The pressure dependence of self-diffusion in lithium and sodium

Roland Arthur Hultsch

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THE PRESSURE DEPENDENCE OF SELF-DIFFUSION IN LITHIUM AND SODIUM

by

Roland Arthur Hultsch

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DOCTOR OF PHILOSOPHY

Major Subject: Physics

Approved:

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In Charge of Major Work

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Iowa State University
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Ames, Iowa

1961
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I. INTRODUCTION

Diffusion in solids is the translational motion of the atoms or molecules among the lattice or interstitial sites. When the diffusing units are identical, except for nuclear mass differences, to the lattice units, the phenomenon is called self-diffusion. Chemical (impurity) diffusion is the term used when the lattice consists of more than one kind of atom or molecule. The research described herein is concerned with the self-diffusion of atoms in the elementary solids lithium and sodium.

That atoms move through the lattice is directly shown by observing the net transport of radioactive tracer atoms. In such experiments tracer atoms initially on the surface of a crystal are found after a time to be inside the crystal. The distribution of these atoms, i.e., the activity profile, is described by the appropriate solution of the classical diffusion equation \( \frac{\partial c(x,t)}{\partial t} = D \nabla^2 c(x,t) \), where \( c(x,t) \) is the tracer concentration and \( D \) is the diffusion coefficient. Simple geometries and boundary conditions are used and the data are analyzed to give \( D(P,T) \) for the particular pressure \( P \) and temperature \( T \) at which the crystal is maintained.

Besides the direct measurement of \( D \) there are several measurable phenomena which depend on \( D \) or are diffusion limited. Examples of these are relaxation of strained
crystals, electrical resistivity anomalies, and nuclear spin relaxation. The last of these has been used in this work.

It is known that certain nuclear spin relaxation times are directly or inversely proportional to the diffusion coefficient. Holcomb and Norberg (1) verified this for lithium and sodium in their measurements of the temperature dependence of the relaxation times. We have been able to measure the pressure dependence of these relaxation times, and hence get a measure of the pressure dependence of the diffusion coefficient.

The specific goal of this research has been to measure the activation volumes for self-diffusion of lithium and sodium. The activation volume $V_a$ is essentially the pressure derivative of the logarithm of $D$. Prior to this work $V_a$ for sodium and lead had been measured using tracer diffusion (2,3). No such experiments are possible with lithium, since the radioisotopes of lithium have inconveniently short half-lives. Thus we were primarily interested in obtaining $V_a$ for lithium, and the sodium measurement was undertaken for comparison with the earlier value and to give us confidence in our method.

Recently a new theory of the pressure dependence of self-diffusion (4) has provided a formula for predicting the activation volume of simple solids. This formula
was found to work well for lead. However, the agreement of theory and experiment for sodium was not clear cut, and required special arguments.

The values of $V_{a}$ for lithium and sodium obtained in the present work agree with the predictions of the new theory, within the uncertainties of the measurements, and the uncertainties of the other quantities in the theory. Thus we feel that besides producing a good value of $V_{a}$ for lithium, we have improved the value of $V_{a}$ for sodium.
II. THEORY OF DIFFUSION AND NUCLEAR SPIN RELAXATION

A. Theory of Diffusion

In measuring the diffusion coefficient using tracers one observes a net transport of atoms from the surface of a crystal into the interior. To account for this transport one postulates random jumping of the atoms between the lattice or interstitial sites. Then it follows from the theory of random flights that the atoms move away from their initial positions. For example, in the case of a particle making jumps of equal length at random in one dimension, after \( N \) jumps the particle has an even chance of being more than \( \sqrt{N} \) steps from its initial position. The main problem of understanding diffusion in solids is to understand the elementary jump mechanism.

Most of the experimental effort has been to determine the temperature dependence of \( D \) in pure metals and binary alloys. It has been found that the Arrhenius equation adequately describes \( D(P, T) \) in the temperature ranges studied. This equation is

\[
D(P, T) = D_o \exp\left(-\frac{H_a(P)}{RT}\right).
\]  

(1)

\( H_a \) is called the activation enthalpy, or loosely, the activation energy. It is independent of temperature and dependent on pressure. \( D_o \) is weakly dependent on both temperature and pressure. Usually Eq. 1 is used to get
$D_0$ and $H_a(P)$ by measuring $D$ at several temperatures at constant pressure, and fitting a straight line to the data, plotted as $\log D(T)$ vs $1/T$.

Derivations of Eq. 1 start with an expression from the theory of random flights in three dimensions (5). This expression is

$$D = \frac{1}{6} \sum_i \nu_i \delta_i^2$$

where $\nu_i$ is the jumping frequency of an atom along the $i^{th}$ direction, and $\delta_i$ is the jump distance. It is recognized that this is only a rough definition of $\nu_i$ (6).

For cubic crystals one assumes that $\nu_i$ is the same for different jumping directions, and for a single mechanism, it is customary to write

$$\frac{1}{6} \sum_i \delta_i^2 = \gamma \alpha^2$$

where $\gamma$ is a constant which depends on the crystal structure and the mechanism, and $\alpha$ is the lattice constant. With these simplifications, the expression for $D$ is

$$D = \gamma \alpha^2 \nu.$$  \hspace{1cm} (4)

From the Theory of Absolute Reaction Rates we get

$$\nu = \nu_0 \exp(-G_a/RT).$$  \hspace{1cm} (5)

Here $\nu_0$ is a constant characterizing the lattice vibration spectrum and is usually taken to be $(10)^{13}$ sec$^{-1}$. $G_a$ is
called the Gibbs free energy of activation. For any jump mechanism we suppose the diffusing atom to pass over a saddle potential configuration. On an atomic basis, if the diffusing atom is confined to a plane perpendicular to the jump direction, \( G_a \) is the isothermal work required to slowly move the plane from a position passing through an equilibrium position (lattice or interstitial site) to a position passing through the saddle point.

To show explicitly the temperature dependence of \( G_a \), we write

\[
G_a = H_a - T S_a
\]

(6)

where \( H_a \) is the activation enthalpy mentioned above, and \( S_a \) is the activation entropy.

Collecting terms again, we have

\[
D = r a^3 \nu_0 \exp \left( \frac{S_a}{R} \right) \exp \left( -\frac{H_a}{RT} \right) = D_0 \exp \left( -\frac{H_a}{RT} \right)
\]

(7)

where \( D_0 \) includes the terms with relatively slight temperature and pressure dependence.

The three most discussed elementary jump mechanisms are:

(a) Vacancy Mechanism. On this model, a lattice has a temperature dependent concentration of vacant sites, onto which the nearest neighbor atoms can jump. Vacancies are formed at surfaces and faults when an atom jumps out of a surface layer into a new atom plane. The vacancy thus formed can migrate into the interior of the crystal as
atoms from successively deeper atom planes jump into the vacancy. This mechanism is probably more important for self-diffusion than for chemical diffusion.

(b) Interstitial Mechanism. According to this picture atoms jump among the interstitial sites. This mode is considered effective in the case of interstitial solid solutions, such as diffusion of carbon in iron.

(c) Interchange Mechanism. This view is that two neighbor atoms on lattice sites can interchange, or that a ring of four atoms can rotate together so that each moves onto its neighbor's position. The ring of four case is considered possible in b.c.c. structures, such as the alkali metals (7).

Besides these individual atom mechanisms others have been suggested which involve the cooperative motion of 10-20 atoms (8). However, these are more difficult for theory to deal with, and have not been considered as much as the single atom mechanisms.

Calculations of $D_0$ and $H_a(P=0) = Q_o$ have been made on these models and the calculated values compared with the experimental values (9,10). The activation energy $Q_o$ has been most used to judge how well a model fits reality. Thus if a calculated value of $Q_o$ were five times the experimental value, the mechanism on which the calculation was based would be considered unlikely, especially if another mechanism gave better agreement. Table 1 gives some experimental and calculated values of $Q_o$ for self-diffusion in copper (11).
Table 1. Calculated and experimental activation energies

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Activation energy (kilo calories/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy</td>
<td>64.6</td>
</tr>
<tr>
<td>Ring-of-four</td>
<td>92.3</td>
</tr>
<tr>
<td>Pair exchange</td>
<td>230.</td>
</tr>
<tr>
<td>Experiment</td>
<td>48.5</td>
</tr>
</tbody>
</table>

Because of the complexity of even the simplest solids, calculations of $Q_0$ require judgements and approximations. Therefore agreement of calculated and experimental values is not considered conclusive evidence for a particular mechanism.

Among efforts to understand diffusion, attempts have been made to find correlations of $Q_0$ with other physical constants of a system. It has been observed that $Q_0$ is approximately proportional to either the melting temperature $T_o$ at one atmosphere, or the heat of fusion $H_m$. Table 2 lists values of the ratios $Q_0/T_o$ and $Q_0/H_m$ for various simple solids. The idea that diffusion and melting may be related has inspired a notion of a local-liquid mechanism for diffusion (8). We shall see below that the values for the activation parameters measured in this work satisfy a fusion-diffusion correlation.
Table 2. Correlation of diffusion and melting parameters

<table>
<thead>
<tr>
<th>Element</th>
<th>Q_o (kcal/mole)</th>
<th>T_o (°K)</th>
<th>H_m (kcal/mole)</th>
<th>Q_o/RT_o</th>
<th>Q_o/H_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>13.2</td>
<td>454</td>
<td>0.715</td>
<td>14.7</td>
<td>18.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>10.0</td>
<td>371</td>
<td>0.624</td>
<td>13.6</td>
<td>16.0</td>
</tr>
<tr>
<td>Copper</td>
<td>47.1</td>
<td>1350</td>
<td>3.08</td>
<td>17.5</td>
<td>15.3</td>
</tr>
<tr>
<td>Lead</td>
<td>24.2</td>
<td>601</td>
<td>1.19</td>
<td>20.4</td>
<td>20.4</td>
</tr>
</tbody>
</table>

A further possibility for deciding among the model mechanisms is provided by a knowledge of the pressure dependence of D. The experiments are usually directed toward measuring the activation volume V_a. Nachtrieb (2) defined this parameter as

\[ V_a = \frac{\partial G_a}{\partial P} \bigg|_T \]  

Using Eqs. 4 and 5 we get the relation between V_a and D;

\[ V_a = -RT \frac{\partial}{\partial P} \ln \left( \frac{D}{a^2 \nu_o} \right) \bigg|_T \]  

In the limit of low pressure where we can neglect the dependence of a^2\nu_o on pressure, V_a is a measure of the pressure dependence of the activation energy. The experimental evidence is that, to a good approximation,

\[ H_a = Q_o + V_a P \]

where Q_o is the activation energy at one atmosphere pressure, which is practically zero pressure for the
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<table>
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<th>Element</th>
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</table>

A further possibility for deciding among the model mechanisms is provided by a knowledge of the pressure dependence of $D$. The experiments are usually directed toward measuring the activation volume $V_a$. Nachtrieb (2) defined this parameter as

$$ V_a = \left. \frac{\partial G_a}{\partial P} \right|_T $$

Using Eqs. 4 and 5 we get the relation between $V_a$ and $D$;

$$ V_a = -RT \left. \frac{\partial \ln \left( \frac{D}{a^2 \nu_0} \right)}{\partial P} \right|_T $$

In the limit of low pressure where we can neglect the dependence of $a^2 \nu_0$ on pressure, $V_a$ is a measure of the pressure dependence of the activation energy. The experimental evidence is that, to a good approximation,

$$ H_a = Q_o + V_a P $$

where $Q_o$ is the activation energy at one atmosphere pressure, which is practically zero pressure for the
approximately ten kilo-atmosphere pressure range used in diffusion experiments. To illustrate the dependence of $H_a$ on pressure, it may be noted that in the case of lithium a pressure of thirty kilo-atmospheres increases the activation energy by thirty percent, assuming the linear relation above.

The activation volume has also been interpreted as a real physical volume. On the model of a point defect, $V_a$ can be considered as the sum of two terms, (a) the volume $V_p$ associated with the formation of the defect, and (b) the volume $V_M$ associated with the dilatation of the lattice when an atom moves onto the defect site. This interpretation actually appears to be inconsistent with the vacancy model (11). On this model, $V_M$ should equal $V_p$, but experiments indicate that $V_M$ is much smaller than $V_p$. This difficulty does not arise with the new dynamical theory (4), since on this view $V_a$ is not considered to be a real physical volume.

The activation volume has been measured for only a few of the simple solids. The experimental values, including the results of this work, are listed in Table 3, along with the ratios of the activation volume to the molar volume $V_m$.

It is interesting to note the ratios of these volumes. The activation volume is a measure of how much the neighbor atoms relax inward on a vacancy. On a hard sphere close-packed model of a solid, the spheres adjacent to a vacancy are not disturbed, and the volume of the vacant site $V_p$
equals the volume of the occupied site $V_m$. (However, on this model, $V_a = 2V_m$, since the volume contribution of $V_M$ above is equal to the molar volume.) But experiments show that $V_a$ is less than the molar volume, so we infer that neighbors are relaxing inward on a vacancy. It is plausible that metal atoms would relax inward since the nearest neighbor forces are repulsive. Creating a vacancy results in an unbalanced force on each atom adjacent to the vacancy tending to displace the atom into the vacancy.

Table 3. Activation volumes for self-diffusion

<table>
<thead>
<tr>
<th>Element</th>
<th>$V_a$ (cm$^3$)</th>
<th>$V_m$ (cm$^3$)</th>
<th>$V_a/V_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>3.6$^a$</td>
<td>13.0</td>
<td>0.28</td>
</tr>
<tr>
<td>Sodium</td>
<td>9.6$^a$</td>
<td>23.7</td>
<td>0.40</td>
</tr>
<tr>
<td>Silver</td>
<td>9.3$^b$</td>
<td>10.3</td>
<td>0.90</td>
</tr>
<tr>
<td>Lead</td>
<td>13.0$^c$</td>
<td>18.2</td>
<td>0.71</td>
</tr>
</tbody>
</table>

$^a$This research

$^b$ (12)

$^c$ (3)

Eq. 5 for $\nu$ is obtained from thermodynamic ideas about energy states of a diffusing atom at the equilibrium and saddle positions. However, the time it takes an atom to jump may be so short that thermodynamic concepts are not valid. This criticism has been made by Rice (6) who has given a dynamical theory of diffusion. This theory has been
extended to include the pressure dependence of diffusion (4), and the results of the theory that are pertinent to our experiment are given by two expressions. The first is

$$\frac{V_a}{H_a} = \frac{\delta V_m}{H_m}$$  \hspace{1cm} (11)

Here $\delta V_m$ is the change of molar volume upon melting. The other relation is

$$\ln D \propto \left( \frac{T_m}{T} \right)^{\delta}$$  \hspace{1cm} (12)

This is called a law of corresponding states since the diffusion coefficient is given by a single variable, $T_m/T$.

The relations of Eqs. 11 and 12 were observed experimentally before they were found to be predicted by theory. It is easy to show how Eq. 11 leads to Eq. 12.

In the limit of low pressure, we can write

$$D = D_0 \exp \left(- \frac{Q_v + V_a P}{RT} \right)$$  \hspace{1cm} (13)

When the pressure dependence of the melting temperature can be described by a linear function,

$$T_m = T_o + KP,$$  \hspace{1cm} (14)

the coefficient $K$ is given by the Clausius-Clapeyron equation:

$$K = \frac{d T_m}{d P} \bigg|_{P=0} = \frac{T_o \delta V_m}{H_m}$$  \hspace{1cm} (15)
If Eq. 14 is solved for P and Eq. 11 is used with Eq. 15, substitution of $P(T_m)$ into Eq. 13 results in

$$D(T_m/T) = D_0 \exp\left(- \frac{Q_o}{RT_0} \frac{T_m}{T}\right). \quad (16)$$

From this relation we get

$$\frac{d \ln D(T_m/T)}{d(T_m/T)} = - \frac{Q_o}{RT_0}. \quad (17)$$

which is the relation expressed by Eq. 12. Further comments on the derivation of Eq. 17 are presented in Appendix A.

In this section we have presented the ideas about diffusion that are necessary to understand our results. A more complete discussion of the theoretical and experimental situation can be found in a recent review of Lazarus (11).

B. Theory of Nuclear Spin Relaxation

When a sample of matter containing nuclei with magnetic dipole moments is placed in a magnetic field, after equilibrium obtains the nuclei are distributed in several Zeeman levels. In the limit of negligible internuclear interaction, each nucleus experiences only the magnetic field $B_0$ produced in the laboratory, and there are $2I + 1$ levels when $I$ is the nuclear spin quantum number. The populations of these levels, given by the Boltzmann
factor, are unequal, and the sample has a net nuclear magnetization $M_0$ parallel to the field $H_0$.

A nucleus with magnetic dipole moment $\mu$ has an angular momentum parallel to $\mu$. In a magnetic field $H_0$ such a nucleus precesses about the direction of $H_0$, just as a top precesses in the earth's gravitational field. The precession frequency is the Larmor frequency $\omega_L$, given by $\omega_L = \gamma H_0$, where $\gamma$ is the ratio of the magnetic moment to the angular momentum of the nucleus and is called the gyromagnetic ratio. The Larmor frequency for nuclei is usually between one and forty megacycles per second with the available laboratory magnetic fields.

In one kind of nuclear magnetic resonance (NMR) experiment, the sample in the strong field $H_0$ is exposed to a weak magnetic field perpendicular to $H_0$, and rotating with the Larmor frequency. This rotating field induces transitions between the Zeeman levels, and because the lower energy levels are more populated, there is a net absorption of power by the sample. If $\omega_L$ is kept constant and $H$ varied continuously through $H_0$, the apparatus will record a sharp power absorption when $H = \omega_L/\gamma$. In many materials, particularly solids, the nuclei have appreciable magnetic dipole-dipole interactions with their neighbors, and the Zeeman levels are not sharp, but are spread practically continuously over narrow energy ranges. Then, in
the experiment described above, the sample absorbs power over a wider range of field values. The dependence of power absorption on field is called the resonance line shape.

An important detail omitted from the above description of an NMR experiment is how the nuclei lose the energy they absorb from the radiofrequency oscillator producing the rotating field. If nuclei excited to higher energy levels never relaxed back to lower levels, the level populations would eventually become equal and no further absorption of power could occur.

Another way to look at this question is to ask how nuclear level populations can become unequal, when they are equal before the sample is placed in the magnetic field. In equilibrium in $H_0$, the nuclear spin system has energy $W = -M_0 H_0$ relative to the zero field situation. How does this energy pass from the spins to the lattice as the level populations approach their equilibrium values?

The most important mechanisms for coupling nuclei to the lattice are:

(a) Nuclear magnetic dipole-electron magnetic dipole coupling when the lattice contains unpaired electron spins, as in metals and paramagnetic materials.

(b) Randomly fluctuating local magnetic fields of nuclei carried about by rotating or translating atoms or molecules.

(c) Nuclear electric quadrupole coupling to the electric
field gradient produced by the lattice electrons.

It is found that the population levels approach their equilibrium values as \( \exp (-t/T_1) \), where \( T_1 \) is called the spin-lattice relaxation time. If there is more than one mechanism for spin-lattice relaxation, the total \( T_1 \) is given by

\[
\frac{1}{T_1} = \sum_i \left( \frac{1}{T_i} \right)
\]

(18)

where the sum is over the different mechanisms.

From the point of view of the magnetization and spin-lattice energy exchange, if \( M_z(t) \) is the magnetization in the laboratory field direction \( z \) at time \( t \), then the energy \( W \) of the spin system after it is placed in the field \( H_o \) at time \( t = 0 \) is

\[
W = -M_z(t)H_o.
\]

(19)

One of the famous Bloch equations (13) in the case of no applied radiofrequency field is

\[
\frac{d}{dt} M_z(t) = -\frac{M_0 - M_z(t)}{T_1}, \quad M_z(0) = 0
\]

(20)

for which the solution is

\[
M_z(t) = M_0 \left[ 1 - \exp \left( -t/T_1 \right) \right].
\]

(21)

Thus the magnetization and magnetic energy of the spin system grow exponentially with time constant \( T_1 \).
There is another relaxation time characterizing the time dependence of $M_x(t)$ and $M_y(t)$, the components of magnetization in the plane perpendicular to $H_0$. In equilibrium with no applied rotating field, $M_x = M_y = 0$.

Suppose we instantaneously tip $M_0$ through $90^\circ$ into the $x$-$y$ plane, and observe $M_{xy} = \sqrt{M_x^2 + M_y^2}$. $M_{xy}(t)$ rotates with the same Larmor frequency as its constituent nuclei.

In general, $|M_{xy}(t)|$ decreases in time, and in some cases, including those of this experiment,

$$|M_{xy}(t)| = M_0 \exp(-t/T_2)$$

(22)

where $T_2$ is called the inverse line width relaxation time. We are considering the magnitude of $M_{xy}(t)$, since we are interested in the time dependence of the amplitude of the rotating vector and not in its radiofrequency variation.

What causes $|M_{xy}|$ to decrease in time? One cause is the return to equilibrium of $M_z$, for if $|M_{xy}(0)| = M_0$, then $M_z(0) = 0$. The other cause, which is usually more effective in decreasing $|M_{xy}|$, is the dephasing of the precessing nuclei which produce $|M_{xy}|$.

As a simple model for the dephasing effect, consider two coplanar vectors of equal magnitude rotating in their plane with the same angular frequency $\omega$. Their phase difference is constant and their resultant is a constant magnitude vector rotating in the plane with frequency $\omega$. 
In this case there is no dephasing.

Now suppose the two vectors have different angular frequencies \( \omega_1 \) and \( \omega_2 \). Then their resultant is a vector which rotates with frequency \( \omega_2 - \omega_1 \) and which has periodic magnitude. In this case there is dephasing, but also rephasing as the magnitude of the resultant grows during half of its cycle.

Finally, for a third model, let the two vectors have angular frequencies which are random functions of time, changing at random intervals and by random amounts. Then the phase difference of the two vectors is not monotonically increasing or decreasing as in the case above. Instead, the vectors are alternately gaining and losing phase difference at varying rates. The usual measure of the dephasing time is the average time it takes the phase difference to change by one radian. Of especial importance is the fact that the more rapidly the random changes occur, the larger is the dephasing time.

Each interaction produces dephasing of the nuclear spins. A separate relaxation time is associated with this dephasing process. Its symbol is \( T_2' \) and it is called the phase memory time. For each interaction, we get \( T_2' \) from

\[
\left( \frac{1}{T_2'} \right) = \left( \frac{1}{T_2} \right) + \left( \frac{1}{2T_1} \right).
\]

(23)

If there is more than one mechanism contributing to \( T_2 \),
Of the relaxation mechanisms mentioned above, (a) and (b) are involved in this experiment. We now discuss these in detail and especially note the pressure and temperature dependences of the relaxation times.

Lithium and sodium lattices include conduction electrons, so the nuclei are coupled to the lattice via the electron magnetic moments. The theory of this is understood (14) and the result of the theory pertinent for us is

\[
\frac{1}{T_1} = \sum_i \left( \frac{1}{T_{1z}} \right)_i.
\]  

(24)

where \( T_{1z} \) is the electronic spin-lattice relaxation time, \( T \) is the temperature in degrees Kelvin, and \( k \) is the Knight shift.

Knight (15) observed that for the same nucleus the resonances in the metallic and non-metallic states occur at different laboratory magnetic fields when the resonances are observed at the same Larmor frequency. The laboratory field is less for the metal and the difference is made up by the internal field in the metal produced by polarization of the conduction electrons. The pressure dependence of \( k \) has been found to be so small (16) in the case of the alkali metals, that we have taken \( T_{1z} \) to be
independent of pressure. The inverse temperature dependence of $T_1 e$ is well established. Concerning $T_2 e$, we only note that the electronic mechanism satisfies the limiting case $T'_2 e = T_1 e$ and $T''_2 e = 2T_2 e$ (1).

For the nuclear dipole-dipole interaction, instead of discussing the pressure and temperature dependences of the relaxation times, we shall consider their dependence on the rate of atom motion. It is this dependence that enables us to study diffusion with NMR techniques.

We shall first consider the phase memory time $T_2^{'} d$. At low temperatures there is no atom motion and the nuclei are fixed on lattice sites in a so-called rigid lattice. Because of the variation of neighboring dipole orientations each nucleus experiences, there is a variety of local fields in the z direction, parallel to the laboratory field. This results in a distribution of Larmor frequencies, referred to above as the resonance line shape.

According to the second model for the dephasing process, nuclei with different frequencies will dephase. If a nucleus retained the same local z field, then its Larmor frequency would not change and there would be rephasing. This was the case with the two vectors in the second model, but it is not the case with nuclei. Throughout the sample nuclei are continually changing energy levels in a dynamic equilibrium which does not change the level
populations. No energy is exchanged with the lattice in this process, but the local z field at each lattice site changes randomly. Because of the large number of nuclei involved, the average distribution of local fields throughout the sample is constant, i.e., the resonance line shape does not change. But the random changes of local z fields result in irreversible dephasing of the precessing nuclei.

In general, resonance line shapes are bell-shaped curves, similar to the Gaussian curve. We define the width $\Delta f$ of a resonance as the frequency range between the frequencies corresponding to the maximum and minimum slopes of the line shape. When $T_2'$ is much smaller than the other relaxation times, $T_2' \approx 1/\Delta f$.

When the temperature of the sample is increased, the atoms can jump through the lattice. The effect of this motion, when it is rapid enough, is to decrease the line width. A criterion for how rapid the motion has to be to produce line narrowing is that the mean time $\tau$ between jumps be of the order of magnitude of the rigid lattice phase memory time.

From the point of view of the local fields we say that the rapidly moving nuclei tend to average the local field variations to zero. From the point of view of the phase memory time, the third model above is appropriate. The more rapidly the nuclei change local field values, the longer they take to change precession phase by a radian.
In general, $T_2'$ increases monotonically from the rigid lattice value as $\tau$ decreases.

A spin-lattice relaxation is also produced by the motion of the atoms carrying the nuclei. Associated with the random fluctuations in time of the nuclear motions is a frequency spectrum of the local magnetic fields. The portion of the spectrum near the Larmor frequency of the nuclei can induce transitions of the nuclei between Zeeman levels. In this way energy passes between the spin system and the moving atoms of the lattice. When the atoms move relatively infrequently, the frequency spectrum is concentrated at frequencies below the Larmor frequency. At this extreme there is little coupling of nuclei to the lattice and $T_1$ is large. When there is extremely rapid atom motion, the frequency spectrum is spread over a broad range, and only a small portion of the spectrum is near the Larmor frequency. For this case also, $T_1$ is large. For an intermediate rate of motion, $T_1$ has a minimum value, occurring approximately when $\omega_L = 1/\tau$.

This brief review of nuclear spin relaxation gives the essential ideas involved in the use of NMR in this experiment. The original explanation of the effect of atom or molecule motion on nuclear spin relaxation times was given by Bloembergen, Purcell, and Pound (17), and their article should be consulted for the details omitted.
from this discussion. Good reviews of nuclear magnetic resonance in general, as well as of nuclear spin relaxation, can be found in the article by Pake (18), and in the books of Andrew (19) and Losche (20).

C. Relation of Diffusion and Relaxation Times

Nuclear motion occurs in lithium and sodium when the atoms carrying the nuclei diffuse through the lattice. When the diffusion coefficient is large enough the nuclear spin relaxation times are affected by the motion, as described above. For lithium and sodium the diffusion rates are significant above about 200° K.

Bloembergen, Purcell, and Pound (17) gave the formulas relating the diffusion coefficient to the dipolar relaxation times. Their formulas, slightly modified by Holcomb and Norberg (1), are:

\[
\left( \frac{1}{T_2'} \right)_d = \frac{4 \gamma^4 \frac{2}{4} I (I+1) N}{5 D a} \quad (26)
\]

\[
\left( \frac{1}{T_1} \right)_d = \frac{14 \pi \gamma^4 \frac{2}{4} I (I+1) N D}{2 \pi \omega a \alpha^5}, \left( \omega, \gamma R \gg 1 \right) \quad (27)
\]

\[
\left( \frac{1}{T_1} \right)_d = \frac{2 \pi \gamma^4 \frac{2}{4} I (I+1) N}{5 D a}, \left( \omega, \gamma R \ll 1 \right). \quad (28)
\]
Here $\delta$ is the gyromagnetic ratio, $N$ is the number of nuclei per unit volume, $D$ is the diffusion coefficient, $a$ is the distance of nearest approach of two nuclei (taken to be the nearest neighbor distance in a solid), and $\omega$ is the Larmor frequency. Eq. 27 is applicable when the atom jump rate is relatively low, and Eq. 28 when the jump rate is high. $\tau_c$ is called the correlation time, and is a more sophisticated measure of the rate of motion than $\tau$, the average time between jumps.

We will show how Eq. 26 is used to get the activation parameters from measurements of relaxation times. If we solve Eq. 26 for $D$, we get

$$D = \text{constant} \frac{(T_2')_d}{a^6 \nu}$$

(29)

where the constant includes terms that are independent of temperature and pressure. We have used the fact that $N \propto N_0/a^3$, where $N_0$ is the total number of nuclei in the sample. Now since

$$H_\alpha = -R \left. \frac{\partial \ln (D/a^6 \nu_0)}{\partial (1/T)} \right|_P,$$

we have

$$H_\alpha = -R \left. \frac{\partial \ln (T_2')_d/a^6 \nu_0}{\partial (1/T)} \right|_P.$$

(30)

Over the narrow temperature range to which this is applied, $a^6 \nu_0$ changes very little compared to the change in $\ln T_2'$, so it is neglected in obtaining $H_\alpha$ from measurements of $T_2'$.
Similarly substituting in Eq. 9,

\[ V_a = -RT \frac{\partial \sqrt{\frac{\ln (T_a')}{d}}}{\partial \rho} \]  

(32)

Here we consider the \( a^6 \nu_0 \) term, since \( a \) and \( \nu_0 \) change significantly over the pressure range used. Thus we have

\[ V_a = -RT \left[ \frac{\partial \ln (T_a')}{\partial \rho} \right]_T - \alpha \frac{\partial \ln \rho}{\partial \rho} - \beta \frac{\partial \ln \nu_0}{\partial \rho} \]  

(33)

The last two terms on the right of Eq. 33 are simplified to a function of the volume compressibility \( \beta \) and the Gruneisen constant \( \gamma_g \), as shown in Appendix B. Then

\[ V_a = -RT \left[ \frac{\partial \ln (T_a')}{\partial \rho} \right]_T + \beta (2 - \gamma_g) \]  

(34)

Manipulation of Eq. 28 gives the same expression as Eq. 34 for \( T_1) \), in the region of high diffusion. From Eq. 27, we get for \( T_1) \), in the region of relatively low diffusion

\[ V_a = -RT \left[ -\frac{\partial \ln (T_a')}{\partial \rho} \right]_T - \beta (2 + \gamma_g) \]  

(35)

Eq. 34 has been used to get the value of \( V_a \) from measurements of \( T_2') \). The relations involving \( T_1) \) have been observed qualitatively.

Since there are two interactions, conduction electron and nuclear dipole, we have to separate the dipolar relaxation times from the measured total relaxation times. To get \( T_2') \) from \( T_1 \) and \( T_2 \), we use Eqs. 18, 23, and 24 to get...
\[ \left( \frac{1}{T_{2'}} \right)_d = \frac{1}{T_2} - \frac{1}{T_1} + \left( \frac{1}{2T_1} \right)_d \quad (36) \]

as shown in Appendix C.

Similarly, we get \( T_1 \) from Eq. 18:

\[ \left( \frac{1}{T_1} \right)_d = \frac{1}{T_1} - \left( \frac{1}{T_1} \right)_e \quad (37) \]

\( T_1 \) was determined by connecting the low and high temperature \( T_1(T) \) data with a smooth curve approximating \( T_1 \) with \( T = \) constant.
III. EXPERIMENTAL METHODS AND APPARATUS

A. Spin Echo Technique

The NMR spin echo experiment (21) differs from the experiment described in Section II-B. There we assumed the radiofrequency magnetic field was weak and applied continuously, whereas with spin echo experiments, the r.f. field is large and applied in pulses of short duration. With continuously applied r.f., we observe the steady state response of the nuclear magnetization. With pulsed r.f., we observe the transient response.

We referred above to tipping the equilibrium nuclear magnetization $M_0$ through $90^\circ$ from the z direction into the x-y plane. This is accomplished by the torque that the rotating magnetic field applies to $M_0$. Since $M_0$ precesses with the Larmor frequency as soon as it is tipped away from the field direction, the applied field vector must rotate with the same frequency or the net torque would be zero. Thus the frequency of the r.f. during the pulse is the Larmor frequency.

To understand how the applied r.f. field rotating at a single frequency can tip nuclei with a variety of Larmor frequencies, consider the nuclei in a coordinate system $(x_r, y_r, z_r)$ rotating with the Larmor frequency of the center of the resonance line shape. In this system, in the absence of applied r.f., the nuclei experience fields
roughly in the range ±5 gauss in the \( z_r \) direction, if the line width is roughly 10 gauss. When a 50 gauss field is applied in the \( x_r \) direction, the smaller \( z_r \) field variations are not important and all nuclei "see" about the same field. Thus, in the laboratory system \( M_0 \) is brought practically intact into the \( x-y \) plane.

The above is a description of the effect of a so-called 90° pulse. If the pulse duration is doubled we get a 180° pulse whose effect is to rotate \( M_0 \) to the direction anti-parallel to the laboratory field.

Immediately following the 90° pulse, \( M_0 \) precesses in the \( x-y \) plane. This precessing vector induces a signal in a coil of a circuit tuned to the Larmor frequency, and we observe the envelope of this signal, called the free induction decay. If the laboratory field is uniform over the sample, in the case of rapid atom motion, this envelope is an exponential with time constant \( T_2 \), the phase memory time. However, if the field is not uniform, the decay envelope is not in general exponential, but reflects the shape of the field gradient. Sufficiently homogeneous fields are not usually available, so this is not a practicable way to measure \( T_2 \).

Before explaining how \( T_2 \) is measured, we shall explain how we measure \( T_1 \). Following a 90° pulse, \( M_z(t) \) is given by Eq. 21. If another 90° pulse is applied at time \( t = \tau \) after the first pulse at time \( t = 0 \), the decay height
after the second pulse depends on $M_z(\tau)$. Thus by observing $M_z(\tau)$ for several values of $\tau$, including $\tau = \infty$, we get $T_1$ from the slope of $\ln(M_0 - M_z(\tau))$ vs. $\tau$.

We will now explain how nuclear spin echoes are produced and used to measure $T_2$. First, the laboratory field must be sufficiently non-uniform over the sample to broaden the resonance by a factor of about two. Suppose the sample is divided into five parts, each part in a different place in the field. In equilibrium $M_0$ is the sum of five different $M_1$'s. Consider the situation in the rotating coordinate system described above after the application of a 90° pulse. All five $M_1$'s are along the $-y_r$ direction because of the applied pulse field in the $x_r$ direction. The $M_1$'s precess about $z_r$ with different frequencies because they are in different laboratory fields, so they fan out isotropically in the $x_r$-$y_r$ plane, and $|M_{x_r y_r}|$ decays to zero. Also each $M_1$ decreases by natural dephasing, as discussed in Section II-B. Suppose a particular $M_1$ has rotated through $\phi_r$ in the $x_r$-$y_r$ plane from the $-y_r$ direction. When a 180° pulse is applied at $t = \tau$, $M_1$ rotates about the $x_r$ axis to the angle $\pi - \phi_r$ from the $-y_r$ direction. From this angle $M_1$ continues to precess as it did before the 180° pulse was applied. All the $M_1$'s are thus manipulated simultaneously, and the result is that they rephase at times near $t = 2\tau$, produce a net $|M_{x_r y_r}|$, and then dephase as they did after the 90°
pulse. This net $|M_{xy}\rangle$ in the rotating system induces a r.f. signal in the laboratory system, and this signal, occurring at $t = 2\tau$, is called the spin echo.

The amplitude of the echo at time $2\tau$ is proportional to $|M_{xy}(2\tau)|$. Therefore by measuring the echo height for several values of $2\tau$, one can obtain the time constant in the relation

$$\epsilon = \epsilon_0 e^{\frac{-2\tau}{T_2}}$$

(38)

where $\epsilon$ is the echo amplitude at time $2\tau$, and $T_2$ is the inverse line-width relaxation time. A plot of $\ln \epsilon$ vs. $2\tau$ can be fitted with a line with slope $-1/T_2$.

B. Spin Echo Apparatus

A diagram of the spin echo apparatus is shown in Fig. 1. It was constructed following a published description (22). With this system we can apply to the sample pulses of r.f. energy at 10 megacycles per second with variable pulse duration, and in a variety of pulse sequences, and detect the nuclear signals following the pulses. The source of r.f. energy is a crystal controlled 5 megacycle oscillator. The pulser provides signals to the first gate, allowing pulses of 5 megacycle energy to enter the doubler-transmitter. The doubler is gated on at the same time the 5 megacycle pulses enter, and 10
Figure 1. Block diagram of the spin echo apparatus. The receiver is the radio-frequency amplifier whose circuit is shown in Fig. 2.
megacycle pulses enter the transmitter. The transmitter is a high power r.f. amplifier, tuned to 10 megacycles, from which the pulses go to the sample circuitry, including the sample coil. The r.f. voltage at the sample coil is several hundred volts, and the rotating magnetic field vector may be as large as 100 gauss.

The same coil is used to transmit the pulsed r.f. to the sample and detect the transient nuclear signals. The r.f. receiver is used to amplify the nuclear signals before display on an oscilloscope screen. We have used a simpler receiver than was described with this system. Our circuit is shown in Fig. 2. The receiver remains blocked for about 100 microseconds after each pulse, and the nuclear decay cannot be observed during this time.

The high power pulses were not of constant amplitude, so that the durations of the 90° and 180° pulses were not related by a factor of two. This was not a limitation, since these pulse durations were determined either by maximizing or minimizing their associated decays, or by maximizing the echo amplitude.

The nuclear signals are detected with a 1N34 diode after amplification by the receiver. It is necessary to calibrate the diode, since its detection characteristic is non-linear. We did this by measuring $T_2$ for protons in water with a small concentration of MnCl$_2$ at room temperature, using both detected and undetected echoes. The
Figure 2. Circuit diagram of 10 megacycle per second amplifier.
RESISTANCE IN OHMS
CAPACITANCE IN MICROFARADS
proton echoes are known to decrease exponentially, as given in Eq. 38, and have large enough amplitude to give good signal to noise ratio even when undetected. The plot of undetected echo amplitude vs. $2^\tau$ on semi-logarithmic graph paper gives a straight line. Because of non-linearity of the diode, the detected echo amplitudes do not plot as a straight line. Fig. 3 shows a typical detected-undetected signal comparison.

We wanted to use detection with lithium and sodium echoes, since this gave a better signal to noise ratio than when the echoes were undetected. Therefore we needed a calibration curve. Such a curve was constructed from the data of Fig. 3 by drawing smooth curves through the points and then collecting pairs of values of echo amplitudes by drawing vertical lines through these smooth curves. Fig. 4 shows a calibration curve, a smoothed plot of these pairs of echo heights.

All of the data were taken by visual observation of the echoes and decays displayed on a Tektronix 545 oscilloscope. The oscilloscope sweep was expanded to make a good judgement of the echo height. Several repetitions of an echo were viewed for each height measurement. In the early part of this research, measurements were made from photographs of the oscilloscope displays. However, visual observation was much more convenient and appeared
Figure 3. Plot of echo amplitudes vs. $2\pi$ for protons in H$_2$O (with dissolved MnCl$_2$) with and without detection. The resonance line shape is Lorentzian, so the undetected echo envelope amplitude is an exponential function with argument linear in the time.
Figure 4. Plot of the detection characteristic of a 1N34 diode. The nuclear signal amplitudes measured from the oscilloscope display were located on the ordinate, and the corrected amplitudes read from the abscissa.
DIODE IN34

AMPLITUDE DETECTED (VOLTS)

AMPLITUDE UNDETECTED (VOLTS)
to be as precise as the photographic technique, so the latter was abandoned.

A run made with lithium is shown in Fig. 5. The echo amplitudes both with and without the use of the calibration curve are shown.

C. Magnets

In the course of this work we have used two magnets. The smaller was adequate for Li$^7$ nuclei which require about 6050 gauss for a Larmor frequency of 10 megacycles per second. This smaller magnet had six inch diameter pole caps, and an air gap of approximately three inches.

The larger magnet was used with both Li$^7$ and Na$^{23}$ nuclei, the latter requiring about 8900 gauss for a 10 megacycle frequency. The pole caps used with this magnet were tapered from twelve inches to six inches, and the air gap was three inches.

Both magnets were manufactured by Varian Associates, Inc.

D. Sample Bomb and Pressure Equipment

The high pressure sample bomb was made of non-magnetic Berylco 25, an alloy of copper and beryllium. Fig. 6 shows the dimensions and details of the r.f. lead in to the bomb and the sample coil. This is essentially a copy of a bomb used by Benedek (23).
Figure 5. Plot of echo amplitude vs. $2\tau$ for lithium at $23^\circ$ C and one atmosphere pressure, both as observed from the oscilloscope display without correction for non-linear detection, and with correction using the calibration curve shown in Fig. 4.
LITHIUM

T = 23 °C
P = 1 atm.

Without calibration: ~

With calibration: ~

\( T_2 = 0.86 \text{ msec.} \)
Figure 6. Full scale drawing of the high pressure non-magnetic sample bomb. The thermocouple is located outside the high pressure region.
SAMPLE BOMB
BERLYCO 25

SAMPLE CIRCUITRY
STAINLESS STEEL PIPE
HEX HEAD
1/4"
9 THREADS / INCH
7/8"
THERMOCOUPLE
RF LEAD
NEOPRENE "O" RING
82°
FIBRE CONE

RF COIL
LUCITE SAMPLE CYLINDER
TEFLON PISTON
5/8"
1/16"
60°
9/16"
18 THREADS INCH

6"
1 1/16"
The r.f. sample coil consisted of about 20 turns of #26 enameled copper wire wound on a 11/64 inch drill. The sample container was a thin walled lucite cylinder, open at one end. Closely fitted into the open end was a teflon or lucite piston. The sample was a dispersion of metal particles in oil, so this arrangement presented hydrostatic pressure to the sample.

The pressure transmitting fluid was a half and half mixture of 2-methyl butane and Stanoil Industrial Oil No. 35, made by the Standard Oil Co. The pressure generating system is shown in Fig. 7. Pumps 1 and 2 are Blackhawk Model P228, and have a capacity of 40,000 psi. The intensifier increases the pressure by a factor of about fifteen. It and the manganin gauge are products of the Harwood Engineering Co. The pressure tubing used was 1/4 inch O.D., 0.065 inch I.D. The Bourdon gauge, made by the Heise Co., was the pressure standard for this work, and was used to calibrate the manganin gauge to 50,000 psi. The calibration was linearly extrapolated to higher pressures. This gauge is a length of manganin wire whose resistance is pressure dependent. The wire resistance was one arm of a Wheatstone bridge. A helipot was used to balance the bridge, and the sensitivity permitted measurement of pressure to ±200 psi.
Figure 7. Block diagram of high pressure generating system including manganin pressure measuring gauge and sample bomb in air gap of electromagnet.
E. Temperature Control and Measurement

The samples were kept at constant temperature by immersing them in liquid baths whose temperatures were regulated. For the measurements of the temperature dependence of the relaxation times, the sample coil was not in the pressure bomb, but was simply a few turns of wire wrapped around a one centimeter diameter vial containing the sample. For the pressure measurements, the entire bomb was immersed in the bath.

For temperatures above room temperature the liquid used for the bath was Dow Corning Corporation 200 Centistoke Silicone Fluid. This was heated with two 100 watt Variac controlled immersion heaters. Usually one heater almost maintained the desired temperature, and the other was turned on and off by the regulator. To regulate we used either a Precision Scientific Co. Micro-set regulating mercury thermometer, or a thermistor whose resistance was strongly temperature dependent. The mercury thermometer was only used above -38°C, the freezing temperature of mercury.

For temperatures below room temperature, the liquid used for the bath was acetone. This was cooled by circulating acetone at -77°C through coils immersed in the tank. The circulated acetone was cooled by a dry ice-acetone mixture. Regulation of the temperature was accomplished
by turning the circulating pump on and off.

The tank used to contain the baths was made of thin brass sheet, and fitted in the air gaps of the magnets with just enough space for a layer of insulation from the pole caps. The liquids were stirred with a propeller driven by a motor mounted outside the gap.

Temperatures were measured with a copper-constantan thermocouple placed as shown in Fig. 6. The thermocouple was forced into contact with the bomb by a teflon wedge (not shown). A dummy run with another thermocouple at the sample site showed that in equilibrium there was an insignificant temperature gradient between the sample site and the thermocouple site outside the high pressure region.

After each change of pressure, the system was allowed about fifteen minutes to come to equilibrium. When the pressure was changed some pressure fluid passed in or out of the temperature bath. The waiting time allowed the pressure fluid temperature to equilibrate and the associated slow transient pressure change to die away.

The temperature values measured are accurate to at least the nearest degree. In the case of the pressure dependence runs, the temperature was held constant to within two tenths of a degree.

F. Sample Preparation

To perform NMR experiments with electrically conducting
materials, it is necessary to divide the sample into particles whose size is less than the skin depth of the radiofrequency radiation at the Larmor frequency used. For 10 megacycles per second, the skin depths of lithium and sodium are 60 microns and 30 microns, respectively.

Dispersions of lithium and sodium were produced by vigorously stirring samples of the molten metals in the Silicone Fluid. This was done in a dry box in an argon atmosphere, which, however, was not very free of water vapor or air. The dry box did provide protection for the operator from the vessel of turbulent molten alkali metal. This was important on the one occasion when a glass vessel, attacked by hot lithium, broke. Subsequent to this accident, the metals were dispersed in stainless steel vessels.

The lithium had less than five millipercent impurity before dispersion, but was probably contaminated by nitrogen and oxygen during dispersion. We also used some commercially available lithium dispersion made by the Lithium Corporation of America. Spectroscopic analysis showed this to contain only trace impurities. This commercial dispersion consisted of particles of which 90 percent had diameter less than 20 microns. We measured the activation volume both in our own dispersion and in the commercial dispersion, and found no sample dependence. Our relaxation times for one atmosphere pressure at different temperatures were in
agreement with the values of Holcomb and Norberg, within the scatter of the measurements. This indicated that our samples were equivalent to Holcomb and Norberg's samples.

The sodium which was dispersed was DuPont Reactor Grade with the only significant impurity being about 100 p.p.m. of potassium. No commercial sodium dispersion was used. The sodium relaxation times at one atmosphere agreed with those of Holcomb and Norberg.
IV. RESULTS

A. Activation Energies

The activation energy $Q_0$ for self-diffusion in lithium and sodium had been measured prior to this research. The earliest NMR work, using line width measurements, was done by Gutowsky (24) on sodium, and by Gutowsky and McGarvey (25) on lithium. Nachtrieb et al. (26) used tracer diffusion to obtain $Q_0$ for sodium. Later Holcomb and Norberg used spin echo techniques to measure $Q_0$ for both metals. The value for $Q_0$ obtained for sodium from the spin echo experiments agreed with the tracer result.

The first objective was to repeat the measurements of Holcomb and Norberg of $T_1(T)$ and $T_2(T)$ for lithium and sodium. We felt that we ought to get activation energy values in agreement with theirs before going on with high pressure experiments to measure the activation volumes. Such agreement would give confidence that the spin echo apparatus was being operated properly, and that our samples were satisfactory.

We were able essentially to duplicate Holcomb and Norberg's $T_1(T)$ and $T_2(T)$ curves for both metals. Our data from these measurements are shown in Figs. 8 and 9. For lithium the $T_1(T)$ curve shows the combination of two spin-lattice relaxation processes. These are the electronic,
Figure 8. Plots of spin-lattice relaxation time $T_1$ and inverse line width relaxation time $T_2$ vs. temperature (°C) for lithium at one atmosphere pressure. The $T_1$ curve shows the minimum due to the dipolar contribution $T_1d$. The predominant mechanism for spin-lattice relaxation is that due to the conduction electrons, for which $T_1e \propto 1/T$. 
Figure 9. Plots of spin-lattice relaxation time $T_1$ and inverse line width relaxation time $T_2$ vs. temperature ($^\circ$C) for sodium at one atmosphere pressure.
for which $T_1^e \propto T^{-1}$, and the nuclear dipole-dipole, with $T_1^d$ having a minimum at about 130° C. For sodium, no $T_1^d$ minimum occurs, since $T_1^e$ is so much smaller than $T_1^d$ that $T_1^e$ dominates the spin-lattice relaxation. This is associated with the larger Knight shift of sodium relative to lithium.

The $T_2(T)$ curves show the increase with temperature as the atom motion increases and $T_2^d$ increases. At high temperatures, $T_2$ is limited by $T_1^e$, as described in Section II-B.

From $T_1(T)$ and $T_2(T)$ one can get $T_2^d$ as a function of temperature, and hence the activation energy, as described in Section II-C. Fig. 10 shows a plot of $\ln T_2^d$ vs. $1/T$ for lithium. This plot includes relaxation times obtained from line width measurements, assuming Lorentzian line shapes for which $T_2 = 1/\sqrt{3} \pi \Delta f$. The data on this plot at low temperatures deviate from the straight line because self-diffusion does not determine the phase memory time when the atom motion is small. From the slope of this line we obtained $Q_0 = H_a(0) = 12.0$ kilocal/mole. This is to be compared with Holcomb and Norberg's value of $Q_0(H & N) = 13.2 \pm 0.4$ kilocal/mole.

The corresponding data for sodium are shown in Fig. 11. The slope of the straight line fitted to this data yields $Q_0 = 9.4$ kilocal/mole. For sodium, Holcomb and Norberg had $Q_0(H & N) = 10.0 \pm 0.6$ kilocal/mole. From tracer experiments
Figure 10. Plot of the logarithm of the phase memory time $T_2' \rho_d$ vs. inverse temperature ($^\circ$K) for lithium at one atmosphere pressure. The values of $T_2' \rho_d$ were calculated from the data of Fig. 8 using Eq. 36. The activation energy $H_a(P = 0)$ is obtained from the slope of the best straight line fitted to the data in the region of exponential dependence of $T_2' \rho_d$ on temperature.
LITHIUM

$H_0 = 12.1$ Kcal/mole

- SPIN ECHO
- LINE WIDTH

$\frac{1}{T}$ (milliseconds) vs. $10^3 \frac{1}{T^* K}$
Figure 11. Plot of the logarithm of the phase memory time $T_2'$ vs. inverse temperature (°K) for sodium at one atmosphere pressure. The values of $T_2'$ are calculated from the data of Fig. 9 using Eq. 36. The activation energy $H_a(P = 0)$ is obtained from the slope of the best straight line fitted to the data.
SODIUM

$^\circ_{T_2}d$

$H_a(0) = 9.4$ kcal/mole
with sodium (26), $Q_0$ (tracer) = 10.4 ± 0.3 kilocal/mole.

The values of $Q_0$ from this work are seen to be systematically smaller than those of Holcomb and Norberg. A second series of $T_1(T)$ and $T_2(T)$ measurements on lithium gave a value of $Q_0$ agreeing with our first value, so the difference between our value and Holcomb and Norberg's value may be significant. However, our data were more scattered and the value of $Q_0$ depends very sensitively on the slope of the line fitted to the $\ln T_2')_d$ vs. $1/T$ data. Since Holcomb and Norberg obtained the same value for $Q_0$ for lithium by several independent uses of their data, their value of $Q_0$ for lithium is probably more reliable than our value above. Similarly for sodium, Holcomb and Norberg's value is to be preferred to our value obtained from $T_1(T)$ and $T_2(T)$ data.

The data taken here in the pressure dependence measurements are more precise than the $T_1(T)$ and $T_2(T)$ data. It will be shown below how this pressure data can be used to give values of $Q_0$ in good agreement with Holcomb and Norberg's values.

B. Activation Volumes

The activation volume for lithium was obtained at five temperatures in the range 35° C to 80° C. Measurements could not be made at lower temperatures because $T_2$ becomes
too small to measure with the spin echo apparatus. Some early work (27) was done at 3° C and 27° C using line width measurements, but this was unreliable owing to inhomogeneity of the magnetic field.

At temperatures above 80° C it is not clear how to obtain $T_2'$ from $T_1$ and $T_2$. Holcomb and Norberg observed that above about 80° C, $\ln T_2'$ falls below the straight line plotted in Fig. 10. This indicates that another interaction is contributing to the nuclear spin relaxation. This interaction is not yet understood, so the activation volume measurements were restricted to the temperature range in which the dipolar relaxation time could be unambiguously separated from the raw data.

To use Eq. 34, $T_2$ was measured at about fifteen pressures between 1 atmosphere and 7000 atmospheres, at a constant temperature. $T_1$ at this temperature was obtained from the data of Fig. 8. Then, using Eq. 36, $T_2'$ was obtained for each pressure. Fig. 12 shows the plots of $\ln T_2'$ vs. pressure for lithium at five temperatures. The data at each temperature were fitted with a straight line by least squares analysis. Using the values of compressibility $\beta$ and Gruneisen constant $\gamma_G$ given in Table 4 and the slopes of the least squares lines, the activation volume was computed for each temperature.
Figure 12. Plots of the logarithm of the phase memory time $T_2'$ vs. pressure for lithium at five different temperatures. The activation volume $V_a$ for each temperature was determined from the slope of the line for that temperature using Eq. 34. The average of the five values of $V_a$ is $3.6 \pm 0.3$ cm$^3$. 
LITHIUM

\[ V_0 = 3.6 \pm 0.3 \text{cm}^3 \]

- 78.0°C
- 70.8°C
- 56.6°C
- 50.0°C
- 36.6°C

\[ \text{PRESSURE} \times 10^{-3} \text{(ATMOSPHERES)} \]

\[ T_{2/1,d} \text{ (MILLISECONDS)} \]
Table 4. Compressibility and Gruneisen constant for lithium and sodium

<table>
<thead>
<tr>
<th>Metal</th>
<th>Compressibility $\beta^a$ (atm)$^{-1}$</th>
<th>Gruneisen constant $\gamma^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.9 (10)$^{-5}$</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium</td>
<td>1.4 (10)$^{-5}$</td>
<td>1.3</td>
</tr>
</tbody>
</table>

$^a(28)$

$^b(29)$

The values of activation volume for lithium are given in Table 5. To the accuracy of the measurements, $V_a$ for lithium is independent of temperature. The average of the five values is $V_a(\text{average}) = 3.6 \pm 0.3 \text{ cm}^3$. As shown in Table 3, this is 28 percent of the molar volume of lithium.

Table 5. Activation volumes for lithium

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Activation volume (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>3.68</td>
</tr>
<tr>
<td>50</td>
<td>3.63</td>
</tr>
<tr>
<td>57</td>
<td>3.61</td>
</tr>
<tr>
<td>71</td>
<td>3.44</td>
</tr>
<tr>
<td>78</td>
<td>3.71</td>
</tr>
</tbody>
</table>

The activation volume for sodium was measured at -42°, -45°, and -50° C. As with lithium we were restricted to a temperature range in which $T_{2'}d$ could be obtained from the $T_1$ and $T_2$ data. This limited the usefulness of measurements above -30° C. The practical lower limit is about -70° C,
where $T_2$ becomes too small to measure with spin echo apparatus.

The pressure dependence of $\ln T_2'$ for sodium is greater than for lithium by a factor of about three. There was no evidence of a pressure dependence of $V_a$ to 3000 atmospheres. Therefore the data for each temperature were fitted with a straight line. Using $\beta$ and $\delta$ from Table 4 and the slopes of the lines in Fig. 13, the activation volume was computed for each temperature. The results are given in Table 6.

Table 6. Activation volumes for sodium

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Activation volume (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-42</td>
<td>9.57</td>
</tr>
<tr>
<td>-45</td>
<td>9.86</td>
</tr>
<tr>
<td>-50</td>
<td>9.26</td>
</tr>
</tbody>
</table>

To the accuracy of the measurements, $V_a$ for sodium is independent of temperature. The average of the three values is $V_a(average) = 9.6 \pm 0.5$ cm$^3$. This is 40 percent of the molar volume of sodium.

C. Correlations with Fusion Parameters

The measured values of $V_a$ can be compared with the predictions of Eq. 11. Table 7 lists the values of $H_m$, $\delta V_m$, $Q_{01}$, and $Q_{02}$. These last two quantities are the activation energies of Holcomb and Norberg, and of this
Figure 13. Plots of the logarithms of the phase memory time $T_2^1$ vs. pressure for sodium at three different temperatures. The activation volume $V_a$ for each temperature was determined from the slope of the line for that temperature using Eq. 34. The average of the three values of $V_a$ is $9.6 \pm 0.5 \text{cm}^3$. 
SODIUM

\[ V_0 = 9.6 \pm 0.5 \text{ cm}^3 \]

-42.2 °C
-45.4 °C
-50.0 °C

\[ T_2 \]
work, respectively. The heats of fusion $H_m$ are the best known values in Table 7 (30,31). Values of $\delta V_m$ are from a published survey of experimental measurements (32). The melting temperatures $T_0$ at one atmosphere pressure have been very precisely determined (30,31). Using $H_m$, $\delta V_m$, and $T_0$ for each metal, the slopes of the melting curves at zero pressure (one atmosphere) were calculated using the Clausius-Clapeyron relation. The calculated slopes were in agreement with the slopes measured from the melting curves (28) shown in Figs. 14 and 15.

Table 7. Fusion parameters and activation energies

<table>
<thead>
<tr>
<th>Metal</th>
<th>$H_m$ (kilocal/mole)</th>
<th>$\delta V_m$ (cm$^3$)</th>
<th>$Q_{01}$ $^a$ (kilocal/mole)</th>
<th>$Q_{02}$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.715$^c$</td>
<td>0.21$^d$</td>
<td>13.2</td>
<td>12.0</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.624$^e$</td>
<td>0.57$^d$</td>
<td>10.0</td>
<td>9.4</td>
</tr>
</tbody>
</table>

$^a$Results of Holcomb and Norberg (1)

$^b$This research

$^c$(30)

$^d$(32)

$^e$(31)
Figure 14. Plot of the melting temperature vs. pressure for lithium (28). The slope of the curve at zero pressure is $3.56 \times 10^{-3} \text{deg cm}^2/\text{kg}$. The value of $T_0 = T_m(P=0)$ does not agree with the more recent determination (30).
MELTING CURVE
LITHIUM

TEMPERATURE (°C)

PRESSURE x 10^3 (kg/cm^2)
Figure 15. Plot of the melting temperature vs. pressure for sodium (28). The slope of the curve at zero pressure is $8.17 \times 10^{-3}$ deg cm$^2$/kg.
MELTING CURVE
SODIUM

TEMPERATURE (°C)

160
140
120
100

PRESSURE x 10^{-3} (kg/cm^2)

2
4
6
The values of $V_a$ calculated with Eq. 11 are compared with the experimental results in Table 8.

Table 8. Comparison of predicted and experimental activation volumes

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\delta V_m Q_{O1}/H_m$</th>
<th>$\delta V_m Q_{O2}/H_m$</th>
<th>$V_a$(experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>3.9</td>
<td>3.5</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>Sodium</td>
<td>9.1</td>
<td>8.6</td>
<td>9.6 ± 0.5</td>
</tr>
</tbody>
</table>

(all units cm$^3$/mole)

The experimental value of $V_a$ for lithium is in better agreement with the prediction than is the value for sodium. The value of $V_a$ for sodium based on the tracer experiments (2) at 90° C is $V_a$(tracer) = 12.4 cm$^3$, in poorer agreement with prediction than the spin echo value. Rice and Nachtrieb (4) recognized this poor agreement and suggested that the large pressure dependence of the compressibility of sodium was responsible for the discrepancy. The evidence from this research is that Eq. 11 is adequate to predict $V_a$ for sodium without extra argument, and that the spin echo result is more reliable than the tracer value.

The other relation from the theory of Rice and Nachtrieb (4), Eq. 17, can also be tested experimentally with our data. A plot of $\ln T_2'/d$ vs. $T_m/T$ includes the data for all pressures and temperatures (not including
the $T_1(T)$ and $T_2(T)$ data of Figs. 8 and 9) obtained for one metal, and yields a single number, the slope of the best straight line fit to the data. The data is plotted in Figs. 16 and 17. The values of $T_m(P)$ were obtained from the melting curves, shown in Figs. 14 and 15 (28). In Table 9 are shown the values of the slopes and the values of $Q_0/RT_0$.

Table 9. Experimental test of Eq. 17

<table>
<thead>
<tr>
<th>Metal</th>
<th>$T_0^0$ (°K)</th>
<th>$Q_{o1}/R T_0$</th>
<th>$Q_{o2}/R T_0$</th>
<th>$d \ln T_2'/d(T_m/T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>453.7$^a$</td>
<td>-14.7</td>
<td>-13.4</td>
<td>-14.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>371.0$^b$</td>
<td>-13.6</td>
<td>-12.8</td>
<td>-13.5</td>
</tr>
</tbody>
</table>

$a$ (30)  
b (31)

The agreement of the experimental values and the values of $Q_{o1}/R T_0$ is remarkably good for both sodium and lithium. The agreement with the values of $Q_{o2}/R T_0$ is satisfactory. It is concluded that Eq. 17 is a valid relation, and that $T_2'/d$ and the self-diffusion coefficient $D$ in the limit of low pressure can be described as functions of the single variable $T_m/T$. Alternatively, presupposing that Eq. 17 is valid, the data yield values for $Q_0$. 
Figure 16. Plot of the logarithm of the phase memory time $T_{2^{'}}_d$ vs. $T_m/T$ for lithium. The slope of the best fitting straight line is -14.5 and with Eq. 17, gives a value for the activation energy $Q_0$ of 13.0 kilocal/mole.
Figure 17. Plot of the logarithm of the phase memory time $T_2' \rho$ vs. $T_m/T$ for sodium. The slope of the best fitting straight line is -13.5 and with Eq. 17, gives a value for the activation energy $Q_0$ of 9.9 kilocal/mole.
SODIUM
-42.2°C
-45.4°C
-50.0°C

$T_2^d$ (MILLISECONDS)

$T_m / T$

1.64
1.68
1.72
1.76
These are $Q_0(Li) = 13.0$ kilocal/mole and $Q_0(Na) = 9.9$ kilocal/mole. It is important to note that the use of Eq. 17 to obtain $Q_0$ requires knowledge of the melting curve so that $T_m$ can be determined for each pressure at which $T_2'$ is measured.

D. Miscellaneous Observations on Lithium

Holcomb and Norberg showed that for lithium one could obtain $T_1 d$ as a function of temperature from the $T_1(T)$ curve. They showed the direct and inverse proportionalities of $T_1 d$ to the diffusion coefficient in the regions of high and low diffusion, respectively, and were able to measure the activation energy from these dependencies.

In principle one can obtain the activation volume from the pressure dependence of $T_1 d$. This was attempted here, but the experimental precision was not sufficient to permit measurement of $V_a$. However, the relations of Eqs. 27 and 28 were observed qualitatively. Fig. 18 shows $\ln T_1 d$ vs. pressure for lithium at $100^\circ C$ in the region of relatively low diffusion where $T_1 d$ is inversely proportional to $D$. The line in Fig. 18 was drawn with slope calculated from Eq. 35 assuming $V_a = 3.6 \text{ cm}^3$.

Similarly Fig. 19 shows $\ln T_1 d$ vs. pressure for lithium at $135^\circ C$ where $T_1 d$ is proportional to $D$ by Eq. 28.
Figure 18. Plot of the logarithm of the dipolar spin-lattice relaxation time $T_1^d$ vs. pressure for lithium at 100.5° C, where $T_1^d \propto 1/D$. The slope of the line was determined using Eq. 35, assuming an activation volume of 3.6 cm$^3$, and the intercept was chosen by inspection to approximate a good fit to the data.
LITHIUM
100.5°C
$T_1 \alpha \frac{1}{D}$

$V_a = 3.6 \text{ cm}^3$
Figure 19. Plot of the logarithm of the dipolar spin-lattice relaxation time $T_1 J_\alpha$ vs. pressure for lithium at $135^\circ$ C, where $T_1 J_\alpha \propto D$. The slope of the line was determined using Eq. 34, assuming an activation volume of 3.6 cm$^3$, and the intercept was chosen by inspection to approximate a good fit to the data.
LITHIUM

\[ T_{1} \text{ d} = D \]

\[ V_a = 3.6 \text{ cm}^3 \]

PRESSURE \( \times 10^{-3} \) (ATMOSPHERES)
Again the line was drawn assuming $V_a = 3.6 \text{ cm}^3$, but with the slope calculated from Eq. 34.

Although $T_2')_d$ for lithium cannot be reliably obtained from $T_1$ and $T_2$ at temperatures above about $80^\circ C$, $T_2$ was measured at several pressures at $100^\circ C$. Using the line drawn in Fig. 18, $T_1')_d$ was estimated for these pressures, and an apparent $T_2')_d$ was calculated using Eq. 36. The third term on the right of this equation could have been neglected, since $T_1')_d$, although pressure dependent, was always at least three times as large as $T_1$.

Using these values of $T_2')_d$ at several pressures, an activation volume was obtained from the slope of a straight line fitted to $\ln T_2')_d$ vs. pressure. The result was $V_a(100^\circ C) = 2.6 \text{ cm}^3$. This must be considered an unreliable value because of the uncertainty involved in determining $T_2')_d$ at this temperature.

At temperatures above about $150^\circ C$, the echo envelope departed from the exponential shape. Fig. 20 shows a plot of echo height vs. $2\tau$ for lithium at $170^\circ C$. The departure of the echo heights from the straight line at the larger values of $2\tau$ is probably due to an $\exp (-k(2\tau)^3)$ term multiplying Eq. 38, the usual expression for the echo envelope. This effect is well understood (21) and the constant $k$ is proportional to the diffusion coefficient and the square of the magnetic field gradient. Attempts to qualitatively vary this non-exponential behavior with high pressure were unsuccessful.
Figure 20. Plot of the echo amplitudes corrected for non-linear detection vs. $2\tau$ for lithium at 170.3°C. The line was drawn to fit the data for small values of $2\tau$. The departure of the data from the line for large values of $2\tau$ is probably due to an $\exp \left(-k(2\tau)^{3}\right)$ term.
V. CONCLUSIONS

The results of this research strongly support Eqs. 11 and 17. These are, in the limit of low pressure,

\[
\frac{V_a}{Q_0} = \frac{\delta V_m}{H_m}
\]

and

\[
\frac{d \ln D}{d (T_m/T)} = - \frac{Q_0}{RT_0}
\]

The only other metal for which there are significant data to test these equations is lead. The activation energy \(Q_0\) and activation volume \(V_a\) for lead were determined with tracer diffusion by Nachtrieb (3,33) and by Hoffman et al. (34). Fusion and diffusion parameters for lead are presented in Table 10. It is seen that the data for lead also support Eq. 11.

<table>
<thead>
<tr>
<th>Table 10. Fusion and diffusion parameters for lead(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_0) (kilocal/mole)</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>24.2</td>
</tr>
</tbody>
</table>

\(^a(3,4)\)
Nachtrieb (3) has given the plot of $\ln D$ vs. $T_m/T$ for lead. The values of $T_m(P)$ were obtained from the melting curve of Butuzov and Gonikberg (35). The slope of the $\ln D$ vs. $T_m/T$ curve in the limit of low pressure is -20.7, and the value of $Q_o/R T_o$ for lead is -20.3. Thus, as Nachtrieb pointed out, in the limit of low pressure, the diffusion coefficient is well described by Eq. 17.

Nachtrieb (2) has remarked that relations among thermodynamic quantities do not provide a basis for deciding the elementary jump mechanism. Thus, although Eq. 11 is experimentally valid, one cannot infer from this any ideas about the microscopic relation of melting and diffusion. Similarly, Eq. 17, which is a new form of the historical correlation of activation energy and melting temperature, merely expresses a relation among thermodynamic quantities. Eq. 17 states that the activation energy for diffusion of the single substance is proportional to the melting temperature of that substance, but that the proportionality constant is different for different substances. This can be seen by equating the arguments of the exponential functions of Eqs. 1 and 16, giving, in the limit of low pressure,

$$H_a(P) = \frac{Q_o}{T_o} T_m(P)$$

(39)

As remarked in Section II-A, tests of diffusion mechanisms have usually consisted of comparisons of
calculated and experimental activation energies, and that on this basis the vacancy mechanism seems most likely in simple structures. For the activation volume, such a comparison is possible with copper, for which Tewordt (36) has calculated the volume change due to interstitial and vacancy defects. Although the activation volume has not been measured for copper, Eq. 11 can be used to estimate a value for comparison with Tewordt's calculations.

Tewordt calculated that for a vacancy in copper, the crystal volume is decreased by about 50 percent, whereas for an interstitial, the crystal volume is increased by about 30 percent. All measured values of the activation volume for simple solids are less than the atomic volume, so that on this comparison, the vacancy defect is more likely.

In Section II-A the activation volume was divided into two parts, one associated with the volume of formation $V_F$ of a defect, and one associated with the volume of motion $V_M$ of a diffusing atom. Tewordt's calculation gives the result that for a vacancy, $V_F$ is 50 percent of $V_m$, the molar volume. Using Eq. 11, $V_a$ for copper is estimated to be $4.5 \text{ cm}^3$, or 65 percent of the molar volume of copper. Thus $V_M$ is estimated to be about 15 percent of $V_m$.

On the hard sphere model, $V_M$ and $V_F$ should both equal
The accepted view seems to be that $V_M$ and $V_F$ should be about equal in real lattices (4,11). Thus the remarks above concerning copper suggest that the vacancy model may not be consistent.

The values of $V_a$ from this research raise doubts about the vacancy model. The most remarkable result from this work is that both $V_a$ and $V_a/V_m$ for lithium are so small. On the vacancy picture these values imply that atoms beyond those adjacent to a vacancy are affected by the vacancy. The concept of a vacancy as a point defect may not be adequate for this situation.

One aspect of Rice's dynamical theory is the calculation of the probability that a lattice dilates enough to permit an atom to jump into a vacancy. It appears that a great deal of cooperative motion of the atoms would be necessary for a lithium atom to jump into a volume which was only one-fourth of the atomic volume.

In summary, it is established by this work and that of others that melting and diffusion phenomena are closely correlated, and that Eq. 11 can be reliably used for predictions of activation volumes in simple structures. It is hoped that the values of activation volume obtained here for lithium and sodium will encourage calculation of this parameter for these metals.
VI. REFERENCES


VII. ACKNOWLEDGEMENTS

The author wishes to thank the persons in his laboratory who assisted in the course of this research. Dr. W. H. Jones, Jr. was very helpful in the early part of the work. Special thanks are due to Mr. R. D. Engardt for assembling the pressure system and instructing the author in its use. Mr. Engardt's humor and experimental skill were invaluable in moments of discouragement.

The author is particularly grateful to Dr. R. G. Barnes for suggesting this research problem and for giving so much helpful advice and encouragement during the progress of the work. The author has benefited greatly from and enjoyed very much his association with Dr. Barnes during several years of graduate research and study.
VIII. APPENDIX A

Given

\[ D = D(P, T), \quad \frac{\partial \ln D}{\partial P} \bigg|_T = -\frac{V_a}{RT}, \quad \frac{\partial \ln D}{\partial (1/T)} \bigg|_P = -\frac{H_a}{R}, \]

change variables from \((P, T)\) to \((z, T)\), where \(z = T_m/T\).

First find

\[ \frac{\partial \ln D(z, T)}{\partial z} \bigg|_T = \frac{\partial \ln D(P, T)}{\partial P} \bigg|_T \quad \frac{\partial P(z, T)}{\partial z} \bigg|_T. \]

Since

\[ \frac{T_m}{T} = \frac{T_0 + KP}{T} = z, \quad K = \frac{T_0}{H_m} = \frac{T_0}{Q_0}, \]

then

\[ P(z, T) = \frac{zT - T_0}{K}, \quad \frac{\partial P(z, T)}{\partial z} \bigg|_T = \frac{T}{K}, \]

and

\[ \frac{\partial \ln D(z, T)}{\partial z} \bigg|_T = \left( -\frac{V_a}{RT} \right) \left( \frac{TQ_0}{T_0 V_a} \right) = -\frac{Q_0}{RT_0}. \]

Now find

\[ \frac{\partial \ln D(z, T)}{\partial (1/T)} \bigg|_T = \frac{\partial \ln D(P, T)}{\partial (1/T)} \bigg|_P \quad \frac{\partial \frac{1}{T}(z, T)}{\partial (1/T)} \bigg|_T + \frac{\partial \ln D(P, T)}{\partial P} \bigg|_T \quad \frac{\partial P(z, T)}{\partial (1/T)} \bigg|_T \frac{\partial \frac{1}{T}}{\partial (1/T)} \bigg|_T \]

\[ \frac{\partial \frac{1}{T}(z, T)}{\partial (1/T)} \bigg|_T = 1; \quad \frac{\partial P(z, T)}{\partial (1/T)} \bigg|_T = \frac{z}{K \frac{1}{T^2}} = -\frac{T^2}{K}. \]
Then
\[ \frac{\partial}{\partial (1/T)} \ln \frac{D(z, T)}{D(z)} \bigg|_{2} = \left( -\frac{H_{q}}{R} \right) + \left( -\frac{V_{q}}{RT} \right) \left( -\frac{T^2 z}{K} \right). \]

As \( P \to 0, \)
\[ \frac{\partial}{\partial (1/T)} \ln \frac{D(z, T)}{D(z)} \bigg|_{2} = -\frac{Q_{v}}{R} + \frac{Q_{v}}{R} = 0 \]

Therefore \( D(z, T) = D(z) = D(T_{m}/T). \)
IX. APPENDIX B

Using
\[ \frac{\partial \ln \alpha}{\partial P} \bigg|_T = -\frac{1}{3} \beta \quad , \quad \nu_0 = \Theta_0 \frac{k}{h} \]

where \( \beta \) is the volume compressibility, and \( \Theta_0 \) is the Debye temperature, we have

\[ \frac{\partial \ln \nu_0}{\partial P} \bigg|_T = \frac{\partial \ln \Theta_0}{\partial P} \bigg|_T = \left( -\frac{\partial \ln \Theta_0}{\partial \ln \nu} \right) \left( -\frac{\partial \ln \nu}{\partial P} \right) \]

Since

\[ \gamma_G = -\frac{\partial \ln \Theta_0}{\partial \ln \nu} \]

where \( \gamma_G \) is the Gruneisen constant,

\[ \frac{\partial \ln \nu_0}{\partial P} \bigg|_T = \gamma_G \beta \]

Then the terms in Eq. 34 become

\[ -6 \frac{\partial \ln \alpha}{\partial P} \bigg|_T - \frac{\partial \ln \nu_0}{\partial P} \bigg|_T = \beta (2-\gamma_G) \]
Starting with Eq. 18,
\[ \frac{1}{T_1} = \sum_i \left( \frac{1}{T_{i1}} \right)_i = \left( \frac{1}{T_{11}} \right)_d + \left( \frac{1}{T_{11}} \right)_e \]
and Eq. 23,
\[ \left( \frac{1}{T_{21}} \right)_d = \left( \frac{1}{T_{12}} \right)_d + \left( \frac{1}{2T_1} \right)_d \]
and Eq. 24,
\[ \frac{1}{T_2} = \left( \frac{1}{T_{22}} \right)_d + \left( \frac{1}{T_{22}} \right)_e \]

solve Eq. 23 for \( T_{21} \) and use Eq. 24 to get
\[ \left( \frac{1}{T_{21}} \right)_d = \frac{1}{T_2} - \left( \frac{1}{T_{22}} \right)_e - \left( \frac{1}{T_{12}} \right)_d \]
Now use \( T_{22} \) and Eq. 18 to get
\[ \left( \frac{1}{T_{21}} \right)_d = \frac{1}{T_2} - \frac{1}{T_1} + \left( \frac{1}{2T_1} \right)_d \]

In the case of sodium the last term on the right of this last equation was neglected.