The Temperature Dependence of Isotope Thermotransport in Liquid Metals

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The isotope effect due to temperature gradient has been investigated in liquid K and Rb, using new type steel capillary cells, convenient for the study of the variation of the effect with temperature. The physical parameters, deduced from the experimentally determined steady state gradient of the isotope separation factor versus reciprocal temperature, agree with earlier results obtained within restricted temperature ranges, and were found to be nearly independent of temperature.

The cells which have hitherto been used for the measurement of isotope thermotransport in liquid metals [1–3] consisted of about 5 cm long capillaries, closed at one end, connected to a large metal reservoir at the other. The temperatures were measured at only two points, the top and bottom of the capillary. No control was available of the temperature gradient along the cell. The two extreme temperatures were, for optimal effectivity and convenience, usually kept about fixed for each metal; the exception was the series in Ga [2], which, however, was performed in glass cells, giving considerable uncertainty concerning the temperature of lower end of capillary.

As the model interpretation of the effect [4] depended on the assumption that certain basic parameters are nearly independent of temperature, it appeared desirable to perform a more quantitative check of the temperature behaviour of the effect. For this purpose the comparatively easily handled K and Rb metals were chosen, and the earlier cell design was somewhat modified. Thus the capillaries were made of stainless steel, 0.6 mm i. d., 0.1 mm wall thickness, about 70 mm long. They were, as before, closed at one end, joined to a "reservoir" at the other. Cromel-alumel thermocouples were welded at four or five points along each capillary. The temperature gradient was obtained by heating the "reservoir" by a closely fitting ceramic oven (stabilised to within 3° at 500 °C), and by cooling the lowest portion of the capillary by a slowly stirred oil bath. The constancy of temperature at all points was safeguarded by shielding the whole capillary inside a 2 cm wide glass tube which reached into the bath, thus preventing erratic cooling by funnel air along the cell. This was considered to be important for reducing any convection effects due to contraction and elongation of the metal column [5].

According to a theoretical model [4],

$$\frac{\partial \ln Q}{\partial \ln T} = \frac{-D\,\Delta M\,a_{\mathrm{w}}\,\varphi(E_{\mathrm{m}}-E_{\mathrm{f}})}{D_{\mathrm{eff}}\,M\,R\,T}, \qquad (1\,\mathrm{a})$$

or

$$\frac{\partial \ln Q}{\partial (1/T)} = \frac{D\,\Delta M}{D_{\mathrm{eff}}\,M}\,T^{*}. \qquad (1\,\mathrm{b})$$

Here Q is the steady-state isotope separation factor at a temperature T, D/D_{eff} the ratio of the molecular self-diffusion coefficient to the effective sum of self-diffusion and convection coefficients, $\Delta M/M$ the relative isotope mass difference and φ a measure of the ratio of the effective radius of the diffusing species (atom or "cluster") to its mean displacement length. The "isotope factor" a_{w} is defined as [6]

$$a_{\mathrm{w}} = \frac{\partial w/w}{\partial M/M} = f^{-1}\,\frac{\partial D/D}{\partial M/M}, \qquad (2)$$

where w denotes frequency of position change, D tracer self-diffusion coefficient and f the Bardeen-Herring correlation factor. The energies E_{m} and E_{f} in Eq. (1 a) pertain to particle motion and to the formation of a void requisite for motion.

In the derivation of theoretical parameters from results of earlier experiments [2] it had to be assumed that D/D_{eff} as well as $T^{*}(=a_{\mathrm{w}}\,\varphi(E_{\mathrm{m}}-E_{\mathrm{f}})/R)$ were temperature independent as one integrated from T_{min} to T_{max}. While experimental precautions vouched for the former ratio being close to unity, the constancy of T^{*} could be guaranteed only after having performed experiments of the kind described in the

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present paper, i. e. after having made sure that a plot of $\ln Q$ versus $1/T$ yields a straight line.

Fig. 1 shows two typical plots for each of the investigated metals. Table 1 gives for each cell the gradients in two temperature ranges, the ratio g_1/g_2 of these two gradients, and the mean gradient. It is seen that the mean of g_1/g_2 is close to unity, i. e. neither in K nor in Rb is there any definite tendency for the gradient, and thus for T^*, to change with temperature.

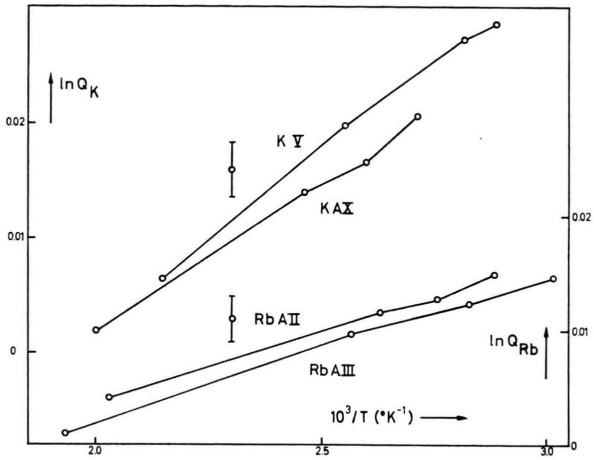

Fig. 1. Steady-state isotope separation factor in dependence of temperature, in thermotransport of liquid K and Rb.

Cell	T_1	g_1	T_1	g_2	g_1/g_2	$\frac{1}{2}(g_1+g_2)$
K III	370	28.0	345	30.5	0.92	29.3
K V	402	31.5	368	26.2	1.20	28.9
KA V	455	22.2	395	26.8	0.83	24.5
K IX	478	24.9	391	31.5	0.79	28.2
KA IX	434	24.5	386	26.7	0.92	25.6
KA X	450	33.2	390	30.0	1.11	31.6
K, mean					**0.96**	**28.0**
RbA II	419	11.8	362	13.0	0.91	12.4
RbA III	420	12.4	359	10.5	1.18	11.5
Rb VI	546	12.4	431	10.0	1.12	11.2
RbA VII	440	16.6	381	17.0	0.98	16.8
Rb X	460	11.2	346	13.9	0.80	12.6
Rb, mean					**1.00**	**12.9**

Table 1. Experimental results. The steady-state gradient g denotes $\partial \ln Q/\partial(1/T)$ at the temperature T [see Eq. (1b) in text]. The indices 1 and 2 denote mean values of higher, resp. lower temperature interval. All T and g values in °K.

In Table 2, the mean values of T^* have been computed from the gradient values, and listed together with the results of other measurements. It can be seen that the earlier results for Rb agree fairly well with those obtained here. For K, it was in fact presumed in Ref. [2] that the effect observed there was too low by some 10%, owing to convection. With this correction the older results for K overlap the present ones just within the limits of experimental error.

Metal	E_D (cal/mole)	T^* (°K)	φ_{min}	$2RT/E_D$
K	2550 [10]	565 ± 30	4.2	0.88
		445 ± 50 [2]		
Rb	1950 [11]	555 ± 35	5.4	1.13
		560 ± 60 [2]		
Li	2850 [12]	720 ± 35 [1]	4.8	1.01
In	2430 [13]	665 ± 65 [3]	5.1	1.08
Ga	1190 [8]	630 ± 40 [2]	10.1	2.12
	2450 [11]		5.2	1.03

Table 2. Model parameters. For definitions of symbols, see text.

Also given in Table 2 are values of the ratio φ, calculated on the assumptions

$$a_w = -0.105, \quad E_m \cong 0 \quad \text{and} \quad E_f \cong E_D$$

(the experimental "activation energy" of self-diffusion), as has been done in the evaluation in Ref. [2]. The assumed value for a_w is rather arbitrary, as this factor has never been directly measured for liquid metals, the figure being derived from analogy with liquid salts [7]. This approach is avoided by recourse to a schematic model discussed in Ref. [4] (last section), correlating "cluster" size and free volume. If the cluster is considered as a partitcle composed of n atoms, vibrating independently of its surroundings throughout the displacement, then the frequency w_i of the "cluster" containing the atom with isotope mass M_i will be proportional to the inverse root of the cluster mass, i. e. to $(M_i + (n-1)\,M)^{-1/2}$, so that one obtains, by using Eq. (2) and performing the differentiation,

$$a_w = -1/2\,n\,. \tag{3}$$

Now, the free volume argument of Ref. [4] leads to the simple relation

$$\varphi \cong n\,, \tag{4}$$

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and so, substituing into the definition of T^* above, one finds

$$E_{\mathrm{f}} - E_{\mathrm{m}} \cong 2\,R\,T^*. \tag{5}$$

The comparison of $2\,R\,T^*$ with E_{D} in Table 2 shows that the assumption $E_{\mathrm{m}} = 0$ seems acceptable in this model (which has the advantage of avoiding semi-arbitrary assumptions concerning a_{w}) for all hitherto investigated metals, with the possible exception of Ga. Now, the activation energy quoted for Ga is based on measurements with "shear cells"[8] within rather a short temperature interval. There are reasons to believe that a considerably higher E_{D} might apply as mean value up to the highest temperature (600°) used in Ref. [2], as the gradients of the Arrhenius plots of all liquid self-diffusion coefficients are expected to increase with temperature. Also, data from viscosity measurements indicate, via a modified Stokes-Einstein relation[9] which applies well to practically all other liquid metals, that the "activation energy" should be at least twice that given in Ref. [8], which would give good agreement for Ga with the other metals in Table 2.

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