Self-Diffusion in Molten Lithium

Isotopic Mass Dependence *, **

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The liquid state self-diffusion coefficients of Li^6 and Li^7 in isotopically enriched Li^6 and Li^7 metal and in several isotopic alloys have been measured by the nuclear magnetic resonance spin echo, pulsed magnetic gradient technique. At the melting point 180.5 °C, the self diffusion coefficients are measured as $D_m{}^6 = (6.8 \pm 0.7) \cdot 10^{-5}$ cm²/sec for Li^6 in 99% Li^6, and $D_m{}^7 = (5.8 \pm 0.6) \cdot 10^{-5}$ cm²/sec for Li^7 in 99.9% Li^7. The ratio of measured values $(D_m{}^6/D_m{}^7) = 1.18 \pm 0.07$, which is greater than the square root of the mass ratio, $(m^7/m^6)^{1/2} = 1.08$. The isotopic ratio of self diffusion coefficients is observed to be less than the ratio of the mutual diffusion coefficients in almost pure Li^6 and almost pure Li^7, $(D_{Mm}{}^6/D_{Mm}{}^7) = 1.35$, and the viscosity ratio, $(\eta^7/\eta^6) = 1.44$. The dependence of D upon isotopic alloy concentration appears to be relatively weak and linear in all but the very low concentrations. As a test of the experimental method, D was measured in liquid Na, H_2O, and D_2O. In liquid sodium at the melting point, $D = (3.7 \pm 0.3) \cdot 10^{-5}$ cm²/sec. The Na measurement and the values of D in water are about 5% below other published data, but they are in agreement within experimental uncertainties. Results of this experiment contain systematic corrections amounting to 15—20% caused principally by the finite size of the droplets of the liquid metal samples. The corrections as well as the limitations of the technique in measurement of self diffusion coefficients in metals are discussed.

1. Introduction

The self-diffusion of Li^6 and Li^7 has been measured in $Li^6 - Li^7$ alloys by the spin-echo method of pulsed nuclear resonance (NMR) with the addition of a pulsed magnetic gradient. A description of the measurement of D in liquid lithium by this technique is given by MURDAY and COTTS [1] (MC).

Self-diffusion in lithium alloys is of particular interest because of anomalous results in measurements of other atomic transport properties in isotopically enriched lithium alloys. The effect of isotopic mass on atomic transport in classical liquids has been studied theoretically by BROWN and MARCH [2]. They conclude that in classical liquids differing only by this isotopic mass, the self-diffusion coefficient is proportional to $m^{-1/2}$. This prediction is in agreement with the Ascarelli-Paskin dense gas model [3] and the Cohen-Turnbull free volume model [4]. The calculations of Brown and March also predict that the shear viscosity of the isotopically pure liquids depends on mass as $m^{1/2}$. Empirically it is found [5] that diffusion and viscosity in liquid metals are related; that is, they obey a Stokes-Einstein type relationship, $D\,\eta = \text{const} \times T$. One would then expect to find for liquid lithium, $D^6/D^7 = \eta^7/\eta^6 = 1.08$. However, the viscosities in 99.8% pure Li^6 and 99.99% pure Li^7 have been measured [6] and give a ratio $\eta^7/\eta^6 = 1.44 \pm .02$ at the melting point. It is of interest to determine whether or not the same mass dependence appears in self-diffusion.

2. NMR Measurement of Self-Diffusion

The relation of self-diffusion to the echo height in the pulsed NMR spin echo technique is developed by HAHN [7], CARR and PURCELL [8], and others [9, 10]

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[1] J. S. MURDAY and R. M. COTTS, J. Chem. Phys. **48**, 4938 [1968].

[2] R. C. BROWN and N. H. MARCH, Phys. Chem. Liquids **1**, 191 [1968].

[3] P. ASCARELLI and A. PASKIN, Phys. Rev. **165**, 222 [1968].

[4] M. H. COHEN and D. TURNBULL, J. Chem. Phys. **31**, 1164 [1959].

[5] H. J. SAXTON and O. D. SHERBY, Trans. Am. Soc. Metals **55**, 826 [1962].

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[7] E. L. HAHN, Phys. Rev. **80**, 580 [1950].

[8] H. Y. CARR and E. M. PURCELL, Phys. Rev. **94**, 630 [1954].

[9] A. ABRAGAM, The Principles of Nuclear Magnetism, Oxford University Press, New York 1961.

[10] H. C. TORREY, Phys. Rev. **104**, 563 [1956].

for steady magnetic gradients and infinite media. The extension to pulsed gradients is given by Stejskal and Tanner [11].

$$\ln M = \ln M_0 - \tfrac{2}{3}\gamma^2 D\, G_0^2 \tau^3 - \gamma^2 D\, G^2 \delta^2 (\tau - \delta/3) - \gamma^2 D\, \mathbf{G}\cdot\mathbf{G}_0\, \delta (\tau^*)^2 \qquad (1)$$

where, $(\tau^*)^2 = (\tau^2 + \tau\,\delta - \tfrac{2}{3}\delta^2)$, M is the spin echo magnitude, γ the gyromagietic ratio, D the self-diffusion coefficient, G the applied gradient, G_0 the background gradient, δ the time duration of the applied gradient G, and τ the time between 90° and 180° pulses. It has been assumed in Eq. (1) that the time lapses between each gradient pulse and the previous RF pulse are equal and very much less than δ.

The value of τ was kept constant throughout a data run so the first two terms of Eq. (1) are constant and may be included in M_0. If one chooses $G\,\delta \gg G_0\,\tau$, only the third term contributes significantly to the degradation of M by the pulsed gradient and $\ln M \sim (G\,\delta)^2$.

The pulsed gradient in Eq. (1) is asumed to have zero rise and fall times. In practice this was not the case. To first order, a correction [12] for the finite rise and fall times is accomplished by replacing $(\tau - \delta/3)$ by $(\tau - \delta/3 + A(2\,\tau/\delta - 1))$. If one considers the product of gradient times time, $G\,\delta$, as an area under the ideal pulse, then A is defined as the difference between the actual area and $G\,\delta$ (see Fig. 1).

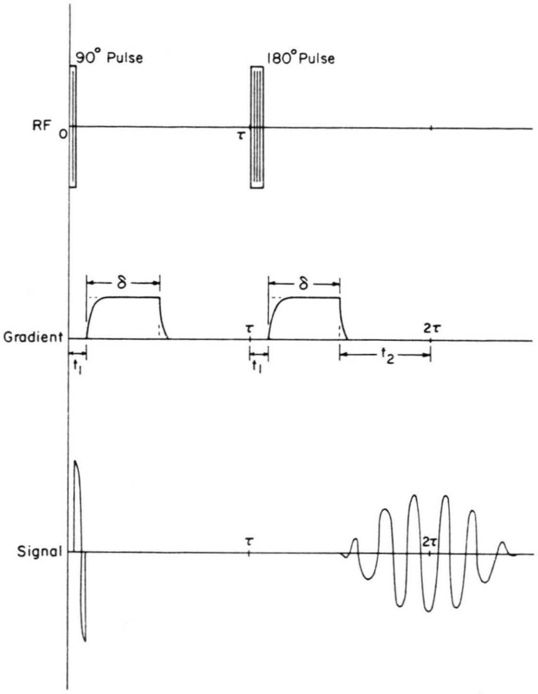

Fig. 1. Sequence of pulses in a pulsed magnetic gradient spin-echo experiment.

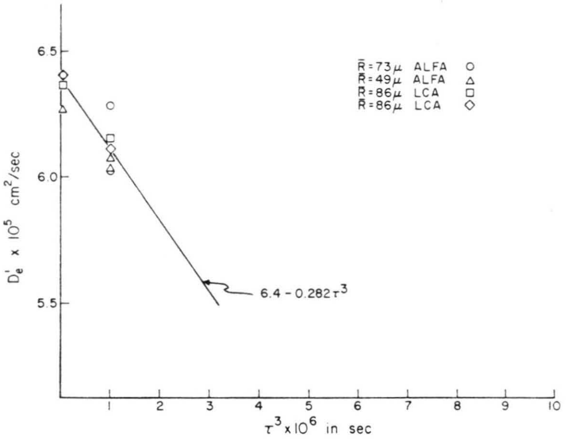

Fig. A. 1. τ dependence of the measured self-diffusion coefficient without the background gradient correction.

Equation (1) needs two additional corrections when applied to the lithium measurements. NMR technique requires penetration into the sample of radio frequency magnetic fields. Lithium, being a metal, has a skin depth of 110 μ at 7 MHz, the frequency at which the experiment was performed. The samples were a powder of particles with diameter on the order of 150 μ or less. The lithium particle diameters were on the order of the distances traversed by the atoms during a measurement of D, so a significant number of atoms collided with a boundary, restricting the diffusion. An extension of a theory by Neumann [1, 13] can account for the bounded media. The new equation describing the system is:

$$\ln M = \ln M_0 - \gamma^2 G^2 \delta^2 (\tau - \delta/3)\; f'(\tau, \delta, R, D)\,,\; f' = \frac{2}{\delta^2(\tau - \delta/3)} \sum_{m=1}^{\infty} [\alpha_m^2(\alpha_m^2 R^2 - 2)]^{-1}$$
$$X\left(\frac{2\,\delta}{\alpha_m^2 D} - \frac{2 + \exp[-\alpha_m^2 D(\tau - \delta)] - 2\exp(-\alpha_m^2 D\,\delta) - 2\exp(-\alpha_m^2 D\,\tau) + \exp[-\alpha_m^2 D(\tau + \delta)]}{(\alpha_m^2 D)^2}\right). \qquad (2)$$

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[11] E. O. Stejskal and J. E. Tanner, J. Chem. Phys. **42**, 288 [1965].

[12] J. S. Murday, Ph. D. Thesis, Cornell University 1970, unpublished.

[13] C. H. Neuman, private communication.

The a_m are a set of constants determined from the solution of Eq. (3).

$$a_m R J'_{3/2}(a_m R) - \tfrac{1}{2} J_{3/2}(a_m R) = 0 . \qquad (3)$$

Equation (2) acounts for bounded media effects only due to the third term in Eq. (1). It would be possible, but very tedious, to apply the Neuman theory to the fourth term. Since the effect of the fourth term is small compared to the third, it was decided that bounded media corrections to it would be insignificant.

A powder of lithium particles has significant inhomogeneous local fields due to contributions by the electron magnetic susceptibility. These fields produce large background gradients [1] which cause term 4 of Eq. (1) to be significant.

If a nucleus experiences background gradient g_{0i}, then it behaves as described by Eq. (1) with $G_0 = g_{0i}$. A suitable average over all nuclei must be made to characterize the signal. The assumptions made in taking this average are: a) the distribution, $\varrho(g_0)$, of background gradients is symmetric about $g_0 = 0$, b) the distribution $\varrho(g_0)$ is continuous, and c) the size of the background gradient experienced by a particle is independent of the particle's volume. The Appendix outlines the steps in the average; its result is that a term $\gamma^4 D^2 \delta^2 \tau^{*4} G^2 \overline{\overline{G_0^2}}$ must be added to Eq. (2).

$$\ln M = \ln M_0 - \gamma^2 G^2 \delta^2 \left(\tau - \delta/3 + A \frac{2\tau}{\delta} - 1\right) f'(\tau, \delta, R, D) + \gamma^4 D^2 \delta^2 \tau^{*4} G^2 \overline{\overline{G_0^2}}. \qquad (4)$$

$\overline{\overline{G_0^2}}$ is an average over the background gradients.

3. Experimental Procedure

The experimental procedure for this series of diffusion measurements was basically the same as described in MC. The significant differences were in temperature control and homogeneity, signal averaging, data processing and gradient calibration [12]. The changes will be briefly described below.

The lithium raw material came from three sources. Natural lithium, 92.6% Li^7 and 7.4% Li^6, was purchased from ALFA Inogranics and Lithium Corporation of America. The former was a piece of bulk lithium, 99.99% pure; the latter a powder of unknown purity. Isotopically enriched materials were purchased from Oak Ridge National Laboratory. All the Oak Ridge lithium was 99.9% free from metallic impurities. The isotopic break-down of the various Oak Ridge material is given in Table 1. The uncertainty of the isotopic concentration is less than 1% from known sources of error. The ALFA Inorganic and Oak Ridge lithium were in bulk form and had to be reduced to powder for use in the NMR experiments. The techniques for powder production are described elsewhere [12]. In addition to the lithium mixtures above, another alloy of 36% Li^7 and 64% Li^6 was prepared by mixing chosen amounts of molten 100% Li^7 and 95% Li^6 in a stainless steel crucible. The alloy was annealed for one half hour in the liquid state (to assure homogeneous mixing) before being powdered. The mixture was measured to be 36% Li_1 and 64% Li^7 by comparing the Li^6 and Li^7 free induction decay (FID) signal magnitudes at the same frequency.

Table 1. Enriched isotope samples.

Nominal	Actual Concentration	
Li^7 100%	99.99% Li^7	0.01% Li^6
Li^6 95%	4.4%	95.6 %
Li^6 99%	0.7 %	99.3 %

Prior to data run the sample tubes were placed in the heated oven for at least an hour to insure temperature homogeneity. The oven consisted of a vacuum flask made from two concentric quartz tubes into which a 20 cm long, non-inductively wound, stainless steel wire heating coil was inserted. At the best spot the temperature inhomogeneity across a 1 cm long sample was less than .½ °C. The temperature was maintained by a proportional controller to better than ½ °C. A copper-constantan thermocouple, taped about 1 cm above the sample top, monitored the temperature. The thermocouple temperature was recorded several times during a run. The sample tube was carefully positioned to put it in the center of the gradient coils.

The values of τ and δ were adusted to within 5 μs and 1 μs respectively of their desired values with aid from a time interval plug-in in a H-P scaler. δ remained stable throughout a run but τ needed to be constantly monitored against 0.1% drift. The repetition rate of the run was chosen to be greater than $5\,T_1$. The separation between the RF and gradient pulses, t_1 (see Fig. 1), was arbitrarily set at 300 μs.

The 90° and 180° RF turning pulses were adjusted and the H_0 field trimmed to place the spin system about 1 to 1.5 kHz off resonance. The off-resonance condition resulted in a beat signal of spins against reference voltage. The beat envelope was a more accurate measure of echo height than an on-resonance echo. With large gradients it often proved impossible to adjust H_0 for a clean on-resonance echo. Evidently trailing fields after a gradient pulse (perhaps due to relaxation transients in the magnetic pole face or some other cause) changed the signal frequency. Off resonance, phase coherence with the reference frequency is not important and the beat pattern envelope reproduced the expected echo shape.

During the run the current in the gradient coils was recorded as one of the seven available fixed values. At each setting, the current in the second pulse was trimmed to make the echo symmetric about 2τ. This adjustment equalizes the two gradient pulses as can be seen by the following illustration. The background gradient usually has a small net component, $\boldsymbol{g}$, parallel or antiparallel to $\boldsymbol{G}$. Suppose compared to the first gradient pulse, the second pulse is slightly smaller by an amount ξ and the background gradient is parallel to $\boldsymbol{G}$. The background will eventually replace the missing spin phase accumulation $\boldsymbol{g}\,(t-2\tau) = \xi\delta$. The echo occurs, but slightly late $t > 2\tau$. When ξ is adjusted to be zero the echo will occur at 2τ. The data was taken with a zero gradient reading every third points. In this way all data points were contiguous to a zero reading and any gain drifts were easily accounted for.

The echo was fed to the NS 513 signal averager. The averager was triggered ON just prior to the peak of the echo. The significant part of the echo then appeared in the beginning channels of the integrator. Once averaged, the signal was read out from the integrator memory via IBM typewriter.

The minimum and maximum values of the typewritten data occurring nearest to 2τ represent the peak to peak echo height. The difference of the two numbers was plotted on a semilog graph paper versus

$$I^2\,\delta^2\left(\tau-\frac{\delta}{3}+A\left(\frac{2\,\tau}{\delta}-1\right)\right).$$

Each set of data consisted of about fifteen $(I\,\delta)$ values, with both I and δ varied. The value of the abscissa at $1/e$ point, t_e, of the data, was found from a least squares fit. When making a least squares fit to an equation for the form $\ln(y)=\ln(a)-b\,x$ it is necessary to pay attention to proper weighting factors. All of the spin echo data in a run was taken at the same gain setting. The amount of noise in the signal was then independent of echo size y and can be considered as an added constant Δy. If x is exact and the magnitude of eror in y is Δy for all values of y, then the point (x, x) should be weighted by y^2 in a logarithmic fit. This follows by noting $\ln(y \pm \Delta y) = \ln(y) \pm \Delta y/y$ and that weighting in least squares goes as the inverse square of the probable error[14].

Two adjustments to t_e were necessary to account for the background gradient and bounded diffusion effects. The adjustment for background gradient was obtained via Eq. (A. 6) with the value of D approximated by $D_e = 1/c^2\,\gamma^2\,t_e$. The corrected value D_e was then inserted into a computer program to calculate a new D from bounded diffusion theory by the same iteration procedure described in MC. Since the initial background gradient correction was proportional to D^2, the complete process was repeated with the new value of D. An equivalent procedure, not used because of a prewritten computer program for the bounded diffusion correction, would be to solve Eq. (4) by an iterative process.

The gradient was produced by "anti-Helmholtz" coils. The gradient was therefore related to the current in the coils by a constant $G=c\,I$. The coil constant was determined four different ways. The methods actually were sensitive to H rather than G and a map of H vs. position yielded G in these cases. In two of the three the beat frequency of an echo from the pulsed NMR spin echo technique was recorded at different positions along the coil axes for a given value of I. The beat frequency was proportional to the field H seen by the sample at its position along the coil axis. In the third H-measuring method, the field separation of two small samples spaced a known distance apart along the axis was measured from recordings of the CW NMR signal of the samples. The current I was measured by either the voltage across a 0.1 ohm, 1% resistor or by a pulse transformer.

The fourth method measured G directly. The FID of a cylindrical sample in a homogeneous gradient is a Bessel function[8]. On resonance, the first zero of the Bessel function depends on the gradient strength in a known way. The gradient is obtained from the slope of a first zero time versus current plot.

As is shown in Table 2, all four method gave results within a 3% spread. An average value of $c=9.58 \pm 0.06$ was chosen.

Table 2. Determination of coil constant c.

Measuring Technique		Value of c
Current	Gradient	(G/cm.amp)
0.1 Ω Resistor	Beat Freq. versus Displacement	9.68 ± 0.1
Pulse Transformer	Beat Freq. versus Displacement	9,40 ± 0.15
0.1 Ω Resistor	Free Induction Decay	9.60 ± 0.1
Pulse Transformer	CW Line	9.58 ± 0.1

All the calibrations of c were carried out at low values of G ($G < 5$ gauss/cm). In order to check the constancy of c for larger values of G (G was up to 200 g/cm in these measurements) both steady gradient (low G) and pulsed gradient (large G) measurements of D in H_2O and D_2O were carried out. Both pulsed and steady gradient techniques gave values of D which agreed to 1% or better.

4. Data and Results

The known sources of error in this experiment were serious enough to warrant careful checking of the technique. Therefore the pulsed gradient was

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[14] A. G. WORTHING and J. GEFFNER, Treatment of Experimental Data, J. Wiley & Sons, Inc., New York 1943, p. 248.

used to measure D in two liquids, H_2O (l. c.[15]) and molten Na (l. c.[16]), in which there are other published measurements of D. In both H_2O and Na the pulsed gradient[12] D was about 5% lower than the other published measurement. It is not known whether the 5% is due to systematic error or is accidental. In any event, the pulsed gradient measurements are at least reasonably (i. e., 5% or better) accurate. The ratio of self-diffusion coefficients of the two lithium isotopes should be very accurate since any systematic errors will be compensated.

The two known major sources of systematic error are the corrections for bounded media and background gradients. The correction to the self-diffusion measurements for the background gradient in their liquid metal dispersions is largely empirical. The theory outlined in Appendix A is at best a rough approximation since the assumptions concerning the gradient distributions are no more than reasonable guesses. The correction turns out to be on the order of $5-8\%$ for Li. As discussed in the Appendix, the correction is uncertain by about 50%. The lithium diffusion coefficients will have about 5% uncertainty because of this ambiguity.

The metal dispersions also have the bounded media correction to D. The correction is about 10% in the $125-177\ \mu$ particle diameter range and 15% in the $74-125\ \mu$ range. The magnitude of the correction is dependent on the average particle radius R chosen to represent the distribution of diameters. In order to get a handle on the particle size distribution three different representative samples were opened and their powders observed under a scanning microscope. The results, Fig. 2, show that the particle preparation has not separated the powders into sharply defined diameter ranges. The bulk of the diameters fall within their nominal limits but fairly substantial tails exist in both the purchased and homemade powders. A measured sample is assumed to represent the diameter distribution of all samples in its class; for instance, all $74-125\ \mu$ homemade lithium powder is assumed to have the distribution in Fig. 2 c. The distributions in Fig. 2 are characterized in Table 3.

It turns out that for the values of D, τ, and R in this experiment the bounded media correction is not very sensitive to R. $\overline{R}$ is known to about 10% in the lithium dispersions; the corresponding error in the correction is 2% in both particle ranges.

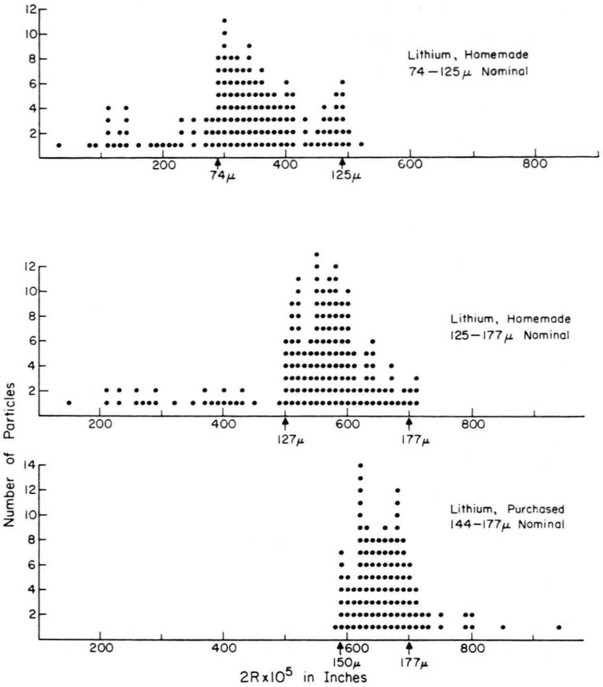

Fig. 2. Histogram of the number of particles in a sample with a given radius versus the magnitude of that radius.

Table 3. Average Radius $\overline{R}$ for the various kind of powdered samples.

Type of Material	ϱ(r) in Range ΔR	$\overline{R}$
homemade	3.4 in 152—177 μ	
lithium powder	10 in 125—152 μ	73 μ
125—177 μ nominal	1 in 50—125 μ	
homemade	3 in 107—125 μ	
lithium powder	7 in 74—107 μ	49 μ
74—125 μ nominal	1.5 in 0— 74 μ	
purchased	0.5 in 185—230 μ	
lithium powder (LCA)	2 in 180—185 μ	86 μ
144—177 μ nominal	8 in 150—180 μ	

Data of the self-diffusion of Li^7 and Li^6 in the several compositions of isotopic lithium is tabulated in Table 4. The value of τ was 10 ms for all measurements except for a few in the natural lithium data. δ was in the range $1.034-1.674$ ms for Li^7 and $1.674-2.934$ ms for Li^6. The value $\tau=10$ ms was chosen as a round number at which Li^6 diffusion could be measured easily. At $\tau=5$ ms the low

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[15] N. J. TRAPPENIERS et al., Phys. Letters **18**, 256 [1965].

[16] R. E. MEYER and N. H. NACHTRIEB, J. Chem. Phys. **23**, 1851 [1955].

Li^6 gyromagnetic ratio required a δ nearly equal to τ if the pulsed gradient were to be effective. δ was kept much less than τ for fear of any trailing fields following the gradient pulses. Figure 3 shows typical data for a Li^7 and a Li^6 diffusion measurement. The tailing off of the Li^7 data at the large $(I\,\delta)^2$ values is not understood. Other species (Li^6, Na and H_2O) showed some signs of such a tail but not so pronounced.

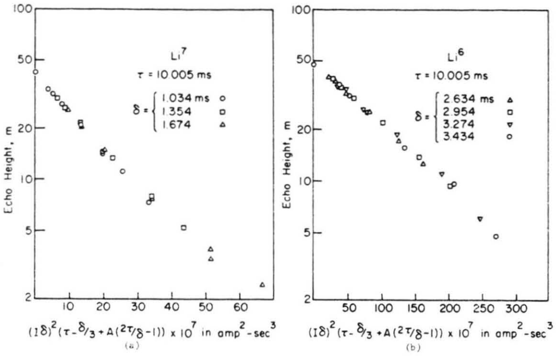

Fig. 3. Typical pulsed magnetic gradient spin-echo lithium data.

In Fig. 4 a graph presents the temperature dependence of self-diffusion for Li^7 in 99.99% Li^7 and Li^6 in 99% Li^6. NACHTRIEB [17] has noted that liquid metal diffusion coefficients have no unique temperature dependence. He found that tin, lead, and indium self-diffusion coefficients could be represented by either D vs. T or $\ln(D)$ vs. $1/T$. Assuming a linear temperature dependence

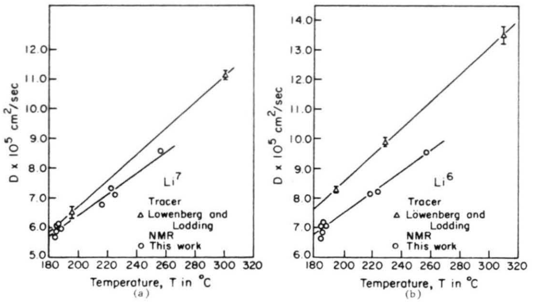

Fig. 4. Self-diffusion and mutual diffusion coefficients of the enriched liquid lithium isotopes as a function of temperature.

$$D = D_m + a(T - T_m),$$

a least square fit of the lithium data yields

$$D_m{}^7 = 5.76 \pm 0.5 \cdot 10^{-5}\ \text{cm}^2/\text{sec},$$
$$a^7 = .036 \pm .003 \cdot 10^{-5}\ \text{cm}^2/\text{sec}\ {}^\circ\text{C}$$

and $D_m{}^6 = 6.80 \pm 0.6 \cdot 10^{-5}\ \text{cm}^2/\text{sec}$,

$$a^6 = .036 \pm .003 \cdot 10^{-5}\ \text{cm}^2/\text{sec}\ {}^\circ\text{C}.$$

The error estimates on these numbers are the square root of the sum of the squares of the various experimental uncertainties, which are taken to be a systematic contribution of ±5% from c and I measurements, bounded diffusion ±2%, background gradients ±5%, and reproducibility ±3%.

If the data is least square fit to the Arrhenius relation $D = D_0 \exp\{-Q/R\,T\}$, $D_0 = 8.3 \pm 1.4 \cdot 10^{-4}$ cm²/sec and $Q = 2380 \pm 160$ cal/mole for Li^7; $D_0 = 6.8 \pm 1.2 \cdot 10^{-4}$ cm²/sec and $Q = 2080 \pm 160$ cal/mole for Li^6. The error estimates affixed on these numbers represent reproducibility only. These fits predict

$$D_m{}^7 = 5.8 \cdot 10^{-5}\ \text{cm}^2/\text{sec}$$

and $(\mathrm{d}D/\mathrm{d}T)_m{}^7 = .034 \cdot 10^{-5}\ \text{cm}^2/\text{sec-}{}^\circ\text{C}$,

$$D_m{}^6 = 6.8 \cdot 10^{-5}\ \text{cm}^2/\text{sec}$$

and $(\mathrm{d}D/\mathrm{d}T)_m{}^6 = .035 \cdot 10^{-5}\ \text{cm}^2/\text{sec-}{}^\circ\text{C}$.

For the purposes of comparing the diffusion coefficients measured internal to this experiment, the systematic error can be eliminated since it is present in all the data. For this reason the ratio of the isotopic diffusion coefficients $D_m{}^6/D_m{}^7 = 1.18 \pm .07$ is better known than either of the two D_m separately. The measurement is close to but greater than the ratio predicted by the theories, $(m^7/m^6)^{1/2} = 1.08$.

5. Discussion and Conclusions

Measurements of mutual diffusion coefficients in isotopically enriched lithium have also been made by LÖWENBERG and LODDING [18] (LL). Their data are also presented in Fig. 4. Their results at the melting point are

$$D_{\mathrm{M}m}{}^6 = (7.8\ \ \pm .2) \cdot 10^{-5}\ \text{cm}^2/\text{sec},$$
$$D_{\mathrm{M}m}{}^7 = (5.75 \pm .3) \cdot 10^{-5}\ \text{cm}^2/\text{sec},$$

where $D_m{}^6$ and $D_m{}^7$ are the mutual diffusion coefficients in the limit of isotopically pure Li^6 and Li^7, respectively. In the limit of diminishing solute concentration the mutual diffusion coefficient ap-

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[17] N. H. NACHTRIEB, Adv. Phys. (GB) **16**, 309 [1967].

[18] L. LÖWENBERG and A. LODDING, Z. Naturforsch. **22 a**, 2077 [1967].

proaches the self-diffusion coefficient of the solute (l. c.[19, 20]).

Thus, the Löwenberg and Lodding data may be presented in terms of self-diffusion, since

in matrix of Li^7 $D_{\mathrm{M}m}{}^7 = D_m{}^6$, and
in matrix of Li^6 $D_{\mathrm{M}m}{}^6 = D_m{}^7$.

The mechanisms of diffusive motion in liquids are not established. So it might be possible that the mass dependence of tracer self-diffusion is determined by the matrix mass and/or tracer mass. Classically, for Li^7 tracer in Li^6, that leaves the possibility for D^7 to be anywhere in the range 1 to 0.92 times D^6. It also follows that for Li^6 tracer in Li^7, D^6 should be from 1 to 1.08 times D^7. With the interpretation of mutual diffusion in terms of self-diffusion and with D proportional to $m^{-1/2}$ the ratio $D_{\mathrm{M}m}{}^6/D_{\mathrm{M}m}{}^7$ would be expected to have a value between 1.08 and 0.92. The measured ratio[19] is equal to $D_{\mathrm{M}m}{}^6/D_{\mathrm{M}m}{}^7 = 1.35$.

In a check on alloy concentraiton dependence the self-diffusion coefficients of Li^6 and Li^7 have been measured as a function of composition using NMR. The data in Fig. 5 show that the self-diffusion coefficients of Li^6 and Li^7 are relatively insensitive to the isotopic concentrations. The self-diffusion of 5% Li^7 in 95% Li^6 gives a value of

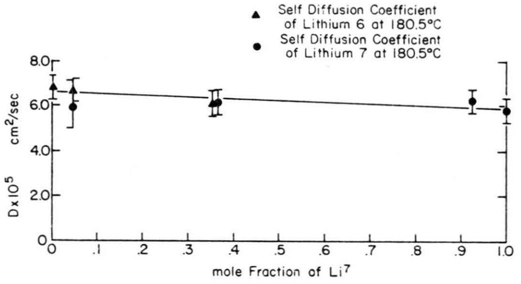

Fig. 5. Self-diffusion coefficients of Li^6 and Li^7 in various isotopic lithium alloys at 180.5 °C.

$$D_m = (5.75 \pm .7) \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{sec}$$

at the melting point. The LL data give the much larger value of $D_{\mathrm{M}m} = (7.65 \pm .15) \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{sec}$ for 7% Li^7 in 93% Li^6. Unfavourable signal to noise prevented any NMR measurement of Li^6 tracer in Li^7. However, from the NMR data, one might expect that in nearly pure Li^7, $D_m{}^6$ is close to $D_m{}^7$. The LL value of $D_{\mathrm{M}m}{}^7 = (5.87 \pm .30) \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{sec}$ in 95% Li^7 agrees very well with our value of $D_m{}^7$. Comparison of $D_{\mathrm{M}m}{}^7$ with $D_m{}^6$ would be preferable here, but unfortunately no NMR data for $D_m{}^6$ could be obtained.

The self-diffusion data of Fig. 5 show that there is little difference between the self-diffusion coefficients of Li^6 and Li^7 atoms in a given isotopic alloy. These data and the LL value of $D_{\mathrm{M}m}{}^7$ are in agreement within this percentage range. However, the $D_{\mathrm{M}m}{}^6$ data of LL fall well outside of this percentage range.

The data for D^7 in natural lithium from $\tau = 5$ msec and $\tau = 10$ msec of Table 4 were adjusted for temperature dependence to obtain an effective

$$D_m = (6.25 \pm 0.6) \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{sec}.$$

This result is lower than the previous result for Li^7 in natural lithium measured by MC,

$$D_m = (6.8 \pm 0.6) \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{sec},$$

but the ranges of uncertainty overlap. The use of improved data recording in the present experiment indicates that current data have a higher reliability.

It is of interest to note in Fig. 5 that there is a strong concentration dependence of self-diffusion for the solvent near both ends of the concentration range. This effect is more pronounced at the Li^7-rich end than at the Li^6-rich end of the concentration range. Examination of the data in Table 4 shows that in these regions the scatter of measured values of D at a given concentration is less than the difference between mean values of D for different concentrations.

The concentration dependence is illustrated in the magnitude of the ratio $(D_m{}^6/D_m{}^7)$ as determined from 95.6% Li^6 and 92.6% Li^7 alloys. For these alloys, $(D_m{}^6/D_m{}^7) = 1.07$ in contrast to the value of the ratio in almost isotopically pure alloys where $(D_m{}^6/D_m{}^7) = 1.18$. The fractional change in D, $[(D_m{}^6/D_m{}^7) - 1]$, decreases by more than 50% for a change of just a few percent in isotope concentration.

In conclusion, our data and the recent results of Krüger et al.[21] demonstrate a smaller isotope mass dependence in D than was suggested by the known larger isotope effect in shear viscosity[6]. Our ob-

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Table 4. Self-diffusion coefficients for Li^6 and Li^7 in various isotopic lithium alloys.

Species and Sample	Matrix	τ (ms)	Avg δ (ms)	$\overline{R}(\mu)$	$t_e \cdot 10^7$ ($Amp^2 - sec^3$)	$D_{unkorr.}$ ($cm^2 \cdot 10^5/sec$)	$D_{corr.}$ ($cm^2 \cdot 10^5/sec$)	T (°C)
Li^7 in Oak Ridge	99.99% Li^7	10	1.35	73	19.5	5.17	5.99	185
	0.01% Li^6	10	1.35	73	19.45	5.18	5.99	188
		10	1.35	49	20.4	4.94	6.11	186
		10	1.35	49	20.3	4.96	6.06	185
		10	1.35	49	20.5	4.91	5.72*	184
		10	1.51	73	16.5	6.11	7.19	225
		10	1.35	49	17.1	5.89	7.41	223
		10	1.35	49	17.4	5.79	6.84*	217
		10	1.35	73	14.16	7.13	8.58	257
Li in ALFA	92.6% Li^7	5	1.35	73	17.0	5.93	6.44	187
	7.4% Li^6	10	1.35	73	18.5	5.45	6.38	184
		10	1.03	73	17.8	5.67	6.65	186
		20	1.03	73	21.1	4.78	—	187
		5	1.35	49	17.9	5.64	6.31	185
		10	1.03	49	19.3	5.21	6.43	185
		10	1.35	49	19.4	5.20	6.39	187
		20	1.03	49	21.5	4.59	—	185
Li in LCA	92.6% Li^7	5	1.67	86	17.1	5.89	6.41	185
	7.4% Li^6	10	1.35	86	18.0	5.61	6.47	186
		20	1.03	86	19.8	5.08	—	185
		5	1.67	86	17.0	5.93	6.44	185
		10	1.35	86	18.1	5.57	6.44	185
		20	1.03	86	20.5	4.91	—	185
		5	1.67	86	12.7	7.93	8.65	248
		10	1.35	86	13.4	7.53	8.92	248
Li^7 in Alloy	36% Li^7	10	1.35	73	19.0	5.31	6.20	187
	64% Li^6	10	1.35	49	18.8	5.36	6.63	189
Li^7 in Oak Ridge	4.4% Li^7							
	95.6% Li^6	5	1.67	49	18.4	5.49	5.91	185
Li^6 in Alloy	36% Li^7	10	2.63	73	130.3	5.39	6.25	185
	64% Li^6	10	2.95	73	133.4	5.27	6.11	184
		10	2.95	49	131.7	5.34	6.63	189
Li^6 in Oak Ridge	4.4% Li^7	10	2.95	73	125.0	5.63	6.62	184
	95.6% Li^6	10	2.95	73	119.7	5.87	6.92	187
		10	2.95	49	125.8	5.58	7.00	185
Li^6 in Oak Ridge	0.7% Li^7	10	2.95	73	119.3	5.89	6.92	186
	99.3% Li^6	10	2.95	73	114.3	6.14	7.26	187
		10	2.95	73	116.8	6.02	7.12	186
		10	2.95	49	132.0	5.32	6.69	185
		10	2.95	49	124.4	5.65	7.14	188
		10	2.95	73	101.7	6.91	8.18	219
		10	2.95	49	108.7	6.47	8.23	224
		10	2.95	73	90.4	7.77	9.55	257

* Data taken at 2 MHz.

served isotope effect is also smaller than that observed for mutual diffusion coefficients. The fundamental reason for the apparent disparity in the magnitudes of the isotope effects is not presently understood.

Appendix

The Appendix deals with the problem of background gradients in dispersions of small metal particles. Not much is known about how these gradients vary from particle to particle within the dispersion. Some assumptions about the distribution will be made, and the effects of the gradients on the measurement of self-diffusion by the spin-echo pulsed magnetic gradient technique will be examined.

The signal detected in this experiment is the sum of the contributions from each particle in a sample. If different particles experience different background gradients, and the third and fourth terms on the right of Eq. (1) are significant, then to describe the signal one must take an appropriate sum over all the particles.

$$M = \sum_i M_i = \sum_i M_{0i} \cdot \exp\left[-\frac{2\tau}{T_2} - \gamma^2 D G^2 \delta^2 (\tau - \delta/3) - \gamma^2 D \mathbf{G} \cdot \mathbf{G}_{0i} \delta \tau^* - \tfrac{2}{3} \gamma^2 D G_{0i}^{2} \tau^3 \right]. \qquad (A.1)$$

Not much is known about the distribution of background gradients, other than their origin in the bulk susceptibility. The following assumptions are made to facilitate performing the sum indicated above.

1) The distribution of background gradients, $\varrho(G_0)\,\mathrm{d}G_0$ = number of particles experiencing gradient between G_0 and $G_0+\mathrm{d}G_0$, is symmetric about $G_0=0$, i. e., for every particle with $+G_0$ there is one with $-G_0$. This assumption is both reasonable and supported by the fact that reversing the applied gradient G causes no observable change in the signal. If $\varrho(G_0)$ were not symmetric, the $(\boldsymbol{G}\cdot\boldsymbol{G}_0)$ term of Eq. (A. 1) would cause such a change.

2) The distribution $\varrho(G_0)$ is continuous. Random packing of the metal particles makes this reasonable.

3) The size of the background gradient experienced by a particle is independent of the particle's volume. This plausible assumption is made principally to allow a transformation of the summation in Eq. (A. 1) from a sum over particles to a sum over gradients. Under these assumptions and the stipulation

$$\gamma^2 D\,\delta\tau^{*2}\,G\,G_1 \ll 1$$

it can be shown that

$$M \cong M_0 \exp\{-2\,\tau/T_2\}\cdot\exp\{-\gamma^2 D\,G^2\,\delta^2(\tau-\delta/3)\}$$
$$(\overline{\exp\{-\tfrac{2}{3}\,\gamma^2 D\,\mathrm{G}_0^2\,\tau^3\}})\,\{1+c_1^2\,\overline{\overline{G_0^2}}\} \quad \text{(A. 2)}$$

where: $c_1=\gamma^2 D\,\delta\tau^{*2}\,G\,,$

$$(\overline{\exp\{-\tfrac{2}{3}\,\gamma^2 D\,G_0^2\,\tau^3\}}) = \frac{\int_{-G_1}^{G_1} \varrho(g_0)\,\exp\{-\tfrac{2}{3}\,\gamma^2 D\,g_0^2\,\tau^3\}\,\mathrm{d}g_0}{\int_{-G_1}^{G_1} \varrho(g_0)\,\mathrm{d}g_0}\,,$$

$$\overline{\overline{G_0^2}} = \frac{\int_{-G_1}^{G_1} \varrho(g_0)\,g_0^2\exp\{-\tfrac{2}{3}\,\gamma^2 D\,g_0^2\,\tau^3\}\,\mathrm{d}g_0}{\int_{-G_1}^{G_1} \varrho(g_0)\,\exp\{-\tfrac{2}{3}\,\gamma^2 D\,g_0^2\,\tau^3\}\,\mathrm{d}g_0}\,,$$

and where G_1 represents the upper bound on the background gradient. The average of the steady gradient term is independent of δ and G. It will be a constant for constant τ and may be lumped into M_0 along with the real T_2 term

$$M_0' = M_0\cdot\exp\left\{-\frac{2\,\tau}{T_2}-\tfrac{2}{3}\,\gamma^2 D\,G_0^2\,\tau^3\right\}. \quad \text{(A. 3)}$$

In the absence of rise and fall corrections and bounded media, Eq. (A. 2) will describe the experimental data. The most effective way of plotting it is $\ln(M)$ versus $I^2\,\delta^2(\tau-\delta/3)$.

$$\ln M = \ln M_0' - c^2\,\gamma^2 D\,\delta^2\;I^2(\tau-\delta/3)\;+\ln(1+c_1^2\,\overline{\overline{G_0^2}})$$
$$\cong \ln M_0' - \left(c^2\,\gamma^2 D - \frac{\gamma^4 D^2\,\overline{\overline{G_0^2}}\,\tau^{*4}\,c^2}{(\tau-\delta/3)}\right) I^2\,\delta^2(\tau-\delta/3)\,. \quad \text{(A. 4)}$$

In Eq. (A. 4) it has been assumed that $c_1^2\,G_0^2 \ll 1$. From the $1/e$ point, t_e, D may be evaluated from

$$D - \frac{\gamma^2\,\overline{\overline{G_0^2}}\,\tau^{*4}\,D^2}{(\tau-\delta/3)} = \frac{1}{c^2\,\gamma^2\,t_\mathrm{e}} \quad \text{(A. 5)}$$

If the $\overline{\overline{G_0^2}}$ term is small as assumed, D can be determined to good approximation as

$$D = D_\mathrm{e}[1+(\gamma^2\,\overline{\overline{G_0^2}}\,\tau^{*4}\,D_\mathrm{e})/(\tau-\delta/3)] \quad \text{(A. 6)}$$

where $D_\mathrm{e}=(c^2\,\gamma^2\,t_\mathrm{e})^{-1}$.

As a test of the magnitude of the $\overline{\overline{G_0^2}}$ term and its dependence upon τ, a special set of experiments were run on Li^7 in natural abundance. Temperature was held fixed at about 185 °C to maintain D essentially constant. The value of t_e was then found for several values of τ. Since $\tau^{*2}\approx\tau^2$, a fit was made to a modified Eq. (A. 5).

$$D_\mathrm{e}' = D - \gamma^2\,\overline{\overline{G_0^2}}\,\tau^3\,D^2 \quad \text{(A. 7)}$$

where D_e' was determined from D_e by adjusting for the bounded medium correction. The latter correction made it possible to compare data from samples having different mean particle radii. Values of τ exceeding 10 msec were not used in making the fit. Data and the fit are shown in Fig. A. 1. It was found

$$D = 6.4\times10^{-5}\ \mathrm{cm^2/sec}$$

and $\gamma^2\,G_0^2 = 7.1\pm3\times10^8\ (\mathrm{cm\ sec})^{-2}$

for Li^7 in an applied magnetic field of 4200 Gauss (Larmor frequency = 7 MHz). Since G_0 will be directly proportional to the applied field, the same value of $\gamma^2\,G_0^2$ applies to observation of Li^6 at the same Larmor frequency.

Consequently Eq. (A. 6) becomes

$$D = D_\mathrm{e}\left[\frac{1+7.1\cdot10^8\,\tau^{*4}\,D_\mathrm{e}}{(\tau-\delta/3)}\right]$$

where D_e is in (cm²/sec) and times τ and δ are in seconds. For $\tau=10$ msec, D differs from D_e by 5% to 8%, depending upon the magnitude of D_e. Therefore the earlier assumption that the $\overline{\overline{G_0^2}}$ term is small for $\tau \leqq 10$ msec appears to be valid.

Furthermore, experimental studies of the spin echo decay without the pulsed gradient confirm that there must be a distribution of background gradients in the sample. A single value of G_0 would lead to a noticeable τ^3 dependence in $\ln M_0'(\tau)$ which is not observed. The observed spin echo envelope decays faster than a simple exponential in a manner consistent with a continuous distribution of background gradients[12].