

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

DIFFUSION IN LIQUID METALS

### Permalink

<https://escholarship.org/uc/item/6p6793vm>

### Authors

Pasternak, A.D.

Olander, D.R.

### Publication Date

1966-09-01

UGRL-17479

University of California

Ernest O. Lawrence  
Radiation Laboratory

DIFFUSION IN LIQUID METALS

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

Berkeley, California

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to:  
A.I.Ch.E. Journal

UCRL-17179

UNIVERSITY OF CALIFORNIA  
Lawrence Radiation Laboratory  
Berkeley, California  
AEC Contract No. W-7405-eng-48

DIFFUSION IN LIQUID METALS

A. D. Pasternak and D. R. Olander

September 1966

DIFFUSION IN LIQUID METALS

A. D. Pasternak and D. R. Olander

Inorganic Materials Research Division, Lawrence Radiation Laboratory,  
Department of Nuclear Engineering, College of Engineering,  
University of California, Berkeley, California

September 1966

ABSTRACT

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  $\pm 25\%$ , 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.<sup>(6,14)</sup> 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<sup>(3,15)</sup> due to Olander,<sup>(9)</sup> 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.<sup>(17)</sup>

Self-diffusion and mutual diffusion in both organic liquids and molten metals have often (but not very successfully) been correlated by the Stokes-Einstein equation:

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

The choice of the constant 4 or 6 in Eq. (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 ( $D \sim 10^{-5}$  cm<sup>2</sup>/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<sup>(7)</sup> have developed an equation for self diffusion based upon the lattice structure of the liquid state. They obtained the equation:

$$\frac{D_{\mu}}{kT} = \frac{\sigma - \tau}{2\sigma} \left( \frac{N_{Av}}{V} \right)^{1/3} \quad (2)$$

The data examined by Li and Chang suggested values of about 6 for  $\frac{kT}{D_{\mu}} \left( \frac{N_{Av}}{V} \right)^{1/3}$ . 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  $\sigma$  and  $\tau$ , Eq. (2) becomes:

$$\left( \frac{D_{\mu}}{T} \right) \left( \frac{4}{k} \right) \left( \frac{V}{N_{Av}} \right)^{1/3} = 1 \quad (3)$$

In the modified form of absolute rate theory, mutual diffusion data in dilute organic systems were correlated by:<sup>(9)</sup>

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

The exponential on the right hand side of Eq. (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 Eq. (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 Eq. (4) becomes:

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

Walls and Upthegrove<sup>(18)</sup> have analyzed self-diffusion in liquid metals by absolute rate theory and obtained the expression:

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

The entropy and enthalpy of activation are obtained from viscosity data by the expression:<sup>(3)</sup>

$$\mu = \frac{N_{Av} h}{V} \exp \left\{ - \frac{\Delta S^*}{R} + \frac{\Delta H^*}{RT} \right\} \quad (7)$$

Equations (6) and (7) can be combined and put in the form of Eq. (5), in which case  $\xi$  is specified as:

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

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 Eq. (6) with self-diffusivity data for mercury. The same value of  $b$  was used for other metals. Introducing  $b = 0.419$  and the configurational constant  $\gamma = 4/3$ , Eq. (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 Eq. (4) to mutual diffusion, the exponential term has been approximated by:<sup>(9)</sup>

$$\frac{\Delta F_{\mu}^*}{\mu} - \frac{\Delta F_D^*}{D} = RT\delta \quad (9)$$



where:

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

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.

Using the value of  $\xi = 5.31$  from Walls and Upthegrove's study of liquid metal self-diffusivities, Eq. (4) becomes:

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

According to Eq. (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:

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

Many diffusion measurements on molten metal systems have been performed below the melting point of the pure solute. Cavalier<sup>(1)</sup> 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  $\Delta H^*$  and  $\Delta S^*$  obtained for pure solute metals above their melting point can probably 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 ref. 11. Calculated values of the entropies and enthalpies of activation and the parameters  $\gamma$  and  $\delta$  are also tabulated. The measurements covered temperatures from 25°C to 1680°C.

Figure 1 is a plot of the data according to Eq. (11). The best line through the points as determined by the method of averages, has a slope of 0.5, which is identical to that observed for organic liquids.<sup>(9)</sup> The fact that the line passes through  $\delta = 0$  at  $\gamma = 1.1$  instead of  $\gamma = 1.0$  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 Fig. 1 represents 25% deviations 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.

#### Corresponding States Theory

Thomae and Itterbeek<sup>(17)</sup> and Rice and coworkers<sup>(5,8)</sup> 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:

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

$\epsilon^*$  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:

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

where:

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

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

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

where:

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

$$\tilde{V} = V/N_{Av} r^{*3} \quad (18)$$

$$\tilde{T} = kT/\epsilon^* \quad (19)$$

By use of a universal equation of state, the three variables in Eq. (16) can be reduced to two, e.g.,  $\tilde{p}$  and  $\tilde{T}$ . Furthermore, one would expect that for liquid metals,  $\epsilon^*$  would be large, and  $\tilde{p}$  very small. The effect of pressure on the diffusivity would be slight. Petit and Nachtrieb<sup>(12)</sup> found the self-diffusivity of gallium decreased by only 20% as the pressure was increased from one to 10,000 atm. Hence, it should be possible to consider the reduced self-diffusivity as a function of reduced temperature only:

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

The reduced diffusivity and temperature depend upon the interaction parameters  $\epsilon^*$  and  $r^*$  for the liquid metals. Recently, Chapman has correlated viscosity data for 21 liquid metals by a corresponding states approach.<sup>(2)</sup> The functional relation developed was:

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

where the reduced viscosity is:

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

In order to establish the function of the right of Eq. (21), Chapman used for  $\epsilon^*$  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 Eq. (22) and plotted according to Eq. (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.

In order to test Eq. (20), the reduced self-diffusivities of nine liquid metals have been computed using 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 Fig. 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 Fig. 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

\* Data references and additional calculational details can be found in ref. 11

upon Fig. 2 suggests that self-diffusion in liquid metals can be adequately described by a corresponding states theorem.

Thomae and Itterbeek developed the following expression relating the mutual diffusivities in two binary systems with a common solvent A:<sup>17</sup>

$$D_{BA} \left( \begin{array}{c} \epsilon_B^* \\ T \frac{\epsilon_B^*}{\epsilon_C^*} \\ \epsilon_C^* \end{array} \right) = D_{CA}(T) \left( \begin{array}{c} \epsilon_B^* \\ \frac{\epsilon_B^*}{\epsilon_C^*} \\ \epsilon_C^* \end{array} \right)^{1/2} \left( \begin{array}{c} r_B^* \\ \frac{r_B^*}{r_C^*} \\ r_C^* \end{array} \right) \left( \begin{array}{c} m_C \\ \frac{m_C}{m_B} \\ m_B \end{array} \right)^{1/2} \quad (23)$$

$\epsilon_B^*$  and  $\epsilon_C^*$  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,  $\epsilon_B^*$  and  $\epsilon_C^*$  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 referency 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:<sup>(13)</sup>

$$\epsilon_B^* = \epsilon_{AB}^* \quad r_B^* = r_{AB}^* \quad (24)$$

Equation (23) simplifies to:

$$D_{BA} \left( \begin{array}{c} \epsilon_{AB}^* \\ T \frac{\epsilon_{AB}^*}{\epsilon_{AA}^*} \\ \epsilon_{AA}^* \end{array} \right) = D_{AA}(T) \left( \begin{array}{c} \epsilon_{AB}^* \\ \frac{\epsilon_{AB}^*}{\epsilon_{AA}^*} \\ \epsilon_{AA}^* \end{array} \right)^{1/2} \left( \begin{array}{c} r_{AB}^* \\ \frac{r_{AB}^*}{r_{AA}^*} \\ r_{AA}^* \end{array} \right) \left( \begin{array}{c} m_A \\ \frac{m_A}{m_B} \\ m_B \end{array} \right)^{1/2} \quad (25)$$

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

$$r_{AB}^* = \frac{1}{2} (r_{AA}^* + r_{BB}^*) \quad (26)$$

There remains only to estimate the energy interaction parameter.

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

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

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 versus temperature.

$D_{AA}(T)$  is also computed from Eq. (27) 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 shown on Fig. 6. The ratios are essentially temperature independent in the experimental range.

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

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

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

Oriani<sup>(10)</sup> and Shimoji<sup>(16)</sup> 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:

$$\text{(Oriani)} \quad \overline{\Delta H}_B = 1.435 N_{AV} Z \epsilon_{AA}^* (-\theta + 4.50\rho^2) \quad (29)$$

$$\text{(Shimoji)} \quad \overline{\Delta H}_B = N_{AV} Z \epsilon_{AA}^* (-\theta + 0.5\rho^2) \quad (30)$$

Where:

$$\theta = (\epsilon_{AB}^* - 0.5\epsilon_{AA}^* - 0.5\epsilon_{BB}^*) / \epsilon_{AA}^* \quad (31)$$

$$\rho = (r_{BB}^* / r_{AA}^*) - 1 \quad (32)$$

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

$$\Delta H_V = \frac{1}{2} N_{AV} Z \epsilon^* \quad (33)$$

Z is the coordination number, usually taken as 12.

Table 1 compares the average values of the energy parameter ratio obtained from Fig. 6 with those calculated from Eqs. (29) and (30). The last column of Table 1 lists values of  $\epsilon_{AB}^* / \epsilon_{AA}^*$  calculated from Eq. (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 Eq. (29) with pure component energies from the heat of vaporization.

Table 1 Comparison of Experimental and Calculated Interaction Parameter Ratios

System	$\epsilon_{AB}^*/\epsilon_{AA}^*$			
	Experimental	Calculated		
		(Oriani) Eq. (29)	(Shimoji) Eq. (30)	Eq. (28)
Sn in Pb	1.231	1.306	1.263	.974
Bi in Pb	.922	1.009	1.005	.872
Sb in Pb	1.160	1.157	1.131	1.158
Cd in Pb	1.108	.834	.758	1.087
Bi in Sn	.954	.921	.830	.898
Sb in Sn	.970	.902	.912	1.190
Pb in In	.946	.959	.902	1.030
Avg. deviation	-	0.079	0.103	0.097

Figures 7, 8, and 9 compare the experimental mutual diffusivity data with those calculated using Eq. (25) and measured self-diffusion coefficients. Goldschmidt atomic diameters were used in calculating  $r_{AB}^*$  from Eq. (26) and the energy parameter ratios were taken from column 3 of Table 1. The agreement between theory and experiment is satisfactory in all cases except Cd in Pb. For the three other solutes in lead, the theory predicts the correct relative size of the diffusion coefficient, i.e.,  $D_{Bi} > D_{Sb} > D_{Sn}$ .

An alternative procedure which is useful when the self-diffusivity of the solvent is not available is to employ the calculated  $\epsilon_{AB}^*$  in conjunction with the general correlation of Fig. 2. The ratio of the



interaction parameters,  $\epsilon_{AB}^*/\epsilon_{AA}^*$ , is calculated from Eq. (29) as described earlier. However, since the generalized plot of Fig. 2 is based on Chapman's viscosity values of  $\epsilon_{AA}^*$ , the interaction parameter  $\epsilon_{AB}^*$  is obtained by multiplying the ratio  $\epsilon_{AB}^*/\epsilon_{AA}^*$  by the viscosity value of  $\epsilon_{AA}^*$ , and not the value derived from the heat of vaporization. The reducing factor for diffusion is computed from Eq. (15) and the reduced temperature from Eq. (19). The value of  $\tilde{D}$  corresponding to  $\tilde{T}$  is taken from Fig. 2 and the diffusion coefficient from Eq. (14). This method is compared with experimental measurements in Table 2.

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 Fig. 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<sup>(2)</sup> or Grosse<sup>(4)</sup> can be used.

Table 2. Calculation of Mutual Diffusion Coefficients in Dilute Liquid Metals Systems Using the Generalized Correlation of Fig. 2.

System	$\frac{\epsilon_{AB}^*}{k}$ ( $^{\circ}\text{K}$ )	$K_{AB}$ ( $10^{-5}$ )	T ( $^{\circ}\text{K}$ )	$\bar{T}$	$\bar{D}$	$D_{\text{cal'd}}$ ( $10^{-5} \text{ cm}^2/\text{sec}$ )	$D_{\text{expt'l}}$ ( $10^{-5} \text{ cm}^2/\text{sec}$ )
Sn in Bi	2900	154	723	.249	.0264	4.1	5.5
			773	.266	.0302	4.6	6.5
			823	.284	.0342	5.3	7.3
			873	.301	.0382	5.9	8.2
Sn in Pb	3660	169	723	.197	.0164	2.8	2.6
			783	.214	.0194	3.3	3.9
			823	.275	.0215	3.6	4.3
			873	.239	.0244	4.1	5.5
Bi in Pb	2820	120	723	.256	.0280	3.3	5.0
			773	.274	.0320	3.8	6.2
			823	.292	.0361	4.3	7.3
			873	.310	.0405	4.9	8.3
Sb in Pb	3240	158	723	.223	.0211	3.3	3.1
			773	.238	.0241	3.8	4.1
			823	.254	.0275	4.3	5.5
			873	.269	.0309	4.9	6.4
Cd in Pb	2330	136	723	.310	.0405	5.5	3.9
			773	.332	.0460	6.3	5.0
			823	.353	.0515	7.0	6.0
			873	.375	.0571	7.8	6.8
Bi in Sn	2440	106	723	.296	.0370	3.9	3.6
			773	.317	.0422	4.5	4.6
			823	.337	.0474	5.0	5.8
			873	.358	.0528	5.6	6.6
Sb in Sn	2390	129	723	.302	.0385	5.0	5.0
			773	.323	.0437	5.6	5.7
			823	.344	.0492	6.4	6.3
			873	.365	.0546	7.0	6.9
Pb in In	2400	103	661	.276	.0325	3.3	3.85
			760	.317	.0422	4.3	4.75

The corresponding states method utilizing the generalized plot of Fig. 2 requires viscosity data for the solvent to determine the parameter  $\epsilon_{AA}^*$ . In the absence of viscosity data,  $\epsilon_{AA}^*$  can be estimated from the melting point.<sup>(2)</sup> 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 inter-comparison of the two methods is possible, only the Bi in Pb system lies completely outside of the 25% confidence limits of Fig. 1. Each of the two corresponding states methods fails significantly for at least one system: the Cd in Pb pair when the reference system method is used and the Bi in Pb 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.

NOTATION

- a radius of solute atom, cm
- b factor in theory of Walls and Upthegrove
- $D_{AA}$  self-diffusion coefficient of solvent,  $\text{cm}^2/\text{sec}$
- $D_{BA}$  mutual diffusion coefficient of solute B in solvent A,  $\text{cm}^2/\text{sec}$
- D diffusion coefficient,  $\text{cm}^2/\text{sec}$
- f factor in Eq. (9)
- $\Delta F^*$  free energy of activation, cal
- h Planck's constant, erg-sec
- $\Delta H^*$  enthalpy of activation, cal
- $\overline{\Delta H}_B$  partial molar heat of solution of B in A at infinite dilution,  $\frac{\text{cal}}{\text{mol}}$
- $\Delta H_V$  heat of vaporization of pure component, cal/mol
- k Boltzmann constant, erg/ $^\circ\text{K}$
- m molecular or atomic mass, gms
- $N_{AV}$  Avogadro's number
- p pressure, dynes/ $\text{cm}^2$
- r interatomic distance, cm
- $r^*$  position of minimum of interatomic potential energy curve, cm
- R gas constant, cal/mol- $^\circ\text{K}$
- $\Delta S^*$  entropy of activation, cal/ $^\circ\text{K}$
- T temperature,  $^\circ\text{K}$
- V molar volume,  $\text{cm}^3/\text{mol}$
- Y defined by Eq. (4)
- Z coordination number

GREEK LETTERS

$\gamma$	configurational factor in theory of Walls and Upthegrove
$\delta$	defined by Eq. (10)
$\epsilon^*$	minimum energy of interatomic potential curve, ergs
$\sigma$	structure factor in Eq. (2)
$\tau$	structure factor in Eq. (2)
$\kappa$	reducing factor for diffusivity, Eq. (15), $\text{cm}^2/\text{sec}$
$\theta$	defined by Eq. (31)
$\mu$	viscosity, poises
$\rho$	defined by Eq. (32)
$\xi$	structural factor in absolute rate theory method
$\Phi(r)$	interatomic potential energy, ergs

Subscripts

A	solvent species
B,C	solute species
AA	interaction between solvent molecules
BB	interaction between solute molecules
AB	solute-solvent interaction
$\mu$	viscosity
D	diffusion

Superscripts

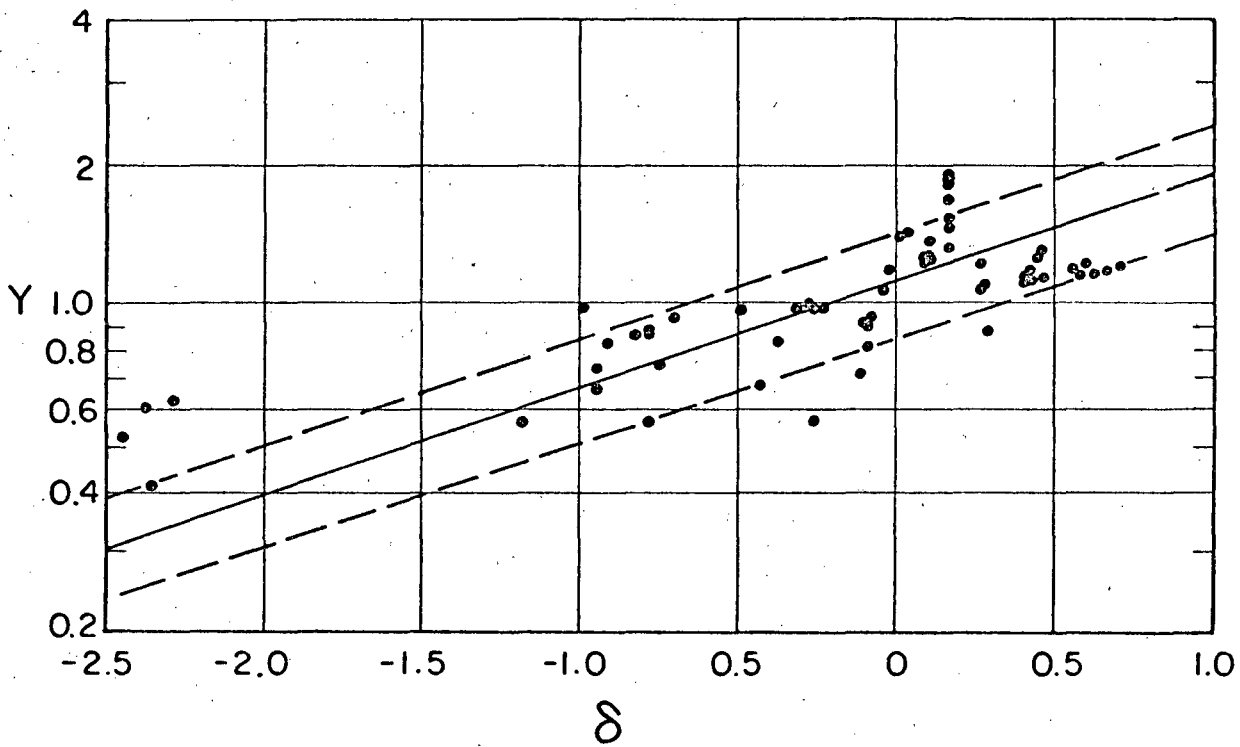
$\sim$	reduced parameter
--------	-------------------

LITERATURE CITATIONS

1. Cavalier, , in The Physical Chemistry of Metallic Solutions and Intermetallic Compounds, Symposium held at the National Physical Laboratory, Teddington, Middlesex, England, p. 54 (1960).
2. Chapman, T. W., AIChE Journal 12, 395 (1966).
3. Glasstone, S., K. J. Laidler, and Henry Eyring, The Theory of Rate Processes, McGraw-Hill, New York (1941).
4. Grosse, A. V., J. Inorg. and Nucl. Chem. 23, 33 (1961); ibid., 24, 317 (1962).
5. Helfand, E., and S. A. Rice, J. Chem. Phys. 32, 1642 (1960).
6. Lawroski, S., and L. Burris, Jr., Atomic Energy Rev. 2, 3 (1964).
7. Li, J. C., and P. Chang, J. Chem. Phys. 23, 518 (1955).
8. Naghizadeh, J. and S. A. Rice, J. Chem. Phys. 36, 2710 (1962).
9. Olander, D. R., J. AIChE, 9, 207 (1963).
10. Oriani, R. A., Acta Met. 4, 15 (1956).
11. Pasternak, A. S., USAEC Rept UCRL 16108 (1966).
12. Petit, J., and N. H. Nachtrieb, J. Chem. Phys. 24, 1027 (1956).
13. Prigogine, I., The Molecular Theory of Solutions, North Holland Publishing Co., Amsterdam, (1957) p. 185.
14. Price, R. D. and L. Burris, Jr., Reactor Technology, (1964) p. 411.
15. Ree, F. H., T. Ree and Henry Eyring, Ind. Eng. Chem. 50, 1036 (1958).
16. Shimoji, M. and K. Niwa, Acta Met. 5, 496 (1957).
17. Thomaes, G. and J. Van Itterbeek, J. Mol. Phys. 2, 372 (1959).
18. Walls, H. A. and W. R. Upthegrove, Acta Met. 12, 461 (1964).

FIGURE CAPTIONS

1. Correlation of mutual diffusion coefficients by the absolute rate theory method.
2. Generalized plot for liquid metal self-diffusion according to corresponding states theory.
3. Comparison of correlations and experiment for self-diffusion in liquid mercury, sodium, and cadmium.
4. Comparison of correlations and experiment for self-diffusion in tin, gallium, and zinc.
5. Comparison of correlations and experiment for self-diffusion in liquid lead, indium, copper, and silver.
6. "Experimental" values of the energy parameter ratio from diffusion data.
7. Comparison of corresponding states theory with mutual diffusion data for bismuth, cadmium, antimony and tin in lead.
8. Comparison of corresponding states theory with mutual diffusion data for antimony and bismuth in tin.
9. Comparison of corresponding states theory with mutual diffusion data for lead in indium.

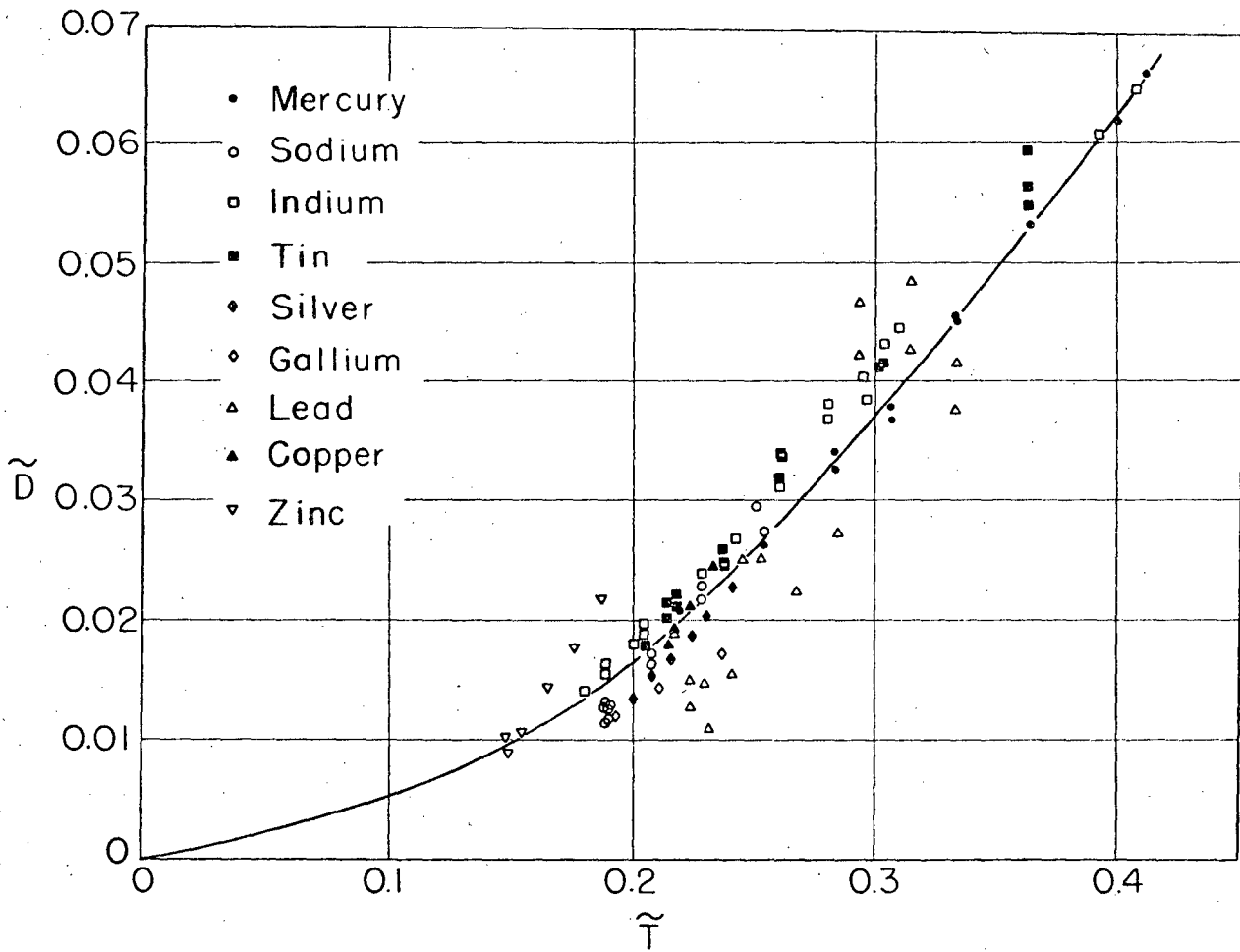


MU-36850

Fig. 1

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

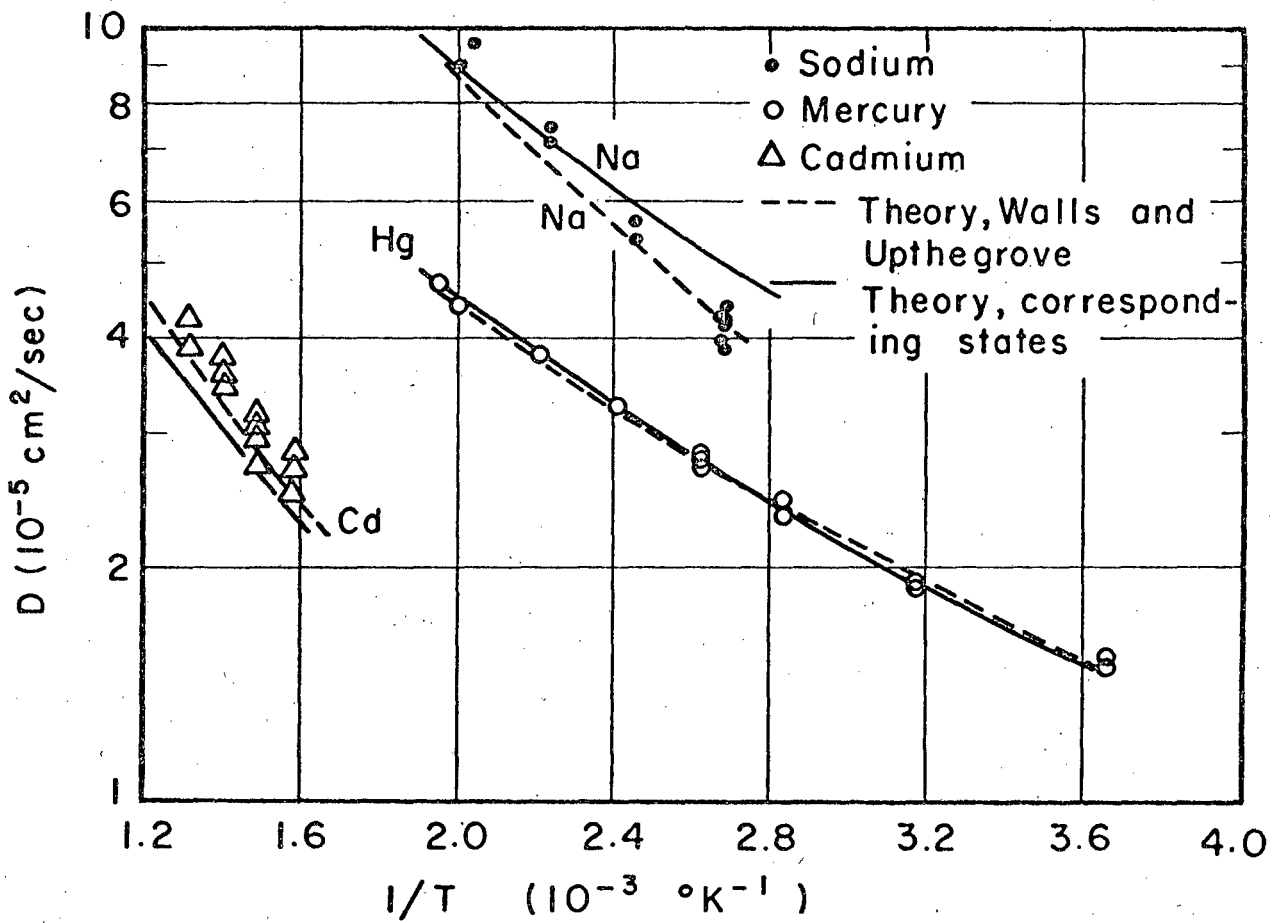




MU-36851

Fig. 2

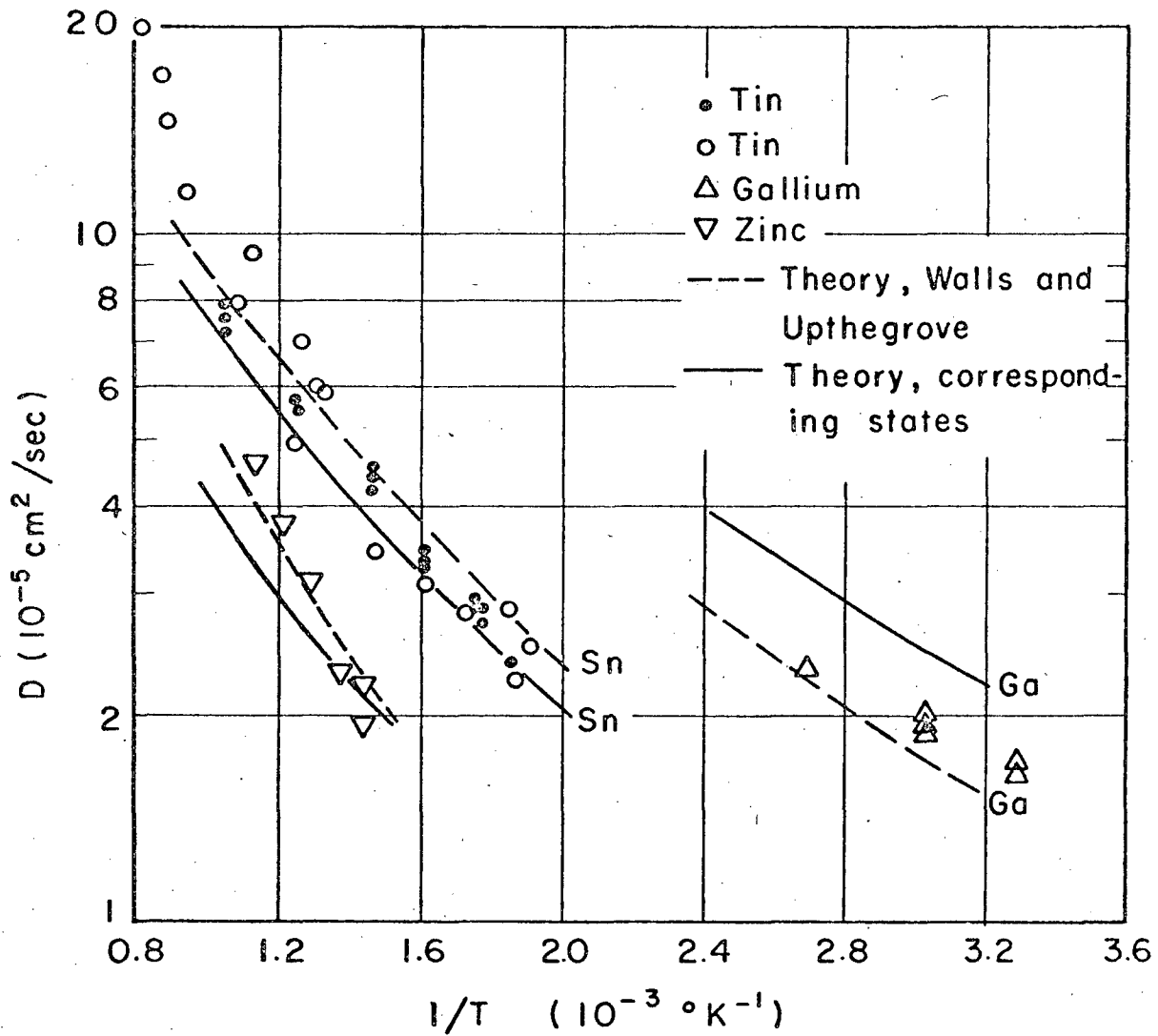
Generalized plot for liquid metal self-diffusion according to corresponding states theory.



MU-36853

Fig. 3

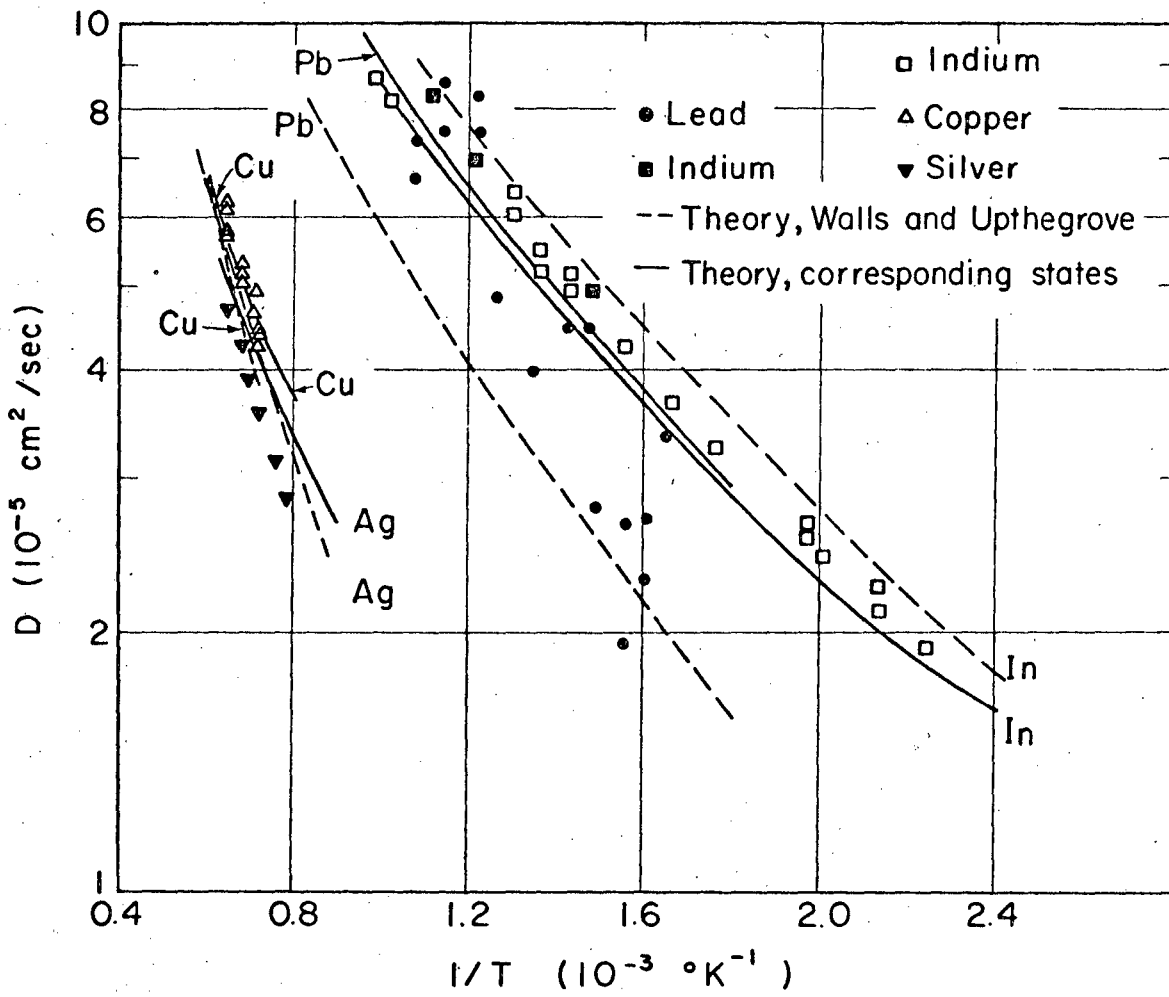
Comparison of correlations and experiment for self-diffusion in liquid mercury, sodium, and cadmium.



MU-36852

Fig. 4

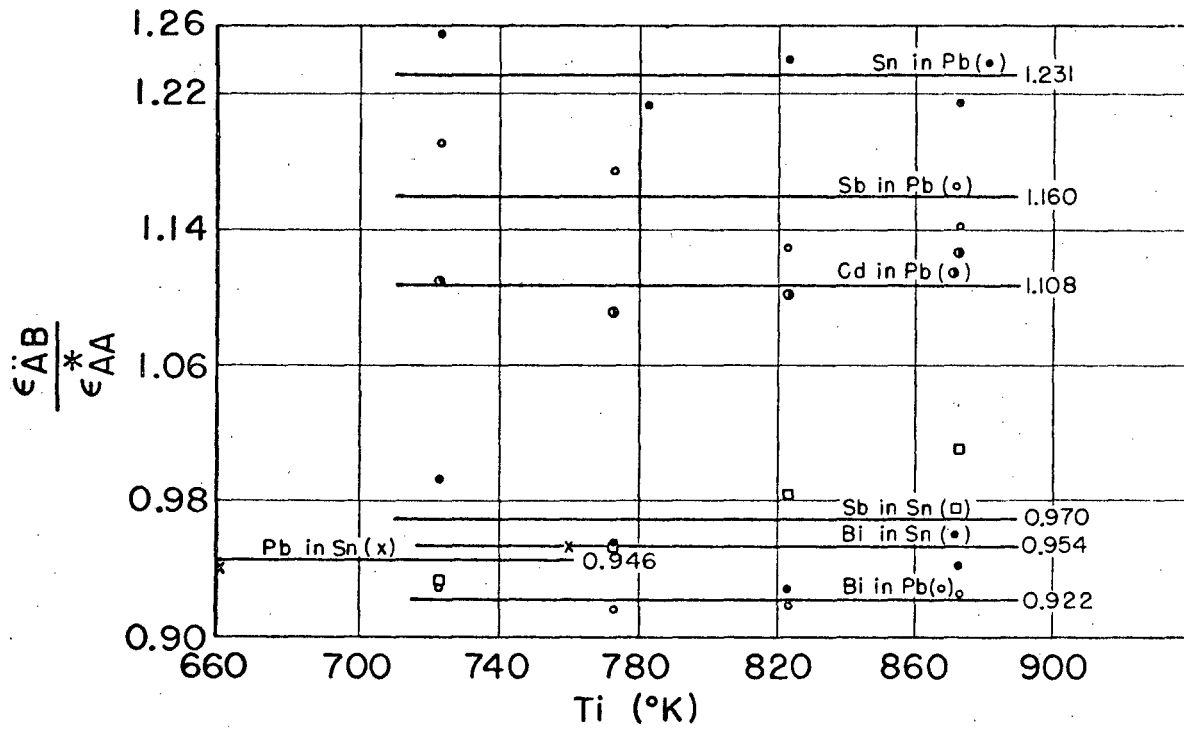
Comparison of correlations and experiment for self-diffusion in tin, gallium, and zinc.



MU-36854

Fig. 5

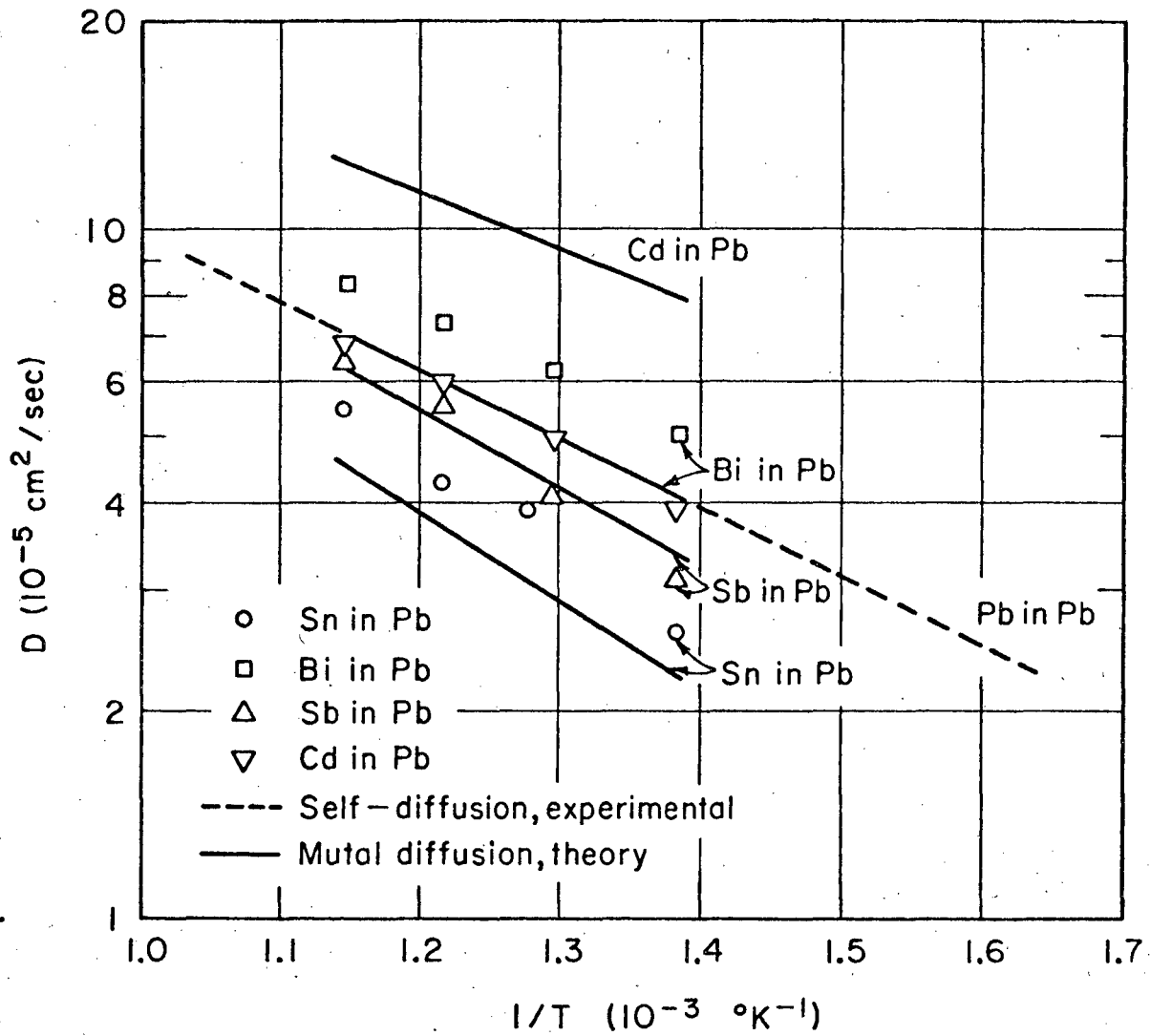
Comparison of correlations and experiment for self-diffusion in liquid lead, indium, copper, and silver.



MUB-10440

Fig. 6

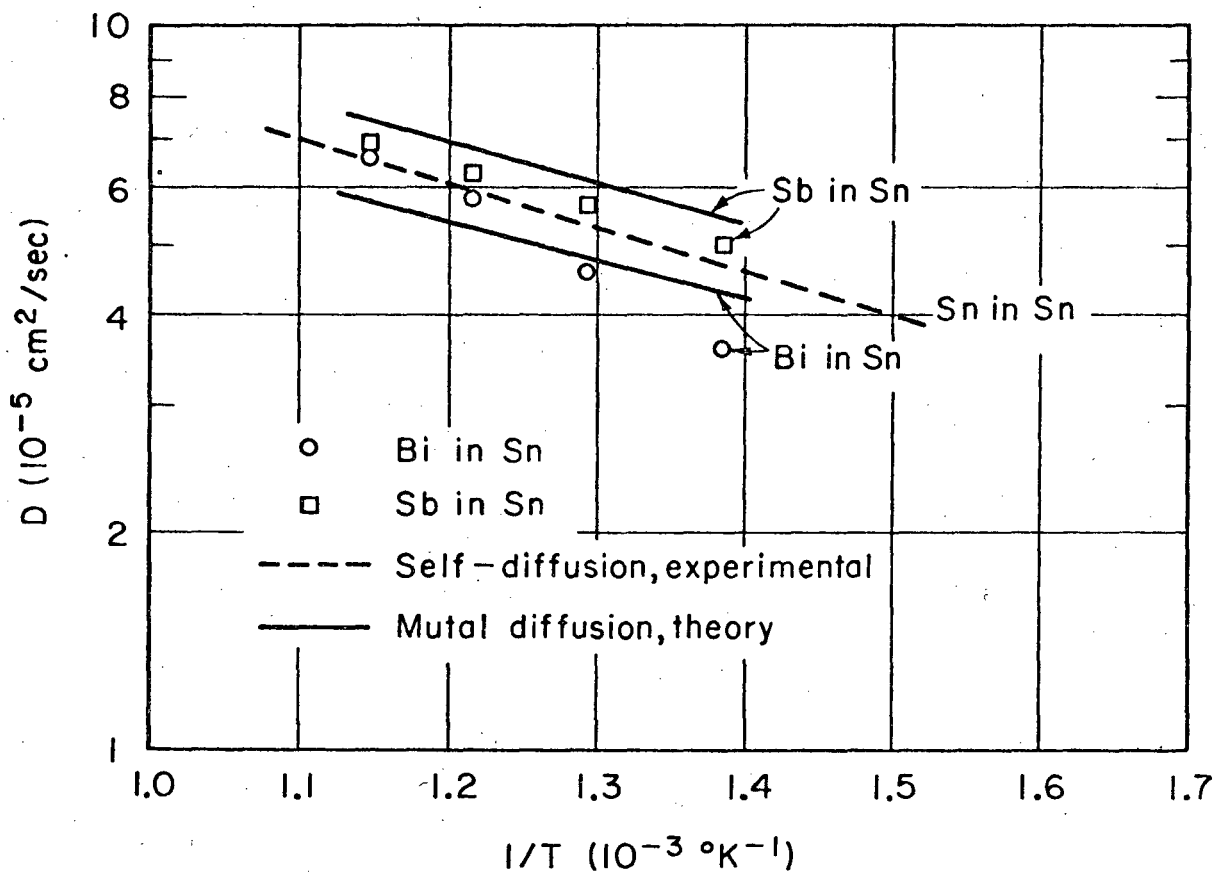
"Experimental" values of the energy parameter ratio from diffusion data.



MU-36887

Fig. 7

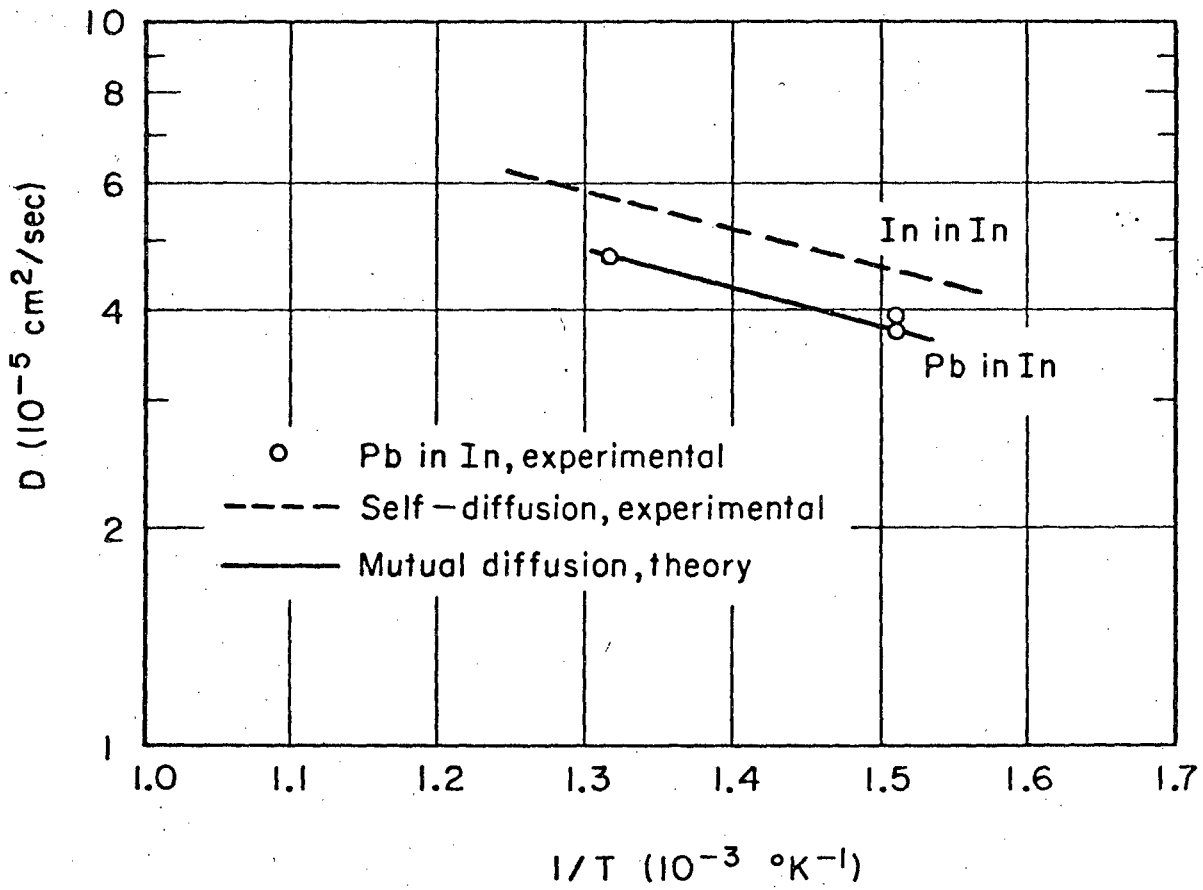
Comparison of corresponding states theory with mutual diffusion data for bismuth, cadmium, antimony and tin in lead.



MU-36888

Fig. 8

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



MU-36889

Fig. 9

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



This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

