Isotope Thermotransport in Liquid Potassium, Rubidium, and Gallium

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Temperature differences ranging from 100 °C to 500 °C were maintained between the top and bottom ends of vertical capillaries containing liquid metal. The light isotope was found to be enriched at the hot end. The steady-sate isotope separation for different temperature ranges were between 1 and 3 per cent, corresponding to the thermal diffusion factors $\alpha_K = 3.1 \times 10^{-2}$, $\alpha_{Rb} = 3.1 \times 10^{-2}$ and $\alpha_{Ga} = 3.8 \times 10^{-2}$. According to a theoretical model, the results imply that the diffusing species is a "cluster" of several cooperating atoms, the mean diffusive displacement of which is considerably less than the effective cluster diameter. The clusters drift into voids given by the statistical fluctuations of free volume.

In 1964 an appreciable de-mixing of isotopes was achieved by maintaining molten Li metal in a temperature gradient [1]. A theoretical model of thermal diffusion of isotopes in simple liquids has been proposed [2]. The present paper deals with thermotransport studies of several metals under varying temperature conditions.

1. Experimental

The metals under investigation were K, Rb and Ga, chosen i. a. because of their low melting points and easy mass-spectrometry. The K and Rb was obtained from Koch-Light Co., grade 3N7, resp. 3N. The Ga, from Alcoa, had a purity of 99.99%.

The diffusion cells consisted of 0.6 mm i. d. Pyrex-Veridia capillaries, 2 mm wall thickness, about 5 cm long. They were closed at one end and connected at the other with a 10 mm wide glass tube, containing the large metal volume. The sealed (lower) end had a 0.57 mm tungsten wire lead-through, reaching about 1 mm into the capillary, its purpose being to ensure good thermal contact between the molten metal and the cold bath. During operation, the cell was vertical, with a small Kanthal-wound oven around the large (abt. 1 cm³) metal volume above, the lower capillary end submerged in a stirred silicone oil temperature bath. The outer end of the fused-in W wire was about 5 cm deep in the oil, the lower end of the liquid metal column about 4 mm below the level of the oil surface. The temperature of the bath was stabilised by means of a contact thermometer relay and monitored by a small Hg-thermometer next to the emerging W lead-through. The oven was kept at constant temperature by a simple thermocouple relay set-up, and the temperature of the large metal volume was recorded via a small glass-sheated thermocouple, inserted through a rubber stopper into the upper tube, and reaching about 1 cm below the metal surface.

The cells were filled with liquid metal by means of a vacuum procedure described earlier (see, e. g., ref. [3]). No breaks occured in the metal column; in the case of K, however, the inner capillary walls were discernibly corroded after a couple of days.

It was required for the quantitative evaluation of these experiments, that steady state be reached. If the length of the capillary column is l, after a critical time

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

(where D_{eff} is the effective self-diffusion, containing a convection term) the composition has changed everywhere in the column. Here each run was conducted for about 8 days, corresponding to about 2 to 20 critical times, even at the lowest measuring temperatures for all metals, and even assuming D_{eff} not greater than D.

The arrangement of the cell with the hottest part up was necessary to limit convection. Mechanical rigidity and absence of intermittent temperature fluctuation were further requirements for the same purpose. Whether the aim $D_{\text{eff}} \cong D$ was actually achieved is difficult to say with certainty, but experience with 0.6 mm Veridia tubes in liquid metal electromigration [4] suggests that in absence of disturbances the convective term should be smaller than some 5 per cent of D. The potassium series possibly has a greater D_{eff}/D ratio than the others, because of chemical attack on the glass walls and corresponding contamination. This series also gave a greater spread of results.

After a concluded run, the metal was allowed to solidify in the cell. The capillary was then cut into pieces a few mm long, the metal was leached out by dilute acid (HNO_3 for the alkali, HBr for gallium) and converted into salt for mass spectrometer analysis. Another sample was made from the "normal" metal from the large volume next to the glass-sheathed thermocouple.

The heavy-to-light isotope ratios were measured by a rapid solid sample mass spectrometer. The isotope analysis apparature and procedure has been briefly de-

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[2] A. Lodding, Z. Naturforschg. 21 a, 1348 [1966].

[3] A. Lodding, Gothenburg Stud. Phys. 1 [1961].
[4] A. Lodding, J. Phys. Chem. Solids, in press.

scribed in another paper in this journal [5] and will be treated in greater detail elsewhere [6]. The reproducibility was about 0.2% for Rb, 0.4% for Ga and 0.5% for K.

2. Computation of Results

Table 1 lists the experimental results as expressed by the isotope separation factor Q, defined as

$$Q = \frac{(c_h/c_l)_C}{(c_h/c_l)_H} \qquad (2)$$

where c_h and c_l are the concentrations of the heavy and the light isotope, and the suffixes C and H refer to the cold, resp. hot capillary end. The denominator is thus the "normal" isotope ratio. The $(Q-1)$ values are positive throughout, indicating that the light isotope has migrated towards the hot end. — The table includes results quoted from an earlier paper [1] on thermal diffusion in liquid Li. In the Li-experiments the thin-walled steel capillaries used ensured nearly perfect thermal contact with the temperature bath. In the present paper the use of small bore glass capillaries entailed several advantages, but a greater inaccuracy was introduced regarding the value of T_C. The temperature difference between the ends of the tungsten lead-through was assessed using heat conductivity values from Liquid Metals Handbook [7] and Rare Metals Handbook [8]. The possible error inherent in these calculations was in a few cases as high as 20 °C, the main reason being the somewhat irregular geometry next to the lead-through inside the capillaries.

From the experimental $(Q-1)$ values the Sôret-coefficients S and thermal diffusion factors α were calculated. Their definitions are:

$$S = \frac{1+(c_h/c_l)_H}{1+(c_h/c_l)_C} \cdot \frac{Q-1}{T_H-T_C} \qquad (3)$$

and $\qquad \alpha = \tfrac{1}{2} S(T_H + T_C).$ (4)

Also listed in Table 1 are the computed ratios relevant to the latest theoretical approach [2]. The errors quoted in the last 3 columns of the table are standard deviations. Searching for definite tendencies among the results which might give a hint as to which of the ways of expressing the effect appears to be most meaningful, one finds that in K and Ga the S-values clearly become smaller as mean tem-

perature increases; the Rb-series contains too few runs and in the Li-series the temperature range is too restricted to show any trend of this kind. For Ga, where temperatures were particularly varied, the percentual error is smallest in the last column. For the other series the spread is about the same in the last three columns.

It should be borne in mind that the obtained separation factors represent the lower limits of theoretically obtainable Q-values, as separation efficiency may be marred by convection. This is a practically unavoidable disadvantage of all steady-state diffusion experiments in liquids (see, e. g. ref. [3]). The "correct" value of each enrichment factor is given by

$$Q-1 = (Q-1)_{exp} \cdot D_{eff}/D, \qquad (5)$$

which means that the experimental values may be too small by a few per cent for Ga and Rb, possibly more than 10% for K and Li.

3. Discussion

On the basis of solid-state arguments, a "heat of transport" Q^* can be calculated [2] from the equation

$$Q-1 = \frac{D}{f D_{eff}} a \frac{\Delta M}{M} \frac{Q^*}{R} (T_C^{-1} - T_H^{-1}). \qquad (6)$$

Here a is an isotope factor known from electromigration, of magnitude $a \cong -0.1$. f is a correlation factor, magnitude $0.8-1.0$. M is the mean atomic mass and ΔM the isotope mass difference. The interpretation of Q^* on a simple vacancy model is $Q^* = E_m - E_v$, where $E_{m,v}$ are the activation energies of defect motion, resp. formation. The self-diffusion activation energy on this model should be $Q_D = E_m + E_v$. It is seen from Table 2 that all investigated liquid metals exhibit a negative Q^*, which indicates that the activation energy required for displacement into a void is small. Moreover, Table 2 shows that the $-Q^*$ values are considerably higher even than experimental Q_D for these metals. While it may be safe to conclude that liquid transport motion is practically non-activated, it is still not easy to explain the fact that the experimental $-Q^*/Q_D$ ratios are much greater than unity (ranging from 3 to 11). It seems evident that the unmodified solid

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[6] I. Holmlid, M. Lövenby, and A. Lodding, Chalmers Handl., to be published.
[7] Liquid Metals Handbook, 2nd ed., NAVEXOS P-733 (Rev.), Washington D.C. 1952.
[8] Rare Metals Handbook, 2nd ed., Reinhold, New York 1964.

Metal	T_C °C	T_H °C	$(Q-1)\times 10^2$	$S\times 10^4$ $(°C)^{-1}$	$\alpha\times 10^2$	$\dfrac{(Q-1)M/\Delta M}{T_C^{-1}-T_H^{-1}}\times 10^{-2}$
Li [1]	340	540	4.6	2.3	16.3	8.0
	351	542	3.3	1.74	12.6	6.1
	366	453	3.2	1.8	13.1	6.5
	354	537	3.3	1.8	12.8	6.9
	384	550	3.9	2.95	17.5	8.8
	378	534	3.6	2.3	16.8	8.4
	338	531	3.8	1.95	13.9	6.7
	371	537	4.0	2.4	17.6	8.7
	361	514	3.1	2.0	14.1	7.0
	340	542	3.9	1.95	13.8	6.7
	358	525	2.6	1.55	11.2	5.5
				Mean: 2.02 ± 0.09	Mean: 14.5 ± 0.7	Mean: 7.2 ± 0.35
K	89 ± 9	271 ± 5	2.6 ± 0.5	1.44	3.78	5.3
	89 ± 9	271 ± 4	1.85 ± 0.6	1.03	2.69	3.8
	91 ± 9	266 ± 3	1.8 ± 0.2	1.03	2.70	4.0
	96 ± 9	336 ± 4	2.85 ± 0.25	1.18	3.68	5.2
	95 ± 9	318 ± 4	2.0 ± 0.2	0.81	2.66	3.8
	96 ± 10	341 ± 4	2.35 ± 0.3	0.83	3.01	4.2
				Mean: 1.05 ± 0.09	Mean: 3.09 ± 0.25	Mean: 4.4 ± 0.4
Rb	130 ± 20	239 ± 2	0.74 ± 0.25	0.68	3.11	5.9
	65 ± 5	270 ± 2	1.36 ± 0.25	0.66	2.93	5.2
	66 ± 5	299 ± 2	1.60 ± 0.25	0.69	3.13	5.7
	66 ± 5	297 ± 2	1.68 ± 0.25	0.73	3.31	6.0
				Mean: 0.69 ± 0.02	Mean: 3.12 ± 0.1	Mean: 5.7 ± 0.2
Ga	84 ± 17	570 ± 12	2.7 ± 0.4	0.55	3.32	5.8
	84 ± 18	590 ± 12	3.4 ± 0.35	0.67	4.08	7.2
	219 ± 12	431 ± 7	1.15 ± 0.25	0.55	3.27	6.6
	74 ± 13	476 ± 8	2.2 ± 0.45	0.55	3.02	5.0
	85 ± 7	279 ± 4	2.05 ± 0.4	1.05	4.78	6.7
	88 ± 8	316 ± 5	2.05 ± 0.3	0.91	4.31	6.3
				Mean: 0.71 ± 0.10	Mean: 3.80 ± 0.35	Mean: 6.3 ± 0.35

Table 1. Experimental results and computed specific isotope separations.
Explanation of symbols: separation factor $Q = (c_h/c_l)/(c_h/c_l)_0$; Sôret coefficient $S \cong (Q-1)/(T_H-T_C)$; thermal diffusion factor $\alpha = S\,T_{mean}$; the suffixes h and l refer to the heavy, resp. light isotope, C and H to the cold, resp. hot end of separation capillary. The experimental values for Li are taken from an earlier paper [1].

state model is not adequate to interpreting transport properties in liquids, and that Q^* in formula (6) has no immediate physical meaning.

A model has been proposed [2], where liquid diffusion is considered as requiring very little activation energy of motion, displacement probability being given by the statistical redistribution of free volume in the liquid. Diffusive motion takes place cooperatively; the value of the isotope factor, $a \cong -0.1$ (see refs. [9] and [10]). This approach, coherent with several differently based liquid models (see, e. g., refs. [11, 12]) also leads to Eq. (6), however

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[10] A. Lodding, Encyclopedia of Electrochemistry, Reinhold, New York 1964, p. 491.

[11] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 [1959].
[12] K. Furukawa, Sci. Rep. Res. Inst. Tohoku Univ., Ser. A, **12**, 368 [1960].

Metal	$-Q^*$	Q_D	φ_{min}	$\psi_{max}(\%)$
Li	13.6	2.85 [5]	4.8	10.4
K	8.3	2.55 [13]	3.3	15.1
Rb	10.8	1.95 [14]	5.5	9.1
Ga	11.9	1.15 [15]	10.3	4.9

Table 2. Calculated transport parameters. Q^* represents the solid state model "heat of transport" [see Eq. (6)]. Q_D is experimental self-diffusion "activation energy"; $\varphi_{min} = -Q^*/Q_D$ a cluster size parameter [see Eq. (7)]. $\psi_{max} = 100/2\,\varphi_{min}$ denotes the calculated mean displacement length in percent of the effective cluster diameter. Q^* has been computed from Eq. (6), using $a \cong -0.105$ (based on ref. [9]), $D/D_{eff} \cong 1$ and $f \cong 1$. All energies in kcal/mole.

with the meaning of Q^* modified according to

$$Q^* = \varphi(E_m - E_v), \qquad (7)$$

where the factor φ can be interpreted as the ratio of the effective cluster radius and the cluster displacement length. As $E_m + E_v$ ($= Q_D$) values are available from self-diffusion measurements, minimal values of φ can be obtained on the assumption $E_m \cong 0$. In Table 2, φ_{min} has been calculated for the four metals via Eqs. (6) and (7). The computed ratios ψ_{max} of the mean displacement and the effective nearest-neighbor distance are also listed.

Whereas the consistency of results in the alkalis is good (the φ_{min} value for potassium should probably be higher by some 10%, owing to convection), the somewhat deviating value in gallium possibly means that the structural similarity of all metals at their melting points may not be quite so far-reaching as is often proposed (see, e. g., ref. [12]). According to the model of ref. [2], the free volume fraction determines the mean cluster size and thus also φ. The "reduced temperature" for equal free volume fraction could quite conceivably be different from the melting point, especially in polyvalent metals like Ga with an anomaly in melting change of volume; already a very small difference of this fraction for Ga as compared with the alkalis would bring the results of all four metals in line. Another possibility, suggested also by isotope electromigration data of liquid metals [4], is that the alkalis have a significant amount of the solid-state transport mechanism still operating in the liquid state, meaning $E_m \neq 0$; this would increase the true value of φ.

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[14] From viscosity data [7], using a formula by H. Eyring and T. Ree, Proc. Nat. Acad. Sci. U.S. 47, 526 [1961].

[15] J. Petit and N. H. Nachtrieb, J. Chem. Phys. 24, 1027 [1956].