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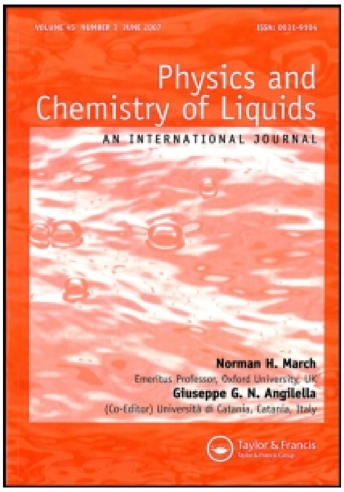

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Self-Diffusion in Liquid Alkali Metals

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Abstract—A recently developed capillary method has been employed to study tracer self-diffusion in liquid Na (102 to 284 °C) and K (97 to 284 °C). The results may be expressed by $D = D_0 \exp(-Q/RT)$, where $10^3 D_{0\mathrm{Na}} = 0.86\ (+0.09, -0.08)$ (cm²/sec), $Q_{\mathrm{Na}} = 2.22 \pm 0.08$ (kcal/mole), $10^3 D_{0\mathrm{K}} = 0.76\ (+0.06, -0.05)$, and $Q_{\mathrm{K}} = 2.02 \pm 0.07$. The reexamination of electrotransport data for Rb (60 to 230 °C) yielded the self-diffusion data $10^3 D_{0\mathrm{Rb}} = 0.66\ (+0.11, -0.09)$ and $Q_{\mathrm{Rb}} = 1.98 \pm 0.16$. For liquid Li, the results of two investigations (195 to 440 °C) have been combined, yielding $10^3 D_{0\mathrm{Li}} = 1.44\ (+0.07, -0.06)$ and $Q_{\mathrm{Li}} = 2.87 \pm 0.07$.

For all four metals the empirical relation $Q \simeq 2.5\ R\bar{T}$ is found to apply ($\bar{T}$ being the mean exp. temp). Also well obeyed is a nearly linear dependence on $(T - 0.72\ T_m)$ (where T_m is the m.p.). Further, the self-diffusion coefficients at the respective melting points can all be expressed by $D_m = 1/6\sqrt{3kT_m/M}\ V_{\mathrm{mol}}^{1/3}\,\beta$, where M is atomic mass, V_{mol} atomic volume and $\beta = 0.11$. Three alternative empirical equations are presented, each about equally well representing the experimental self-diffusion data in Li, Na, K, and Rb.

The diffusion characteristic of cesium, as predicted from these regularities, is found to obey, as do those of the four other alkali metals, a modified Stokes–Einstein type relation connecting diffusion with viscosity. Accordingly, self-diffusion parameters may be computed also for Cs, $10^3 D_{0\mathrm{Cs}} = 0.48$ and $Q_{\mathrm{Cs}} = 1.86$ kcal/mole.

1. Introduction

The mechanism of self-diffusion in liquids is of topical interest.(1–5) Accurate experimental data are relatively few; additional systematic measurements are needed to allow adequate theories to be developed and tested. Within a class of closely related liquids, such as the alkali metals, such systematics would appear especially valuable.

Hitherto, the capillary-reservoir method(6) has been used to study self-diffusion in Li,(7a,b) Na(8,9) and K.(10) NMR has been applied to Li⁽¹¹⁾ and Na.⁽¹²⁾ For Rb, an isotope electrotransport method has been utilized.⁽¹³⁾

The NMR measurements exhibit somewhat too great a scatter to give quantitative systematics for wide ranges of temperature. Of the capillary-reservoir measurements the two series obtained for Na show so good mutual agreement that they should serve as a criterion of accuracy for any new method. The results for K show a dependence on capillary diameter, suggesting convective side-effects. The two series of Li-data (actually isotope interdiffusion measurements) are performed with sufficient accuracy and within a sufficient temperature range to offer clues concerning the shape of the temperature characteristic. Finally, the results quoted for Rb are semi-quantitative, but appear suitable for subsequent refinement.

The purpose of the present investigation was (a) to test a new method by applying it to Na; (b) to use the method for obtaining reliable measurements on K; (c) to recalculate the combined capillary-reservoir data⁽⁷ᵃ·ᵇ⁾ for Li in order to further reduce the uncertainty margins; (d) to re-examine and refine the self-diffusion data for Rb; and (e) to formulate, if possible, empirical systematics applicable to self-diffusion in all alkali metals.

2. Experiments and Results, Na and K

The new capillary method was first developed for liquid Ga,⁽⁴·¹⁴⁾ and subsequently tested for In.⁽¹⁵⁾ In experimental details, the present method has been described in Ref. 16. The length of anneal was chosen and evaluation effected as in Ref. 14. The results are shown in Table 1, corrected for thermal expansion. This correction

TABLE 1. Results, expressed in the form $D = D_0 \exp(-Q/RT)$, with D_0 in cm²/sec and Q in kcal/mole. Values for Cs computed via Eq. (4).

Metal	Li	Na	K	Rb	Cs
Measuring range, °K	469–713	376–557	371–557	330–510	—
$D_0 \cdot 10^3$	$1.44^{+0.07}_{-0.06}$	$0.86^{+0.09}_{-0.08}$	$0.76^{+0.06}_{-0.05}$	$0.66^{+0.11}_{-0.09}$	(0.48)
Q	2.87 ± 0.07	2.22 ± 0.08	2.02 ± 0.07	1.98 ± 0.16	(1.86)

(the square of the ratio of density at room temperature to that during anneal) amounted to about 20% at the highest anneal temperatures.

In Fig. 1, the result for Na and K are shown in an Arrhenius plot and compared with earlier measurements. It can be seen that the agreement with the combined results of Meyer and Nachtrieb(8) and Ozelton and Swalin(9) is very good. The agreement with the K data obtained by Rohlin and Lodding(10) is good at the lowest temperatures, but barely fair at the highest. The older investigation was probably affected by convection due to temperature fluctuation effects as discussed in Ref. 13.

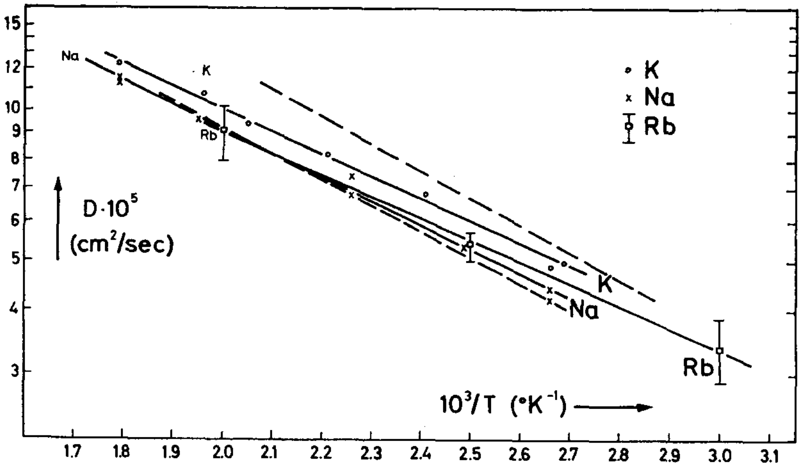

Figure 1. Arrhenius representation of experimental results in Na, K and Rb. Dashed lines: for Na the combined result of Refs. 8, 9, for K Ref. 10. Rb data corrected from Ref. 13.

The parameters D_0 and Q in the Arrhenius representation, $D = D_0 \exp(-Q/RT)$, of the Na and K data are listed in Table 1.

3. Re-Evaluation of Measurements on Li and Rb

Ott and Lodding(7a) have investigated the interdiffusion of ^{7}Li and ^{6}Li in isotopically nearly normal (about 6% ^{6}Li) liquid lithium, between 196° and 440 °C. The results were expressed as

$$D = (1.41 \pm 0.12)\ 10^{-3} \exp \frac{-2825 \pm 90}{RT}\ (\mathrm{cm}^2/\mathrm{sec}).$$

Löwenberg and Lodding(7b) used the same capillary-reservoir technique to study the influence of isotope composition on D. At the 6.5% ^{6}Li concentration good agreement was found with the earlier investigation, but a slight temperature dependence of the slope of the Arrhenius diagram is suggested on comparison of the two sets of data. The two investigations together yield 37 points in the plot of ln D vs T^{-1} (see Fig. 2). The effective activation energy, obtained by least squares analysis, listed in Table 1, is very slightly different from that given in Ref. 7a.

Nordén and Lodding(13) obtained the effective self-diffusion of Rb between 60° and 230 °C by analysis of electrotransport data. From the non-steady-state isotope enrichment, due to a certain current, the corresponding relative isotope velocity Δv was obtained, while the steady-state concentration profile gave $\Delta v/D_{\mathrm{eff}}$. The effective diffusion coefficient D_{eff} was obtained by comparison at each temperature. The electro-convective part of D_{eff} could be assessed by comparing experiments at different current densities; extrapolation to zero current gave a corrected entity, expressed as

$$D_{\mathrm{corr}} = (0.57 \pm 0.23)\ 10^{-3} \exp \frac{-1910 \pm 300}{RT}\ (\mathrm{cm}^2/\mathrm{sec}).$$

It was pointed out, however, that this effective self-diffusion still contained a current-independent convective term of the order of 3% at the highest, 1% at the lowest temperature. Further, no correction was made for the fact that the steady-state profile, from which $\Delta v/D_{\mathrm{eff}}$ was computed, corresponded to a solid Rb column at room temperature, not to the experimental conditions. A density correction (linear; cf. the quadratic correction in the technique described above for Na and K) increases D_{corr} by $11 \pm 1\%$ at the highest temperature, 4 ± 1 at the lowest. Combining this with the above-mentioned correction for convection, one obtains the result plotted as staples in Fig. 1. As seen in Table 1, the effective activation energy turns out only about three percent higher than that given for D_{corr} in Ref. 13.

4. Results as Expressed in the Arrhenius Representation. Comparison with Viscosity

When the experimental points shown in Figs. 1–2 are treated by least-squares analysis, the best straight lines correspond to the D_0 and Q values listed in Table 1.† Although the most exact recent measurements of liquid-metal self-diffusion (see Ref. 1) have suggested a certain curvature in the Arrhenius plot, the representation $D = D_0 \exp(-Q/RT)$ has nevertheless been found convenient and rather adequate for most metals. Possible deviations from a straight-line Arrhenius relationship for the present data will be discussed in the next section.

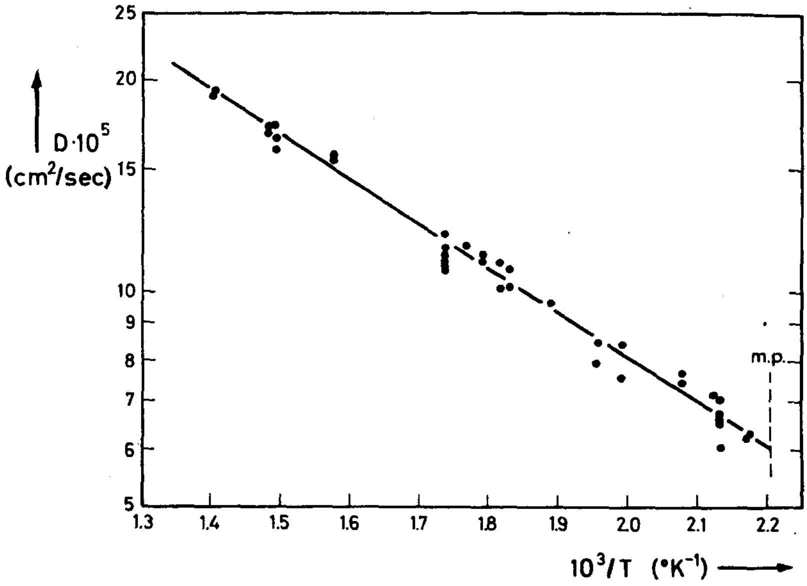

Figure 2. Arrhenius representation of self-diffusion in Li. Combined result of Refs. 7a, b.

In Fig. 3, these results are plotted as ln D vs. T_m/T. Several workers$^{(17,18)}$ have pointed out the interrelation between diffusion

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† For the least-squares treatment of the Rb data, each staple in Fig. 3 was replaced by two equivalent points at 80% of the maximal staple deviation from the mean.

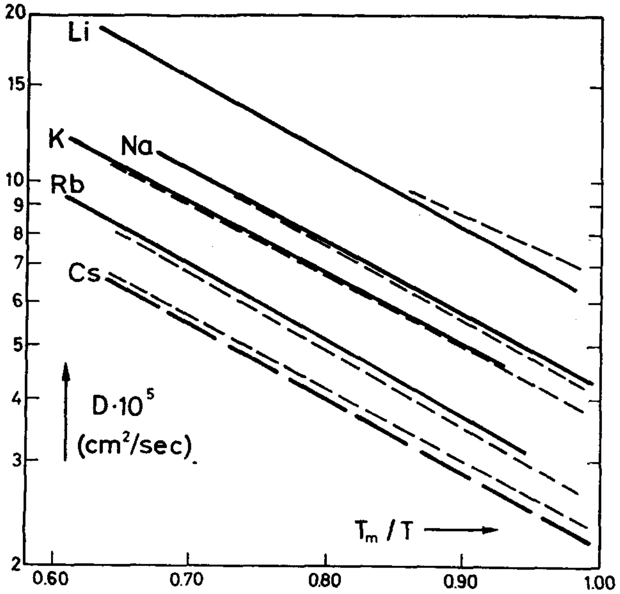

Figure 3. Melting-point-scaled Arrhenius plot of self-diffusion in Li, Na, K, Rb and Cs. Full-drawn lines: from diffusion measurements. Dashed lines from viscosity via Eq. (1). Lowest dashed line: computed diffusivity for Cs, via Eq. (4).

and viscosity by means of a modified Stokes–Einstein relation of the form

$$D = (\eta)^{-1} \frac{kT}{\xi (V_{\mathrm{mol}})^{1/3}} \tag{1}$$

where η is kinematic viscosity, V_{mol} the mole volume and ξ a constant between 5 and 6. The viscosities of the alkali metals have been measured over fairly wide ranges of temperature.(20) If Eq. (1) with $\xi = 5.3$(7a) is applied to the experimental viscosity data, and a linear dependence of ln D on $T/V_{\mathrm{mol}}^{1/3}$ is assumed, one can compute the dashed lines in Fig. 3. It is seen that for Na, K and Rb the predictions of Eq. (1) are very well obeyed. The apparently less perfect agreement for Li may be due to the relatively short temperature range of available η values in this metal, as will be discussed in the next section.

5. Discussion; Diffusion Systematics in Liquid Alkali Metals

(A) TEMPERATURE DEPENDENCE OF D

In Fig. 3, where ln D_0 is plotted against T_m/T, it can be seen that nearly parallel lines are obtained for all alkali metals. This applies both to the data from diffusion measurements and to the computed D-values from viscosity measurements (the latter also performed for Cs). That the effective activation energies are in fact nearly proportional to the respective melting points can be seen quantitatively in Table 2. The mean of Q/RT_m is 3.10 for the D-measurements, with a standard deviation of about 3%. For the viscosity-computed D-values the corresponding value is 2.98, with about 9% error, the greater scatter mainly due to the deviation for Li.

TABLE 2. Diffusion parameters, as obtained from direct measurements (left in column) and as computed via Eq. (1) from viscosity data (right in column) meaning of β, see Eq. (3).

Metal	T_m	T_{mean}	Q	Q/RT_m	Q/RT_{mean}	$D_m \cdot 10^5$	β
Li	454	566	2.87	3.18	2.54	5.98	0.100
		504	2.38	2.64	2.37	6.65	0.104
Na	371	448	2.22	3.01	2.50	4.23	0.116
		438	2.28	2.10	2.63	4.07	0.111
K	337	445	2.02	3.02	2.30	3.72	0.113
		428	1.99	2.97	2.34	3.70	0.113
Rb	312	400	1.98	3.19	2.49	2.72	0.118
		382	1.99	3.21	2.62	2.60	0.113
Cs	302	—	(1.86)	(3.10)	(2.46)	(2.14)	(0.112)
		387	1.78	2.97	2.31	2.32	0.118

" Mean " alkali metal:	Q/RT_m	Q/RT_{mean}	β
From direct measurements	3.10 ± 0.10	2.46 ± 0.10	0.112 ± 0.008
From viscosity	2.98 ± 0.25	2.45 ± 0.16	0.112 ± 0.005

Available theories of liquid diffusion$^{(1-5,17-21)}$ do not predict D to vary with temperature simply according to a solid-state-type Boltzmann-term law. The suggested expressions can usually be reduced to the form

$$D = \text{const} \cdot T^n \exp(-A/RT), \tag{2}$$

where A may be zero and n is between 1/2 and about 2. The plot of such an expression in an Arrhenius diagram exhibits a temperature dependent slope with an apparent activation energy $Q = A + nRT$.

The possibility that A may be zero and $n \simeq 2.5$ is suggested (see Table 2) from the fact that the ratio Q/T_{mean}, where T_{mean} corresponds to the middle of the measuring range in T^{-1}, is nearly the same for all alkali metals. From the diffusion measurements, this ratio is 2.46, with only 4% standard error, while from viscosity one gets 2.45, with an error of about 7%.

Nachtrieb(1) has suggested $D = \text{const}. T$, or $n = 1$. This is obviously contradicted by the present results, but a linear relation with an intercept on the T-axis gives quite a good representation of the present experiments. This can be seen in Fig. 4. The broken curve corresponds to the logarithmic behaviour with $Q = 3.1\ RT$,

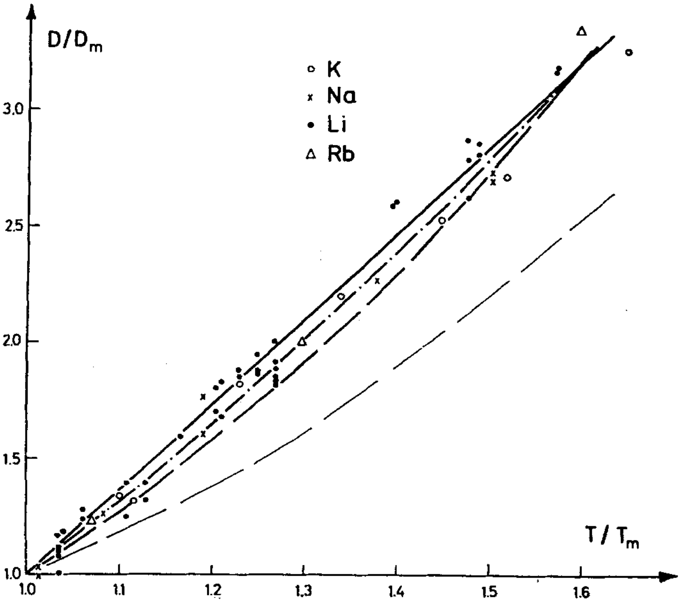

Figure 4. D/D_m vs. T/T_m for Li, Na, K and Rb. Broken curve corresponds to Eq. (4), dashed curve to Eq. (5) and full line to Eq. (6). The experimental points correspond to those in Figs. 1 to 3. Thin dashed line: from Ref. 3.

the dashed curve to the $n=2.5$ behaviour, and the dotted line to $D/D_m = 3.65\ (T/T_m - 0.725)$. The three curves intersect at $T/T_m = 1.6$, i.e. near the upper end of the temperature ranges investigated. In this representation of D/D_m vs. T/T_m the experimental points are not seen to favour any of the three curve shapes before the others. The points for Li and Rb may perhaps best be reconciled with the $T^{2.5}$ characteristic, while those for Na and K appear to follow the linear relation better.†

(B) D-VALUES AT THE MELTING POINT

According to recent considerations by several authors(2–4,7a,21) the diffusion coefficient D_m at the melting point of a pure metal should be expressible by a relation of the form

$$D_m = \tfrac{1}{6}\sqrt{\frac{3kT_m}{M}}\,(V_{\text{mol}})^{1/3}\beta, \tag{3}$$

where k is Boltzmann's constant, M the atomic mass and V_{mol} the atomic volume. The factor β is expected to be nearly constant for all liquid metals. On the basis of thermotransport and melting arguments, one predicts(4,22) $\beta \simeq 0.1$. It can be seen in Table 2 that experiments on the alkali metals strongly support this: D_m values from direct diffusion measurements as well as from viscosity yield $\beta = 0.112$, with only 7%, respectively 5%, standard error.

(C) EMPIRICAL FORMULAE FOR DIFFUSION IN THE LIQUID ALKALI METALS

On the basis of the above systematics of D_m and the temperature behaviour of D, one can formulate three alternative expressions each acceptably representing the experimentally obtained self-diffusion data for the alkali metals.

The Arrhenius-type equation is

$$D = 6.4 \cdot 10^{-5} \cdot (T_m/M^{1/2}(V_{\text{mol}})^{1/3} \exp(-3.09T_m/T) \tag{4}$$

(M in a.u., V_{mol} in Å^3).

The dependence on T^n is expressed by

$$D = 0.29 \cdot 10^{-5}(T_m/M)^{1/2}(V_{\text{mol}})^{1/3}(T/T_m)^{2.46}. \tag{5}$$

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† The thin curve in Fig. 4 corresponds to the predictions of Ascarelli and Paskin.(8)

The linear relation is

$$D = 1.05 \cdot 10^{-5}(T_m/M)^{1/2}(V_{\text{mol}})^{1/3}(T/T_m - 0.725). \qquad (6)$$

The relation (6) gives particularly good agreement with recent model arguments(21) by Lodding.

In Fig. 3, the self-diffusion characteristic has been computed also for Cs from Eq. (4) (dashed line). It can be seen that this " theoretical " line lies near to that computed from the experimental viscosity data for Cs. Assuming that Eq. (4) is indeed applicable also to Cs, one can derive the parameters D_0 and Q for this liquid metal, as listed in Table 2. The uncertainty margin of these figures can be estimated from the scatter in the measured Q/RT_m values to be about the same as quoted for Rb, i.e. less than 10% in Q.

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