

Determination of Diffusivities in Liquid Metals by Means of Temperature Gradient Zone Melting

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discussed previously [see Eq. (9)], the identical diagonal matrix elements occur in different matrices as indicated by the plus and minus designation. The $k_1 = +3$ and the $k_1 = -3$ matrix elements are connected by off-diagonal terms involving a sum of the barrier and the asymmetry, $V_6/4 + f(J, K)(B - C)$, while the $k_1 = +3^+$ and the $k_1 = -3^+$ elements are connected by the difference between the barrier and the asymmetry. As a result, these energy levels have a large splitting approximately quadratic in the barrier, and the frequencies of the transitions have a strong and approximately linear dependence on the barrier. The effect of a sixfold barrier term upon the $K = 1$, $k_1 = 3$, $J = 1$ to $J = 2$ transitions is illustrated in Fig. 1.

The experimentally determined splitting of these lines is approximately 1800 Mc/sec, and this corresponds to a barrier height, V_6 , of 6.03 ± 0.03 cal/mole (2.11 cm^{-1}). In a similar way, the splitting of the $K = 0$, $k_1 = \pm 6$ lines could be used to determine the V_{12} component in the barrier. Experimentally the $k_1 = \pm 6$ lines were not split, so there is no evidence for any V_{12} term. From the resolution of the spectrograph and the sensitivity of the method, an upper limit to V_{12} can be set as 0.05 cal/mole.

The barrier in CD_3NO_2 is not unreasonable when one considers that the low barrier is the result of a cancellation of large interaction terms. A change in the zero-point vibration of the methyl group, particularly the symmetrical $\text{H}-\text{C}-\text{H}$ bending mode, could alter the large interactions only slightly, but it could lead to an appreciable change in the barrier. In particular, the greater hydrogen motion is associated with the larger barrier.

It is difficult to estimate the magnitude of the interaction of a single oxygen with the methyl group, but it must be of the order of magnitude of one or two kcal/mole. Since the barrier in nitromethane is much smaller than this, and since the V_{12} term is so much smaller than the V_6 term, we conclude that the series given by Eq. (1) converges rapidly and that a simple cosine barrier is an excellent approximation to the barrier in nitromethane.

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Determination of Diffusivities in Liquid Metals by Means of Temperature-Gradient Zone Melting

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Diffusivities of liquid alloys of Ge-Al, Ge-Au, and Si-Al have been measured by a new technique. Called temperature-gradient zone melting, the technique involves passing extremely thin molten zones through a solid crystal by means of a temperature gradient. Preliminary values of the diffusivities fall in the $10^{-5} \text{ cm}^2/\text{sec}$ range at temperatures of 530°C to 700°C .

THE temperature-gradient zone-melting technique¹ has certain unique advantages for determining diffusivities in liquid metals.² One major advantage is that the experimental difficulties inherent in high-temperature liquid-metal diffusion studies are reduced. The molten zones employed can be quite small so that convection is negligible. Preliminary quantitative measurements of the diffusivities of liquid alloys of Ge-Al, Ge-Au, and Si-Al by this technique are described in this paper.

In temperature-gradient zone melting, a molten zone is moved through a solid by the establishment of a temperature gradient. For example, by placing a thin

layer of a solvent element A between two sections of a solute element B whose melting point is lowered by A , as shown in Fig. 1(a), and raising the sandwich to a temperature T_1 , the A layer will dissolve B until its composition is given by C_1 . By establishing a temperature gradient, the portion of the molten zone at the highest temperature becomes undersaturated in B . Consequently, this portion of the molten zone dissolves more B , setting up a concentration gradient across the layer. As a result B flows from the hot interface to the cool interface and A flows in the other direction by virtue of the precipitation of B at the cool interface of the molten zone. This solution-diffusion-precipitation process results in a movement of the molten zone through the solid toward the region of higher tempera-

¹ W. G. Pfann, *J. Metals* 7, 961-964 (1955).

² H. Reiss, Bell Telephone Laboratories (private communication).

ture. The travel rate is a direct measure of the flux of diffusing element through the zone.

Preliminary diffusion data were obtained for the Ge-Al, Si-Al, and Ge-Au systems using Al and Au wires of 3 mil and 2 mil diameter, respectively, as the solvent elements. Figure 1(b) illustrates the experimental arrangement for obtaining a desired temperature gradient. Figures 1(c) and 1(d) illustrate, respectively, the semiconductor specimen dimensions and the method of determining the temperature gradient. The surface temperatures of the specimen were calculated by assuming a linear change in temperature through the block.

Specimens of a given solute-solvent system were maintained in a known temperature gradient for varying periods of time. After each experiment, the semiconductor block was cut transversely into four or five sections. The transverse surfaces were polished and etched, and the depths of penetration of the molten zone were measured microscopically. Figure 2 contains the penetration-time data for the Ge-Al, Ge-Au, and Si-Al systems. Straight lines were drawn through the experimental points because, as a first approximation, the flux was assumed constant. In this work, the slope of the liquidus curve was essentially constant, and the diffusivity was assumed constant over the temperature and concentration range in question. The temperatures shown are the mean temperatures of the blocks. Each point on the curves represents an arithmetical average of the penetrations observed on the transverse surfaces

examined for a given specimen. In more than half of the runs, the number of penetrations used for averaging was equal to the number of transverse surfaces examined. Transverse surfaces not containing the wire in its cross section (no penetration) or containing a split wire were rejected for averaging. There was a variation in penetration from section to section, which in most cases amounted to 26%. In a few extreme cases the variation was as much as 60%. This was probably resulting from the nonuniformity of contact between the specimen surfaces and graphite end sections and to nonuniformity in wetting. This nonuniformity in contact and wetting, together with variations in contact pressure from run to run, could account for the spread in the points for a given curve. It is expected that these sources of error will be eliminated in future work.

The high-temperature heater was maintained above the low-temperature heater in one Ge-Al run at a mean temperature of 666°C. The average penetration obtained for this run is shown on the foregoing curve by the point denoted by an inverted delta. This supports the idea that convection is negligible in the small molten zones.

The steady-state diffusion equation

$$F = Ddc/dx \quad (1)$$

was used to calculate the diffusion coefficient D ; F is the flux of diffusing element in atoms/cm²-sec. It is the product of the concentration of solid solute B in atoms/cm³ and penetration rate. The concentration-gradient, dc/dx , was replaced by the product $dT/dx \cdot dc/dT$ for these approximate calculations. The temperature gradient, dT/dx , was known, and dc/dT , the inverse slope of the liquidus, was determined from the known equilibrium diagram. A linearly weighted density was used to calculate the concentrations. Note that the tem-

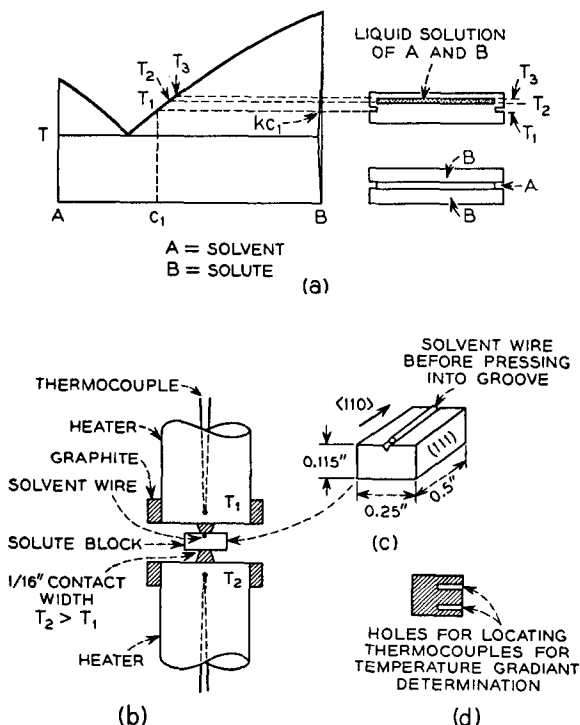


FIG. 1. Principle of the temperature-gradient zone-melting technique and experimental setups.

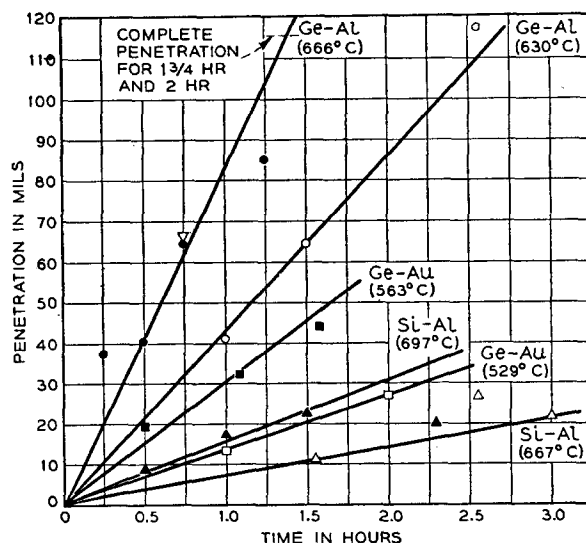


FIG. 2. Penetration-time data for the Ge-Al, Ge-Au, and Si-Al systems.

TABLE I. Diffusion coefficient data.

	Penetration rate mils/hr	Mean temp. °C	Temperature gradient $\frac{dT}{dx}$ (deg/cm)	Mean atom fraction	Inverse slope of liquidus $\frac{dc}{dT} \times 10^{-20} \left(\frac{\text{atoms}}{\text{cc-deg}} \right)$	Concentration gradient $\frac{dc}{dx} \times 10^{-21} \left(\frac{\text{atoms}}{\text{cm}^4} \right)$	Diffusivity $D \times 10^6$ (cm ² /sec)
Ge in Al	41	630	114	0.484	1.2	14.0	9.2
Ge in Al	82	666	111	0.532	1.4	15.1	17.1
Si in Al	7.5	667	126	0.177	0.5	6.5	4.0
Si in Al	16	697	123	0.198	0.5	6.5	8.7
Ge in Au	13.5	529	83	0.419	1.0	8.3	5.1
Ge in Au	30	563	105	0.456	1.2	12.1	7.8

perature gradient establishes, and subsequently maintains, the concentration gradient. The concentration gradient is being considered as the only driving force for these calculations. The temperature gradient, as a driving force (Soret effect³) is not being considered.

Table I contains the diffusion coefficients together with the temperature gradients, mean temperatures, and mean concentrations. For precise D values, liquid density data and a non-steady-state equation with proper boundary conditions, with consideration given to the temperature gradient as a driving force, must be employed. The diffusion coefficients are comparable with those values obtained for diffusion in other liquid-metal systems.^{3,4} The data are too meager for calculating true activation energies. However, the two diffusivity values for each system yield activation energies that are rather high when compared to values obtained in other liquids.

There is no theoretical basis for predicting the direction of the flux of diffusing element due to the temperature gradient alone. A rough measure of this flux can be obtained by considering a solution of uniform concentration at the moment a temperature gradient is impressed upon the solution. For this case,³

$$F = D'cdT/dx, \quad (2)$$

where D' , the thermal diffusion coefficient, appears to be a thousand times smaller than that obtained for ordinary diffusion.³ By choosing a value of 10^{-8} cm²/sec-degree for D' , and utilizing the mean concentrations and temperature gradients shown in Table I, the fluxes resulting from the temperature gradient alone amount to about 2% of the observed flux for Ge in Al, and about 4% for Si in Al and for Ge in Au. It appears, therefore, that the observed flux is essentially due to the concentration gradient.

³ W. Jost, *Diffusion in Solids, Liquids, and Gases* (Academic Press, Inc., New York, 1952).

⁴ C. J. Smithells, *Metals Reference Book* (Interscience Publishers, Inc., New York, 1949).

In the diffusion equations applicable to nonideal or real solutions, the partial molar free-energy or activity gradient, rather than the concentration gradient, is considered as the driving force for diffusion.^{3,5} By using the partial molar free-energy gradient, the equation for the flux³ becomes

$$F = -MkT[d(\ln a)/d(\ln N)](dc/dx), \quad (3)$$

where a =activity, N =atom fraction, K =Boltzmann's constant, T =absolute temperature, and M =mobility. The mobility M generally varies with the composition.³ The ratio, $d \ln a/d \ln N$, is a measure of the deviation of the solution from ideality. From thermochemical data,⁶ the free energies of fusion for Ge and Si were determined as functions of temperature, from which activities along the liquidus curve were calculated, using supercooled liquid as the reference state. This activity gradient was used to calculate the above ratio by assuming that the change in chemical potential along the liquidus was essentially due to the change in concentration and not to the change in temperature. This appears reasonable if one assumes that the solutions are regular.⁷ This ratio is about 1.8 for Ge-Al solutions, 1.6 for Si-Al solutions, and 2.6 for the Ge-Au solutions.

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Thanks are due H. Reiss for helpful discussions of the theory and W. G. Pfann for his help and interest in this research.

Note.—Since the preparation of this paper for publication, preliminary data have been obtained for the movement of a molten Al-rich wire zone across the surface of single crystal Ge. There appears to be a crystal orientation effect on the movement of the molten zone. This is being investigated further.

⁵ A. D. LeClaire, "Diffusion of metals in metals," B. Chalmers, editor, *Progress in Metal Physics* (Butterworth Scientific Publications, London, 1949), Vol. 1.

⁶ O. Kubaschewski and E. L. L. Evans, *Metallurgical Thermochemistry* (Butterworth-Springer Ltd., London, 1951).

⁷ J. Chipman, "Activities in liquid metallic solutions. The physical chemistry of process metallurgy," *Discussions of the Faraday Society*, No. 4 (Gurney and Jackson, London, 1948).