# NOTIZEN

## Isotope Inter-Diffusion in Solid Lithium

A. Ott, J. N. Mundy *, L. Löwenberg, and A. Lodding

Physics Department, Chalmers University of Technology, Gothenburg, Sweden

Isotope inter-diffusion in lithium metal of normal isotopic composition has been measured between 60 °C and 170 °C, using a thin film technique and mass spectrometric analysis. The diffusion coefficient is given by the equation

$$D = 0.12^{+0.06}_{-0.04} \exp \frac{-12{,}620 \pm 210}{R\,T} .$$

Preliminary measurements in lithium of "reversed" isotopic composition show diffusion rates approximately 20% slower than the above values.

A systematic investigation of the atom transport properties of lithium metal is being conducted at this laboratory. The experiments include the observation of electrotransport [1], thermotransport [2-3] and impurity diffusion in lithium [4-6]. In such a survey, an exact knowledge of self diffusion is naturally of central importance.

Four sets of lithium self diffusion measurements have been reported, three by NMR [7-9] and one by a diffusion couple sectioning method [10]. As can be seen from Table 1, the mutual agreement of these data is not satisfactory. In particular it is noticeable that the values for the activation energy, $Q$, tend to fall in two groups, one indicating a $Q$ above 13 kcal mol$^{-1}$, the other $Q \approx 12$ kcal mol$^{-1}$. Ailion and Slichter [9] suspected that this difference might be due to sample dependence.

As the techniques of alkali metal sectioning and mass spectrometric analysis are well established in this research group, a re-investigation of lithium self diffusion by a method similar to that used for the impurity diffusion was therefore considered to be a worthwhile project. The lithium (3N5) of normal isotopic composition was obtained from Foote Comp. On a cylinder of this material we evaporated a thin film of lithium of "reversed" composition (95.6% Li, supplied by Oak Ridge National Laboratory, 3N5 purity). The anneal and sectioning procedure has been described in connection with self and impurity diffusion work on several alkali metals [6, 11]. The mass spectrometric analyses were performed as in recent diffusivity measurements on liquid lithium [12]. The diffusion coefficient is a function of $^6$Li concentration, but in our experiment the $^6$Li concentration is high only in the very beginning of the anneal period in and near the thin evaporated film. The diffusion coefficient at low $^6$Li concentration can therefore be evaluated from "penetration profiles" given by the equation

$$-\delta \ln (c^* - c_0)/\delta (x^2) = (4\,D\,t)^{-1} .$$

Here $c^*$ is the concentration of solute ($^6$Li) in a slice at a distance $x$ from the surface of the cylindrical sample, $c_0$ is the solute concentration in the sample outside the diffusion zone, and $t$ is the anneal time.

The accuracy of all concentration measurements was better than 0.4% throughout; the relative error of the difference $(c^* - c_0)$ increased, however, with penetration depth (the concentration $c_0$ here playing a role analogous to background activity in radioactive analysis). The anneal times were arranged so that eight

| Reference | Method | Concentration % $^6$Li | $D_0$ cm$^2\cdot$sec$^{-1}$ | $Q$ kcal$\cdot$mol$^{-1}$ | $D \times 10^9$ 70 °C | $D \times 10^9$ 170 °C |
|---|---|---|---|---|---|---|
| 10 | Diffusion Couple | 50 | $0.39^{+0.04}_{-0.02}$ | $13.49 \pm 0.07$ | 0.99 | 86 |
| 8 | NMR | 7.4 | $0.24^{+0.17}_{-0.10}$ | $13.20 \pm 0.40$ | 0.94 | 74 |
| 7 | NMR | 7.4 | — | 12.0 | — | — |
| 9 | NMR | 7.4 | — | $11.79 \pm 0.28$ | — | — |
| Present Work | | 8.3 | $0.12^{+0.06}_{-0.04}$ | $12.62 \pm 0.21$ | 1.09 | 72 |

Table 1. Arrhenius Parameters and the Diffusion Coefficients at 70 °C and 170 °C.

* Present Address: Metallurgy Division, Argonne National Laboratory, Argonne, Illinois 60 439.

[1] P. Thernquist and A. Lodding, Z. Naturforsch. 23 a, 473 [1968].

[2] A. Lodding and P. Thernquist, Z. Naturforsch. 21 a, 857 [1966].

[3] P. Thernquist and A. Lodding, Z. Naturforsch. 22 a, 837 [1967].

[4] J. N. Mundy, A. Ott, and L. Löwenberg, Z. Naturforsch. 22 a, 2113 [1967].

[5] A. Ott and A. Nordén-Ott, Z. Naturforsch., in print.

[6] J. N. Mundy, A. Ott, L. Löwenberg, and A. Lodding, to be published.

[7] R. A. Hultsch and R. G. Barnes, Phys. Rev. 125, 1832 [1962].

[8] D. F. Holcomb and R. E. Norberg, Phys. Rev. 98, 1074 [1955].

[9] D. C. Ailion and C. P. Slichter, Phys. Rev. 137, A 235 [1965].

[10] A. N. Naumov and G. Ya. Ryskin, Zh. Techn. Fiz. 29, 189 [1959].

[11] J. N. Mundy, L. W. Barr and F. A. Smith, Phil. Mag. 14, 785 [1966].

[12] L. Löwenberg and A. Lodding, Z. Naturforsch. 22 a, 2077 [1967].

to ten slices of some 0.1 mm thickness gave a meaningful profile. As in corresponding impurity diffusion measurements in lithium and other alkali metals, the first and sometimes the second slice gave points somewhat above the straight profile line, owing to oxide or nitride blocking.

As in earlier experiments, the penetration depth $x$ was determined by dividing the weight per unit area of the slices by the metal density. In this particular investigation, special precautions had to be taken as the density varied according to the solute concentration. The concentrations in the slices after annealing usually ranged between 7.5% and 10% $^6$Li. Exact density data for the separated $^7$Li and $^6$Li metals are available [13], so that the correct density of each slice could be interpolated.

The experimental results are shown in Fig. 1 and Table 2. The values have been corrected for thermal expansion and for heating and cooling times. The individual errors quoted were determined from the known error in the mass spectrometric analyses; the error determined from the standard deviation to the slope of the profiles was approximately 50% smaller and unrealistic.
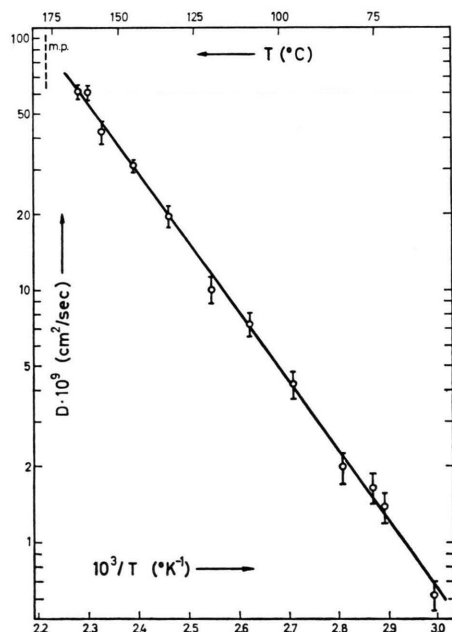
| $T$ (°C) | $D \cdot 10^9$ (cm²/sec) | $D' \cdot 10^9$ (cm²/sec) | $D/D'$ |
|---|---|---|---|
| 165.5 | 61.3 ±4.0 | 50.6 | 1.21 |
| 162.0 | 60.9 ±4.0 | 51.6 | 1.18 |
| 156.8 | 42.3 ±4.6 | | |
| 145.3 | 31.1 ±1.8 | | |
| 133.5 | 19.5 ±1.9 | 17.0 | 1.15 |
| 119.9 | 10.1 ±1.3 | 7.40 | 1.36 |
| 108.3 | 7.35 ±0.54 | 5.85 | 1.26 |
| 96.2 | 4.23 ±0.57 | | |
| 83.1 | 1.99 ±0.29 | 1.90 | 1.05 |
| 75.6 | 1.65 ±0.24 | | |
| 73.0 | 1.38 ±0.19 | | |
| 61.2 | 0.615 ±0.077 | 0.464 | 1.33 |

Table 2. Experimental Results. $D$ denotes the diffusion coefficient in normal lithium, $D'$ (preliminary values) that in lithium with 95% $^6$Li.

In Table 1, the Arrhenius parameters $D_0$ and $Q$ in the equation $D = D_0 \cdot \exp(-Q/RT)$ have been computed by a least squares treatment of the points in Table 2. They are compared with the results of earlier investigations. It can be seen that the present value for the activation energy lies in the middle of the range of the two previous groupings, showing an acceptable agreement with the results obtained by HOLCOMB and NORBERG [8], but not with the other values. It should be mentioned that the work of HULTSCH and BARNES [7] did not give a firm value for $Q$. In the work of NAUMOV and RYSKIN [10], no account appears to have been taken of the residual concentration, $c_0$, nor of the fact that the denlity along the diffusion zone ranged from 0.46 to 0.53 gm/cm³. It is not easy to understand the low value of AILION and SLICHTER [9] obtained with lithium of similar purity to that used in the present work. The NMR measurements follow the motion of $^7$Li atoms in an environment of $^7$Li atoms, whereas the present work observed the motion of $^6$Li atoms in an environment of $^7$Li atoms. One might expect from the inverse root mass relationship that the latter motion would be some 8% faster than the former.

We are presently extending the temperature range of these measurements and also investigating the diffusion in lithium of "reversed" composition (95% $^6$Li). Preliminary measurements at seven temperatures (see Table 2) indicate that interdiffusion at high $^6$Li concentrations is about 20% slower than at low $^6$Li concentrations. This tendency is opposite to that found in liquid lithium [12].

Fig. 1. Arrhenius Plot of the Diffusion Coefficient in Lithium of Normal Isotopic Composition

[13] D. D. SNYDER and D. J. MONTGOMERY, J. Chem. Phys. 27, 1033 [1957].