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Journal of Alloys and Compounds 234 (1996) 119–124

Journal of
ALLOYS
AND COMPOUNDS

Thermodynamics of Au–Gd melts and percolation theory application for compound-forming liquid alloys

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Received 10 March 1995

Abstract

Concentration dependence of activity $a(c)$ in liquid Au–Gd alloys was measured at 1623 K by the Knudsen effusion method and reveals strong ordering effects. The percolation theory is proposed for analysis and calculation of activity data using concentration correlation function $S_{cc}(0)$ for several metallic solutions with chemical short range ordering (CSRO). The basic equations take into account the concentration difference factor $c - c_0$ where c_0 is the mean concentration at which the percolation threshold and maximum CSRO exist. The theoretical calculations of $a(c)$ from given $S_{cc}(0)$ and vice versa are in satisfactory agreement with experimental data. The percolation theory was shown to be suitable for correct interpretation and prediction of activity and $S_{cc}(0)$ data in ordered melts.

Keywords: Activity; Associate; Correlation function; Ordering; Percolation

1. Introduction

In a previous publication [1] it was shown that percolation theory may be successfully applied for the description of thermodynamic properties of liquid alloys possessing chemical short-range ordering (CSRO). The important results from Ref. [1] are the determination of the formulae for the concentration correlation function $S_{cc}(0)$ of binary melts proceeding from the schematic dependence of activity $a(c)$ for two regions of concentration divided by the percolation threshold. The activity was proposed to be treated as the analogy with an infinite cluster formation probability, the critical index β being directly connected with mean concentration c_0 at which the percolation threshold and the maximal CSRO exists. Computation of β from c_0 showed a good agreement with theoretical results of framework [2].

The purpose of the present paper is to give a detailed analysis of the concentration dependence of activity and $S_{cc}(0)$ using the percolation theory approach for liquid alloys possessing CSRO. A further problem exists in determination of the mathematical relations for computation of activity $a(c)$ from known

concentration dependence of $S_{cc}(0)$, and vice versa, according to the basic equations [3]

$$S_{cc}(0) = \frac{1 - c}{\left(\frac{\partial \ln a}{\partial c} \right)_{p, T}} \quad (1)$$

reflecting the principal relation between thermodynamic and microscopic properties of liquid alloys, because $S_{cc}(0)$ may be determined from structural measurements. We shall assume that the deviations of both $a(c)$ and $S_{cc}(0)$ from ideality when $a^{id}(c) = c$ (Raoult's law) and $S_{cc}^{id} = c(1 - c)$ depend on the concentration difference factor $|c - c_0|$ thus allowing us to derive the formulae for calculation of $a(c)$ and $S_{cc}(0)$ for several binary melts, including the newly studied Au–Gd system, given in Section 2 (c corresponds to the second component). In Sections 3, 4, 5 and 6 we present the calculations of $a(c)$ and $S_{cc}(0)$ derived from percolation theory (branching network, infinite cluster model) for liquid alloys with CSRO and phase separation tendency reflecting the different types of component interactions in metallic solutions. In Section 7 a short discussion of

results and a comparison with ideal associated solution (IAS) model is made.

2. Activity measurements in liquid Au–Gd alloys

The Knudsen effusion measurement technique and the method of activity calculations for liquid alloys containing rare earth metals have been described elsewhere [4]. The thermodynamic activity was measured at 1623 K over a wide range of composition for liquid Au–Gd alloys except the heterogeneous field around the intermetallic compound AuGd [5]. The activity of gold was calculated from the formula

$$a_{\text{Au}} = \frac{v_{\text{Au}}}{v_{\text{Au}}^0}$$

where v_{Au}^0 and v_{Au} are the evaporation rates of pure gold and the alloy respectively, which can be determined from the equation

$$v = \frac{m}{Kst}$$

where m is the mass of effused metal, t is the time of exposure, s is the effusion orifice area and K is the Clausing factor. The X-ray fluorescent analysis of the condensate obtained after the evaporation of the alloys did not show the presence of gadolinium; therefore, gold was supposed to be the only volatile component in the melts. Activity of gadolinium was calculated by integration of the Gibbs–Duhem equation [4]. Partial molar Gibbs energies of formation were computed using the activity data ($\Delta\bar{G}_i = RT \ln a_i$) and are listed in Table 1. These data, as well as the thermochemical measurements for liquid Au–Gd alloys [5], show the strong chemical ordering in the studied melts.

3. Activity calculation using the branching model

As shown in Ref. [1], the activity of a component in a melt may be treated analogously to the one com-

Table 1
Thermodynamic properties of liquid Au–Gd alloys at 1623 K

c_{Au}	a_{Au}	a_{Gd}	$-\Delta\bar{G}_{\text{Au}}$ (kJ mol ⁻¹)	$-\Delta\bar{G}_{\text{Gd}}$ (kJ mol ⁻¹)
0.981	0.951	0	0.7	319.0
0.968	0.880	0	1.7	250.1
0.907	0.683	0	5.2	195.7
0.869	0.510	0	9.1	163.6
0.828	0.340	0	14.6	132.3
0.763	0.178	0.001	23.3	97.3
0.679	0.079	0.006	34.3	69.0
0.3	0.004	0.596	73.7	7.0
0.2	0.0035	0.757	76.1	3.7
0.1	0.0030	0.890	79.0	1.6

ponent cluster formation probability. Therefore, the determination of analytical dependence of $a(c)$ reduces to the branching model [6] in connection with the percolation site problem. Following Ref. [6], we consider a tree-like network having free q channels, where q is connected with c_0 so that $c_0 = 1/q$. In compound forming melts, negative deviations of $a(c)$ from ideality are due to the destruction of pure component infinite cluster (blocking effects in the network) when the second component is added. This deviation, $c - a$, is proportional to the blocking probability $(1 - a)^q$ for q channels. So, one can write

$$c - a = c(1 - a)^q \quad (2)$$

The multiplier c in right hand side follows from the standard condition $a(0) = 0$. For real melts when $q > 1$ there are the non-trivial solutions of Eq. (2) at $c_0 < c \leq 1$, except the case $a = 0$ for all c , which, however, is suitable at $0 \leq c \leq c_0$. Taking into account these solutions for both concentration regions, one can obtain the total activity curve. We calculated activities using Eq. (2) for liquid Ag–Nd and Au–Gd alloys, the values of q were taken from experimental $c_0 = 0.33$ [4] and $c_0 = 0.40$ respectively. The results of calculations are compared with the experimental data in Figs. 1 and 2. Further analysis of Eq. (2) leads to the hypothetical network with $q \rightarrow \infty$. In this case $(1 - a)^q$ tends to zero, and, hence, $a(c) = c$ for all c (ideal solution). To explain this result one can imagine that there will be a sufficient quantity of branches at $q \rightarrow \infty$ to form an infinite cluster regardless of blocking effects due to the CSRO. At $q = 1$ from Eq. (2) it

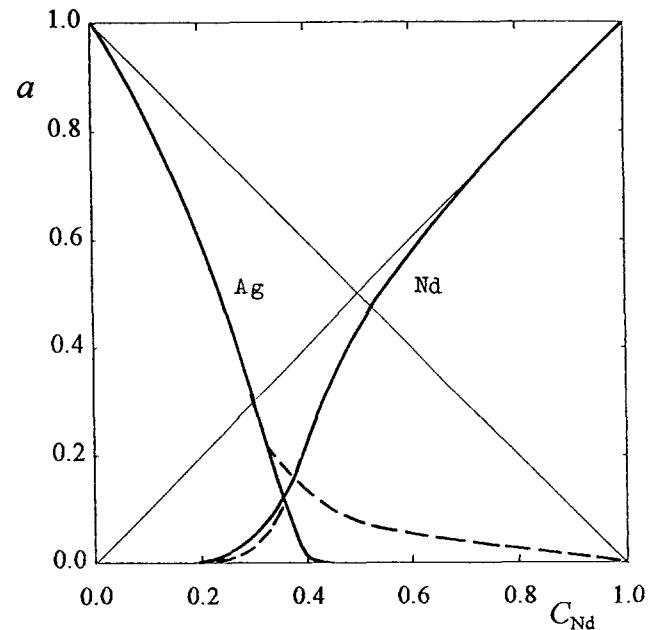


Fig. 1. Activities for liquid Ag–Nd alloys: —, calculated from Eq. (2); ---, experimental data at 1363 K.

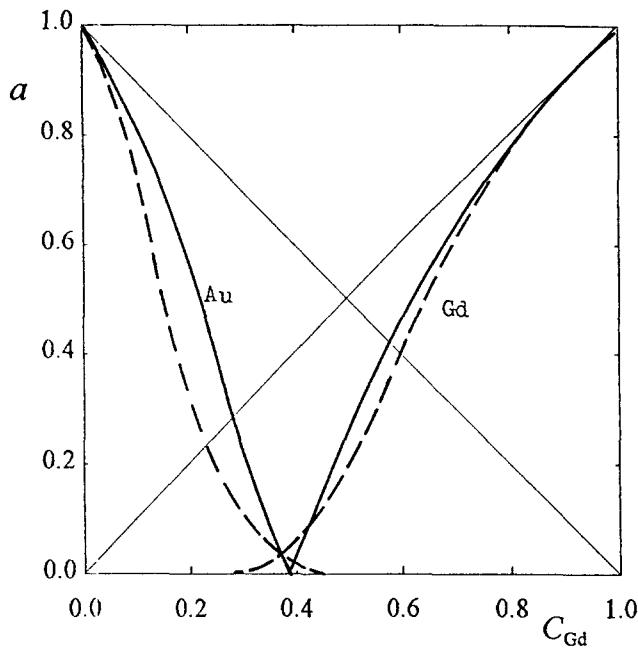


Fig. 2. Activities for liquid Au–Gd alloys: —, calculated from Eq. (2); ---, experimental data at 1363 K. Data for $0.41 < c_{\text{Gd}} < 0.6$ are extrapolated for undercooled liquid alloys.

follows that $a(c) = 0$ for all c , so the thermodynamic activity in the linear chain is equal to zero; this is in line with general properties of fully localized one-dimensional systems [7].

4. Activity calculation from $S_{cc}(0)$ data

In Ref. [1] the deviation of $S_{cc}(0)$ from the ideal value $c(1 - c)$ in ordered liquid alloys was shown to be proportional to the concentration difference factor $|c - c_0|$. For $c > c_0$ let

$$S_{cc}(0) = c(1 - c)(c - c_0) \quad (3)$$

To determine the activity from $S_{cc}(0)$ data we use Eq. (1) in the form:

$$\ln a(c) = \int \frac{1 - c}{S_{cc}(0)} dc = \int \frac{dc}{c(c - c_0)}$$

After the integration one obtains ($a = a(c)$):

$$\ln a = A \ln c + B \ln(c - c_0) + \text{const}$$

where the parameters $A = -B = 1/c_0$, $\text{const} = -B \ln(1 - c_0)$ were determined from the normalization condition $a(1) = 1$, and we may write

$$a = \left[\frac{c - c_0}{c(1 - c_0)} \right]^{1/c_0}$$

For the concentration region $c_0 > c$ Eq. (3) may be written in the form

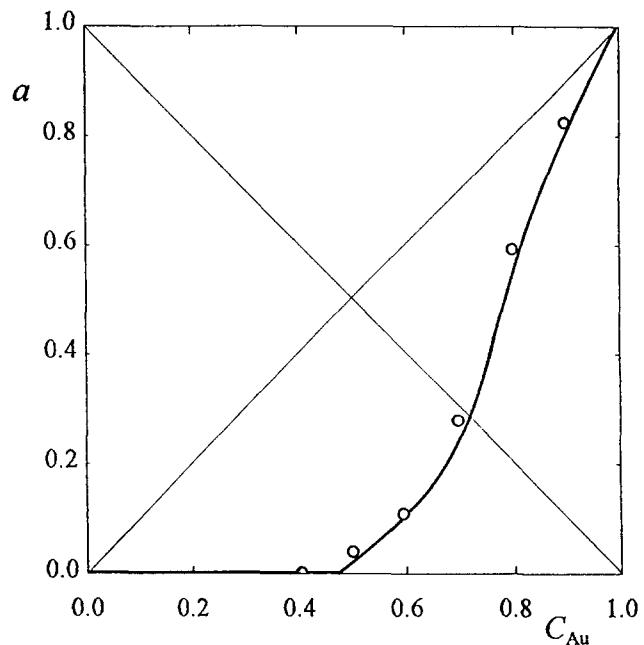


Fig. 3. Activity of aluminum for liquid Al–Au alloys: —, calculated from Eqs. (5) and (6); ○, experimental data at 1400 K.

$$S_{cc}(0) = c(1 - c)(c_0 - c) \quad (4)$$

from which for the activity we obtain

$$a = [c(c_0 - c)]^{1/c_0} \quad (5)$$

The unified expression for computation of activity over the total concentration region is

$$a = \begin{cases} \left[\frac{c - c_0}{c(1 - c_0)} \right]^{1/c_0} & c_0 < c \leq 1 \\ [c(c_0 - c)]^{1/c_0} & 0 \leq c < c_0 \end{cases} \quad (6)$$

Eqs. (5) and (6) describe the typical behavior of the $a(c)$ -curve. Analyzing Eq. (6) one can see that $a(c)$ is too small in comparison with the measured activity data of liquid-compound forming alloys for $c \leq c < c_0$. Using Eqs. (5) and (6) we calculated the activities in liquid Al–Au and Hg–Na alloys. According to the experimental data we used, $c_0 = 0.5$ for the Al–Au system [8] and $c_0 = 0.33$ for the Hg–Na system [9], the last one corresponding to liquid intermetallic Hg_2Na [10]. Both results are given in Figs. 3 and 4 and show good agreement with experimental results. We also calculated $S_{cc}(0)$ for the Hg–Na system using Eqs. (3) and (4) and obtained the excellent agreement with thermodynamic calculations of this function (reported in Ref. [10]).

5. Activity in melts with intermediate ordering

We consider the liquid alloy with CSRO for which the activity values are only very small near $c = 0$, as one can see in Figs. 5 and 6(a). The model interpreta-

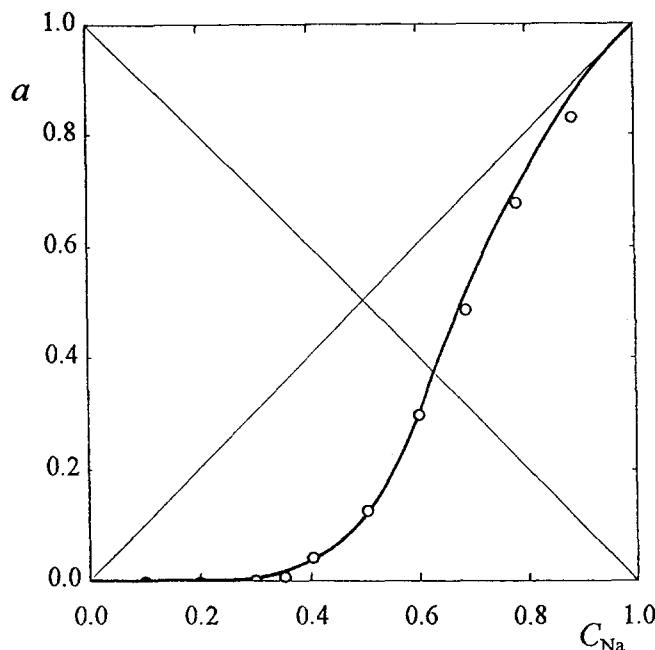


Fig. 4. Activity of sodium for liquid Hg–Na alloys: —, calculated from Eq. (8); ○, experimental data at 648 K.

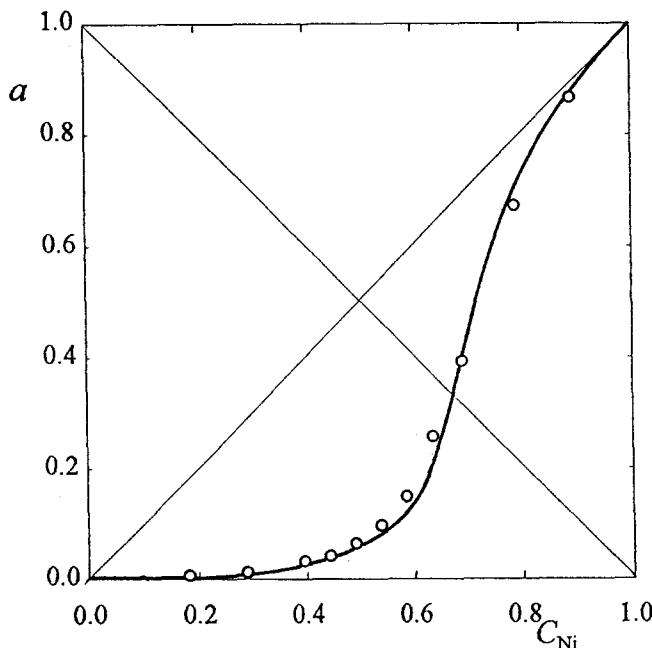


Fig. 5. Activity of nickel for liquid Ge–Ni alloys: —, calculated from Eqs. (5) and (6); ○, drawn from experimental data at 1623 K.

tion of such dependencies seems to be based on the correlation function $\Gamma(R)$, which takes account of the infinite cluster formation and relaxation at $c \rightarrow 0$ when the only small clusters exist [7]:

$$\Gamma(R) = \Gamma_\infty + R^{-1} \exp\left(-\frac{R}{\delta}\right) \quad (7)$$

where R is the reduced interatomic distance and δ is the correlation radius. Analogously to Eq. (7) for the

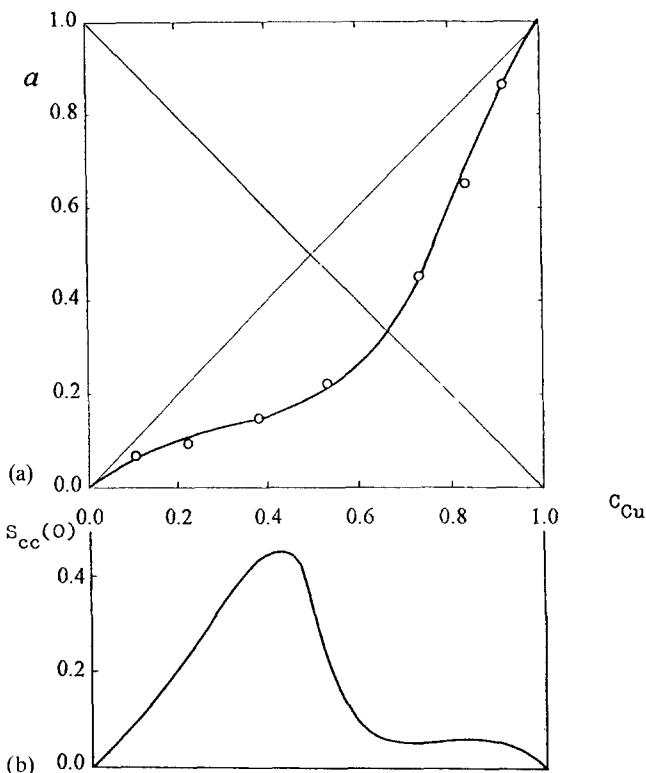


Fig. 6. (a) —, activity of copper for liquid Ge–Cu alloys calculated from Eq. (8); ○, experimental data at 1500 K; (b) —, correlation function $S_{cc}(0)$ for liquid Ge–Cu alloys calculated from Eq. (9).

evaluation of c -dependence of the activity coefficient ($\gamma = a/c$) using the parameters c_0 , δ , γ^0 (limiting value at $c = 0$) and the requirement $\gamma(1) = 1$ one may propose the equation

$$\gamma(c) = \gamma^0(1 - c) + \left[1 + \exp\left(\frac{c_0 - c}{\delta}\right)\right]^{-1} \quad (8)$$

Here δ is given in terms of concentration. The condition $\gamma(1) = 1$ holds when the term $\exp[(c_0 - c)/\delta]$ tends to zero at $c \rightarrow 1$ if correlation radius δ (concentration limit of ordering in an alloy) is sufficiently small. The calculations of activity from Eq. (8) were carried out for liquid Ge–Cu alloys (associate Cu_3Ge , $c_0 = 0.75$, $\delta = 0.08$, $\gamma^0 = 0.6$ [11]). We also calculated the activity of Ni in liquid Ge–Ni alloys using $c_0 = 0.7$ (average value for Ni_3Ge and Ni_5Ge_3 compounds), $\delta = 0.05$, $\gamma^0 = 0.12$ [12]. The results of calculation (see Figs. 5 and 6(a)) are in proper agreement with experiments, as well as the data on Ge–Cu liquid alloys. The knowledge of analytical c -dependence of activity allows as to obtain the formula for calculation of $S_{cc}(0)$ using Eqs. (1) and (8):

$$S_{cc}(0) = c(1 - c) \frac{A[\gamma^0(1 - c)A + 1]}{1 + \gamma^0(1 - 2c)A^2 + (A - 1)(1 + c\delta^{-1})} \quad (9)$$

where $A = 1 + \exp [(c_0 - c)/\delta]$. The computation of $S_{cc}(0)$ for Ge–Cu melts (Fig. 6(b)) indicates that $S_{cc}(0)$ values are rather small in the neighborhood of the Cu_3Ge compound and rather large in Ge-rich composition region, where, by the way, a tendency toward self-association of liquid germanium could occur [13].

6. Phase separation and $S_{cc}(0)$ concentration dependence

A number of liquid alloys indicate the complicated character of the concentration dependence of $S_{cc}(0)$ possessing the minimum in associate formation region at c_0 as well as the phase separation tendency evidenced by the peak at certain concentrations, say c_* [14]. The calculation of $S_{cc}(0)$ from activity data for the $0 < c < c_0$ region using Eqs. (1) and (6) leads to the formula

$$S_{cc}(0) = \frac{c(1-c)(c_0-c)}{c_0-2c} \quad (10)$$

Hence, if the activity follows Eq. (6) the break on the $S_{cc}(0)$ vs. c curve must emerge at $c_* = c_0/2$. However, Eq. (3) for $S_{cc}(0)$ shows that in region $c_0 < c < 1$ such an effect cannot take place. To obtain the unified formula for $S_{cc}(0)$ over the total region we must take account that $S_{cc}(0) \geq 0$, so that

$$S_{cc}(0) = c(1-c) \left| \frac{c-c_0}{2c-c_0} \right| \quad (11)$$

It is of interest to apply this equation, for computation of $S_{cc}(0)$ and activity, in the liquid Tl–Te alloys in which there is the liquid associate Tl_2Te and a miscibility gap in the Tl-rich region according to the phase diagram [15,16]. The formula for activity in the region $c_0 < c < 1$ follows from Eqs. (1) and (11):

$$a(c) = \frac{c(c-c_0)}{1-c_0} \quad (12)$$

For the estimation of activity over the total composition region we must introduce an additional term into Eq. (12), which is analytical at $c = c_0$, as has been made in Eq. (8). For detailed reconstruction of the activity curve it is necessary to take account of its behavior at small c , which is conditioned by the normalization constant $\gamma^0 = \gamma(0)$, so that

$$a(c) = \gamma^0 c(1-c) + \frac{c|c-c_0|}{1-c_0} \quad (13)$$

The results of calculations of $S_{cc}(0)$ and activity of tellurium from Eqs. (11) and (13) for Tl–Te melts are given in Figs. 7 and 8 and show rather good agreement with experimental data for $S_{cc}(0)$ [14] and $a(c)$ [16]. In calculations we used $c_0 = 0.33$ [16] in Eq. (11); γ_{Te}^0 was

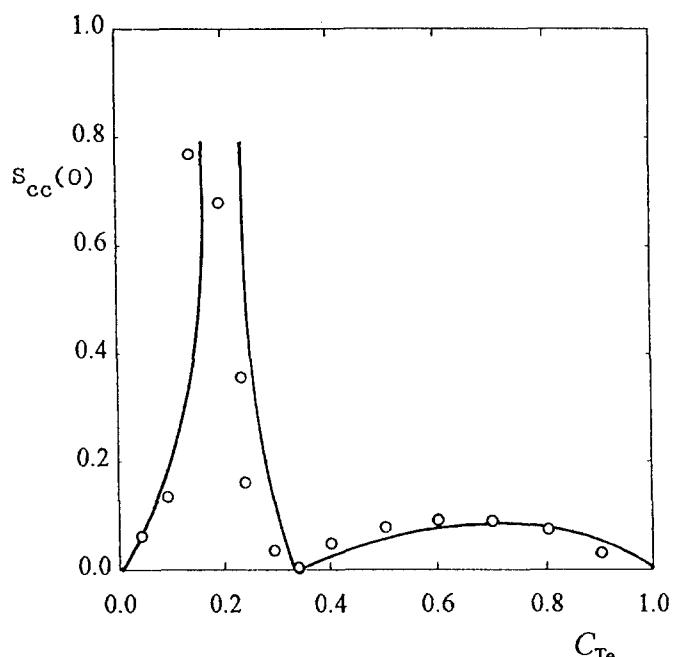


Fig. 7. Correlation function $S_{cc}(0)$ for liquid Tl–Te alloys: ○, calculated from Eq. (11); —, drawn from experimental data.

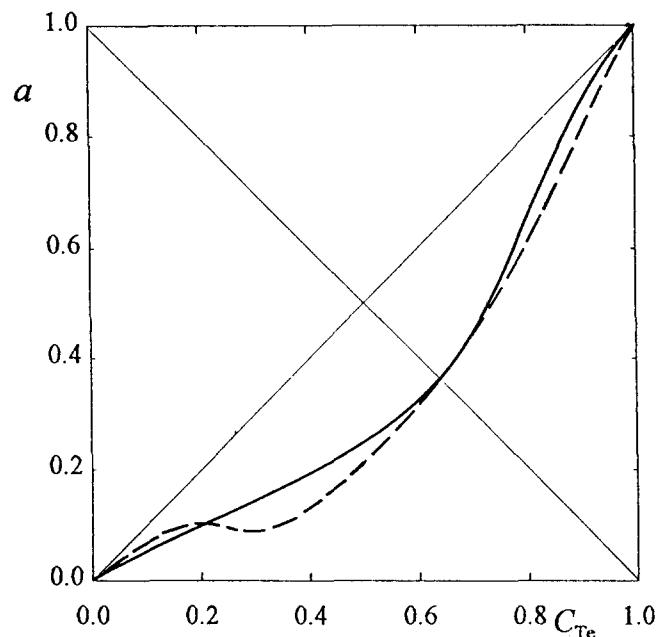


Fig. 8. Activity of tellurium for liquid Tl–Te alloys: ---, calculated from Eq. (13); —, drawn from experimental data at 1181 K.

computed to be 0.42 from data of Ref. [16]. It should be noted that in the Tl-rich region the behavior of the calculated activity curve seems to predict a phase separation tendency, which, however, does not coincide with activity data at 1181 K [16]. The differences between calculated and experimental activity curves may be caused by fluctuation probability scattering, which arises sharply at $c = c_*$ (Fig. 7). Alternatively, in the CSRO concentration region around

Tl₂Te, the small $S_{cc}(0)$ does not make the agreement between both branches of the activity curve worse (Fig. 8).

7. Discussion

The calculation of activity and correlation function $S_{cc}(0)$ demonstrate, in general, the successful attempt of the application of percolation theory for typical liquid alloys with strong CSRO, intermediate ordering and phase separation tendency. All the calculated concentration dependencies of $a(c)$ and $S_{cc}(0)$ reflect the main features of the experimental data sets; however, the results for a_{Ag} (Fig. 1) and a_{Au} (Fig. 2) are unsatisfactory. This weak point of the theory is due to the only single parameter limitation in calculations (Eq. (2)). This seems to be insufficient even though that it gives $\gamma^0 = 0$, while for real melts this parameter is non-trivial and serves as a standard point. Since the adjustable parameter δ must be introduced in several cases to hold the shape of the $a(c)$ curve, the three values (c_0 , γ^0 and δ) in general provide the correct results. All these parameters may be determined or estimated from thermodynamic, structural and phase equilibrium data.

The successful application of the percolation problems to liquid alloys allows us to make certain considerations about the structure of metallic melts. Using the concentration dependence of activity (Figs. 1–3) one can propose the coherent cluster formation at $c > c_0$, the scaling transformation around c_0 when the infinite cluster decomposes into finite size blocks, and a solution of small clusters (associates) at $0 < c < c_0$. This hypothesis of cluster formation is in formal agreement with the idea of microinhomogeneity of liquid alloys in frames of the well-known IAS model for the activity [17]. Furthermore, drawing the analogy with the IAS model, one can choose the corresponding pairs of principal values:

- (1) percolation threshold → mean CSRO point;
- (2) probability of a cluster formation → activity, $a(c)$;
- (3) blocked atoms fraction → associates fraction, $\xi(c)$.

Using the notation suited to the IAS model, we may write the equation (for an arbitrary associate $A_a B_b$, $c_0 = a/(a + b)$)

$$a(c) = c - c_0 \xi(c) \quad (14)$$

which has been derived by Shklovski and Efros [18] in terms of percolation theory. Earlier the IAS model was successfully applied for numerous binary liquid alloys, included the above studied Ag–Nd [4], Ge–Cu [11] and Ge–Ni [12], using percolation theory. The detailed inspections of theoretical activity curves [17] show that the IAS model could reproduce the activities, obtained from percolation theory (Eqs. (2), (5) and (6)), even for very sharp bends, if the IAS model parameters reach the critical limits.

In this paper we have shown an equivalence between certain networks with the percolation threshold and liquid alloy with CSRO for interpreting concentration dependencies of activity and concentration correlation function. The percolation model, which does not take into account the electronic structure of the material, may be used to obtain analytical results for calculation of thermodynamic functions and for estimation of the structure of liquid alloys.

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