

Diffusion of Gold in Solid Lithium

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The diffusion of gold in lithium metal of normal isotopic composition has been measured between 45 °C and 150 °C, using a thin film plating and sectioning method. The data fit the Arrhenius relation $D=D_0 \exp(-Q/RT)$ where $D_0=0.21 \pm 0.08 \text{ cm}^2 \text{ sec}^{-1}$ and $Q=10.99 \pm 0.18 \text{ kcal} \cdot \text{mol}^{-1}$. These results are in contrast to those obtained for other impurities in lithium, and can not be readily interpreted by any existing theory. Measurements of gold diffusion in lithium of the “reversed” isotopic composition show diffusion rates approximately 8% higher than in “normal” lithium.

In order to shed light upon the phenomena of diffusion in the alkali metals and the dependence of the diffusion parameters on valency, atomic size and electron core differences between solute and solvent atoms, we have undertaken a study of diffusion of gold in lithium metal of normal isotopic composition (92.5% ^7Li , 7.5% ^6Li) and in lithium metal of the nearly reversed isotopic composition (4.4% ^7Li , 95.6% ^6Li).

This investigations was a part of a systematic study of impurity diffusion in the lithium lattice. We have earlier studied the diffusion of sodium¹, silver², zink³ in lithium and the self-diffusion of lithium⁴. The experimental procedure and evaluation of the present results was similar as in earlier work, and need not be discussed here. The “normal” lithium metal was from the Foote Lithium Corporation. The “reversed” lithium metal was from Oak Ridge. Both metals were of 3N5 grade. The ^{195}Au was from the New England Nuclear Corporation and free from radioactive impurities.

The experimental values of the diffusion coefficient, D , are given in Table 1 and plotted in Fig. 1.

T (°C)	$D \cdot 10^9$ (cm ² /sec)	$D' \cdot 10^9$ (cm ² /sec)	D'/D
152.5	460.6 ± 10.5		
144.0	357.5 ± 7.5		
137.0	261.9 ± 3.0		
125.9	200.2 ± 4.0	215.2 ± 4.0	1.07
113.8	118.5 ± 2.5		
106.7	92.87 ± 2.0		
98.1	60.87 ± 1.5	65.69 ± 1.5	1.08
85.2	38.81 ± 1.0	42.90 ± 1.3	1.10
78.9		30.05 ± 1.5	
75.8	27.05 ± 0.05		
54.5	10.18 ± 0.15		
49.8	7.579 ± 0.02		
46.8	5.801 ± 0.15		

Table 1. Experimental Results. D denotes the diffusion coefficient in normal lithium, D' that in lithium with 95% ^6Li .

¹ J. N. MUNDY, A. OTT, and L. LÖWENBERG, Z. Naturforsch. **22 a**, 2113 [1967].
² A. OTT and A. NORDÉN-OTT, Z. Naturforsch. **23 a**, 473 [1968].
³ J. N. MUNDY, A. OTT, L. LÖWENBERG, and A. LODDING, to be published.

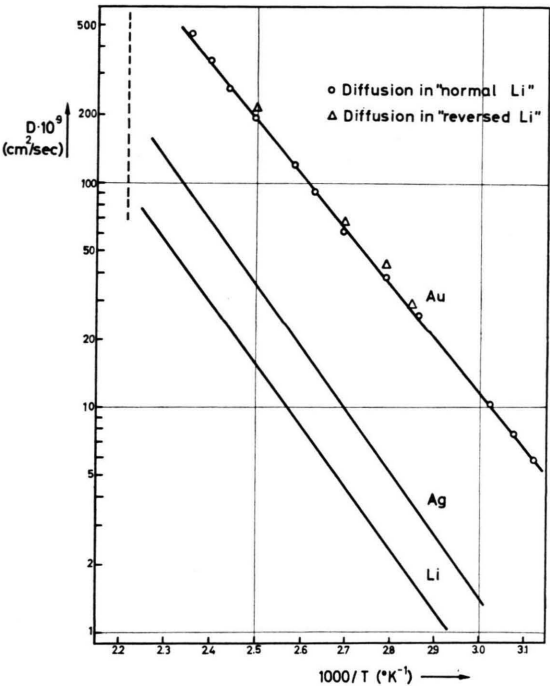


Fig. 1. Arrhenius plot of diffusion in lithium metal. The present work is here compared with the diffusion results for $\text{Ag}^{110\text{m}}$ and ^6Li tracers in Li.

From the slope in the $\log D$ versus $1/T$ diagram we obtained the activation energy Q , and from the intercept on the $1/T$ axis we got the D_0 term in the Arrhenius equation for D . These are listed in Table 2 together with the other known values of diffusion parameters in lithium.

	D_0 (cm ² sec ⁻¹)	Q (kcal · mol ⁻¹)	Reference
Li in Li	0.12 ± 0.05	12.62 ± 0.21	4
Na in Li	0.41 ± 0.09	12.61 ± 0.15	1
Zn in Li	0.57 ± 0.30	12.98 ± 0.24	3
Ag in Li	0.37 ± 0.13	12.83 ± 0.25	2
Au in Li	0.21 ± 0.08	10.99 ± 0.18	

Table 2. Impurity diffusion data in lithium.

Supposing that the gold tracer is univalent, the homovalent theory by LeCLAIRE⁵ can be applied to the present results. This theory aims, as do other theories of impurity diffusion in solid metals, at calculating the difference ΔQ between the activation energies of impurity respectively self-diffusion:

$$\Delta Q = Q_2 - Q_0.$$

⁴ A. OTT, J. N. MUNDY, L. LÖWENBERG, and A. LODDING, Z. Naturforsch. **23 a**, 771 [1968].
⁵ A. D. LeCLAIRE, Phil. Mag. **10**, 641 [1964].



Q_2 and Q_0 are the activation energies for solute resp. solvent atoms.

The treatment entails the calculation of a perturbation potential U at the impurity atom. A positive U means a potential "well" at the impurity atom, electrons are attracted into this well, charging it negatively, and thus repelling vacancies, which in a monovalent metal have an effective negative unit charge. If U is negative, electrons are repelled from the impurity atom, vacancies are attracted and diffusivity enhanced. U is not directly comparable with ΔQ , but they should be of the same sign. This potential U is expressed as a function of the heat of sublimation, the mean Fermi energy and the ionization potentials for the solute and solvent. In our experiment we find that ΔQ is negative, but the theoretical potential U is positive. This discrepancy for the homovalent theory might indicate that gold dissolved in lithium is ionized to a higher order than the first.

As gold may also occur with the chemical valency of three, it should be interesting to regard the consequence of gold as a heterovalent impurity with a valency difference of +2 and to apply the LeCLAIRE heterovalent theory⁶ to such a case. According to this theory, and assuming a vacancy mechanism for diffusion, the difference in activation energy for the solute and solvent ΔQ can be expressed as

$$\Delta Q = \Delta E_f + \Delta E_m - C.$$

ΔE_f , ΔE_m are the solute-solvent differences in formation resp. motion energy of an adjacent vacancy. C accounts for the temperature dependence of the impurity correlation factor f .

Performing the arithmetic operations⁷ we get

$$C = \frac{\Delta E_m}{1 + 2.27 w_0/w_2}.$$

If gold is three-valent in lithium, the coulombic attraction between a gold atom and a vacancy might make the jump frequency w_2 considerably higher than the jump frequency w_0 . This, however, would make C about the same as ΔE_m and ΔQ will be about equal to ΔE_f .

According to LeCLAIRE ΔE_f can be evaluated from the expression

$$\Delta E_f = -2 \alpha Z (e^2/a) \cdot \exp(-q a)$$

where $(-Ze)$ is the excess charge of the impurity, e is the unit electronic charge, a is the nearest neighbour distance, α is a constant of the order of unity⁸, q is the screening parameter $(4\pi N_e)^{1/2}$, where N_e is the density of states at the Fermi level. For Li q is about 1.6 \AA^{-1} , a is 3.1 \AA . Using the valency $Z = +2$ for Au we get ΔE_f to about -1.8 kcal/mole . This is in acceptable agreement with the experimental value of -1.6 kcal/mole .

There are reasons to believe, however, that any quantitative agreement with LeCLAIRE's theory should be impaired by the fact that lithium is a very "open" metal. Measurements⁹ have revealed that considerable relaxation occurs in the lattice. As all electrostatic forces are very dependent on the distance between charges, a model not taking account for these effects can not be expected to explain the experimental results too rigorously.

The present results reveal a much greater diffusivity and a much smaller activation energy for Au in Li than has been found for Ag in Li (see Fig. 1). This seems remarkable, as both the atomic size and elasticity parameters are about the same for Ag and Au. Obviously any theory based solely on such parameters¹⁰ appears incomplete in this context.

The diffusion of gold has been measured (s. Table 1) both in lithium of normal composition and in lithium of reversed isotopic composition. As can be seen there is a distinct difference between the diffusion values in the two cases. The diffusion in the normal lithium is about 8% slower than in the reversed lithium. A different relation has been observed in self-diffusion⁴. These results naturally stimulates the interest for further study of isotopic differences in lithium.

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⁶ A. D. LeCLAIRE, *Phil. Mag.* **7**, 141 [1962].

⁷ L. W. BARR, J. N. MUNDY, and F. A. SMITH, *Phil. Mag.* **16**, 1139 [1967].

⁸ K. UEDA and S. KOBAYASHI, *J. Phys. Soc. Japan* **13**, 148 [1958].

⁹ R. A. HULTSCH and R. G. BARNES, *Phys. Rev.* **125**, 1832 [1962].

¹⁰ R. A. SWALIN, *Acta Met.* **5**, 443 [1957]; *Z. Naturforsch.* **23a**, 805 [1968].