

Self-Transport, Electro-Convection and Effective Self-Diffusion in Liquid Rubidium Metal

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Isotope electrotransport in liquid Rb has been measured. Results of earlier measurements of the mass effect μ have been confirmed and their accuracy further improved. μ ranges from 2×10^{-5} at the m.p. to 10^{-4} at 400°C . Up to about 200°C the temperature dependence of μ is similar to that of the (theoretically computed) self-diffusion coefficient. At higher temperatures the apparent "activation energy" increases.

With the aid of electrotransport, electro-convection in the liquid metal has been studied. Analysis of data at three different currents indicates that in horizontal 0.5 mm i.d. capillaries, at less than some 9 Amps, the main source of electro-convection in Rb is an I^2 sensitive mechanism, probably electro-osmosis. At higher currents an I^4 dependent mechanism may become dominant. A relatively small current independent term may influence the effective self-diffusion. The zero-current values of the effective self-diffusion coefficients are computed. Between 333° and 500°K they can be represented by $(D_{\text{eff}})_0 = 5.7 \times 10^{-4} \exp(-1910/RT)$, with about 15 percent error margin in "activation energy". These values are in good agreement with self-diffusion coefficients as calculated from experimental viscosity.

The main object of this paper is to study electro-convection, i. e. the convective stirring caused by the passage of electric current in a liquid metal. The first investigation of this phenomenon was made by one of the authors¹; isotope electrotransport was utilized to measure the effective self-diffusion coefficients of liquid K, Rb and In in horizontal 0.6 mm i. d. capillaries, carrying a current of 10 Amps. The results have been discussed theoretically²; magneto-hydrodynamic stirring and electro-osmosis have been suggested as plausible mechanisms of electro-convection. More recently, investigations have been made in liquid Pb and Sn³ using radioactive tracers, and in Ga⁴ using electrotransport. The subject has also been discussed in connection with zone melting⁵.

Liquid Rb is known to be suitable for accurate measurements of isotope electrotransport ("HAEFFNER-effect") within a rather wide temperature range. In earlier investigations of Rb, the exactness at higher temperatures was considered¹ to be somewhat uncertain, owing to the possibility of exceeded critical time (see below); the present investigation offered an opportunity to check the earlier results.

Another reason to choose Rb for an electro-convection study is the comparatively high electro-osmotic mobility found in liquid alkali metals⁶.

1. Experimental Method and Results

The procedure employed in the determination of effective self-diffusion coefficients was similar to that first used in ref. ¹, and has also been discussed in detail in ref. ⁴. It is sufficient here to sketch the general principles:

Direct current was passed through liquid Rb in horizontal capillaries, with fused-in electrodes at their ends. The isotope enrichment at different points along the capillaries, due to the transported charge, was then determined, using a mass spectrometer.

Two kinds of cell geometry were adopted:

a) The relative transport velocity Δv of the isotopes was determined from the change in isotopic composition in "long" capillaries, where the duration of experiment was kept considerably shorter than the "critical time", given by

$$\tau = l^2 / \pi D_{\text{eff}}, \quad (1)$$

¹ A. LODDING, Gothenburg Stud. Phys. 1 [1961].

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³ P. P. KUZMENKO, paper submitted at symposium „Elektrotransport und Thermoeffusion in Metallen“, Münster 1965.

⁴ A. LODDING, J. Phys. Chem. Solids, in press.

⁵ J. D. VERHOEVEN, Trans. Met. Soc. AIME 233, 1156 [1965].

⁶ S. I. PATYANIN and A. R. REGEL, Fiz. Metal. Metalloved. 19, 845 [1965].



l being the capillary length and D_{eff} the effective self-diffusion coefficient. It is known from earlier experiments¹ that with 10 Amps in 0.6 mm capillaries the maximal D_{eff} in Rb could be nearly 10^{-3} cm²/sec. Presently the capillary diameter was 0.5 mm (Pyrex-Veridia precision bore), and the maximum current 8 Amps, so that convection should be smaller. Deeming, however, $D_{\text{eff}} \cong 10^{-3}$ to be a satisfactory safety value, with $l = 17$ cm one obtains $\tau_{\text{max}} \cong 25$ hrs. Therefore the duration of each "long capillary" run was not allowed to exceed some 20 hrs. The actual D_{eff} values, subsequently determined, proved this precaution to have been more than ample.

b) The $\Delta v/D_{\text{eff}}$ ratio was determined from the slope of the enrichment curve in "short" capillaries (7 cm), where the duration of experiment was long enough ($> \cong 4\tau$) to establish a steady state. Each of these runs was thus conducted for at least a week with uninterrupted constant current and temperature. The capillary diameter was 0.51 ± 0.015 mm, with a measured concivity of 0.20 ± 0.04 percent/cm. The $\Delta v/D_{\text{eff}}$ values were measured at temperatures between the m.p. and about 300 °C, using three different currents, 7.98, 5.25, and 2.97 Amps.

The various sources of error have been discussed in connection with the Ga work, ref. 4. In the present investigation the percentual combined error in Δv was about the same as in Ga, i. e. between 8 and 18 percent; the better accuracy in mass-spectrometry (reproducibility of $^{87}\text{Rb}/^{85}\text{Rb}$ better than 0.25 percent) was cancelled out by somewhat greater difficulty in weigh measurement. For the "short capillary" runs no weighing was required, and the relative accuracy of $\Delta v/D_{\text{eff}}$ was therefore better, 5 to 12 percent.

The experimental results are shown in Tables 1 and 2, and in Figs. 1 and 2. The isotope transport velocity is directly obtainable from the mass effect μ , defined as

$$\mu = \frac{\Delta v/j}{\Delta M/F\gamma} \quad (2)$$

where j is the current density, F the FARADAY constant, γ the density and ΔM the isotope mass number difference.

From the steady-state gradient of the isotope separation factor Q , the ratio $\Delta v/D_{\text{eff}}$ is obtained:

$$d(\ln Q)/dx = \Delta v/D_{\text{eff}} \quad (3)$$

$T(^{\circ}\text{C})$	$\mu \cdot 10^5$
63 ± 1	2.00 ± 0.35
64 ± 1	2.35 ± 0.4
76 ± 1	2.30 ± 0.5
99 ± 1	2.65 ± 0.35
125 ± 3	3.15 ± 0.6
130 ± 4	2.75 ± 0.7
150 ± 2	3.05 ± 0.4
174 ± 8	3.85 ± 0.6
268 ± 2	7.10 ± 0.9
276 ± 2	5.60 ± 0.9
375 ± 5	8.25 ± 0.9
390 ± 5	9.60 ± 1.0

Table 1. Results of mass-effect measurements.

I (Amps)	$T(^{\circ}\text{C})$	$10^6 \frac{d(\ln Q)}{dx} \cdot j_{(\text{cm/Amp})}^{-1}$
2.97 ± 0.03	46 ± 1	4.26 ± 0.25
	94 ± 2	4.85 ± 0.7
	110 ± 2	4.57 ± 0.25
	111 ± 2	4.52 ± 0.4
	185 ± 2	4.63 ± 0.4
	241 ± 2	5.76 ± 0.55
5.25 ± 0.05	246 ± 2	5.41 ± 0.3
	53 ± 2	2.15 ± 0.15
	53 ± 2	2.37 ± 0.15
	110 ± 2	2.80 ± 0.2
	123 ± 2	2.64 ± 0.15
	123 ± 2	2.85 ± 0.35
7.98 ± 0.02	215 ± 4	3.85 ± 0.4
	256 ± 3	4.05 ± 0.45
	61 ± 2	1.04 ± 0.1
	61 ± 2	1.24 ± 0.1
	123 ± 3	1.63 ± 0.35
	142 ± 4	1.64 ± 0.2
	228 ± 4	2.88 ± 0.25
	261 ± 4	2.65 ± 0.3

Table 2. Results of steady state measurements at different currents. All gradients normalized to unit current density j . Error given in I is standard deviation.

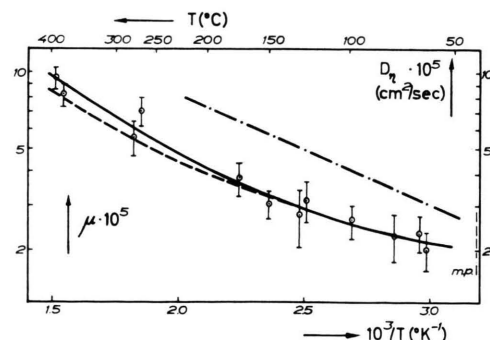


Fig. 1. Isotope electrotransport in liquid Rb, in dependence of temperature. Definition of mass-effect μ , see Eq. (2) in text. Dashed curve: results of earlier measurements¹. Broken line: self-diffusion in liquid Rb, computed^{7,8} from viscosity data, drawn for comparison of slopes.

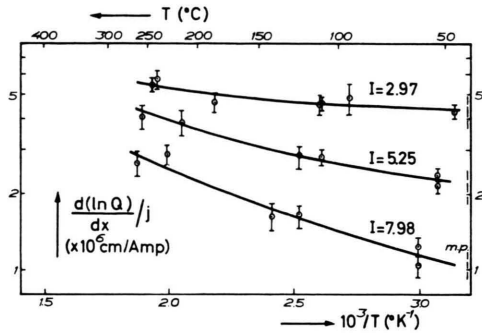


Fig. 2. Gradient of isotope separation factor, in dependence of temperature and current. See Eq. (3) in text. The gradients are normalized to unit current density j .

where x is the capillary length axis. The gradient per unit current is given in Table 2 and Fig. 2 at the three different currents.

Obviously the effective self-diffusion coefficients can be obtained from the experimental entities in Eqs. (2) and (3), so that

$$D_{\text{eff}} = \frac{\mu j}{d(\ln Q)/dx} \cdot \frac{\Delta M}{F \gamma} \quad (4)$$

In Fig. 3 (the three upper curves), computed D_{eff} values are shown as functions of inverse temperature for the three currents. The smoothed curves of Figs. 1 and 2 have been used for the computation; the shaded bands represent the margins of uncertainty.

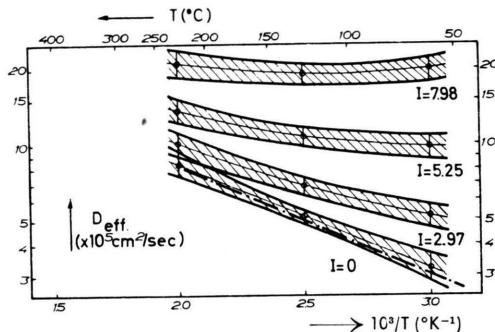


Fig. 3. Effective self-diffusion coefficients at different currents. The three upper curves are computed from the smoothed curves in Fig. 1 and 2. The lowest whole-drawn curve represents D_{corr} extrapolated for zero current, via Eq. (6), from the three D_{eff} curves. Shaded zones show margins of error. Broken line: self-diffusion coefficient D_n , computed^{7,8} from viscosity data.

2. Discussion

a) Isotope Transport

In Fig. 1 the dashed curve shows the results obtained in ref. ¹ before correction for possibly exceeded critical time. The agreement with the present work is evidently good, and the reproducibility of the method gratifying.

The broken line shows the self-diffusion coefficient of liquid Rb, as computed from experimental viscosity⁷ η via a modified STOKES-EINSTEIN type relation due to EYRING and REE⁸:

$$\eta D = k T / \xi V_m^{1/3} \quad (5)$$

Here $\xi \cong 5.6$, k is BOLTZMANN'S constant and V_m is the mole volume. So far no direct measurement of D is available, but Eq. (5) does well represent experimental data for all liquid metals where both η and D have been measured⁹. D_n in Fig. 1 thus gives a notion of the slope of an ARRHENIUS diagram. It can be noted, that the experimental μ values in this temperature range, within their individual error margins, could be represented by a line with the same slope as D_n . Physically this implies that the temperature dependence of the force exerted by the charge carriers on a diffusing atom is small. At higher temperatures (where η has not been measured) the gradient of the ARRHENIUS representation of μ appears to increase. For a detailed discussion of the mechanism of isotope transport, see ref. ⁴.

b) Electro-Convection and Effective Self-Diffusion

The mechanisms suggested²⁻⁴ as plausible causes of electro-convection should contribute to D_{eff} by terms proportional either to I^2 , or to I^4 (I being the total current). It is useful, as a first step, to see which power of the current the observed convection (D' in $D_{\text{eff}} = D + D'$) in Rb is proportional to. The calculations at three temperatures are seen in Table 3. D' appears approximately proportional to $I^{2.05}$ (as $75.2:30.6:10 = 7.98^{2.05}:5.25^{2.03}:2.97^{2.06}$). The main mechanism is thus obviously square in I , but the presence of a secondary term in I^4 cannot be completely ruled out.

⁷ "Liquid Metals Handbook", Navexos P 733 (Rev.), p. 42 and 43 [1954].

⁸ H. EYRING and T. REE, Proc. Nat. Acad. Sci. U.S. **47**, 526 [1961].

⁹ H. A. WALLS and W. R. UPTHEGROVE, Acta Met. **12**, 461 [1964].

$T^{-1} \cdot 10^3$	$D_\eta \cdot 10^5$	$D_{\text{eff}} \cdot 10^5$			$D'_{7.98} : D'_{5.25} : D'_{2.97}$
		$I = 7.98$	$I = 5.25$	$I = 2.97$	
2.0	8.25	21.30	13.70	10.05	72.5:30.3:10
2.5	4.95	19.10	10.70	6.85	74.5:30.3:10
3.0	3.05	19.95	9.75	5.20	78.5:31.2:10
					Mean: 75.2:30.6:10

Table 3. Effective self-diffusion and electro-convection at different currents and temperatures. D' values are here obtained by subtracting D_η from D_{eff} . All D 's in cm^2/sec .

$T^{-1} \cdot 10^3$	$D_\eta \cdot 10^5$	$D_{\text{corr}} \cdot 10^5$	I	$AI^2 \cdot 10^5$	$BI^4 \cdot 10^5$	$b \cdot 10^2$	$\delta \cdot 10^2$
2.0	8.25	8.40 ± 1.05	7.98 2.97	11.7 ± 3.0 1.6 ± 0.4	1.1 ± 1.0 0.02 ± 0.02	17 ± 2	0.5 ± 0.5
2.5	4.95	5.15 ± 0.40	7.98 2.97	11.8 ± 0.6 1.7 ± 0.1	2.1 ± 1.9 0.035 ± 0.03	18 ± 1	0.7 ± 0.6
3.0	3.05	3.25 ± 0.45	7.98 2.97	13.7 ± 0.6 1.9 ± 0.1	3.0 ± 2.2 0.05 ± 0.035	19 ± 1	1.0 ± 0.7

Table 4. Effective self-diffusion at zero current, electro-convective contributions and model parameters. D_η from viscosity data^{7,8}. D_{corr} , AI^2 and BI^4 from Eq. (6). All diffusion and convection in cm^2/sec , electro-osmotic mobility b [see Eq. (7)] in cm^2/Vs , effective conicity δ [see Eq. (8)] in cm^{-1} .

A more detailed treatment is given by the equation

$$D_{\text{eff}} = D_{\text{corr}} + AI^2 + BI^4. \quad (6)$$

Here D_{corr} denotes the effective self-diffusion coefficient extrapolated to zero current, and the constants A and B determine the shares of the I^2 resp. I^4 dependent contributions to D' . As results are available at three distinct currents, all three terms on r.h.s. can be computed at each temperature. The results of the calculations are seen in Table 4. It is shown, that the term in I^4 may account for some 20 percent of total D' at 8 Amps and 333 °K, but only about one percent at 3 Amps and 500 °K.

Of the three current-sensitive mechanisms hitherto discussed, only that of electro-osmosis gives a contribution (D'_{EO}) proportional to I^2 . It has been derived² that

$$D'_{\text{EO}} = \frac{I^2 b^2 \varrho^2}{48 \pi^2 r^2 D} \quad (7)$$

where ϱ is the resistivity in $\Omega \text{ cm}$, r the capillary radius in cm, D molecular self-diffusion coefficient in cm^2/sec and b the electro-osmotic mobility¹⁰. Substituting AI^2 for D'_{EO} in Eq. (7), one finds (see Table 4) that to justify this the mobility would

have to be about $0.18 \text{ cm}^2/\text{Vs}$ at all temperatures in question. This is about 40 times as much as the greatest b value found in Hg¹⁰. However, according to recent measurements by PATYANIN and REGEL⁶, in a mixture of molten alkali metals b does indeed turn out to be of the order $10^{-1} \text{ cm}^2/\text{Vs}$. It thus appears probable, that the major part of electro-convection in Rb under the present experimental conditions is due to electro-osmosis.

Two mechanisms giving rise to an I^4 sensitive term have been suggested. REGIERER (quoted in ref. ³) has treated convection due to ohmic heat development in the column. Calculations reveal, however^{3,4}, that this contribution cannot account for more than about half a percent of total D' in Rb, even at the highest currents used here. The other mechanism is magneto-hydrodynamic stirring², for which one obtains

$$D'_{\text{MHD}} = \frac{I^4 r^2 \delta^2}{6.912 \times 10^8 \pi^2 \eta^2 D}. \quad (8)$$

Here η is the viscosity in poise and δ , in cm^{-1} , represents the effective conicity of the capillary cell. If one substitutes BI^4 for D'_{MHD} , it turns out that

¹⁰ H. KNOF and A. KLEMM, Z. Naturforschg. **14a**, 1020 [1959].

δ would have to be of the order 0.7 percent/cm (see Table 4). Under microscope the actual conicity of the capillaries has been found to be only 0.2 percent/cm, but it should be stressed, that δ represents all deviations from perfectly cylindrical cell profile including irregularities at electrode ends. The obtained δ values thus do not appear unreasonable. Qualitatively they agree well with those similarly computed for Ga⁴. These two investigations are not, of course, the final proof of the MHD mechanism, but evidently present indications. Other support has been furnished by VERHOEVEN⁵: in a suspended drop (container-less) of liquid metal, current passage appears to give rise to a vehement stirring proportional to a high power of I , supposedly related to the curvature ("conicity") of the drop.

The extrapolated zero-current values of D_{eff} [i. e. D_{corr} in Eq. (6)] can be seen in Table 4 and in Fig. 3 (lowest shaded zone). As seen in the figure, within their accuracy limits they agree with molecular self-diffusion coefficients D_η , as computed from experimental viscosity by Eq. (5). A straight ARRHENIUS line can be constructed, yielding

$$D_{\text{corr}} = (5.7 \pm 2.1) \cdot 10^{-4} \exp \left(-\frac{1910 \pm 300}{RT} \right) \quad (9)$$

for T between 333° and 500 °K (plus sign in the pre-exponential term corresponds to plus in the "activation energy", and vice versa).

Provided no sizable current-independent convection is present, this represents the first measurement of molecular self-diffusion in liquid Rb. As a possible current independent factor one may consider either thermal convection or stirring due to expansion or contraction of the metal column. The former mechanism can, according to ref. ³, be neglected with the geometry of the present work. For the thermal expansion contribution, D'_{TE} , first presented in ref. ⁴, has been obtained:

$$D'_{\text{TE}} = v_{\text{TE}}^2 r^2 / 48 D \quad (10)$$

where v_{TE} is the mean flow velocity in the capillary due to contraction or elongation of the column, e. g. because of imperfect temperature stabilization or intermittent disturbances. While the small temperature fluctuations in the present steady-state experiments can be shown⁴ to be unimportant, the effect of cooling and solidification at the conclusion of a run will be briefly discussed here.

After the current passage is stopped, the metal is cooled from the nominal temperature T of the run down to the freezing point T_m . This takes a time t_1 , usually between 30 and 300 seconds. The flow velocity during this period in the half-way portion of the capillary, length l , will be

$$v_1 = \frac{1}{2} l \beta (T - T_m) / t_1$$

where β is the bulk expansion coefficient. Substitution of present experimental data into this relation, and then of v_1 into Eq. (10), shows that the resulting D'_{TE} is small in comparison with molecular D , and thus the self-diffusion coefficient for the temperature $\frac{1}{2}(T + T_m)$ is about representative for the back-diffusion during time t_1 . The column then solidifies rather rapidly, during a time, t_2 , of the order of a second. The corresponding flow velocity is

$$v_2 = \frac{1}{2} l \cdot \Delta V / V t_2$$

where $\Delta V/V$ is the relative volume change in freezing, for Rb 2.5 percent. Substitution of v_2 into Eq. (10) yields D'_{TE} of the order 10^{-3} during solidification. Obviously during the periods t_1 and t_2 the isotope enrichment at the electrodes "diffuses away", and thus the subsequently determined D_{eff} becomes too great, say, by an amount ΔD_{eff} . As the range of diffusive change in time t is of the order $(\pi D t)^{\frac{1}{2}}$, one can put, approximately,

$$\Delta D_{\text{eff}} / D_{\text{eff}} \cong \frac{(\pi D_1 t_1)^{\frac{1}{2}} + (\pi D_2 t_2)^{\frac{1}{2}}}{l} \quad (11)$$

where D_1 is some 5×10^{-5} and D_2 about 10^{-3} . Substituting $t_1 \cong 100$, $t_2 \cong 1$, $l \cong 7$, one finds that the order of magnitude of $\Delta D_{\text{eff}} / D_{\text{eff}}$ is 2 percent. The experimental D_{eff} values used for computations should be corrected (lowered) by this amount. While such a correction definitely falls within the accuracy limits of this work (a correction by 2 percent would make agreement with D_η even better) and hardly changes the "activation energy" of D_{corr} , it might possibly become appreciable in other experiments, with great volume changes and with wide or long capillaries.

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