Application of the Hard Sphere Theory to the Diffusion of Binary Liquid Alloy Systems

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On the basis of the van der Waals concept of Ascarelli and Paskin the hard sphere theory of self diffusion is extended to binary liquid alloys. Using only the melting temperature of the pure metals and the densities, component self-diffusion coefficients and, with the help of Darken's equation, mutual diffusion coefficients were calculated. Agreement with experimental results is good in (Bi, Sn), and excellent in (Sn, Zn) and (Li, Ag). Impurity diffusion in liquid Cu, Sn and Pb is predicted better than by the theory of Protopapas et al. Deviations in (Hg, Zn) and (Li, Pb) are tentatively attributed to strong particle interactions in one component (Hg) or in the alloy (Li, Pb).

1. Introduction

Transport phenomena in liquid metals and alloys are of ever increasing interest: Many technological processes and corrosion phenomena depend directly on transport quantities and, on the other hand, transport data contribute to our knowledge of the liquid state.

The starting point for any theoretical description of transport phenomena in liquids is the solid state theory or the kinetic theory of gases. Nachtrieb [1] presented several models of diffusion in liquid metals, of which the hole-, the free volume-, the fluctuation-, and the itinerant oscillator theories are derived from the solid state theory, whereas the dense gas formulation, the corresponding states correlation and the molecular dynamic calculations have their origin in the kinetic theory of gases. When self-diffusion coefficients are calculated, theories of both sorts give good agreement with experimental results. For the treatment of chemical diffusion, however, only a few models are suitable, of which the dense gas formulations offer good possibilities for adaption to mixtures, and especially to alloys.

The modified hard sphere theory, originally developed by Dymond and Alder [2] on the basis of the ENSKOG-theory, and successfully applied to the calculation of self-diffusion coefficients of liquid metals, can be used, with a minimum of specific parameters, to establish a frame of reference for diffusion in liquid alloys.

In Sect. 2 the different procedures for calculating self-diffusion coefficients (DC) in liquid metals on the basis of the hard sphere (HS) theory are summarized. In section 3 the equations of component self-DCs and mutual DCs of binary liquid alloys are developed and compared with other similar approaches. The theoretical predictions are compared with experimental results in Sect. 4 and discussed in Section 5.

2. Hard Sphere Theory of Self Diffusion in Liquid Metals

2.1. *Basic Concepts of the Theory*

A HS fluid is completely described by its particle mass and diameter and the intensive parameters, temperature and density. Diffusion in such a fluid is described exactly by the ENSKOG-theory [3]. The applicability of the model of a HS fluid to real liquids depends on two basic postulates: a) the particles of the liquid must be nearly spherical, b) attractive forces between the particles must be negligible.

The calculation of self-DCs is possible by the ENSKOG-theory using some corrections, obtained from molecular dynamics calculations [4]. According to the approximation of ENSKOG

$$D_\mathrm{E} = D_\mathrm{g}/\chi\,. \tag{1}$$

D_g is the self-DC of a dilute HS gas and χ a correction, which decreases the DC because of the greater particle density of a HS fluid. χ equals the pair

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correlation function $g(r)$ at $r = \sigma$ (σ: HS diameter), which for HSs is a simple function of the compressibility factor Z

$$\chi = g(\sigma) = f(Z). \tag{2}$$

In order to allow for variable packing fractions η (ratio of the particle volume to the total volume of the liquid) a correction factor $C(\eta)$ has been calculated by computer simulation (see below)

$$D = C(\eta) D_E. \tag{3}$$

In the final expression

$$D = \frac{l}{2}\left(\frac{\pi RT}{M}\right)^{1/2} \frac{C(\eta)}{Z-1}. \tag{4}$$

M is the molar mass of the particles and $l = \sigma/2$ the HS radius.

The application of (4) for the calculation of self-DCs of liquid metals requires methods for determining appropriate values of l and Z. These quantities can be obtained in different ways [5, 6]. In numerous empirical studies it was recognized [5, 7, 6], that η has the same value for all liquid metals at the melting point: $\eta_m = 0.45$ [5] or 0.472 [6].

The HS radius, which is obtained from elementary considerations by

$$l = \left(\frac{3\eta M}{4\pi N_L \varrho}\right)^{1/3} \quad (\varrho\text{: density}) \tag{5}$$

is T-dependent, in contrast to the original theory [5, 7], where l was calculated at the melting point T_m with ϱ_m and the general value η_m. The ad hoc hypothesis of [6], which is based on a soft sphere potential, leads to a temperature dependence somewhat smaller (~ 75%) than in (5). Like other authors, who emphasized its high precision, we use the Carnahan-Starling equation of state [8, 7, 6]

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}. \tag{6}$$

We represented the reverse function as a polynomial of the forth degree.

$$\begin{aligned}\eta = &-3.57 \cdot 10^{-2} + 1.367 \cdot 10^{-1} Z \\ &- 1.747 \cdot 10^{-2} Z^2 + 1.225 \cdot 10^{-3} Z^3 \\ &- 3.508 \cdot 10^{-5} Z^4.\end{aligned} \tag{7}$$

Ascarelli and Paskin [5] introduced the van der Waals concept of fluids on the basis of the theory of Dymond and Alder [2]. They equated the HS repulsive pressure P_{HS} with the van der Waals cohesive pressure

$$Z = \frac{P_{HS} V_m}{RT} = \frac{a}{V_m RT} = \frac{a d}{RT} \tag{8}$$

(a: T-independent van der Waals constant; V_m: molar volume, d: molar density).

For $\eta_m = 0.45$, (6) yields $Z_m = 9.385$; with this value a can be eliminated in (8)

$$Z = \frac{Z_m T_m \varrho}{T \varrho_m}. \tag{9}$$

With the aid of (9), (7) and (5) it is possible to calculate the temperature dependent self-DC. Good agreement with experimental results was obtained using the correction factor [5, 7]

$$C(\eta) = 0.73\, \eta_m/\eta. \tag{10}$$

2.2. *Theory of Protopapas, Andersen and Parlee [6]*

Although the application of (4) yields quite good numerical results, the authors of [6] especially criticized the use of the van der Waals concept. On the basis of a soft sphere potential curve they deduced an expression for the T-dependent HS diameter without reference to the van der Waals equation:

$$\sigma(T) = \sigma_0 (1 - B\sqrt{T/T_m}). \tag{11}$$

(σ_0: distance of HS in the potential minimum, $B = 0.112$: empirical constant for all liquid metals). σ is used to calculate

$$\eta = \frac{\eta_m \varrho \sigma^3}{\varrho_m \sigma_m^3} \tag{12}$$

Upon introducing (6) in (4) an analogous formula for the self-DC is obtained:

$$D = \frac{l}{4}\left(\frac{\pi RT}{M}\right)^{1/2} C_{AW}(\eta) \frac{(1-\eta)^3}{\eta(2-\eta)}. \tag{13}$$

$C_{AW}(\eta)$ is the Alder-Wainwright correction factor [9], whose dependence on η is plotted in [6]. (13) yielded better agreement with the empirical temperature dependence of self-DCs, when compared with the original formula of Ascarelli and Paskin.

3. Extension of the HS Theory to Binary Liquid Alloys

3.1. *Darken Equation*

It is generally accepted that the relation between the mutual DC $\tilde{D}$ of a binary mixture AB and both component self-DCs, D_A^{AB} and D_B^{AB}, is given by the Darken equation [10].

$$\tilde{D} = [D_A^{AB}(1-x) + D_B^{AB}x]\frac{\mathrm{d}\ln a^*}{\mathrm{d}\ln x}, \quad (14)$$

$$\tilde{D} = D_r f_t. \quad (15)$$

(a^*: thermodynamic activity of A; x: mole fraction of A).

According to (15) $\tilde{D}$ can be split into the reduced mutual DC D_r and into the thermodynamic factor $f_t = \mathrm{d}\ln a^*/\mathrm{d}\ln x$, which represents the non-ideality of the mixture. All quantities in (14) are dependent on concentration. At infinite dilution $\tilde{D}$ equals the component self-DC of one component

$$D_A^B = \lim_{x_A \to 0} \tilde{D}. \quad (16)$$

3.2. *First Approach* [11]

Bertucci and Flygare [11] used the HS theory to describe mutual diffusion of binary mixtures without employing (14). They supposed on the basis of the extended ENSKOG-theory [3], a relation similar to (1):

$$D_E^{AB} = D_g/g(\sigma_{AB}) \quad \text{with} \quad \sigma_{AB} = l_A + l_B, \quad (17)$$

where D_g is the mutual DC of a dilute gas mixture. They obtained the final expression

$$\tilde{D} = \frac{3}{8 N_L d_{AB} \sigma_{AB}^2 g(\sigma_{AB})}\left(\frac{kT}{2\pi\mu}\right)^{1/2} C(\eta) A \quad (18)$$

with

$$\mu = \frac{m_A m_B}{m_A + m_B}.$$

In the correction factor $C_{AW}(\eta)$ the packing fraction η is taken as the weighted sum of the individual packing fractions of the components. The correction A allows for deviations from the ideal spherical shape. An expression for $g(\sigma_{AB})$ of alloys was developed on the basis of the Carnahan-Starling equation of state [12]. The concentration dependence of mutual diffusion of binary organic solvent mixtures calculated using (18) was in very good agreement with experimental results [11]. (18) has not yet been used to calculate DCs over the whole concentration range of a binary liquid alloy, but only for impurity diffusion in liquid copper (see Section 4.4) [13, 14].

3.3. *Present Approach*

The theory of Ascarelli and Paskin can, on the basis of the van der Waals concept, be extended to binary liquid alloys. The primary results are component self-DCs and their concentration dependences, which by using (14) yield the mutual DC over the whole concentration range.

The application of the HS theory [5, 7] to binary liquid alloys, which are considered as mixtures of two HS liquids, requires some additional assumptions

A1) The change of the compressibility factor Z_x is caused by the concentration dependence of the density ϱ_x and the van der Waals constant a_x.

A2) The HS radii, l_A and l_B do not change on alloy formation and are independent of the concentration.

A3) The mixture is regarded as thermodynamically ideal, $f_t = 1$, i.e. special particle interactions (clusters, associates, etc.) are not considered.

Concerning A3 it is to be expected that the calculated DCs will deviate from empirical results of non-ideal alloy systems to an extent which is determined by the degree of non-ideality. According to A1 Z_x follows from (8):

$$Z_x = \frac{a_x d_x}{RT} \quad (19)$$

with

$$d_x = \varrho_x/\bar{M}, \quad \bar{M} = x M_A + (1-x) M_B. \quad (20)$$

The concentration dependence of a_x can be expressed by [15]

$$a_x = x^2 a_A + 2x(1-x) a_{AB} + (1-x)^2 a_B, \quad (21)$$

where the coefficient in the mixed term is given by the Berthelot relation [16]

$$a_{AB} = \sqrt{a_A a_B}. \quad (22)$$

The constants a_A and a_B are obtained from the melting point data of the pure metals A and B using (8) with $Z_m = 9.385$. The resulting compressibility factor Z_x is thus given by

$$Z_x = \frac{Z_m \varrho_x}{\bar{M} T} \cdot \left(\sqrt{\frac{M_A T_{mA}}{\varrho_{mA}}}\, x + \sqrt{\frac{M_B T_{mB}}{\varrho_{mB}}}\,(1-x)\right)^2. \quad (23)$$

With A2, (4) directly yields the component self-DC of A (analogously for B):

$$D_{\mathrm{A}}^{\mathrm{AB}} = \frac{l_{\mathrm{A}}}{2}\left(\frac{\pi RT}{M_{\mathrm{A}}}\right)^{1/2} \frac{C(\eta)}{Z_x - 1}\,. \qquad (24)$$

(24) corresponds to a physical picture, in which particles A characterized by l_{A} and M_{A} diffuse in a liquid mixture characterized by d_x and a_x. Besides the melting temperature of the pure metals A and B, their density and its temperature dependence (for l_{A} and l_{B}), and the densities d_x of the liquid alloys (for Z_x) are also required. When not available [17], these data were interpolated with respect to temperature and concentration.

If experimental component self-diffusion data are known, a direct comparison with the predictions of (24) is possible. In most cases only the mutual DCs have been determined, so that the Darken equation (14) must be used to perform a comparison. In the case of non ideal systems the thermodynamic factors f_t are introduced.

4. Comparison between Calculated and Experimental Diffusion Data

4.1. The System (Bi, Sn) (Fig. 1)

At $T = 773$ K the system (Bi, Sn) is nearly ideal over the whole concentration range and the experimental mutual DC shows an almost linear change with concentration [18] (cf. Figure 1). This behaviour corresponds to the Darken relation, (14), supposing the component self-DCs, $D_{\mathrm{Bi}}^{\mathrm{BiSn}}$ and $D_{\mathrm{Sn}}^{\mathrm{BiSn}}$, to show no concentration dependence, and also $f_t = 1$. At lower temperatures (e.g. 613 K), however, the system deviates from ideality [19], and $\tilde{D}$ exhibits a minimum, caused by positive deviations from Raoults law, i.e. $f_t < 1$. This behaviour is typical, in so far as positive deviations from Raoults law often cause minima in the curves $\tilde{D} = f(x)$ and vice versa. In the calculation we therefore used $f_t = 1$ at 773 K and f_t of [19] at 613 K. The best agreement between the experimental and calculated $\tilde{D}$ values was obtained with $C(\eta) = 1$ in (24) (see 4.2). The greater deviation at infinite dilution, where differing experimental values have been found [18, 19, 20], are possibly caused by experimental errors (see 4.3).

4.2. The System (Sn, Zn) (Fig. 2, Fig. 3, Fig. 4)

In the liquid alloys (Sn, Zn) the amount of experimental diffusion data is very large [21]. Additionally, precise values for the thermodynamic factors [21] and the densities [17] of the alloys have been determined. Positive deviations from Raoults law, $f_t < 1$, again cause a minimum in the mutual DC (cf. Figure 2). A comparison of the experimental component self-DCs, $D_{\mathrm{Sn}}^{\mathrm{SnZn}}$ and $D_{\mathrm{Zn}}^{\mathrm{SnZn}}$, with the calculated ones, shows a good agreement with respect to their concentration dependence (cf. Figures 3 and 4). The upper curves calculated with $C(\eta) = 1$ fit the experimental values best, but on approaching the pure component the experimental values are closer to the lower curves calculated with $C(\eta)$ from (10). $C(\eta)$ has its greatest influence near the melting point ($\eta \approx \eta_{\mathrm{m}}$) and increases with the temperature. Though its use in $D_{\mathrm{A}}^{\mathrm{A}}$ is necessary, in the case of alloys the agreement with experimen-

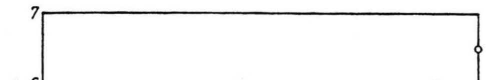

Fig. 1. Mutual diffusion coefficient $\tilde{D}$ of the system (Bi, Sn). Experimental: 773 K [18]; 613 K [19]. Calculated: —— Eq. (24); --- Eq. (24) $C(\eta) = 1$.

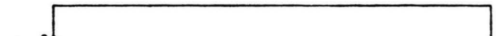

Fig. 2. Mutual diffusion coefficient $\tilde{D}$ of the system (Sn, Zn) [21]. Experimental: ● ● ● 713 K; ○ ○ ○ 793 K; Calculated: —— Eq. (24); --- Eq. (24) $C(\eta) = 1$.

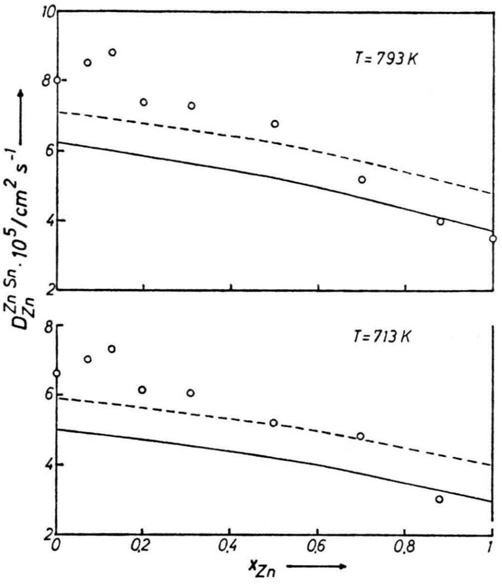

Fig. 3. Component self-diffusion coefficient $D_{\mathrm{Zn}}^{\mathrm{SnZn}}$ [21]. Experimental: ○ ○ ○; Calculated: —— Eq. (24); - - - Eq. (24) $C(\eta) = 1$.

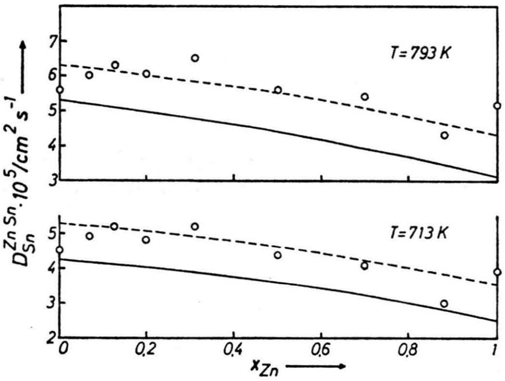

Fig. 4. Component self-diffusion coefficient $D_{\mathrm{Sn}}^{\mathrm{SnZn}}$ [21]. Experimental: ○ ○ ○; Calculated: —— Eq. (24); - - - Eq. (24) $C(\eta) = 1$.

tal results is sometimes better if $C(\eta)$ is set equal to unity. This cannot be explained at present, nor can the fact that for calculated component self-DCs at infinite dilution, the "impurity diffusion coefficients" are too small compared with experimental values. On the other hand these quantities are often extremely sensitive to experimental errors, so that it is not possible to decide whether the deviations are really attributable to a weakness of the model (see 4.3 and 4.4). The agreement of the mutual DCs, at 713 K and at 793 K (Fig. 2) is excellent in the middle of the concentration region and less satisfactory at the boundaries as a consequence of the behaviour of the self-DCs mentioned above.

4.3. *"Impurity" Diffusion in Liquid Cu, Bi and Pb (Fig. 5)*

In order to check the model when describing diffusion at infinite dilution we compare calculated results with measurements on Ag, Sn, Sb, Au in liquid copper [13, 14] and on Cd, Tl, Sn and Sb in liquid Bi and Pb [20].

The data collected in Table 1 are interesting in many respects. The experimental results from the two sources differ by up to 30%. Since the shear-cell method [13] is experimentally superior to the capillary reservoir method [20, 13], the results of [13] are possibly more reliable. In any case it is questionable if the errors given in [20] (cf. Table 2) are really the total uncertainty. The calculated values of [13] and [14] on the basis of (18) agree

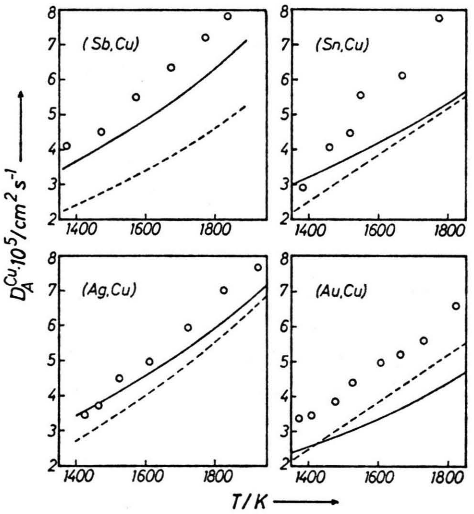

Fig. 5. Impurity diffusion coefficients $D_{\mathrm{A}}^{\mathrm{Cu}}$. Experimental: ○ ○ ○ [13]; Calculated by Eq. (18) - - - [13]; Calculated by Eq. (24) ——.

Table 1. "Impurity" diffusion coefficients $D_{\mathrm{A}}^{\mathrm{Cu}}$ at 1473 K in liquid copper.

	$D_{\mathrm{A}}^{\mathrm{Cu}} \cdot 10^5/\mathrm{cm}^2\,\mathrm{s}^{-1}$				
	Ref. [14]		Ref. [13]		this work
	Exp.	Eq. (18)	Exp.	Eq. (18)	Eq. (24)
(Ag, Cu)	3.32	3.32	3.70	3.15	3.80
(Sn, Cu)	4.27	3.11	4.10	3.00	3.50
(Sb, Cu)	3.06	2.69	4.48	2.75	4.10
(Au, Cu)	2.98	3.42	3.83	3.00	2.85

Table 2. "Impurity" diffusion in liquid bismuth D_A^{Bi} and in liquid lead D_A^{Pb}.

	$D_A^B \cdot 10^5/\mathrm{cm^2\,s^{-1}}$ B = Bi, Pb					
	673 K		973 K		1173 K	
	Ref. [20]	Eq. (24)	Ref. [20]	Eq. (24)	Ref. [20]	Eq. (24)
(Cd, Bi)	3.1 ± 0.9	3.26	14.1 ± 4.8	7.34	48.7 ± 1.9	11.5
(Tl, Bi)	3.3 ± 0.1	2.62	7.5 ± 1.2	5.90	13.7 ± 2.2	9.3
(Sn, Bi)	3.1 ± 0.1	3.31	7.4 ± 0.2	7.39	10.4 ± 1.3	11.6
(Sb, Bi)			9.3 ± 1.5	8.19	22.5 ± 0.9	13.0
(Cd, Pb)	2.3 ± 0.4	2.77	10.9 ± 1.2	6.09	36.7	9.4
(Tl, Pb)	2.4 ± 0.1	2.22	8.0 ± 0.6	4.89	18.7 ± 1.6	7.5
(Sn, Pb)	3.5 ± 0.5	2.81	8.1 ± 1.0	6.13	14.9 ± 1.4	9.4
(Sb, Pb)			8.9 ± 0.7	6.79	12.9 ± 0.6	10.6

within about 10% with one another, but the agreement with the experimental data is, in general, only moderately good. In contrast, the results of (24) are on the average substantially better. The same can be said about the T-dependence of D_A^{Cu} (Figure 5). With the exception of (Au, Cu), the curves based on (24) lie nearer to the empirical ones (but still below) than those of the authors [13] calculated with (18). In all cases the deviations between calculated and measured data increase with temperature; this is also to be seen in Table 2. Here, however, the deviations are so pronounced in the cases of D_{Cd}^{CdBi} and D_{Cd}^{CdPb} at 973 K and at 1173 K that the empirical values may be doubted. The high Cd vapour pressures could possibly have caused systematic errors.

4.4. *Component Self-diffusion and Mutual Diffusion in (Hg, Zn) (Fig. 6)*

Diffusion measurements* were performed in the small Zn solubility range in liquid Hg near room temperature. The calculated mutual and self-diffusion coefficients (from (24)) are by about 50% higher than the experimental values (cf. Figure 6). (24) predicts the linear change of D_{Hg}^{HgZn} with concentration, but it does not reproduce the curvature in D_{Zn}^{HgZn} and in $\tilde{D}$.

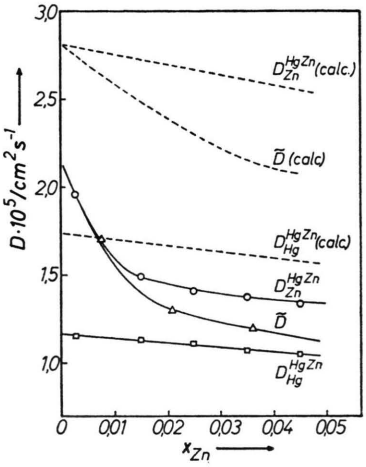

Fig. 6. Mutual ($\tilde{D}$) and component self-diffusion coefficients (D_{Zn}^{HgZn}, D_{Hg}^{HgZn}) in the system (Hg, Zn) at 30 °C [22]. Calculated by Eq. (24) ---.

The failure of (24) is not, in the case of Hg alloys, surprising. Because, as was stated earlier, the HS theory postulates rigid spherical particles with negligible attractive forces. These assumptions are not justified in the case of Hg and Ga [25]. Groups of atoms, either pairs or chains, are thought to be in dynamic equilibrium with atoms in their neighbourhood [26]. Thus, the special structure of Hg seems to be responsible for:

1. The self-DC of Hg being 50% lower than calculated in contrast to the observations with (Sn, Zn) (4.2.)
2. The self-diffusion of Zn being retarded by the Hg-Hg bonding which results in decreased strongly concentration dependent values of D_{Zn}^{ZnHg}, in contrast to the satisfactory results obtained for impurity diffusion in 4.3.

4.5. *Mutual Diffusion in Liquid (Li, Pb) and (Li, Ag) alloys (Fig. 7)*

It is obvious from thermodynamic measurements [27, 28], that there are extreme deviations from ideality in the (Li, Pb) system and less strong deviations in the (Li, Ag) system. These deviations are paralleled by structural anomalies [29]. One can therefore expect the diffusion in the two systems to show different degrees of divergence from HS dif-

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* The data of [22] are to be regarded as rather certain, because the limiting value D_{Zn}^{Hg} has been confirmed [23, 24].

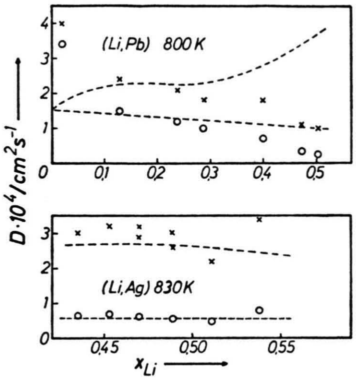

Fig. 7. Mutual ($\tilde{D}$) and reduced diffusion coefficients (D_r) in the system (Li, Pb) and (Li, Ag) [23]; $\tilde{D}$: × × × ; D_r ○ ○ ○. Calculated by Eq. (24) ---.

fusion. Indeed, in the (Li, Pb) system measured and calculated values behave contrarily (Fig. 7), the former falling from $D_{\mathrm{Li}}^{\mathrm{Pb}} = 4.5 \cdot 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ to $\tilde{D} = 1.0 \cdot 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, whereas the latter rise from $D_{\mathrm{Li}}^{\mathrm{Pb}} = 1.5 \cdot 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ to $\tilde{D} = 3.7 \cdot 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ at $x_{\mathrm{Li}} = 0.5$. In the (Li, Ag) system, however, the experimental points lie on the calculated curve. Though Darken's excess stability in (Li, Ag) exhibits a peak at $x_{\mathrm{Li}} \approx 0.5$ [23], which indicates association, an irregularity such as a minimum in the experimental D_r-curve has not been demonstrated, possibly since only a small composition range has been investigated. In the case of (Li, Pb) a salt like compound Li_4Pb formes [28]. The high mobility of Li^+-ions, created by charge transfer, may be responsible for the high value of $D_{\mathrm{Li}}^{\mathrm{Pb}}$, which is three times the calculated one. At higher concentrations, however, where Li^+ alone is not the only species responsible for transport, the compound formation may impede the diffusion, thus causing the experimental and theoretical curves to intersect and leading to a growing divergence of both curves.

5. Conclusion

For liquid alloys, in which no strong bonding occurs, the HS theory in the present elaboration permits the calculation of DCs and their temperature dependence in good agreement with experiment over the whole concentration range. The melting temperature of the components, their melting point density and the density of the alloys, are the only specific parameters of the alloy system which are needed. The use of the thermodynamic factor in the calculation of mutual DCs is not a part of the HS theory but the result of the conventional solution of the diffusion laws. Since the model even holds at moderate deviations from thermodynamic ideality, i.e. the system remains "ideal" in the sense of (24), it can be concluded that the thermodynamic mixing parameters, e.g. the activity coefficients, the thermodynamic factor, etc., are more sensitive to deviations from statistical particle distributions and specific interactions than diffusion data. From a theoretical stand point the success of the model proves that to a good approximation the special features of metals and alloys, e.g. the electronic structure, the geometrical order, the vibrational frequencies, etc., are included in the macroscopic parameters T_m and ϱ. A failure of the model indicates strong particularities of either one component, e.g. Hg, or the mixture, as discussed for (Li, Pb) alloys. The model should enable very useful predictions to be made for a great variety of alloy systems especially in the case of impurity diffusion, which plays an important part in metallurgy.

Acknowledgements

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[1] N. H. Nachtrieb, Ber. Bunsenges. **80**, 678 (1976).
[2] J. H. Dymond and B. J. Alder, J. Chem. Phys. **45**, 2061 (1966).
[3] F. Kohler, The Liquid State, Verlag Chemie, Weinheim 1972.
[4] S. Chapman and T. G. Cowling, Mathematical Theory of Non-Uniform Gases, Cambridge 1970.
[5] P. Ascarelli and A. Paskin, Phys. Rev. **165**, 222 (1968).
[6] P. Protopapas, H. C. Andersen, and N. A. D. Parlee, J. Chem. Phys. **59**, 15 (1973).
[7] C. J. Vadovic and C. P. Colver, Phil. Mag. **21**, 971 (1970).
[8] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).
[9] B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. **18**, 988 (1967).
[10] L. S. Darken, Trans. AIME **175**, 184 (1948).
[11] S. J. Bertucci and W. H. Flygare, J. Chem. Phys. **63**, 1 (1975).
[12] P. Protopapas and N. A. D. Parlee, Chem. Phys. **11**, 201 (1975).
[13] A. Bruson and M. Gerl, Phys. Rev. B **19**, 6123 (1979).
[14] T. Ejima, T. Yamamura, N. Uchida, S. Takano, and T. Honda, J. Japan. Inst. Met. **41**, 1041 (1977) and J. Japan. Inst. Met. **42**, 453 (1978).

[15] J. D. van der Waals, Z. Physik. Chem. **5**, 133 (1890).

[16] J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, Regular and Related Solutions, van Nostrand Reinhold Comp., New York 1970.

[17] Landolt-Börnstein, Eigenschaften der Materie in ihren Aggregatzuständen, 2. Bd., 1. Teil, Mech. therm. Zustandsgrößen, Springer-Verlag, Berlin 1971.

[18] K. Niwa, M. Shimoji, S. Kado, Y. Watanabe, and T. Yokokawa, J. Metals, Trans. AIME **209**, 96 (1957).

[19] C. H. Buell and F. O. Shuck, Metall. Trans. **1**, 1875 (1970).

[20] G. I. Onoprienko, P. P. Kuzmenko, and E. I. Kharkov, Ukr. Fiz. Zh. **12**, 39 (1967).

[21] W. Pippel and W. Lange, Z. Phys. Chem. **238**, 239 (1968); **239**, 104 (1969).

[22] H. W. Schadler and R. F. Grace, Trans. AIME **215**, 559 (1959).

[23] W. Becker, Dissertation, Saarbrücken **1979.**

[24] G. Langen, Diplomarbeit, Saarbrücken **1979.**

[25] V. G. Leak and R. A. Swalin, Trans. AIME **230**, 426 (1964).

[26] V. G. Rivlin, R. M. Waghorne, and G. I. Williams, Phil. Mag. **13**, 1169 (1966).

[27] M. L. Saboungi, J. Marr, and M. Blander, J. Chem. Phys. **68**, 1375 (1978).

[28] W. Becker, G. Schwitzgebel, and H. Ruppersberg, Z. Metallkde. **72**, 186 (1981).

[29] K. Goebbels and H. Ruppersberg, The Properties of Liquid Metals, S. Takeuchi, ed. Taylor and Francis, London 1973.