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Diffusion of Antimony in Silver*

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The diffusion coefficient of antimony tracers in single crystals of pure silver has been measured as a function of temperature over the range 468–942°C. The relation $D=D_0\exp(-H/RT)$ was found to be obeyed with $H=38\,320$ cal/mole and $D_0=0.169$ cm^2/sec. These values are in marked disagreement with those appearing in the literature. The data suggest, in addition, that any variation with temperature in D_0 of the form $D_0=D_0'T^n$ is such that n probably lies in the range 0 to $+\frac{1}{2}$. This implies that any temperature variation of H is probably less than 1 cal/mole deg.

I. INTRODUCTION

THE availability of radioactive isotopes has made it possible to perform diffusion experiments in essentially pure solvent metals with a much greater reproducibility than in the past. Moreover, tracer experiments do not require the large concentration differences so necessary to the older techniques.[1] With this in mind, this laboratory embarked upon a comprehensive investigation of diffusion in substitutional alloys, one aim being to obtain a comparison of diffusion in the silver lattice of tracers of those elements neighboring silver in the periodic table. The present experiment, preliminary results of which have been reported earlier,[2] represents part of this program. It was felt that careful measurements with single crystals, over as large a temperature range as possible, would be of basic importance in assessing the applicability of the equation $D=D_0\exp(-H/RT)$, in which the activation energy H is taken to be temperature independent.

EXPERIMENTAL

Specimens were prepared from 99.99 percent Handy and Harmon silver, melted, degassed, and grown in vacuum into single crystals of diameter $\frac{3}{4}$ in. These were then cast in plaster of Paris and cut into half-inch long cylinders with a cut-off wheel.[3] The worked layer was removed, simultaneously flattening the surface, by polishing on emery paper, followed by electropolishing. The electropolishing bath was the type employed by Francis and Colner.[4] Current was supplied as pulsating dc from a simple rectifier. The crystals were next annealed for 24 hours, the temperature rising slowly from 200°C to 700°C, to remove any residual strains. A subsequent cyanide etch[5] served to show whether the specimen were still a single crystal. The good specimens were then each plated with about 1 microcurie of high specific activity antimony (layer about 100A thick), sealed off in evacuated vycor tubes, and placed in the diffusion annealing furnaces. A description of the annealing, the sectioning of the specimens on a lathe, and the analysis of these sections has been previously published.[6]

RESULTS

A total of 13 diffusion runs were performed, ten on single crystals and three, for comparison, on polycrystals (grain size about 0.1 mm). The two higher temperature measurements on polycrystals involved only volume diffusion; not until 550°C (the third polycrystalline run) did any contribution from grain boundary diffusion appear. Of the single crystal measurements, the previously reported[2] run at 935°C was discarded because of an excessive deviation: when all four runs in the range 935°C–942°C were normalized to a common temperature, the deviation of the suspect measurement was 70 times that of the other three from their average; moreover, this point differs from the best fit of all the data by more than seven times the standard deviation. The discrepancy is explainable by a possible error of one hour in recording the time of diffusion.

The penetration curves for all volume diffusion runs showed a strict proportionality between the logarithm of the activity and the square of the penetration depth. The plots were similar to those previously published[2] and hence are not repeated here.

The diffusion coefficients calculated from these plots are given in Table I. These diffusion coefficients were not "corrected" for the fact that all distances were measured at room temperature rather than at the temperature of diffusion. Since the fundamental process of diffusion should be described in terms of atomic jumps rather than the length of each jump, such a "correction" would actually introduce an extraneous variation of D with temperature. Figure 1 shows the data plotted as log$D$ *versus* the inverse of the absolute temperature. The straight line that best fits the data

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[1] A. D. LeClaire, in *Progress in Metal Physics*, edited by B. Chalmers (Butterworth Scientific Publications, London, 1949 and 1953), Vols. I and IV; F. Seitz, in *Phase Transformations in Solids*, edited by J. Smoluchowski *et al.* (John Wiley and Sons, Inc., New York, 1951).

[2] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. 23, 1405 (1952).

[3] We are indebted to Dr. J. Marx, now of Phillips Petroleum Company, for the suggestion of this method of protecting the crystals while being cut.

[4] H. Francis and W. Colner, J. Electrochem. Soc. 97, 237 (1950).

[5] G. Kehl, *Principles of Metallographic Laboratory Practice* (McGraw-Hill Book Company, Inc., New York, 1949).

[6] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. 23, 1032 (1952).

is given by the equation

$$D = 0.169 \exp(-38\,320/RT) \text{ cm}^2/\text{sec}.$$

The individual diffusion measurements are good to ±2 percent. This precision, together with the large number and range of the measurements, statistically determines the activation energy to 0.001 percent, a figure probably negligible relative to possible systematic errors of unknown origin. Statistically, D_0 is precise to 2 percent; this, too, seems overly optimistic.

DISCUSSION

The present results differ greatly from earlier measurements made on the same system by Seith and Peretti.[7] These workers reported an activation energy of 21 700 cal/mole and a D_0 equal to 5.3×10^{-5} cm^2/sec. The discrepancy cannot lie in the fact that they used polycrystals since our polycrystal runs agree with measurements on single crystals down to reasonably low temperatures (about 600°C). Moreover, their low value of the activation energy cannot be ascribed to some other "short-circuiting path," as suggested by Nowick,[8] since near the melting point their value of the diffusion coefficient is considerably less (by a factor of 5) than ours. It seems probable, then, that the discrepancy may lie in the fact that Seith and Peretti, having no tracers, observed the diffusion of antimony from a 2-percent alloy into pure silver. The effects of both the larger concentration of antimony and the presence of an appreciable gradient of the concentration are now being investigated.

TABLE I. Summary of data.

D(cm^2/sec)	Temperature (°C)	Specimen
2.15×10^{-8}	942.4	Single crystal
2.07×10^{-8}	940.2	Single crystal
2.06×10^{-8}	940.0	Polycrystal
1.44×10^{-8}	908.2	Single crystal
4.92×10^{-9}	838.6	Single crystal
1.14×10^{-9}	754.9	Single crystal
4.12×10^{-10}	698.3	Polycrystal
1.34×10^{-10}	648.5	Single crystal
1.70×10^{-11}	564.9	Single crystal
2.53×10^{-12}	500.5	Single crystal
8.50×10^{-13}	468.5	Single crystal

That these concentration effects may quite generally have been a dominant factor in much of the older work is borne out by recent tracer experiments on the diffusion of Cd, In, and Sn in silver.[9] In these new measurements, as in the present case, the activation energies are found to be much closer to the 45 500 cal/mole for self-diffusion than given by the earlier, nontracer experiments. The theory of solute-vacancy complexes[10] has been the basis for the interpretation of the former results that in a given metal almost all solutes diffused with an activation energy much smaller (by about 50 percent) than that for self-diffusion. It now appears, however, that the binding energy between a solute atom and a vacancy may be much less than previously considered. A theory to explain the 7200-cal/mole difference in activation energy between that for self-diffusion and for antimony in silver, as found in this work, has been formulated by Lazarus.[11]

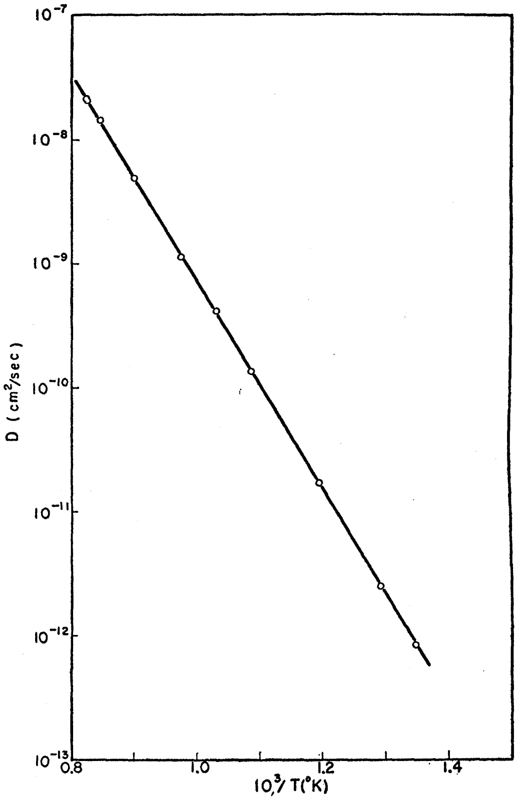

FIG. 1. Diffusion data plotted as log$D$ *versus* $1/T$.

Another marked disagreement between our work and that of Seith and Peretti lies in the value of D_0. It has been predicted[12] that the reported values of the order of 10^{-5} cm^2/sec would be revised upwards about four or five powers of ten; the present results are consistent with this prediction.

In order to obtain information concerning the temperature dependence of D_0 (H being assumed to be constant over the range of temperature), expressions of the form

$$D = D_0' T^n \exp(-H'/RT)$$

have been tested by computing the best H' and D_0' for a given n and then evaluating the standard deviation

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[7] W. Seith and E. Peretti, Z. Elektrochem. **42**, 570 (1936).

[8] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[9] C. T. Tomizuka, Bull. Am. Phys. Soc. **28**, No. 6, 18 (1953); C. T. Tomizuka and L. Slifkin (to be published).

[10] C. Wagner, Z. physik. Chem. **B38**, 325 (1938); R. P. Johnson, Phys. Rev. **56**, 814 (1939).

[11] D. Lazarus, following paper [Phys. Rev. **93**, 973 (1954)].

[12] C. Zener in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley *et al.* (John Wiley and Sons, Inc., New York, 1952).

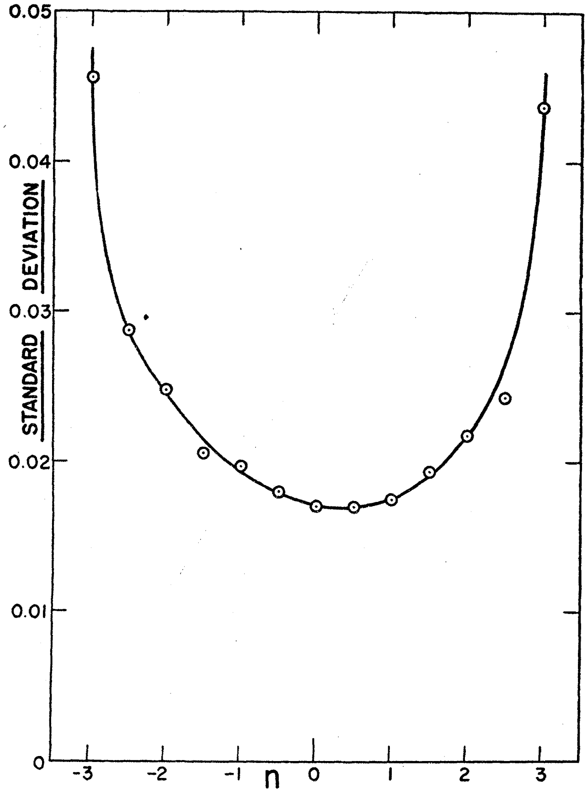

FIG. 2. Standard deviation of the data from the relations $D=D_0'T^n\exp(-H'/RT)$ as a function of n. *Note added in proof.* —The ordinate in this figure is actually the probable error rather than the standard deviation.

of the data. The probable error thus obtained is shown as a function of n in Fig. 2. These results rule out any strong dependence of D_0 on T and, in fact, indicate that n probably does not lie far from the range 0 to $+\frac{1}{2}$. Values of H', D_0', and the probable error for $-\frac{1}{2}\leqslant n\leqslant +1$ are given in Table II.

From this limitation on the temperature dependence of D_0, information can be obtained concerning the possible temperature variation of the enthalpy of activation H. One can write[1]

$$D=a^2\nu e^{S/R}e^{-H/RT},$$

where a is the lattice parameter, ν is a lattice vibration frequency, and S and H refer to the activation process of the elementary diffusion act. If one expands H as a power series in T, all terms higher than the linear one may be neglected since no curvature appears in Fig. 1:

$$H=H_0+H_1T.$$

Employing the relation

$$(\partial H/\partial T)_p=T(\partial S/\partial T)_p,$$

one obtains

$$S=S_0+H_1\ln(T/T_0),$$

where S_0 is the entropy of activation at some reference temperature T_0. Then,

$$D=a^2\nu\left(\frac{T}{T_0}\right)^{H_1/R}\exp\left(\frac{S_0-H_1}{R}\right)\exp(-H_0/RT).$$

TABLE II. Best values of H' and D_0' for various values of n.

n	H'(cal/mole)	D_0'(cm²/sec-deg^n)	Probable error in $\ln D$
$-\frac{1}{2}$	39 270	0.274	0.0180
0	38 320	0.169	0.0170
$+\frac{1}{2}$	37 380	0.104	0.0170
1	36 420	0.064	0.0174

Since we have not corrected our D's for temperature variation of the lattice parameter, the a^2 term is constant. Also, if one assumes ν to be independent of temperature, the only term in D_0 dependent on T is $T^{H_1/R}$. Referring to the previous paragraph H_1/R must be equated to n. Thus, $0\leqslant H_1\leqslant R/2$ and H varies by no more than 1 cal/mole degree.

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