Diffusion in Liquid Metals

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Mutual diffusion coefficients in dilute liquid metal solutions have been correlated by methods based upon absolute rate theory and the theory of corresponding states. Both correlations reproduce the experimental data to approximately ±25%, but the absolute rate theory method is simpler to use and is applicable to a larger number of systems.

In the past decade, there has been increasing interest and activity in the pyrometallurgical reprocessing of spent fuel from nuclear reactors (*7, 17*). Since these methods invariably involve processing the fuel as a liquid metal, knowledge of the transport properties of molten metals is required for rational prediction of transfer rates.

The purpose of this study is to discuss two techniques for correlating diffusion coefficients in liquid metals. The first, a modification of Eyring's absolute rate theory (*4, 18*) due to Olander (*12*), has been developed for correlating mutual diffusion data in dilute binary organic systems. The second is an application of the principle of corresponding states, which was applied to liquified rare gases and some organics by Thomaes and Itterbeek (*21*).

Self diffusion and mutual diffusion in both organic liquids and molten metals have often been correlated by the Stokes-Einstein equation (*3, 11*):

$$\frac{D\mu}{kT} = \frac{1}{4\pi a} \quad \text{or} \quad \frac{1}{6\pi a} \tag{1}$$

The choice of the constant 4 or 6 in Equation (1) depends on taking this hydrodynamic model so seriously as to imagine that either a slip or no-slip condition prevails as the solute sphere moves through a continuous fluid. The Stokes-Einstein equation gives a correct order of magnitude ($D \sim 10^{-5}$ sq.cm./sec.) if a reasonable choice is made for the radius of the diffusing solute atom. For liquid metals it has been found that the ionic rather than the atomic radius of the solute atom is more appropriate.

ABSOLUTE RATE THEORY

Li and Chang (*8*) have developed an equation for self diffusion based upon the lattice structure of the liquid state. They obtained the equation

$$\frac{D\mu}{kT} = \frac{\sigma - \tau}{2\sigma}\left(\frac{N}{V}\right)^{1/3} \tag{2}$$

The data examined by Li and Chang suggested values of about 6 for $\frac{kT}{D\mu}\left(\frac{N}{V}\right)^{1/3}$. It was concluded that most liquids have approximately a cubic packing structure, for which $\tau = 4$ and $\sigma = 6$. The single point for self diffusion in lead gave a value of 3.8 for the same group, leading to the conclusion that liquid metals have a structure for which $\sigma = 12$ and $\tau = 6$. With these values of σ and τ, Equation (2) becomes

$$\left(\frac{D\mu}{T}\right)\left(\frac{4}{k}\right)\left(\frac{V}{N}\right)^{1/3} = 1 \tag{3}$$

In the modified form of absolute rate theory, mutual diffusion data in dilute organic systems were correlated by (*12*)

$$Y = \left(\frac{D\mu}{T}\right)\left(\frac{\xi}{k}\right)\left(\frac{V}{N}\right)^{1/3} = \exp\left\{\frac{\Delta F_\mu^* - \Delta F_D^*}{RT}\right\} \tag{4}$$

The exponential on the right-hand side of Equation (4) represents the difference between the free energies of activation of the viscous and diffusive processes. An empirically determined value of $\xi = 5.6$ was used in connection with Equation (4) for organic systems, but this figure need not apply to liquid metals. Equation (3), for example, suggests a value of $\xi = 4$.

For self diffusion $\Delta F_\mu^* - \Delta F_D^*$, and Equation (4) becomes

$$Y = \left(\frac{D\mu}{T}\right)\left(\frac{\xi}{k}\right)\left(\frac{V}{N}\right)^{1/3} = 1 \tag{5}$$

Walls and Upthegrove (*22*) have analyzed self diffusion in liquid metals by absolute rate theory and obtained the expression

$$D = \frac{kT\gamma^{-1/3}}{2\pi hb(2b+1)}\left(\frac{V}{N}\right)^{2/3}\exp\left\{\frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}\right\} \tag{6}$$

The entropy and enthalpy of activation are obtained from viscosity data by the expression (*4*)

$$\mu = \frac{Nh}{V}\exp\left\{-\frac{\Delta S^*}{R} + \frac{\Delta H^*}{RT}\right\} \tag{7}$$

Equations (6) and (7) can be combined and put in the form of Equation (5), in which case ξ is specified as

$$\xi = 2\pi b\,(2b+1)\,\gamma^{1/3} \tag{8}$$

Although the parameter b has a theoretical interpretation as the ratio of the atomic diameter to the interatomic distance, Walls and Upthegrove used the value of 0.419 obtained by comparing Equation (6) with self-diffusion data for mercury. The same value of b was used for other metals. Introducing $b = 0.419$ and the configurational constant $\gamma = 4/3$, Equation (8) yields a value of $\xi = 5.31$, which is quite close to the value of 5.6 determined empirically from diffusivity data in organic liquids.

In applying Equation (4) to mutual diffusion, the exponential term has been approximated by (*12*)

$$\Delta F_\mu^* - \Delta F_D^* = RTf\delta \tag{9}$$

where

$$\delta = \left(\frac{\Delta F^*_{AA}}{RT}\right)\left[1 - \left(\frac{\Delta F^*_{BB}}{\Delta F^*_{AA}}\right)^{1/2}\right] \tag{10}$$

The parameter f is the fraction of the total free energy of activation attributed to the "jump" of a molecule from one site to another. The subscripts AA and BB refer to

solvent-solvent and solute-solute interactions, respectively.

With the value of $\xi = 5.31$ from Walls and Upthegrove's study of liquid metal self diffusivities, Equation (4) becomes

$$Y = \left(\frac{D\mu}{T}\right)\left(\frac{5.31}{k}\right)\left(\frac{V}{N}\right)^{1/3} = e^{f\delta} \qquad (11)$$

According to Equation (7) the enthalpy and entropy of activation of a pure component can be obtained from the intercept and slope of an Arrhenius plot of the viscosity against temperature. The free energy of activation is then determined by

$$\Delta F^* = \Delta H^* - T\Delta S^* \qquad (12)$$

Many diffusion measurements on molten metal systems have been performed below the melting point of the pure solute. Cavalier (*1*) has measured the viscosities of many liquid metals in the supercooled liquid state and found that the data above and below the melting point fell on the same Arrhenius line. Thus, values of ΔH^* and ΔS^* obtained for pure solute metals above their melting points probably can be safely used at temperatures below the melting point where the diffusion experiments were conducted.

A summary of data for mutual diffusion in dilute liquid metal systems for which viscosity data are available for both the pure solute and solvent is presented in reference *14*. Calculated values of the entropies and enthalpies of activation and the parameters Y and δ are also tabulated. The measurements covered temperatures from 25° to 1,680°C.

Figure 1 is a plot of the data according to Equation (11). The best line through the points as determined by the method of averages (*14*) has a slope of 0.5, which is identical to that observed for organic liquids (*12*). The fact that the line passes through $\delta = 0$ at $Y = 1.1$ instead of $y = 1.0$ suggests that the constant $\xi = 5.31$ is somewhat large. A value of 4.8 would have brought the line through the origin. This behavior is also similar to that observed for organic liquids.

The dashed line in Figure 1 represents 25% deviation from the best line. The scatter here is greater than in the corresponding plot for organic liquids, which in part reflects the accuracy of the measured diffusion coefficients. Diffusivity measurements are considerably more difficult in molten metals at elevated temperatures than in organic liquids at room temperature.

Recently Swalin and Leak (*20*) have compared the predictions of the fluctuation model and the hole theory with the measured ratios of the diffusivities of various solutes in silver to the self-diffusion coefficient in liquid silver. The solute-solvent interaction was attributed to the additional Coulomb repulsion energy due to the difference in valence between the two species, which was computed from the Thomas-Fermi potential. Their treatment of the hole theory is of particular interest, since this model also forms the basis of the correlation presented here. In both cases the ratio of the mutual to self-diffusion coefficients is an exponential function of an interaction parameter; in the Swalin and Leak analysis this parameter is the Coulomb energy mentioned above, in which the only solute property which enters is the ionic valence. In the present analyses the interaction parameter is $\frac{1}{2}\delta$, which depends upon the molar volume and viscosity of the pure solute. The comparison of theory and experiment given by Swalin and Leak has been extended to include the predictions of the present analysis, and the results are shown in Table 1.

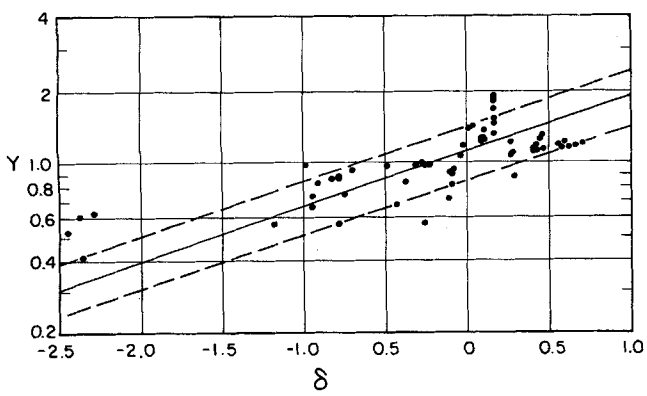

Fig. 1. Correlation of mutual diffusion coefficients by the absolute rate theory method.

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL MUTUAL TO SELF-DIFFUSION COEFFICIENT RATIOS FOR VARIOUS SOLUTES IN SILVER AT 1,200°C. EXPERIMENTAL DATA, FLUCTUATION MODEL, AND HOLE THEORY FIGURES ARE FROM REFERENCE *20*

	D_{AB}/D_{AA}			
Solute in Silver	Exp	Fluctuation model	Hole theory	Present analysis
Indium	1.36	1.12	1.42	1.36
Tin	1.39	1.16	1.59	1.26
Antimony	1.49	1.33	1.73	1.24

The average deviation of the fluctuation model from the measured ratios is 15%; for the hole theory as treated by Swalin and Leak, the deviation is 11%; for the present analysis, the average deviation is 9%. The hole theory, in conjunction with the Thomas-Fermi potential, reproduces the few data in Table 1 nearly as well as does the proposed correlation. However, wide application of the Swalin and Leak method is limited by the need for parameters such as the screening constants, which may not be readily available for many metals.

CORRESPONDING STATES THEORY

Thomaes and Itterbeek (*21*) and Rice and co-workers (*6, 10*) have attempted to establish a theorem of corresponding states for the diffusion coefficient and viscosity of pure liquids and solutions. Reduced viscosity or diffusivity of similar substances should be universal functions of reduced temperature and pressure if the molecules are simple (monatomic or spherical) and if the potential energy of interaction can be represented by a universal two-parameter function of the type

$$\Phi(r) = \epsilon^* F(r/r^*) \qquad (13)$$

ϵ^* and r^* are the energy and distance coordinates of the function minimum. These parameters and the mass m completely characterize the molecular species.

The reduced diffusivity is given by

$$\tilde{D} = D/\kappa \qquad (14)$$

where

$$\kappa = \epsilon^{*1/2}\, r^*/m^{1/2} \qquad (15)$$

If a theorem of corresponding states is valid for the substances under consideration

$$\tilde{D} = \tilde{D}(\tilde{p}, \tilde{V}, \tilde{T}) \qquad (16)$$

where

$$\tilde{p} = pr^{*3}/\epsilon^* \qquad (17)$$

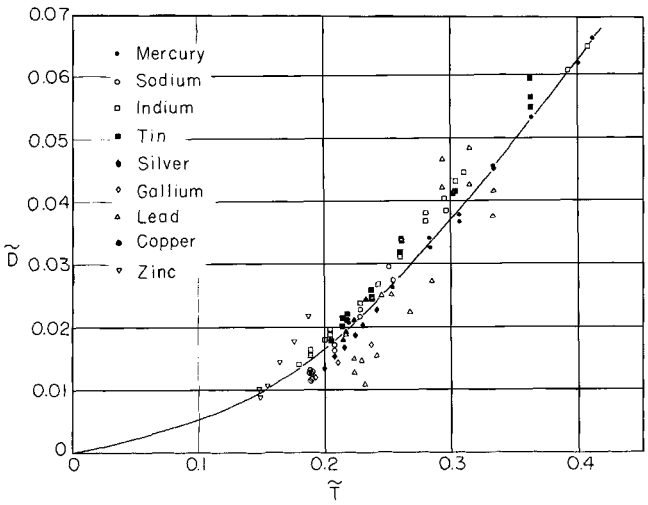

Fig. 2. Generalized plot for liquid metal self diffusion according to corresponding states theory.

$$\tilde{V} = V/Nr^{*3} \tag{18}$$

$$\tilde{T} = kT/\epsilon^* \tag{19}$$

By use of a universal equation of state, the three variables in Equation (16) can be reduced to two, for example, $\tilde{p}$ and $\tilde{T}$. Furthermore, one would expect that for liquid metals ϵ^* would be large and $\tilde{p}$ very small. The effect of pressure on the diffusivity would be slight. Petit and Nachtrieb (*15*) found the self diffusivity of gallium decreased by only 20% as the pressure was increased from 1 to 10,000 atm. Hence, it should be possible to consider the reduced self diffusivity as a function of reduced temperature only:

$$\tilde{D} = \tilde{D}(\tilde{T}) \tag{20}$$

The reduced diffusivity and temperature depend upon the interaction parameters ϵ^* and r^* for the liquid metals. Recently Chapman correlated viscosity data for twenty-one liquid metals by a corresponding states approach (*2*). The functional relation developed was

$$\tilde{\mu}\tilde{V}^2 = f(1/\tilde{T}) \tag{21}$$

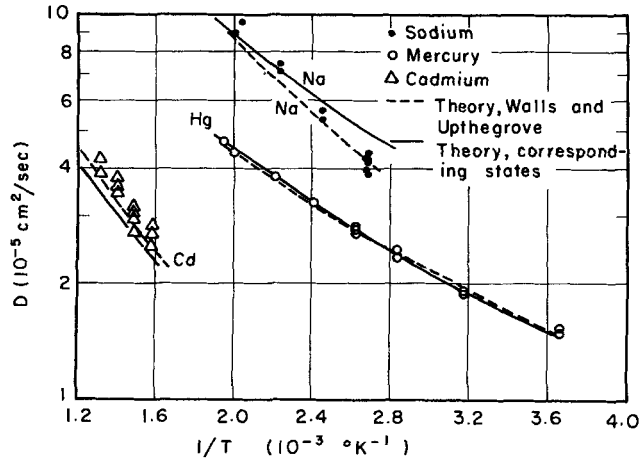

Fig. 3. Comparison of correlations and experiment for self diffusion in liquid mercury, sodium, and cadmium.

where the reduced viscosity is

$$\tilde{\mu} = \frac{\mu}{\tilde{T}^{1/2}}\left[\frac{r^{*2}}{(m\epsilon^*)^{1/2}}\right] \tag{22}$$

To establish the function of the right-hand side of Equation (21), Chapman used for ϵ^* the effective Lennard-Jones parameters for liquid sodium and potassium as determined from experimental x-ray scattering data. Goldschmidt atomic diameters were used for r^*. The viscosity data for sodium and potassium were reduced as indicated by Equation (22) and plotted according to Equation (21). The resulting curve was used to establish the energy parameters for the other liquid metals, which were found to be a linear function of the melting point.

To test Equation (20) the reduced self diffusivities of nine liquid metals have been computed with Chapman's values for the energy parameter and the Goldschmidt atomic diameters for r^*. The dependence of $\tilde{D}$ on $\tilde{T}$ is shown in Figure 2, where the best line has been drawn through the points for mercury.†

Figures 3, 4, and 5 compare the self diffusivities calculated from the line of Figure 2 with the data and with the theory of Walls and Upthegrove. While the latter method is somewhat better (except for silver and copper), the agreement between the data and the method based upon Figure 2 suggests that self diffusion in liquid metals can be adequately described by a corresponding states theorem.

Thomaes and Itterbeek developed the following expression relating the mutual diffusivities in two binary systems with a common solvent A (*21*):

$$D_{BA}\left(T\frac{\epsilon^*_B}{\epsilon^*_C}\right) = D_{CA}(T)\left(\frac{\epsilon^*_B}{\epsilon^*_C}\right)^{1/2}\left(\frac{r^*_B}{r^*_C}\right)\left(\frac{m_C}{m_B}\right)^{1/2} \tag{23}$$

ϵ^*_B and ϵ^*_C are effective interaction parameters of solutes B and C in the $B - A$ and $C - A$ mixtures, respectively. Since both solute-solvent and solute-solute interactions are involved, ϵ^*_B and ϵ^*_C are functions of composition. The diffusion coefficient in the $B - A$ system at a temperature $T\epsilon^*_B/\epsilon^*_C$ is determined by the diffusivity in the $C - A$ system at temperature T and the ratios of the interaction parameters and the masses. Instead of the arbitrary reference system $C - A$, the pure solvent (system $A - A$) will be used. The interaction parameters of the reference system become the pure component parameters of the solvent. Furthermore, if the $B - A$ system is very dilute in B, interactions of B atoms with each other are unimportant and only $B - A$ interactions need be considered (*16*):

$$\epsilon^*_B = \epsilon^*_{AB} \qquad r^*_B = r^*_{AB} \tag{24}$$

Equation (23) simplifies to

$$D_{BA}\left(T\frac{\epsilon^*_{AB}}{\epsilon^*_{AA}}\right) = D_{AA}(T)\left(\frac{\epsilon^*_{AB}}{\epsilon^*_{AA}}\right)^{1/2}\left(\frac{r^*_{AB}}{r^*_{AA}}\right)\left(\frac{m_A}{m_B}\right)^{1/2} \tag{25}$$

The distance parameter r^*_{AB} is taken as the arithmetic average of the pure component values:

$$r^*_{AB} = \frac{1}{2}(r^*_{AA} + r^*_{BB}) \tag{26}$$

There remains only the energy interaction parameter to be estimated. Equation (25) will be applied to experi-

† Data references and additional calculational details can be found in reference *14*.

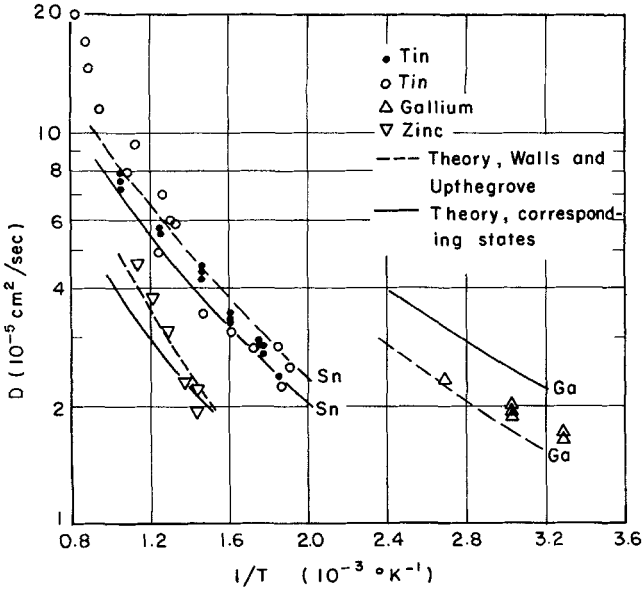

Fig. 4. Comparison of correlations and experiment for self diffusion in tin, gallium, and zinc.

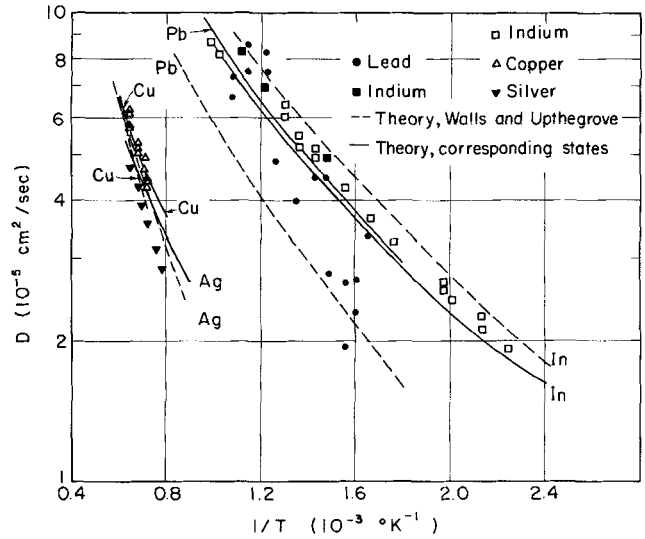

Fig. 5. Comparison of correlations and experiment for self diffusion in liquid lead, indium, copper, and silver.

mental self- and mutual diffusion measurements to compute ϵ^*_{AB}. These experimental values will then be compared with several methods of predicting ϵ^*_{AB} from thermodynamic or transport property data. Solving Equation (25) for $D_{AA}(T)$

$$D_{AA}(T) = D_{BA}\left(T\frac{\epsilon^*_{AB}}{\epsilon^*_{AA}}\right)\left(\frac{m_B}{m_A}\right)^{1/2}\left(\frac{\epsilon^*_{AA}}{\epsilon^*_{AB}}\right)^{1/2}\left(\frac{r^*_{AA}}{r^*_{BB}}\right) \quad (27)$$

Beginning with the experimental mutual diffusivity at a temperature $T\epsilon^*_{AB}/\epsilon^*_{AA}$, a trial value of $\epsilon^*_{AB}/\epsilon^*_{AA}$ is assumed and divided into the experimental temperature to give T. Then $D_{AA}(T)$ is obtained from the experimental curve of the self-diffusion coefficient vs. temperature. $D_{AA}(T)$ is also computed from Equation (27) by using the assumed value of $\epsilon^*_{AB}/\epsilon^*_{AA}$. When the two values of $D_{AA}(T)$ match, the correct $\epsilon^*_{AB}/\epsilon^*_{AA}$ has been chosen. The energy parameter ratios determined in this manner for seven binary liquid metal systems are essentially temperature independent in the experimental range.

The most common method for obtaining the binary interaction parameters is to take the geometric mean of the pure component values:

$$\epsilon^*_{AB} = (\epsilon^*_{AA}\ \epsilon^*_{AB})^{1/2} \quad (28)$$

Table 2. Comparison of Experimental and Calculated Interaction Parameter Ratios

	$\epsilon^*_{AB}/\epsilon^*_{AA}$			
		Calculated		
System	Experimental	(Oriani) Equation (29)	(Shimoji) Equation (30)	Equation (28)
Sn in Pb	1.231	1.306	1.263	0.974
Bi in Pb	0.922	1.009	1.005	0.872
Sb in Pb	1.160	1.157	1.131	1.158
Cd in Pb	1.108	0.834	0.758	1.087
Bi in Sn	0.954	0.921	0.830	0.898
Sb in Sn	0.970	0.902	0.912	1.190
Pb in In	0.946	0.959	0.902	1.030
Avg. deviation	—	0.079	0.103	0.097

This approach has been utilized in deriving Equation (10) in the absolute rate theory method.

A sounder approach to estimate ϵ^*_{AB} is to account explicitly for solute-solvent interactions by a thermodynamic quantity which directly reflects this interaction. Ma and Swalin (9) have noted that a correspondence exists between the partial molar heats of solution and mutual diffusion coefficients of various solute metals in tin. Since the corresponding states approach to mutual diffusion expresses the solute-solvent interaction by the force constant ϵ^*_{AB}, a link between this quantity and the heat of solution is required.

Oriani (13) and Shimoji (19) have extended the cell model theories of Prigogine to the prediction of excess thermodynamic properties of metallic solutions. From these studies it is possible to extract the binary interaction parameters from the thermodynamic data on liquid alloys. In particular, the partial molar heats of solution at infinite dilution are given by

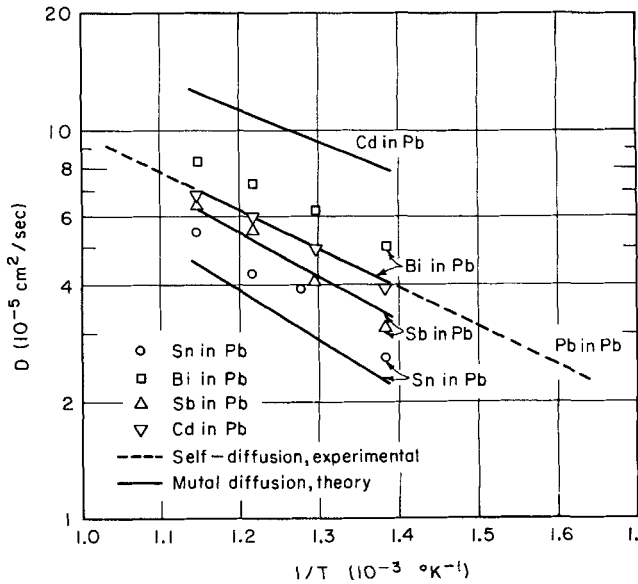

Fig. 6. Comparison of corresponding states theory with mutual diffusion data for bismuth, cadmium, antimony, and tin in lead.

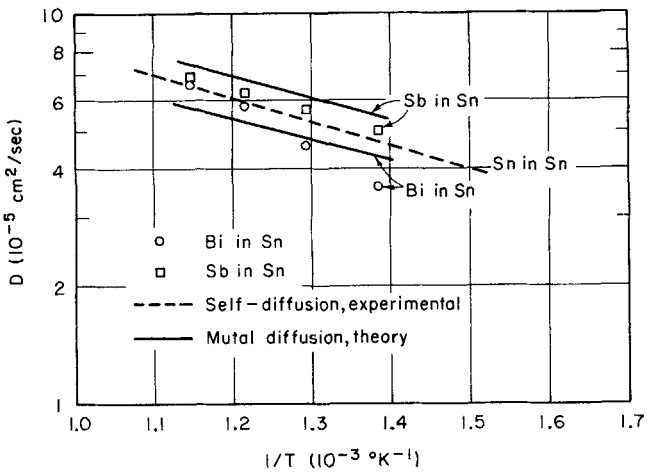

Fig. 7. Comparison of corresponding states theory with mutual diffusion data for antimony and bismuth in tin.

Oriani:

$$\overline{\Delta H}_B = 1.435\ N\ Z\ \epsilon^*_{AA}\ (-\theta + 4.50\rho^2) \qquad (29)$$

Shimoji:

$$\overline{\Delta H}_B = N\ Z\ \epsilon^*_{AA}\ (-\theta + 0.5\rho^2) \qquad (30)$$

where

$$\theta = (\epsilon^*_{AB} - 0.5\epsilon^*_{AA} - 0.5\epsilon^*_{BB})/\epsilon^*_{AA} \qquad (31)$$

$$\rho = (r^*_{BB}/r^*_{AA}) - 1 \qquad (32)$$

The pure component parameters are calculated from the heat of vaporization:

$$\Delta H_V = \frac{1}{2} N\ Z\ \epsilon^* \qquad (33)$$

Z is the coordination number, usually taken as 12.

Table 2 compares the average values of the energy parameter ratio obtained from diffusivity data with those calculated from Equations (29) and (30). The last column of Table 2 lists values of $\epsilon^*_{AB}/\epsilon^*_{AA}$ calculated from Equation (28) and Chapman's viscosity-based pure component parameters. Significant deviations from the experimental ratios have been underlined, and the average deviation of each method is shown. For the seven systems examined, the best agreement is obtained from Oriani's

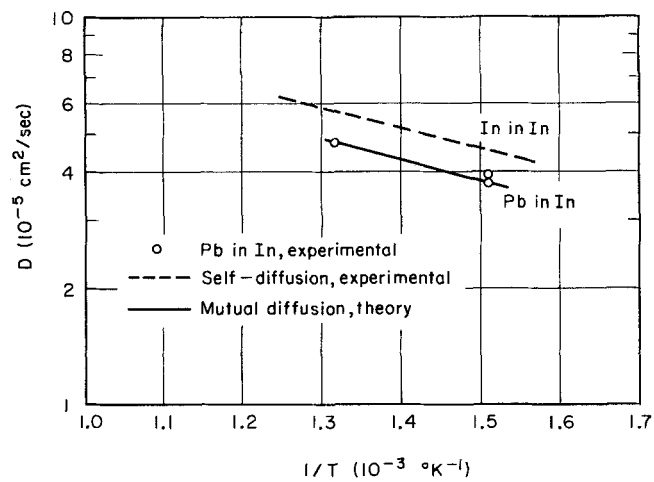

Fig. 8. Comparison of corresponding states theory with mutual diffusion data for lead in indium.

TABLE 3. CALCULATION OF MUTUAL DIFFUSION COEFFICIENTS IN DILUTE LIQUID METALS SYSTEMS WITH THE GENERALIZED CORRELATION OF FIGURE 2

System	ϵ^*_{AB}/k, °K.	κ_{AB}, 10^{-5}	T, °K.	$\tilde{T}$	$\tilde{D}$	D_{calc} 10^{-5} sq. cm./sec.	D_{exp} 10^{-5} sq. cm./sec.
Sn in Bi	2,900	154	723	0.249	0.0264	4.1	5.5
			773	0.266	0.0302	4.6	6.5
			823	0.284	0.0342	5.3	7.3
			873	0.301	0.0382	5.9	8.2
Sn in Pb	3,660	169	723	0.197	0.0164	2.8	2.6
			783	0.214	0.0194	3.3	3.9
			823	0.275	0.0215	3.6	4.3
			873	0.239	0.0244	4.1	5.5
Bi in Pb	2,820	120	723	0.256	0.0280	3.3	5.0
			773	0.274	0.0320	3.8	6.2
			823	0.292	0.0361	4.3	7.3
			873	0.310	0.0405	4.9	8.3
Sb in Pb	3,240	158	723	0.223	0.0211	3.3	3.1
			773	0.238	0.0241	3.8	4.1
			823	0.254	0.0275	4.3	5.5
			873	0.269	0.0309	4.9	6.4
Cd in Pb	2,330	136	723	0.310	0.0405	5.5	3.9
			773	0.332	0.0460	6.3	5.0
			823	0.353	0.0515	7.0	6.0
			873	0.375	0.0571	7.8	6.8
Bi in Sn	2,440	106	723	0.296	0.0370	3.9	3.6
			773	0.317	0.0422	4.5	4.6
			823	0.337	0.0474	5.0	5.8
			873	0.358	0.0528	5.6	6.6
Sb in Sn	2,390	129	723	0.302	0.0385	5.0	5.0
			773	0.323	0.0437	5.6	5.7
			823	0.344	0.0492	6.4	6.3
			873	0.365	0.0546	7.0	6.9
Pb in In	2,400	103	661	0.276	0.0325	3.3	3.8
			760	0.317	0.0422	4.3	4.7

Equation (29) with pure component energies from the heat of vaporization.

Figures 6, 7, and 8 compare the experimental mutual diffusivity data with those calculated with Equation (25) and measured self-diffusion coefficients. Goldschmidt atomic diameters were used in calculating r^*_{AB} from Equation (26) and the energy parameter ratios were taken from column 3 of Table 2. The agreement between theory and experiment is satisfactory in all cases except for cadmium in lead. For the three other solutes in lead, the theory predicts the correct relative size of the diffusion coefficient, that is, $D_{Bi} > D_{Sb} > D_{Sn}$.

An alternative procedure which is useful when the self diffusivity of the solvent is not available is to employ the calculated ϵ^*_{AB} in conjunction with the general correlation of Figure 2. The ratio of the interaction parameters, $\epsilon^*_{AB}/\epsilon^*_{AA}$, is calculated from Equation (29) as described earlier. However, since the generalized plot of Figure 2 is based on Chapman's viscosity values of ϵ^*_{AA}, the interaction parameter ϵ^*_{AB} is obtained by multiplying the ratio $\epsilon^*_{AB}/\epsilon^*_{AA}$ by the viscosity value of ϵ^*_{AA}, and not the value derived from the heat of vaporization. The reducing factor for diffusion is computed from Equation (15) and the reduced temperature from Equation (19). The value of $\tilde{D}$ corresponding to $\tilde{T}$ is taken from Figure 2 and the diffusion coefficient from Equation (14). This method is compared with experimental measurements in Table 3.

The method utilizing the generalized correlation is about as accurate as that using self-diffusivity data as the reference system. The latter technique generally gives a better estimate of the temperature dependence of the mutual diffusion coefficient, but on the basis of the seven systems

compared here, there is little to choose between the two methods in terms of predicting absolute values of the diffusion coefficient. However, the method based on the generalized plot of Figure 2 has the decided advantage of not requiring self-diffusion data of the solvent.

COMPARISON OF ABSOLUTE RATE AND CORRESPONDING STATES THEORIES

The absolute rate and corresponding states theories can be compared for ease of use, amount of data required, and general accuracy. The absolute rate theory method requires only pure component viscosity and density data, which are available for many liquid metals. For those metals for which viscosity data are lacking, the correlations of Chapman (2) or Grosse (5) can be used.

The corresponding states method utilizing the generalized plot of Figure 2 requires viscosity data for the solvent to determine the parameter ϵ^*_{AA}. In the absence of viscosity data, ϵ^*_{AA} can be estimated from the melting point (2). If solvent self diffusivity is used in the reference system method, self-diffusion coefficients are required; such data are available for only nine liquid metals. Both of the methods based on the corresponding states approach require partial molal heat of mixing data, which may not be available for the binary alloy of interest. The method based on absolute rate theory, on the other hand, requires only pure component data. It is thus the simpler of the two methods and can be applied to more systems.

The accuracy of the absolute rate and corresponding states methods is about the same. Of the eight systems for which intercomparison of the two methods is possible, only the bismuth in lead system lies completely outside the 25% confidence limits of Figure 1. Each of the two corresponding states methods fails significantly for at least one system: the cadmium in lead pair when the reference system method is used and the bismuth in lead pair when the generalized correlation is employed.

On all counts the absolute rate method is preferable to the corresponding states method for estimating mutual diffusion coefficients in dilute liquid metal systems.

ACKNOWLEDGMENT

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NOTATION

a = radius of solute atom, cm.
b = factor in theory of Walls and Upthegrove
D_{AA} = self-diffusion coefficient of solvent, sq.cm./sec.
D_{BA} = mutual diffusion coefficient of solute B in solvent A, sq.cm./sec.
D = diffusion coefficient, sq.cm./sec.
f = factor in Equation (9)
ΔF^* = free energy of activation, cal.
h = Planck's constant, erg/sec.
ΔH^* = enthalpy of activation, cal.
$\overline{\Delta H}_B$ = partial molar heat of solution of B in A at infinite dilution, cal./mole
ΔH_V = heat of vaporization of pure component, cal./mole
k = Boltzmann constant, erg/°K.
m = molecular or atomic mass, g.
N = Avogadro number
p = pressure, dynes/sq.cm.
r = interatomic distance, cm.
r^* = position of minimum of interatomic potential energy curve, cm.
R = gas constant, cal./(mole) (°K.)
ΔS^* = entropy of activation, cal./°K.
T = temperature, °K.
V = molar volume, cc./mole
Y = defined by Equation (4)
Z = coordination number

Greek Letters

γ = configurational factor in theory of Walls and Upthegrove
δ = defined by Equation (10)
ϵ^* = minimum energy of interatomic potential curve, ergs
σ = structure factor in Equation (2)
τ = structure factor in Equation (2)
κ = reducing factor for diffusivity, Equation (15), sq. cm./sec.
θ = defined by Equation (31)
μ = viscosity, poises
ρ = defined by Equation (32)
ξ = structural factor in absolute rate theory method
$\Phi(r)$ = interatomic potential energy, ergs

Superscripts

A = solvent species
B, C = solute species
AA = interaction between solvent molecules
BB = interaction between solvent molecules
AB = solute-solvent interaction
μ = viscosity
D = diffusion

Subscript

$\sim$ = reduced parameter

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