements, specific heat data lack internal consistency. Therefore, Singh and Sommer[3] suggested that $S_{cc}(0)$ should be determined from the optimized[9] set of data which are usually procured by the least squares method taking into account all the experimental data found in literature. Here the excess free energy of mixing (G_M^{xs}) is expressed as

$$G_M^{XS}(c, T) = \sum_{l=0}^{m} K_l(T) c_A c_B (c_A - c_B)^l \tag{6}$$

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The coefficients $K_i(T)$ are temperature dependent whose values for Bi-In, Cd-Ga and Al-In can be found in references[3,4,10] respectively. Equation (6) is used in Eq. (2) to determine the temperature dependence of $S_{cc}(0)$ and hence that of D from Eq. (5).

In order to exhibit the temperature dependence of diffusion coefficients, DD_{id}^{-1} computed from Eq. (5) for the critical compositions $Bi_{0.15}Zn_{0.85}$, $Cd_{0.5}Ga_{0.5}$ and $Al_{0.65}In_{0.35}$ are plotted in Figures (1)–(3) respectively as a function of T^{-1}. The results clearly suggest that

$$\frac{D}{D_{\text{id}}} \sim T \tag{7}$$

Equation (7) is obviously in disagreement with the Arrhenius type of temperature dependence which is usually considered to express the temperature dependence of the diffusion coefficient of pure liquid metals, i.e.

$$D = D_0 e^{-Q/RT}, \tag{8}$$

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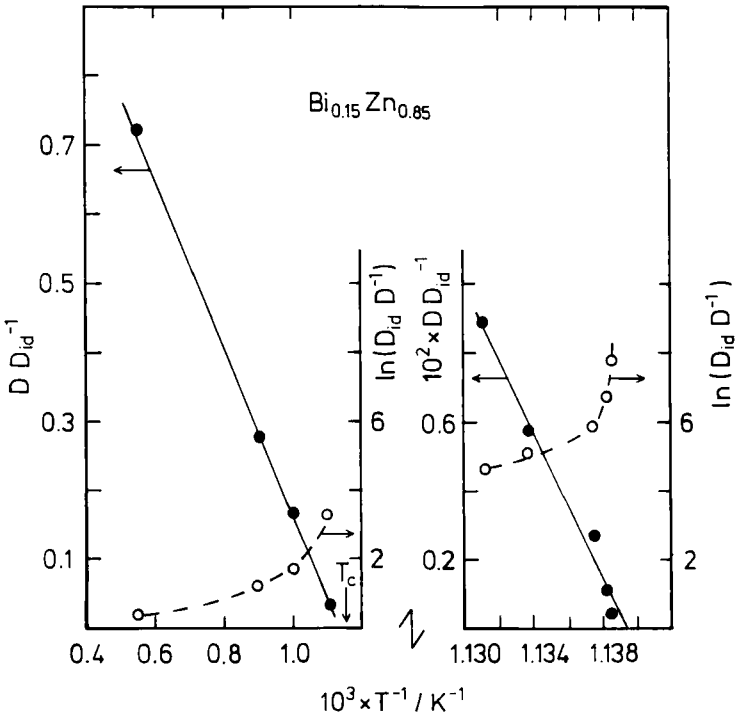

Figure 1 Diffusion coefficients versus temperature for the liquid $Bi_{0.15}Zn_{0.85}$ alloy: —●—●—● (DD_{id}^{-1} vs T^{-1}), ○ ○ ○ - ($\ln (D_{id}D^{-1})$ vs T^{-1}). Curve (b) is an expanded scale in the region of criticality. T_c (=863.8 K) corresponds to the critical temperature.

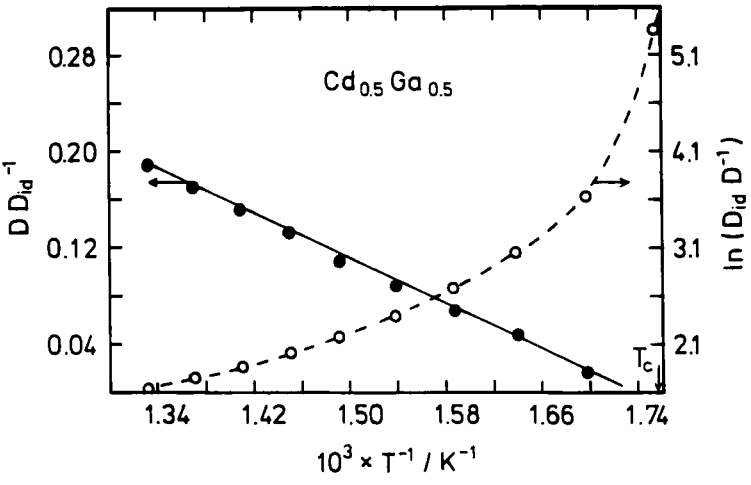

Figure 2 Diffusion coefficients versus temperature for the liquid $Cd_{0.50}Ga_{0.50}$ alloy: —●—●—● — (DD_{id}^{-1} vs T^{-1}), —○—○—○— (ln ($D_{id}D^{-1}$) vs T^{-1}. T_c (= 568.6 K) is the critical temperature.

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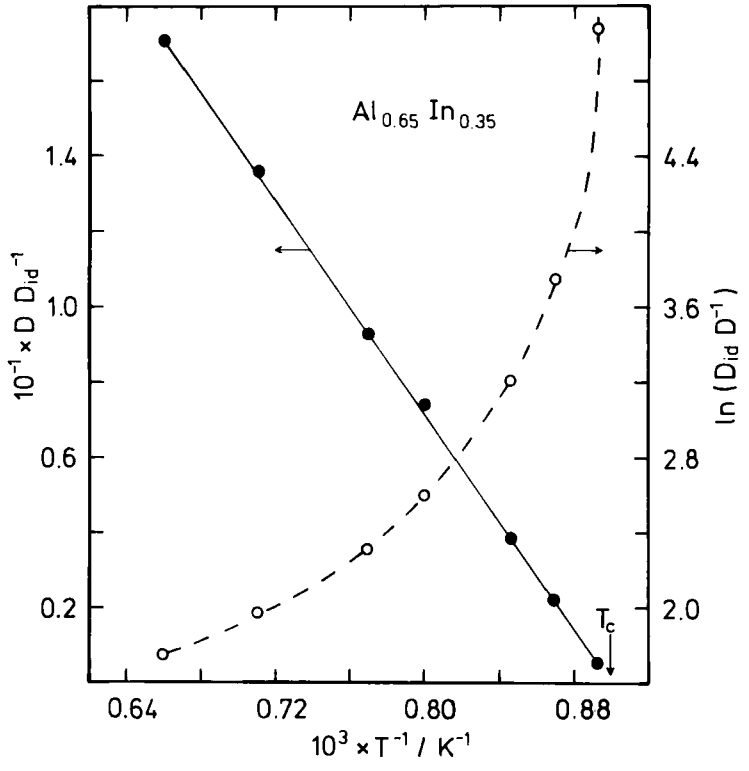

Figure 3 Diffusion coefficients versus temperature for the liquid $Al_{0.65}$ $In_{0.35}$ alloy: —●—●—● — (DD_{id}^{-1} vs T^{-1}), —○—○—○— (ln ($D_{id}D^{-1}$) vs T^{-1}. T_c (= 1110 K) is the critical temperature.

where D_0 is constant and Q is the activation energy. To be explicit, we have therefore, also shown a plot of $\ln(D_{id}D^{-1})$ vs T^{-1} in the same figures. Obviously $\ln(D_{id}D^{-1}) \sim T^{-1}$ curves are far from straight line behaviour. In particular, the deviations are quite significant as $T \to T_c$, however, in very high temperature region it displays a straight line behaviour. The diffusion data of pure liquid metals have been reviewed by Nachtrieb[11] and it was also observed that Eq. (8) is deficient in reproducing the temperature dependence of D over a wide range of temperature. A similar observation is also made for metals in the liquid[12] and undercooled liquid state[13].

Recently, Herwig and Hoyer[14] have measured viscosity of liquid Al-In alloys over a wide range of concentration and temperature. Viscosity data exhibit a non Arrhenius type of temperature dependence as one finds for D for Al-In (see Fig. 3). We intend to discuss the problem of diffusion and viscosity in demixing binary liquid alloys in detail, in forthcoming[15] publication.

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