Self-Diffusion in Solid Argon*

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The self-diffusion coefficient $D = D_0 \exp(-Q/RT)$ for solid argon has been measured in thin specimens of large grain size by a tracer technique. The results, $D_0 = 0.2 \pm 0.4 \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 3600 \pm 150 \text{ cal mole}^{-1}$, are lower than those obtained in previous investigations. The value of $Q$ agrees reasonably well with a two-body absolute-rate calculation for vacancy migration, but not with calculations based on divacancy or interstitial mechanisms. The results suggest that vacancy diffusion takes place, and that many-body forces in solid argon are either very small, or else may satisfactorily be accounted for in an empirical two-body potential.

I. INTRODUCTION

The lattice self-diffusion coefficient

$$D = D_0 \exp(-Q/RT)$$

for the solidified inert gases is of interest for two reasons. First, these solids provide a good test for diffusion theory because the atomic interactions may reasonably be represented by a sum of two-body central forces in the form of simple semiempirical potentials. Calculations of the activation energy $Q$ may thus be compared with experimental results as a realistic test of the various mechanisms and models proposed for diffusion. By contrast, in metals there is much greater uncertainty in the interatomic potential. Second, diffusion studies in these solids provide general information about the validity of the interatomic potentials themselves.

The coefficient of self-diffusion in solid argon has previously been measured by Bernè et al. The results, $D_0 = 4 \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 3865 \pm 200 \text{ cal mole}^{-1}$, are somewhat uncertain because of the difficulties experienced by the investigators in accounting for grain-boundary effects. Their value of $Q$ is consistent with a law-of-corresponding-states comparison of NMR measurements of self-diffusion in solid xenon, but not with the recently determined vacancy-formation energy $E_v^0$ in solid krypton assuming a vacancy-diffusion mechanism, $Q = E_v^0 + E_m^0$.

When the present experiments were begun, there existed only one calculation of the activation energy $Q$ by Fieschi et al. This was an absolute-rate calculation for the vacancy mechanism using a Lennard-Jones (12,6) potential giving $Q = 3210 \text{ cal mole}^{-1}$ at 80K. The discrepancy between this value and the observed one was assumed to be due to either experimental error, the inadequacy of the interatomic potential, or, as suggested by Rice, the inadequacy of the absolute-rate theory itself. Subsequently, the Rice and absolute-rate theories seemed to be shown to be equivalent. Also, because of the large expansivity of solid argon, it seems important to calculate $Q$ over a temperature range and to compare the extrapolation of these values to $T = 0 \text{K}$ with the observed $Q$. Following this procedure, Glyde obtained $Q = 3790 \text{ cal mole}^{-1}$ using a (12,6) potential and rate theory. Subsequent calculations at $T = 0 \text{K}$ give nearly identical values. Using similar potentials, calculations of $Q$ for the divacancy and interstitial mechanisms give $Q_{2v} = 4850$ and $Q_{si} = 5400 \text{ cal mole}^{-1}$, respectively.

A preliminary study of the procedures employed by Bernè et al. to measure the self-diffusion coefficient in solid argon led us to believe that they could be modified so as to produce more accurate results. In view of the need to obtain more reliable data, in particular an accurate value for $Q$ to check recent calculations, we undertook the present investigation.

II. EXPERIMENTAL METHOD

The diffusion coefficient was measured by means of a tracer method using the stable isotope Ar. An argon crystal (Ar) of thickness $l = 10 \mu$ and surface area $(A_s) = 12 \text{ cm}^2$ was slowly condensed ($\sim 2 \text{ h}$) directly from the vapor onto a cold copper block mounted inside a liquid-nitrogen cryostat. The vapor in equilibrium with the crystal was confined to a volume $V$ immediately above the solid. Because the vapor is fast relative to diffusion rates in the solid $(D_{mol} = 10^{-11} \text{ cm}^2 \text{ sec}^{-1})$, the system may be regarded as a semi-infinite solid in contact with a well-stirred fluid. To initiate the diffusion process Ar atoms are introduced into the vapor under constant-pressure conditions at time $t = 0$. The condition

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for thermodynamic equilibrium at the solid surface for
small concentrations is that \( \varepsilon(t) = kc(t) \), where \( \varepsilon(t) \) and
\( c(t) \) are the number of densities of the tracer in the vapor
and solid phases, respectively, and \( k \) is the ratio of the
partial vapor pressures of the impurity \( p_e \) and host \( p_h \)
atoms in the lattice;

\[
k = \frac{p_e}{p_h} \left[ \frac{c(1-c)}{1} \right],
\]

where \( c \) is the impurity concentration on the solid
surface.

Solution of the diffusion equation for these boundary
conditions is\(^{12}\)

\[
\frac{\varepsilon(t) - kc(0)}{\varepsilon(0) - kc(0)} = \exp \left[ \frac{\rho_s^2 \left( \frac{A^2 D}{t} \right)}{\rho_s^2 \left( \frac{1}{k^2 V} \right)} \right]
\times \text{erfc} \left[ \frac{\rho_s \left( \frac{A}{k} \sqrt{D} \right)}{\sqrt{t}} \right],
\]

where \( \rho_s \) and \( \rho_h \) are the densities of the solid and vapor,
and \( c(0) \) is the concentration of the tracer in the solid
at \( t=0 \) (i.e., the natural abundance \( \sim 0.34\% \)). \( A \) is
the effective area of the crystal, which for a polycrystalline
specimen is not, in general, well determined. \( k \) for \( ^{26} \text{Ar} \)
in \( ^{13} \text{Ar} \) is known to be 0.993 \( \pm 1 \).\(^{13}\)

The time dependence of \( \varepsilon(t) \) was determined by
monitoring the concentration of \( ^{26} \text{Ar} \) by means of a
mass spectrometer. The quantity \( D^{12}A \) was evaluated
by fitting the experimental data to Eq. (1) by the
method of least squares. The result of a typical run
is shown in Fig. 1.

![Fig. 1. Output of typical experimental run and computer-fitted curve [Eq. (2)].](image)


The apparatus and experimental techniques are
reported in greater detail elsewhere.\(^{14}\)

### III. SPECIMEN GEOMETRY

Measurements were made on thin well-annealed
specimens of grain size \( \sim 100 \mu \). Since the activation
energy for grain boundary and surface diffusion is
\( \sim 0.5 \) that for lattice diffusion,\(^{10,16}\) \( D_{\text{GB}} \approx 10^5 D_{\text{lat}} \approx 10^{-2} D_{\text{vap}} \). Thus for thin specimens, the \( ^{26} \text{Ar} \)
concentration in the boundaries will rapidly reach equi-
librium with the vapor. The effect of the grain bounda-
ries is therefore to increase the effective surface area
of the solid exposed to the vapor. This contrasts with
the usual effect of grain boundaries on lattice dif-
fusion.\(^{13,16}\) Since the average grain diameter \( d \gg l \), the
semi-infinite solid condition remains unaffected. There-

![Fig. 2. Variation of \( D^{12}(^{26} \text{Ar} + ^{13} \text{Ar}) \) with the time \( t_0 \) that the solid
was annealed prior to \( t=0 \) at 66.4 and 78.4 K.](image)

Thus, provided that this extra area \( A_E \) may be deter-
mined, or at least kept constant for each sample,
the effect of finite grain size can be eliminated.

### IV. RESULTS—ACTIVATION ENERGY \( Q^0 \)

Results for runs carried out at \( T = 78.4 \) and 66.4 K
are shown in Fig. 2, where \( D^{12}(^{26} \text{Ar} + ^{13} \text{Ar}) \) is shown
plotted as a function of the time \( t_0 \) during which the
specimen was annealed prior to the experiment. Since
all the measurements were carried out on specimens of
the same thickness (\( l = 12 \mu \)) and surface area \( A_s \), the
observed decrease in \( D^{12}(^{26} \text{Ar} + ^{13} \text{Ar}) \) at 66 K must be
due to recrystallization processes causing grain growth.

\(^{16}\) E. E. Hoffmann and D. Turnbull, J. Appl. Phys. 22, 634
(1951).
and hence reducing $A_B$. From Fig. 2 it may be seen that when $t_a \geq 6$ h, $A_B$ appears to have reached an equilibrium value. Grain growth at 78°C is so rapid that equilibrium is reached quickly, and $D^{12}A$ does not appear to change during the range of $t_a$ studied.

All our observations and Fig. 2 indicate that the grain size for specimens of a particular thickness at a given temperature depends primarily on the anneal time $t_a$. The results suggest also that a pseudo-equilibrium state is reached where further grain growth is inhibited by the geometry of the specimen. Under these conditions, the total grain area of a specimen of given thickness is probably independent of temperature, although there might be a slight negative temperature dependence.

Assuming that the grain size is independent of temperature, $DA^2 = D_0 A^2 \exp(-Q^0/RT)$. In Fig. 3, $\ln DA^2$

![Fig. 3. Plot to determine $Q^0$ and $D^0$ from experimental results on well-annealed specimens.](image)

is plotted versus $1/T$, which leads to a value of $Q^0 = 3550 \pm 90$ cal mole$^{-1}$. Because $A_B$ might be slightly temperature-dependent, this value should be regarded as a lower limit for $Q^0$.

**V. GRAIN SIZE DEPENDENCE AND $D_0$**

Previous investigations have shown that in thin well-annealed samples the grain boundaries traverse the specimen in the shortest possible direction, and thus the grain-boundary area $A_B$ will be proportional to the specimen thickness. If $d$ is the average grain diameter of the crystal, $A_B = A_S (4d/d)$ and the total effective surface is $A = A_S + A_B = A_S (1 + 4d/d)$. In Fig. 4, $D^{12}A$ is plotted versus $l$ for measurements made at three temperatures. The slope gives an average value at each temperature of 100 μ with a maximum difference of 20 μ over the investigated temperature range. That the points for each temperature lie on a straight line within experimental error confirms that $A_B$ depends only on the sample thickness over the small range of $l$ studied.

Taking the observed values of $A_B$ for $l = 12$ μ, $D_0 = 0.2 \pm 0.14 \times 10^{-4}$ cm$^2$ sec$^{-1}$ and a revised $Q^0 = 3600 \pm 150$ cal mole$^{-1}$ are obtained. The revised $Q^0$ and error were obtained by using the maximum difference of 20 μ in $d$ to provide an upper limit ($Q^0 = 3750$ cal mole$^{-1}$) and the value of Sec. IV to provide a lower limit. The correction to $Q^0$ is thus small, although the error is considerably increased. This confirms the suggestion that $d$ is approximately constant for well-annealed specimens. Thus we believe that $Q^0$ should lie within the limits quoted in Sec. IV, but our determination of $A_B$ is not accurate enough to demonstrate this beyond doubt.

**VI. DISCUSSION**

The values of $D_0$ and $Q_0$ obtained in the present investigation are slightly lower than results obtained previously for solid argon by Bernè et al. ($D_0 = 4$ cm$^2$ sec$^{-1}$, $Q_0 = 3855 \pm 200$ cal mole$^{-1}$), but agree within estimated experimental error. The present values should be more reliable, however, because $D$ has been measured over a wider range of temperature and the average grain size of the specimen is greater, with a corresponding decrease in the uncertainty due to grain-boundary correction. In addition, the results are more consistent because each sample was annealed to its equilibrium grain size; this allows a more satisfactory

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procedure to be used to determine or eliminate $A_{0}$ than that employed previously. A law-of-corresponding-states comparison with the NMR results of Yen and Norberg\textsuperscript{4} for xenon gives $Q^{0} = 3830 \pm 100$ cal mole\textsuperscript{-1} in argon.\textsuperscript{8}

The present experimental value for $Q^{0}$ is also consistent within experimental error with $Q^{0} = 3700$ and $Q^{0} = 3811$ cal mole\textsuperscript{-1}, the rate-theory calculations for vacancy diffusion based on the Lennard-Jones (12,6) potential. It is not consistent, however, with calculations for the interstitial or divacancy mechanisms.

Assuming that diffusion in solid argon is by vacancies, the agreement of $Q^{0}$ suggests that many-body force effects are small or, alternatively, that they are well accounted for (over large changes in interatomic spacing) by using an empirical two-body potential of the Lennard-Jones type. This is in contradiction with the conclusion reached on comparing the calculated and experimental values for the vacancy formation energy $E_{s}^{0}$ in solid krypton\textsuperscript{2} where $E_{s}^{0}$(observed) $\approx 0.7 E_{s}^{0}$(calculated).

For vacancy diffusion in close-packed solids, one expects $E_{s}^{0} = 0.5 Q^{0}$. Using observed values of $Q^{0}$ for argon and xenon to estimate $Q^{0}$ for krypton, $E_{s}^{0}$(obs.) $= 0.38 Q^{0}$. Although it would require detailed model calculations to determine exactly how many body contributions to the potential would affect $E_{s}^{0}$ and $Q^{0} = (E_{s}^{0} + E_{w}^{0})$, one might expect both quantities to be changed in roughly similar proportions. Thus the results of the diffusion and vacancy-concentration investigations do not appear to be consistent if diffusion is by single vacancies.

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**Comments and Addenda**

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**Influence of Band Structure on the Nonlocal Conductivity of Metals and the Anomalous Skin Effect**

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The conductivity kernel entering into the expression for the surface impedance of a metal is calculated for a separable band structure. In the anomalous-skin-effect region, Pippard’s expression is found when the Gaussian curvature on the Fermi surface is nonzero, and modifications are indicated when this is not the case.

The anomalous skin effect in layer lattices has been discussed by Gerlach\textsuperscript{1} by calculating the wave-vector-dependent conductivity for such a metal to second order in the periodic potential. He found, in particular, that when the Fermi surface intersects the zone boundaries, a term going as the inverse square of the wave number can appear in the conductivity. This can contribute a different frequency dependence to the surface impedance than the inverse wave-vector dependence given by Pippard’s\textsuperscript{3} expression. In this paper a derivation of the conductivity kernel is given, which is “exact” for layer lattice, i.e., correct to all orders in the lattice potential. It is shown that the $q^{-2}$ dependence found by Gerlach is due to the existence of a “flat” (having vanishing Gaussian curvature) portion of the Fermi surface, for which case Pippard’s ineffectiveness expression breaks down.

We consider an electromagnetic wave having wave vector $\mathbf{q}$ and frequency $\omega$ incident normally on a metallic surface lying in the $x$-$y$ plane, so $\mathbf{q} = (0,0, q)$. In terms of this coordinate system the metal is to be composed of noninteracting electrons possessing the band structure

$$\delta(k) = \epsilon_{x}(k_{x}) + \epsilon_{y}(k_{y}) + \epsilon_{z}(k_{z}),$$

where the $\epsilon_{n}$ are arbitrary one-dimensional band structures. Since (1) is to be considered as an approximation to an actual three-dimensional band structure, $\epsilon_{n}(k)$ may possess in-band critical points, which cannot occur in one-dimensional lattices. The electrons are assumed

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\textsuperscript{1} E. Gerlach, Phys. Rev. 163, 527 (1967).