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EFFECT OF PRESSURE ON ANISOTROPIC SELF-DIFFUSION IN ZINC

by

Mary Ann Cerella Norton

A Dissertation Submitted to the Faculty of the DEPARTMENT OF PHYSICS
In Partial Fulfillment of the Requirements For the Degree of DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1973
I hereby recommend that this dissertation prepared under my direction by Mary Ann Cerella Norton entitled Effect of Pressure on Anisotropic Self-Diffusion in Zinc be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy.

After inspection of the final copy of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:

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SIGNED: Mary Ann Cerella Norton
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>12</td>
</tr>
<tr>
<td>RESULTS</td>
<td>18</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>26</td>
</tr>
<tr>
<td>Determination of Activation Volume</td>
<td>26</td>
</tr>
<tr>
<td>Phenomenological Theories</td>
<td>30</td>
</tr>
<tr>
<td>Isotope Effect</td>
<td>34</td>
</tr>
<tr>
<td>Basal Plane Activation Volume</td>
<td>40</td>
</tr>
<tr>
<td>Motional Volumes</td>
<td>41</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>49</td>
</tr>
<tr>
<td>LIST OF REFERENCES</td>
<td>50</td>
</tr>
<tr>
<td>Figure</td>
<td>Illustration/Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Illustration of the Gibb's free energy barrier as an atom moves from one equilibrium site to another</td>
</tr>
<tr>
<td>2.</td>
<td>Geometry of the hcp lattice and representative jump vectors for diffusion parallel and perpendicular to the σ-axis</td>
</tr>
<tr>
<td>3.</td>
<td>Cross-sectional view of the internal furnace for measurement of zinc diffusion at 360° and 410°C</td>
</tr>
<tr>
<td>4.</td>
<td>Penetration curves for self-diffusion in zinc parallel to the σ-axis at 360°C</td>
</tr>
<tr>
<td>5.</td>
<td>Penetration curves for self-diffusion in zinc perpendicular to the σ-axis at 360°C</td>
</tr>
<tr>
<td>6.</td>
<td>Penetration curves for self-diffusion in zinc parallel to the σ-axis at 410°C</td>
</tr>
<tr>
<td>7.</td>
<td>Penetration curves for self-diffusion in zinc perpendicular to the σ-axis at 410°C</td>
</tr>
<tr>
<td>8.</td>
<td>Variation with pressure of the diffusion coefficients at constant temperature</td>
</tr>
<tr>
<td>9.</td>
<td>Saddle point configuration for jumps parallel to the σ-axis</td>
</tr>
<tr>
<td>10.</td>
<td>Saddle point configuration for jumps perpendicular to the σ-axis</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. c/a Ratio of hcp Elements</td>
<td>8</td>
</tr>
<tr>
<td>II. Raw, Time Corrected and Temperature Corrected D's</td>
<td>23</td>
</tr>
<tr>
<td>III. Uncorrected Activation Volumes</td>
<td>30</td>
</tr>
<tr>
<td>IV. Corrected Activation Volumes</td>
<td>30</td>
</tr>
<tr>
<td>V. Values of n</td>
<td>39</td>
</tr>
<tr>
<td>VI. Activation Volumes</td>
<td>42</td>
</tr>
</tbody>
</table>
ABSTRACT

The effect of pressure in the \( \frac{1}{2} \) to 10 kbar range on the self-diffusion coefficients of single crystal zinc has been investigated. Standard tracer techniques have been employed to determine diffusion coefficients parallel and perpendicular to the \( c \)-axis at 360°C and 410°C. The volume of activation parallel to the \( c \)-axis has been found to be equal to 4.23 cm\(^3\)/mole at 360°C and 4.41 cm\(^3\)/mole at 410°C. The volume of activation perpendicular to the \( c \)-axis has been found to be equal to 4.16 cm\(^3\)/mole at 360°C and 4.50 cm\(^3\)/mole at 410°C. The equation for \( \Delta K \) of the isotope effect derived by Le Claire has been reexamined and a new equation has been derived. The results of this new relation have been compared to the present experiment. An expression for the difference in motional volumes between jumps in the basal plane and jumps between basal planes has been derived and applied to the results of this experiment with the result that no difference has been found.
INTRODUCTION

The movement of atoms in solids has been the subject of many experimental and theoretical investigations over the past years. Work in diffusion has yielded considerable information on the mechanisms of atomic migration. It is well established that in most solids crystalline imperfections are necessary for atomic migration. The most common mechanisms of diffusion are now thought to be vacancy, divacancy, interstitial and interstitialcy.

The diffusion coefficient, $D$, for diffusion in the $x$ direction is defined by

$$ J = -D \frac{\partial c}{\partial x} \quad (1) $$

where $J$ is the net mass flow per cross-sectional area and $c$ is the concentration. The continuity equation combined with Eq. (1) yields the diffusion equation

$$ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \quad (2) $$

For the case where $D$ is independent of $x$ this simplifies to

$$ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3) $$
When an experimental investigation of diffusion results in a temperature dependence of the diffusion coefficient given by

\[ D = D_0 \exp \left[ -\frac{Q}{RT} \right], \quad (4) \]

where \( R \) is the gas constant and \( T \) is the absolute temperature, \( D_0 \) is called the frequency factor and \( Q \) is referred to as the activation energy. \( D_0 \) and \( Q \) are usually found to be independent of temperature. Behaviour of the type found in Eq. (4) is commonly found in face-centered cubic (fcc), body-centered cubic (bcc) and hexagonal close-packed (hcp) metals over limited temperature ranges.\(^2\) Comparison of experimentally obtained activation energies with those obtained theoretically has been made in order to establish the mechanism of migration. Theoretical calculations carried out for the noble metals indicate that the vacancy mechanism is responsible for diffusion.\(^3\)

Zener\(^4\) has developed an expression for the diffusion coefficient in terms of atomic quantities. It is assumed that the migrating particle is constrained to move in a plane normal to the path over the Gibbs free energy barrier, as is illustrated in Fig. 1. The plane is moved slowly enough to maintain thermal equilibrium between the lattice and a surrounding temperature bath. The work done in moving
Fig. 1. Illustration of the Gibb's free energy barrier as an atom moves from one equilibrium site to another.
the particle from a Gibbs free energy minimum to a Gibbs free energy maximum is $\Delta G$. The expression derived by Zener for the diffusion coefficient is

$$D = \gamma a^2 \nu f \exp[-\Delta G/RT]$$

(5)

where $\gamma$ is a constant determined by the geometry of the lattice, $a$ is the lattice constant, $\nu$ is an effective vibrational frequency in the direction of the jump and $f$ is the correlation factor to be discussed below. Vineyard has shown that the same form as Eq. (5) can be obtained by generalizing Zener's treatment to include many-body effects but finds that the effective frequency is the ratio of the product of the $N$ normal frequencies at the start of the transition to the $N-1$ normal frequencies of the constrained system at the saddle point. Though the correlation factor $f$ was not originally included by Zener, its inclusion is necessary to take into account the fact that each jump of an atom may not be perfectly random. That each jump of a migrating atom may not be independent of its past history can easily be seen by considering movement via the vacancy mechanism. After one interchange with a neighboring vacancy the new neighbors of the diffusing atom are not identical. Since one of its neighbors is the vacancy it is most likely to make a return jump with that same vacancy. This correlated motion is taken into account by including a factor $f$ which
may take on values between zero (no net movement) and one (completely random movement); the actual value is determined by the geometry of the lattice and the type of diffusive mechanism.  

Since the Gibbs free energy $G$ is related to the enthalpy $H$ by

$$G = H - TS$$

where $S$ is the entropy, we may rewrite Eq. (5) as

$$D = \gamma a^2 \nu f \exp[\Delta S/R] \exp[-\Delta H/RT] .$$

By comparison of Eq. (7) with Eq. (4) the following identifications can be made

$$D_0 = \gamma a^2 \nu f \exp[\Delta S/R]; Q = \Delta H .$$

In order to include the effects of pressure on diffusive processes, the thermodynamic relationship

$$V = [\partial G/\partial P]_T$$

is used to obtain what is customarily defined as the activation volume, $\Delta V$,

$$\Delta V = -RT \left( \frac{\partial \ln D}{\partial P} \right)_T + RT \left( \frac{\partial \ln (\gamma a^2 \nu f)}{\partial P} \right)_T .$$
The first term on the right may be obtained from the experimental data from the slope of a plot of the natural logarithm of the diffusion coefficient $D$ versus the pressure $P$ and the second term is usually a small correction term and will be discussed in more detail later. Since different mechanisms of diffusion are expected to require different activation volumes the comparison of experimentally and theoretically obtained activation volumes is an effective way to distinguish between different mechanisms of diffusion.

When the diffusion process is via a mechanism which requires the formation of a defect, the total Gibbs free energy of diffusion, $\Delta G$, is the sum of the energy of formation, $\Delta G_f$, and the energy of motion, $\Delta G_m$, of the defect. $\Delta G_f$ is the difference in Gibbs free energy before and after the defect is formed. $\Delta G_m$ is the difference in Gibbs free energy between the state where the diffusing atom is found on one normal site and the state where the diffusing atom is found at a saddle point site. Because of Eq. (9) the activation volume is also the sum of two terms: $\Delta V_f$, the formation volume, and $\Delta V_m$, the motional volume. The activation volume measured in conventional diffusion studies is the sum of $\Delta V_f$ and $\Delta V_m$. Nuclear magnetic resonance techniques have been employed to determine $\Delta V$ and also the study of high temperature creep at high pressure yields values of $\Delta V$. 
It is possible to obtain values of $\Delta V_f$ and $\Delta V_m$ separately from quenching studies\textsuperscript{11-13} at high pressures in which a thin wire is rapidly cooled from high temperatures. The quenched-in resistivity is monitored to determine the formation volume and the subsequent annealing of the quenched-in defects is followed in order to determine the motional volume.

It is well established that diffusion in fcc solids proceeds via a vacancy mechanism.\textsuperscript{1} Generally it is found that the activation volumes in these solids are greater than 60% of the molar volume which lends support to the vacancy mechanism. Since hcp solids are close-packed as are the fcc solids they are commonly treated together in theoretical discussion. However, the hcp structure introduces a new consideration; it is a non-isotropic structure. Experimental evidence from diffusion studies\textsuperscript{14-18} on some hexagonal solids indicates that the vacancy mechanism is the predominant mechanism of diffusion. There have been no reliable experimental determinations of activation volumes for hcp solids. It is the purpose of the present work to determine experimentally activation volumes for self-diffusion in a representative of the hcp system. Table I lists the $\sigma/a$ ratio of divalent hcp elements along with the ratio for the ideal hexagonal close-packed lattice. The lattice constant in hexagonal direction is $\sigma$, and $a$ is the
Table I. $c/a$ Ratio of hcp Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>1.568</td>
</tr>
<tr>
<td>Mg</td>
<td>1.622</td>
</tr>
<tr>
<td>ideal</td>
<td>1.633</td>
</tr>
<tr>
<td>Zn</td>
<td>1.856</td>
</tr>
<tr>
<td>Cd</td>
<td>1.886</td>
</tr>
</tbody>
</table>

Because of the non-isotropic crystalline structure of the hexagonal system the rate of diffusion is dependent upon crystallographic direction.\textsuperscript{14} It has been found\textsuperscript{14} that in this system diffusion can be specified by two diffusion
coefficients which behave as functions of temperature as

\[ D_{||} = D_{0_{||}} \exp \left[ -\frac{Q_{||}}{RT} \right] \quad (11) \]

and

\[ D_{\perp} = D_{0_{\perp}} \exp \left[ -\frac{Q_{\perp}}{RT} \right], \quad (12) \]

where the subscript \( || \) refers to diffusion parallel to the hexagonal or \( c \)-axis and the subscript \( \perp \) refers to diffusion perpendicular to this axis (or in the basal plane). By using oriented single crystals it is possible to determine diffusion coefficients both parallel and perpendicular to the \( c \)-axis and consequently it is possible to determine activation volumes both parallel and perpendicular to the \( c \)-axis. Hence, it will be determined from this work to what extent the activation volume for zinc is dependent upon crystallographic direction.

In the hexagonal system two atomic jump frequencies must be considered; jumps in the basal plane and jumps between basal planes may have different frequencies. The diffusion coefficients \( D_{||} \) and \( D_{\perp} \) in this case can be described as

\[ D_{||} = \frac{1}{2}a^2 \nu_B \exp \left[ -\frac{\Delta G_B}{RT} \right] \quad (13) \]

and

\[ D_{\perp} = \frac{1}{2}a^2 \left[ 3\nu_A \exp \left( -\frac{\Delta G_A}{RT} \right) + \nu_B \exp \left( -\frac{\Delta G_B}{RT} \right) \right] \quad (14) \]
Where the subscript $A$ refers to jumps within the basal plane and subscript $B$ refers to jumps between two adjacent basal planes. The latter type of jumps has a component both along the $\sigma$-axis and in the basal plane, as can be seen in Fig. 2. To include the effects of correlation it is now necessary to allow for three possible correlation factors: one for jumps within the basal plane, one for the component along the $\sigma$-axis of the jumps between adjacent basal planes and one for the component on the basal plane of the same jumps.

Equations (13) and (14) can be manipulated to isolate the contribution of basal plane jumps. We obtain the following for the diffusion coefficient in the basal plane (BP)

\[
D_{BP} = \frac{3}{2} \alpha^2 \nu_A \exp[-\Delta G_A/RT] \quad (15)
\]

or

\[
D_{BP} = D_\perp - \frac{2}{3} \frac{\alpha^2}{\sigma^2} D_\parallel . \quad (16)
\]

From the experimentally determined diffusion coefficients $D_\parallel$ and $D_\perp$ it is possible to determine the activation volume in the basal plane using Eqs. (16) and (10).
Fig. 2. Geometry of the hcp lattice and representative jump vectors for diffusion parallel and perpendicular to the $c$-axis.
EXPERIMENTAL

Zinc single crystals of 99.999% purity were purchased from Nuclear Elements, Aremco and Materials Research Corporation. The crystals were oriented within 2° of the directions parallel and perpendicular to the c-axis by the back-reflection Laue method. Cutting and shaping of the crystals was done with a Servomet spark machine, with the crystal immersed in a 100°C oil bath throughout the process to reduce possible damage to the crystals. The crystals were cut into wafers of approximately 0.55 to 0.60 cm thickness. The crystals were then reduced in diameter to about 0.95 cm and spark-planed on both sides in the oil bath. The final step in surface preparation was a chemical polish to remove the damaged layers left from spark-planing. The final crystal length was approximately 0.54 cm for the 410°C runs and 0.48 cm for the 360°C runs. Crystals showing no surface imperfections under examination with an optical microscope were then preannealed at 400°C for 2$\frac{1}{2}$ hours to remove any remaining strains. Since all attempts at a preanneal in an evacuated capsule or in an evacuated capsule loaded with extra zinc chips resulted in a noticeable thermal etching which left a roughened and pitted
surface, the preanneal was done in an argon atmosphere at a pressure of $\frac{1}{2}$ kbar after which there was no evidence of thermal etching. The crystals were then given another chemical etch immediately preceding electroplating the radioactive zinc isotope. Radioisotope Zn$^{65}$ was obtained from International Chemical and Nuclear Corporation in the form of ZnCl$_2$. It was electroplated from a plating bath with the sample as the cathode and a Pt anode. The plated layer was estimated to be no more than 200Å thick.

The diffusion anneal was carried out in a gas pressure system as described by Dickerson, Lowell and Tomizuka using 99.999% pure argon* as the pressure medium. For this experiment the internal furnace had been modified so that the internal core pieces and the winding piece were of high-purity alumina. The sample was positioned with the diffusion axis parallel to the furnace axis.

The diffusion samples for the 410°C runs fit into an alumina ring with the face to be sectioned in contact with a 0.008 cm thick Pt disc on which a chromel, type 3G-345, alumel, type 3G-178, † was spot welded. The opposite face was similarly in contact with a Pt disc. In an attempt to decrease the temperature gradients across the sample, the

---

*Matheson Gas Products.
†Hoskins Manufacturing Company.
diffusion samples for the 360°C runs were held in a copper cup with the face to be sectioned in contact with the bottom of the cup. Chromel-alumel thermocouple wires were pressed into pre-drilled 0.3 mm deep holes in the base of the cup. These furnace configurations are shown in Fig. 3. All thermocouples were preannealed at 540°C for 35 minutes per instructions of the manufacturer to remove the effects of any strain introduced during fabrication of the thermocouple. A new thermocouple was used for each run. The indicated temperature was monitored with the chromel-alumel thermocouple and was maintained within 0.5°C of the desired temperature. Three of the runs at 410°C were also monitored with a Pt-Pt10%Rh thermocouple in order to determine whether thermocouple deterioration was a serious problem at this temperature. Pt-Pt10%Rh was chosen as a comparison since previous work\textsuperscript{22,23} indicated that this thermocouple is the most stable thermocouple at high pressure. All chromel-alumel thermocouples were subsequently calibrated against a new annealed thermocouple from the same spool of wire which had previously been calibrated against a standard Pt-Pt10%Rh thermocouple which had been calibrated against the melting points of standard metals supplied by the National Bureau of Standards.

Pressure was inferred from the resistance measurement of a manganin coil which was calibrated against the freezing
Fig. 3. Cross-sectional view of the internal furnace for measurement of zinc diffusion at 360° and 410°C.
pressure, 7.565 kbar of mercury, at 0°C. Pressure was maintained within ± 0.030 kbar for the entire diffusion anneal, including the process of warm-up and cooling.

Warm-up time to a preset temperature was kept to about 5 minutes as was the cooling time. The effective time, $t_{\text{eff}}$, at the anneal temperature was computed by requiring $t_{\text{eff}}$ to satisfy the condition

$$D(T_0) t_{\text{eff}} = \int_0^{t_{\text{actual}}} D(T(t)) dt$$  \hspace{1cm} (17)

where $T_0$ is the preset temperature. This gives

$$t_{\text{eff}} = \int \frac{\exp[\frac{\Delta H}{RT(t)}] dt}{\exp[-\frac{\Delta H}{RT_0}]}$$  \hspace{1cm} (18)

where

$$\Delta H = \Delta H_0 + PAV[1 - T(t)\alpha]$$  \hspace{1cm} (19)

$\Delta H_0$ was calculated from the work of Peterson and Rothman, and $\alpha$ is the volume expansion coefficient. The integral is approximated by a sum of terms.

Each diffused sample was mounted on a precision lathe in a chuck specially designed for rapid alignment of the diffusion surface. A layer of thickness approximately equal to $6\sqrt{Dt}$ was removed from the sides to eliminate any contribution from surface diffusion. About 15 sections were
turned off in thicknesses of 0.002 cm for the 410°C runs and in thicknesses of 0.001 cm for the 360°C runs with a tool bit shaped and sharpened to remove the material cleanly and with no appreciable burr. The 1.14 MeV gamma peak of Zn$^{65}$ was counted with a NaI(Tl) scintillator used with a RIDL Model 34.12B 400-channel analyzer. Each section was weighed with a Mettler Microbalance.
RESULTS

A total of twenty-two successful diffusion anneals were completed. The applicable solution to Eq. (3) is the solution for a thin film source at $t = 0$ on a semi-infinite medium given by

$$c = \frac{\alpha}{2\sqrt{\pi D t}} \exp\left[-\frac{x^2}{4Dt}\right] \quad (20)$$

where $\alpha$ is the initial concentration per unit area at $x = 0$ and $x$ is the distance in the direction normal to the initial thin film. From Eq. (20) it follows that a plot of the logarithm of the activity versus the square of the penetration distance yields a straight line. It is seen in Figs. 4 to 7 that straight lines are obtained. The diffusion coefficients calculated from the slope of the penetration plots using the calculated $t_{eff}$ are listed in Table II. Fig. 8 shows the pressure dependence of the diffusion coefficients for each temperature and crystallographic direction.
Fig. 4. Penetration curves for self-diffusion in zinc parallel to the c-axis at 360°C.
Fig. 5. Penetration curves for self-diffusion in zinc perpendicular to the \( \sigma \)-axis at 360°C.
Fig. 6. Penetration curves for self-diffusion in zinc parallel to the c-axis at 410°C.
Fig. 7. Penetration curves for self-diffusion in zinc perpendicular to the \( \sigma \)-axis at 410°C.
Table II. Raw, Time Corrected and Temperature Corrected D's

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Temp. (°C)</th>
<th>Pressure (Kb)</th>
<th>Raw D (cm²/sec)</th>
<th>Time Corrected D' (cm²/sec)</th>
<th>Temp. Corrected D_T (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR 8</td>
<td>360</td>
<td>1</td>
<td>$2.83 \times 10^{-9}$</td>
<td>$2.82 \times 10^{-9}$</td>
<td>$2.88 \times 10^{-9}$</td>
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<tr>
<td>MR 6</td>
<td>360</td>
<td>3</td>
<td>$2.52 \times 10^{-9}$</td>
<td>$2.50 \times 10^{-9}$</td>
<td>$2.55 \times 10^{-9}$</td>
</tr>
<tr>
<td>MR 3</td>
<td>360</td>
<td>5</td>
<td>$2.05 \times 10^{-9}$</td>
<td>$2.03 \times 10^{-9}$</td>
<td>$2.07 \times 10^{-9}$</td>
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<tr>
<td>MR 7</td>
<td>360</td>
<td>7</td>
<td>$1.77 \times 10^{-9}$</td>
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<tr>
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<td>360</td>
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<tr>
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<tr>
<td>MR 4</td>
<td>360</td>
<td>3</td>
<td>$1.48 \times 10^{-9}$</td>
<td>$1.46 \times 10^{-9}$</td>
<td>$1.45 \times 10^{-9}$</td>
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<tr>
<td>MR 1</td>
<td>360</td>
<td>5</td>
<td>$1.25 \times 10^{-9}$</td>
<td>$1.24 \times 10^{-9}$</td>
<td>$1.26 \times 10^{-9}$</td>
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<td>7</td>
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<td>$1.10 \times 10^{-9}$</td>
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<tr>
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<td>$0.968 \times 10^{-9}$</td>
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<tr>
<td>NE 3</td>
<td>410</td>
<td>0.5</td>
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<td>$1.08 \times 10^{-8}$</td>
<td>$1.07 \times 10^{-8}$</td>
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<tr>
<td>NE 1</td>
<td>410</td>
<td>2</td>
<td>$0.880 \times 10^{-8}$</td>
<td>$0.868 \times 10^{-8}$</td>
<td>$0.850 \times 10^{-8}$</td>
</tr>
<tr>
<td>MR 5</td>
<td>410</td>
<td>3</td>
<td>$0.930 \times 10^{-8}$</td>
<td>$0.924 \times 10^{-8}$</td>
<td>$0.858 \times 10^{-8}$</td>
</tr>
<tr>
<td>A 2</td>
<td>410</td>
<td>4</td>
<td>$0.814 \times 10^{-8}$</td>
<td>$0.816 \times 10^{-8}$</td>
<td>$0.808 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
Table II, Continued

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Temp. (°C)</th>
<th>Pressure (Kb)</th>
<th>Raw $D$ (cm$^2$/sec)</th>
<th>Time Corrected $D'$ (cm$^2$/sec)</th>
<th>Temp. Corrected $D_T$ (cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR 1$\parallel$</td>
<td>410</td>
<td>5</td>
<td>$0.828 \times 10^{-8}$</td>
<td>$0.812 \times 10^{-8}$</td>
<td>$0.801 \times 10^{-8}$</td>
</tr>
<tr>
<td>A 1$\parallel$</td>
<td>410</td>
<td>6</td>
<td>$0.725 \times 10^{-8}$</td>
<td>$0.712 \times 10^{-8}$</td>
<td>$0.688 \times 10^{-8}$</td>
</tr>
<tr>
<td>MR 4$\parallel$</td>
<td>410</td>
<td>8</td>
<td>$0.600 \times 10^{-8}$</td>
<td>$0.588 \times 10^{-8}$</td>
<td>$0.572 \times 10^{-8}$</td>
</tr>
<tr>
<td>NE 5$\perp$</td>
<td>410</td>
<td>0.5</td>
<td>$0.739 \times 10^{-8}$</td>
<td>$0.730 \times 10^{-8}$</td>
<td>$0.704 \times 10^{-8}$</td>
</tr>
<tr>
<td>NE 4$\perp$</td>
<td>410</td>
<td>3</td>
<td>$0.570 \times 10^{-8}$</td>
<td>$0.564 \times 10^{-8}$</td>
<td>$0.570 \times 10^{-8}$</td>
</tr>
<tr>
<td>NE 3$\perp$</td>
<td>410</td>
<td>6</td>
<td>$0.458 \times 10^{-8}$</td>
<td>$0.459 \times 10^{-8}$</td>
<td>$0.444 \times 10^{-8}$</td>
</tr>
<tr>
<td>NE 7$\perp$</td>
<td>410</td>
<td>7.5</td>
<td>$0.432 \times 10^{-8}$</td>
<td>$0.430 \times 10^{-8}$</td>
<td>$0.424 \times 10^{-8}$</td>
</tr>
<tr>
<td>NE 6$\perp$</td>
<td>410</td>
<td>9</td>
<td>$0.384 \times 10^{-8}$</td>
<td>$0.375 \times 10^{-8}$</td>
<td>$0.362 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
Fig. 8. Variation with pressure of the diffusion coefficients at constant temperature.
DISCUSSION

Determination of Activation Volume

According to the recent work of Getting and Kennedy on the effect of pressure on the emf of various thermocouples, the effect of pressure on chromel-alumel couples for operating conditions similar to the present one amounts to less than 0.5°C. Since this corresponds to approximately a 1% correction to the diffusion coefficient, it has been neglected.

The runs monitored with chromel-alumel and Pt-Pt10%Rh thermocouples indicate that deterioration of the chromel-alumel couples over the two to three hour runs at these temperatures is not a problem. The deterioration that does occur is approximately linear in time. Consequently the diffusion coefficients are temperature-corrected by taking one-half the full magnitude of deterioration and normalizing to the temperature of interest, T₁, using the following relation

\[ D_{T₁} = D_T \exp\left[ - \frac{H}{R}\left( \frac{1}{T₁} - \frac{1}{T} \right) \right] \]  

(21)

The temperature corrected values are found in Table II.

There are many sources of error in the measurement of each diffusion coefficient. The error in the mass of
each section is less than ± 0.5%. The error in the penetration depth is a result of errors in the measurement of the sample diameter, misalignment of the sample during sectioning, uncertainty in the thickness of the first cut and mass of the section and is estimated to be ± 1.5%. This results in an error in D of approximately ± 2%. The error introduced due to the finite time of warm-up and cooling and counting is less than ± 1%. The total error in D due to these sources is approximately ± 2.5%.

The largest source of error in determining the pressure dependence of the diffusion coefficients, \( D_\parallel \) and \( D_\perp \), is uncertainty in the diffusion temperature. The error in the isothermal values of \( D_\parallel \) and \( D_\perp \) due to uncertainty in the diffusion temperature is typically ± 3% at 360°C and ± 4.5% at 410°C.

The method of least squares is used to determine the slopes and intercepts of the straight lines of Fig. 8. The activation volumes are determined from the slopes of these straight lines according to Eq. (10). The effect of the second term on the right of Eq. (10) is either neglected by many authors or is treated as follows. It is assumed that there will be no change in \( f \) with pressure as long as there is no change in diffusion mechanism. Since \( \gamma \) is a constant dependent only on crystal structure the second term becomes
Using the definition of isothermal volume compressibility, $K = -\left[(1/V)(\partial V/\partial P)\right]_T$, we can rewrite the first term on the right of Eq. (22) to obtain

$$\text{RT}\left(\frac{\partial \ln(a^2vf)}{\partial P}\right)_T = \text{RT}\left(\frac{\partial \ln a^2}{\partial P}\right)_T + \text{RT}\left(\frac{\partial \ln v}{\partial P}\right)_T. \quad (22)$$

The Grüneisen constant, $\gamma_g$, is defined as $\gamma_g = -\frac{\partial \ln V}{\partial \ln P}$.

Using the definition of $K$ and $\gamma_g$ we can treat the second term as follows

$$\text{RT}\left(\frac{\partial \ln a^2}{\partial P}\right)_T = \frac{\text{RT}}{V^{2/3}}\left(\frac{\partial V^{2/3}}{\partial P}\right)_T = \frac{2}{3} \frac{\text{RT} (\partial V)}{V} = -\frac{2}{3} \text{RT} K. \quad (23)$$

Combining Eqs. (23) and (24) the final form for the activation volume with the correction term becomes

$$\Delta V = -\text{RT}\left(\frac{\partial \ln \bar{D}}{\partial P}\right)_T + \text{RT} (\gamma_g) (-K) \quad (25)$$

Recently Jeffery and Lazarus have pointed out that Eq. (25) is true only if the actual laboratory processes of measuring the diffusion coefficient (such as determination of the penetration depth) are actually carried out at the temperature and pressure of the diffusion anneal. They have
reanalyzed the problem as follows. For each plane of constant specific activity of the tracer, the penetration distance, \( x \), of Eq. (20) is an integral multiple of the lattice parameter, i.e., \( x = n \alpha \), \( n \) an integer. Then at the temperature and pressure of the diffusion anneal we have \( x(T,P) = n \alpha(T,P) \). For sectioning at room temperature and pressure, \( x_0 = n \alpha_0 \). These relations are substituted into Eq. (20) to obtain

\[
\frac{D(T,P)}{\alpha^2} = \frac{D'(T,P)}{\alpha_0^2}
\]  

(26)

where \( D' \) is the value of the diffusion coefficient determined from sectioning at room temperature and pressure. Eq. (26) is substituted into Eq. (10) giving

\[
\Delta V = -RT \left( \frac{\partial \ln D'}{\partial P} \right)_T + RT \left( \frac{\partial \ln \nu}{\partial P} \right)_T = -RT \left( \frac{\partial \ln D'}{\partial P} \right)_T + RT \nu \alpha_0 G \nu
\]

(27)

since \( \left( \frac{\partial \alpha_0}{\partial P} \right)_T = 0 \). Thus when the diffusion coefficient is determined by sectioning at ambient temperature and pressure, the \( 2/3 \) factor of Eq. (25) is not to be included in the correction term.

Uncorrected activation volumes calculated by a least squares analysis and using only the first term on the right of Eq. (27) are listed in Table III.
Table III. Uncorrected Activation Volumes

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\Delta V_{\parallel}$ (cm$^3$/mole)</th>
<th>$\Delta V_{\perp}$ (cm$^3$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>$4.06 \pm 0.18$</td>
<td>$3.99 \pm 0.18$</td>
</tr>
<tr>
<td>410</td>
<td>$4.23 \pm 0.35$</td>
<td>$4.32 \pm 0.16$</td>
</tr>
</tbody>
</table>

The corrections to the activation volume determined from the second term on the right of Eq. (27) amount to less than 5% of the total activation volume. The corrected activation volumes calculated according to Eq. (27) using the Grüneisen constants of Grüneisen and Goens$^{28}$ and the compressibility data of Bridgman$^{29}$ are listed in Table IV.

Table IV. Corrected Activation Volumes

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\Delta V_{\parallel}$ (cm$^3$/mole)</th>
<th>$\Delta V_{\perp}$ (cm$^3$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>$4.23 \pm 0.18$</td>
<td>$4.16 \pm 0.18$</td>
</tr>
<tr>
<td>410</td>
<td>$4.41 \pm 0.35$</td>
<td>$4.50 \pm 0.16$</td>
</tr>
</tbody>
</table>

Phenomenological Theories

It is informative to compare these experimentally obtained values to those values predicted by various semi-empirical relationships developed by various authors.
Rice and Nachtrieb\textsuperscript{30} have extended Rice's dynamical theory\textsuperscript{31} of diffusion to include the effects of pressure. They find that if the melting temperature, $T_m$, is linear in the applied pressure, then what they call a law of corresponding states exists. This law is expressed as

$$\lim_{T_m \to T_m(P=0)} D \propto \frac{T_m}{T} .$$  \hfill (28)$$

Making use of the Clapeyron equation they establish the following relation

$$\frac{\Delta H}{\Delta H_m} = \frac{\Delta V}{\Delta V_m}$$  \hfill (29)$$

where $\Delta H_m$ and $\Delta V_m$ are respectively the enthalpy and volume change of melting. If we use Kaufman's data\textsuperscript{32} for $\Delta H_m$ and $\Delta V_m$ and Peterson and Rothman's values\textsuperscript{15} of $\Delta H_\parallel$ and $\Delta H_\perp$, values of 4.95 cm$^3$/mole and 5.20 cm$^3$/mole are obtained for the activation volume parallel and perpendicular to the $c$-axis, respectively. These predicted values differ from the experimental values by 15\% and 20\%, respectively.

Keyes\textsuperscript{33,34} considered the effect of pressure on activated processes by means of continuum models and by means of atomic models. Keyes has succeeded in obtaining the following general expression for the activation volume
\[ \Delta V = 4K\Delta G \] (30)

by considering different models of lattice defects. As an example we consider the result of one model. He has shown that the continuum strain energy model of Zener leads to the following expression for the activation volume:

\[ \Delta V = 2(\gamma_G - \frac{1}{3})K\Delta G . \] (31)

Equation (31) is valid in the Grüneisen approximation in which it is assumed that all vibrational frequencies of the crystal depend upon the volume in the same way. Using the Grüneisen constants of Grüneisen and Goens and compressibility data of Bridgman and activation energies of Peterson and Rothman we obtain \( \Delta V_\parallel = 4.39 \text{ cm}^3/\text{mole} \) and \( \Delta V_\perp = 5.56 \text{ cm}^3/\text{mole} \) which differ from the present experimental values by 2% and 28%, respectively.

Sherby, Robbins and Goldberg have recently compiled a table of experimentally obtained activation volumes from self-diffusion measurements and creep studies. Furthermore they have developed a semi-empirical relation for calculation of the activation volume for any crystalline solid which is given by

\[ \Delta V = R(k_0 + \nu) \frac{\Delta V_m}{\Delta S_m} \] (32)
where \( k_0 \) is a constant which depends upon the crystal structure, \( v \) is the valence of the element and \( \Delta V_m \) and \( \Delta S_m \) are, respectively, the volume change and entropy change on melting. To arrive at Eq. (32) they have used the following relation for the activation energy

\[
Q = RT_m (k_0 + v)
\]

(33)

where \( T_m \) is the melting temperature. Equation (33) was derived semi-empirically by Sherby and Simnad as follows: using available diffusion data they made a plot of \( \log D \) versus \( T_m/T \). They observed a division of the data into three groups: bcc group, fcc - hcp group and diamond group. Furthermore, within each group they find that the more electropositive an element the higher the diffusivity. From these observations they proposed Eq. (33). With the use of Eq. (33) and the Clapeyron equation Sherby, Robbins and Goldberg arrive at Eq. (32). From Eq. (32) and using a \( k_0 \) equal to 16 for hcp crystals they predict an activation volume of 5.43 cm\(^3\)/mole for zinc. To take into account any possible anisotropy in the activation volumes of hcp crystals they suggest using Eq. (33) along with the experimentally determined values of \( Q_{\parallel} \) and \( Q_{\perp} \) to calculate directionally dependent values for \( (k_0 + v) \). Thus from Eq. (33) we obtain

\[
(k_0 + v)_{\parallel \ or \ \perp} = \frac{Q_{\parallel \ or \ \perp}}{R T_m} \ .
\]

(34)
When we substitute Eq. (34) into Eq. (32) we obtain Eq. (29) of Rice and Nachtrieb. Thus, this procedure will not predict a value for $\Delta V_\parallel$ and $\Delta V_\perp$ different from that already calculated from Eq. (29).

**Isotope Effect**

In recent years the isotope effect has been actively studied in an effort to determine the mass dependence of the atomic jump rate, $w$, and to determine the correlation factor, $f$. In 1959 Schoen\textsuperscript{38} proposed the following equation to describe the effects of isotopic mass on tracer diffusion for tracer isotopes $\alpha$ and $\beta$

\[
\left( \frac{D_\alpha}{D_\beta} - 1 \right) = f^\alpha \left( \frac{w_\alpha}{w_\beta} - 1 \right)
\]

(35)

where $f^\alpha$ is the correlation factor for isotope type $\alpha$. Equation (35) can be used to determine $f$ provided that the ratio of the jump rates is known. The simplest assumption considered follows from the work of Zener\textsuperscript{4}; it is that the jump frequencies satisfy the relation

\[
\frac{w_\alpha}{w_\beta} = \left( \frac{m_\beta}{m_\alpha} \right)^{1/2}
\]

(36)

which is equivalent to the assumption of uncoupled harmonic oscillators. Consideration of the coupling between the diffusing atom and the lattice led Muilen\textsuperscript{7} to modify
Eq. (35) to
\[
\left( \frac{D^\alpha}{D^B} - 1 \right) = r^\alpha \Delta K \left( \frac{m^B}{m^\alpha} \right)^{\frac{1}{2}} - 1
\]  
(37)

where $\Delta K$ is the fraction of the total translational kinetic energy possessed by the jumping atom as it passes through the saddle point configuration.

Le Claire\(^{39}\) has rederived Mullen's expression and has found his interpretation of $\Delta K$ to be oversimplified. For motion about the saddle point, there is one unstable mode which, when excited, leads to the passage of the atom through the saddle point configuration. Le Claire finds that $\Delta K$ represents the fraction of the total kinetic energy of the unstable mode possessed by the jumping atom.

In 1966 Mundy, Barr and Smith\(^{40}\) collected together the then existing data on isotope effects and relative activation volumes (ratio of activation volume, $\Delta V$, to molar volume, $\Omega$). This data suggested a correlation between $\Delta V/\Omega$ and $\Delta K$. Furthermore, they argue, the correlation should be between $\Delta K$ and the formation activation volume rather than the total activation volume since it is in effect the formation volume which moves during the atom's jump.

Le Claire\(^{39}\) has argued further in this direction as follows: whenever $\Delta K$ is less than one, more atoms than the
jumping atom must participate in the decomposition mode. Hence there will be motion of neighboring atoms towards new positions as the migrating atom completes its jump. Since motion associated with $\Delta V_f$ will have a component in the jump direction and motion associated with $\Delta V_m$ will be mostly orthogonal to the jump direction, one expects to find a correlation of $\Delta K$ with $\Delta V_f$. Now it is assumed that the kinetic energy of an atom participating in the decomposition is directly proportional to the distance it has to move to reach its final position. If $K.E. = \text{constant} \times r$ where $r$ is the atomic radius for the migrating atom, and $K.E. = \text{constant} \times \ell$ where $\ell/r$ is the relaxation strain around the defect for the other atoms, then $\ell/r \approx \frac{1}{3} \left| \left[ 1 - \left( \frac{\Delta V_f}{\Omega} \right) \right] \right|$. Then the following expression is obtained by Le Claire for $\Delta K$

$$
\Delta K \approx \frac{r}{r + n\ell} \approx \frac{1}{1 + \frac{n}{3} \left| \left( 1 - \frac{\Delta V_f}{\Omega} \right) \right|} \tag{38}
$$

where $n$ is a number considered to be of the order of the number of atoms that relax for the passage of the atom through the saddle point.

The present experimental results can be applied to calculate $n$ for zinc under the assumption that the motional volume is a small fraction of the total activation volume.
If we use Peterson and Rothman's value for $\Delta K$ given by $\Delta K_{||} = 0.926$ and $\Delta K_{\perp} = 0.944$ then we obtain $n_{||} = n_{\perp} = 0.4$. Since it does not appear very likely that less than one atom participates in the decomposition mode the present experimental results do not support the relation of Eq. (38) derived by Le Claire. If our assumption that $\Delta V_f \gg \Delta V_m$ is incorrect, then Eq. (38) will yield values for $n$ even more unlikely than those just derived.

Let us reconsider Le Claire's assumptions in obtaining Eq. (38). He assumed that the kinetic energy of an atom participating in the decomposition mode is directly proportional to the distance it moves to reach its final position. The form of the potential energy used in determining the normal mode frequencies of the crystal in its equilibrium configuration and in determining the normal mode frequencies of the crystal with a migrating atom in the saddle point configuration is usually taken to be harmonic. Thus we will assume that the kinetic energy of an atom participating in the decomposition mode is directly proportional to the square of the distance moved in reaching its final position. Using this assumption we arrive at the following expression for $\Delta K$

$$
\Delta K \approx \frac{1}{1 + \frac{n}{9} \left( 1 - \frac{\Delta V_f}{\Omega} \right)^2}.
$$

(39)
Table V contains values of n calculated from Le Claire's expression for $\Delta K$ given by Eq. (38) with values of n computed from the present expression, Eq. (39). The formation volumes for zinc and sodium are obtained by assuming that the motional volume is a small fraction of the total activation volume and hence that the formation volume is approximately equal to the total activation volume. The formation volume for silver is obtained by assuming that it is the same fraction of the total volume as it is for gold, namely 0.75. From Table V it is seen that only in the case of Na is the n value obtained by Le Claire at all likely. For Na n = 6 is actually equal to the number of neighbors a migrating atom has at the saddle point, but in fact, it is likely that more than 6 atoms actually relax. In the fcc and hcp cases it is unlikely that so few atoms be involved in the relaxation. If we consider the values of n obtained from the present relationship, the numbers obtained are more reasonable than Le Claire's numbers in all cases. In the bcc case, n = 39 corresponds to considering nearest neighbors, next nearest neighbors and third nearest neighbors. In the fcc case, n = 16 corresponds to considering nearest neighbors and next nearest neighbors. In the hcp case, n = 2 does not correspond to considering even nearest neighbors, but the present value at least corresponds to considering 2 of the 4 nearest neighbors at the saddle point positions.
Table V. Values of n

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>$\Delta K$</th>
<th>$\Delta V_f/\Omega$</th>
<th>$n_{\text{Le Claire}}$</th>
<th>$n_{\text{present}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>bcc</td>
<td>0.50$^a$</td>
<td>0.52$^b$</td>
<td>6</td>
<td>39</td>
</tr>
<tr>
<td>Ag</td>
<td>fcc</td>
<td>0.86$^c$</td>
<td>0.70$^d$</td>
<td>1.6</td>
<td>16</td>
</tr>
<tr>
<td>Zn</td>
<td>hcp</td>
<td>0.93$^e$</td>
<td>0.47$^f$</td>
<td>0.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$^a$Mundy et al.$^40$
$^b$Nachtrieb et al.$^42$
$^c$Peterson and Barr.$^43$
$^d$Bonanno and Tomizuka.$^44$
$^e$Peterson and Rothman.$^15$
$^f$Present experiment.
Thus, from the present relation given by Eq. (39) we have been able to improve the values for $n$ over those given by the expression of Le Claire's in Eq. (38). More experimental data is needed in order to establish the usefulness of Eq. (39).

**Basal Plane Activation Volume**

Empirical relations obtained from the present experiment are given by:

\[
\ln D_{360°} = (-0.0770 \pm 0.0033)P - 19.586 \pm 0.019 \quad (40)
\]

\[
\ln D_{360°} = (-0.0758 \pm 0.0033)P - 20.093 \pm 0.019 \quad (41)
\]

\[
\ln D_{410°} = (-0.0745 \pm 0.0062)P - 18.348 \pm 0.029 \quad (42)
\]

\[
\ln D_{410°} = (-0.0761 \pm 0.0029)P - 18.745 \pm 0.017 \quad (43)
\]

These equations together with Eq. (16) yield equations for the pressure dependence of diffusion in the basal plane

\[
\ln D_{BP,360°} = (-0.0755 \pm 0.0145)P - 20.469 \pm 0.049 \quad (44)
\]

and

\[
\ln D_{BP,410°} = (-0.0765 \pm 0.0144)P - 19.078 \pm 0.034 \quad (45)
\]
These are the lines shown in Fig. 8. The activation volumes determined from these equations are given by

\[
\begin{align*}
(360°) & \quad \Delta V_{\text{BP}} = 3.98 \text{ cm}^3/\text{mole} \pm 0.76 \text{ cm}^3/\text{mole} \\
(410°) & \quad \Delta V_{\text{BP}} = 4.35 \text{ cm}^3/\text{mole} \pm 0.82 \text{ cm}^3/\text{mole} .
\end{align*}
\]

The corrected values as determined by Eq. (27) are given by

\[
\begin{align*}
(360°) & \quad \Delta V_{\text{BP}} = 4.15 \text{ cm}^3/\text{mole} \pm 0.76 \text{ cm}^3/\text{mole} \\
(410°) & \quad \Delta V_{\text{BP}} = 4.53 \text{ cm}^3/\text{mole} \pm 0.82 \text{ cm}^3/\text{mole} .
\end{align*}
\]

A tabulation of all calculated activation volumes is found in Table VI.

**Motional Volumes**

Consider Eqs. (13) and (14) and let us separate the activation energy into the sum of the formation energy and motional energy. Since the energy of formation of a vacancy is independent of direction, we obtain

\[
D_{||} = \frac{3}{2} a^2 \nu_B \exp[-\Delta G_f/RT] \exp[-\Delta G_m^B /RT] 
\]

\[
D_{\perp} = \frac{1}{2} a^2 \left[ 3 \nu_A \exp(-\Delta G_f/RT) \exp(-\Delta G_m^A /RT) + \nu_B \exp(-\Delta G_f/RT) \exp(-\Delta G_m^B /RT) \right] 
\]

Using \(D_{||}\) and \(D_{\perp}\) as given by Eqs. (46) and (47) in Eq. (16) we obtain
Table VI. Activation Volumes

| T (°C) | ΔV|| (cm³/mole) | ΔV⊥ (cm³/mole) | ΔV_Bp (cm³/mole) |
|--------|----------------|----------------|-----------------|
| 360    | 4.06 ± 0.18    | 3.99 ± 0.18    | 3.98 ± 0.76     |
| 410    | 4.23 ± 0.35    | 4.32 ± 0.16    | 4.35 ± 0.82     |

Corrected

| T (°C) | ΔV|| (cm³/mole) | ΔV⊥ (cm³/mole) | ΔV_Bp (cm³/mole) |
|--------|----------------|----------------|-----------------|
| 360    | 4.23 ± 0.18    | 4.16 ± 0.18    | 4.15 ± 0.76     |
| 410    | 4.41 ± 0.35    | 4.50 ± 0.16    | 4.53 ± 0.82     |

\[
D_{BP} = \frac{3}{2} a^2 v_A \exp[-\Delta G_f/RT] \exp[-\Delta G_m^A/RT] \quad (48)
\]

and

\[
D_\parallel = \frac{3}{2} a^2 v_B \exp[-\Delta G_f/RT] \exp[-\Delta G_m^B/RT] . \quad (49)
\]

Taking the logarithm of the ratio of Eqs. (48) and (49) we get

\[
\ln \frac{D_{BP}}{D_\parallel} = \ln \left\{ \frac{2 \frac{a^2}{e^2} v_A}{v_B} \right\} - \left( \frac{\Delta G_m^A - \Delta G_m^B}{RT} \right) . \quad (50)
\]

If we take the derivative of Eq. (50) with respect to pressure at constant temperature we obtain
Hence a plot of $\ln\left(\frac{D_{BP}}{D_{\parallel}}\right)$ versus pressure will yield the difference in motional volume of jumps in the basal plane versus jumps between basal planes if the contribution of the first two terms on the right can be neglected (or corrected for).

Consider the first term on the right of Eq. (51). High pressure data on the variation of lattice parameter of Zn is not available. In the work of Drickamer et al. the variation of lattice parameters of solids at very high pressures data on cadmium has been included. Since the $c/a$ ratio for Cd is similar but greater than that of Zn we will use the low pressure data of Drickamer et al. to obtain an upper limit on this term. We obtain a less than 1% contribution for this term. Now the second term on the right of Eq. (51) will be considered. If we take $\nu_A$ and $\nu_B$ equal to the Debye frequencies in the respective directions and use the definition of the Grüneisen constant we obtain

$$\left(\frac{\partial \ln \nu_A/\nu_B}{\partial P}\right)_T = -\frac{1}{RT} \left(\Delta V_{m_A} - \Delta V_{m_B}\right).$$  

(52)
Using the values of $\gamma_G^A$ and $\gamma_G^B$ of Grüneisen and Goens\textsuperscript{28} this term also makes a less than 1% contribution.

Using Eqs. (40) and (44) for 360° and Eqs. (42) and (45) for 410°, we obtain the following equations for the dependence of $\ln(D_{BP}/D_\parallel)$ on pressure

360°: $\ln[D_{BP}/D_\parallel] = (+0.0015 \pm 0.0176)P - (0.883 \pm 0.068)$

(53)

410°: $\ln[D_{BP}/D_\parallel] = (-0.0020 \pm 0.0206)P - (0.730 \pm 0.063)$

(54)

From these equations we obtain the following for the difference in motional volume between jumps in the basal plane and jumps between basal planes:

at 360° $[\Delta V_{m_A} - \Delta V_{m_B}] = (0 \pm 1) \text{ cm}^3/\text{mole}$

at 410° $[\Delta V_{m_A} - \Delta V_{m_B}] = (0 \pm 1) \text{ cm}^3/\text{mole}$.

Thus within the limits of error of this experiment significant difference in value of the motional volumes between jumps within the basal plane and jumps between basal planes cannot be observed.

From the point of view of simple geometric arguments this result of directional independence in motional volumes is unexpected as can be seen from the following. In Fig. 2
representative nearest neighbor jumps are shown, one for movement parallel to the $c$-axis and one for movement perpendicular to the $c$-axis. In Fig. 9 the configuration of the surrounding atoms in the saddle point position for an atom making a jump parallel to the $c$-axis is shown. In Fig. 10 the configuration of the surrounding atoms in the saddle position for an atom making a jump perpendicular to the $c$-axis is shown. Now if we treat the problem of the diffusing atom moving through the saddle point position in the hard sphere approximation, then we see that the diffusing atom has to "fit" through an area the size of which is dependent upon the type of jump. If we take the radius of the zinc atom to be $r = 1.32\AA$ and using the value for the lattice constants given by $a = 2.65\AA$ and $c = 4.93\AA$ then we find that for a jump in the basal plane there is $0.38\AA^2$ to spare as the atom moves through the saddle point. But for a jump perpendicular to the basal plane the diffusing atom will not fit through and an extra $1.9\AA^2$ is needed for the atom to pass through the saddle point barrier. Hence in this model we would expect that the motional volume for a jump in the basal plane to be greater than the motional volume for a jump out of the basal plane. In fact treating $1.9\AA^2$ as if it were the cross section of a sphere we find that a motional volume of approximately $0.2$ of an atomic volume is expected for jumps in the basal plane.
Fig. 9. Saddle point configuration for jumps parallel to the c-axis.
Fig. 10. Saddle point configuration for jumps perpendicular to the \( c \)-axis.
To get further information of the possible existence of a small difference between the activation volumes parallel and perpendicular to the $c$-axis it will be necessary to improve the experimental accuracy. The greatest source of error in the present experiment is knowledge of the diffusion temperature. Though thermocouple deterioration has not been a serious problem in this work the presence of temperature gradients across the sample is a serious problem which must be overcome if further accuracy is to be achieved. A possible solution to this problem might be attained by winding the heater directly onto a metal core or by the addition of a metal cylinder directly under the winding core.
SUMMARY

The activation volumes for single crystalline zinc have been determined for diffusion parallel and perpendicular to the \( \sigma \)-axis at 360°C and 410°C. Within the resolution of this experiment no anisotropy has been observed in activation volumes. The activation volumes determined in this experiment are independent of temperature.

Le Claire's expression for \( \Delta K \) has been reexamined and an alternative expression for \( \Delta K \) has been proposed. The present expression for \( \Delta K \) is in better agreement with the experimental data presently available.
LIST OF REFERENCES


