ascribed mainly to the effect of the admixed end wall flows.

The point of inversion (neg./pos.) varies rapidly with d_h/d_c (Fig. 4) because Θ_0, as shown by experiment [8], increases rapidly with d_h/d_c.

The numerical values of the maximum and/or minimum tend to increase with decreasing orifice diameter (Fig. 5); the model relates this change to the fact that higher tangential velocities are obtained in the separating region the smaller the orifices are (see [9]).

In [10] it is, furthermore, shown that the theory accounts in a satisfactory manner for the dependence of the separation on tube length, i. e. the experimental finding that maximum separation is obtained with relatively short tubes [9] (see also [6]).

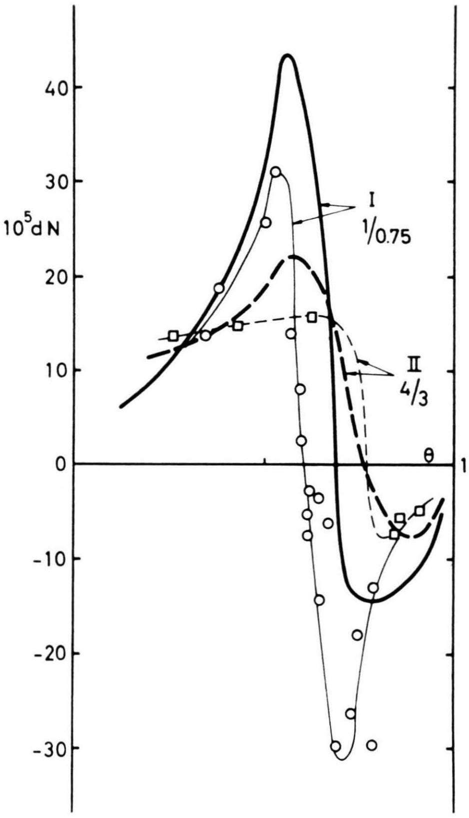

Fig. 5. Comparison between calculated and experimental gas separation effect $d_h/d_c = 1.33$; otherwise as Fig. 4.

Isotope Transport along a Temperature Gradient in Li Metal

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It has been found that, when a temperature gradient is maintained along a Li metal rod, the light isotope becomes enriched in the hot portion. This is contrary to expectation, as it is known that thermotransport motion of Li atoms relative to the lattice is directed towards the cold portion. It is inferred that isotope thermotransport and bulk thermotransport are governed by two different mechanism. The isotope factor [defined as $a = (\Delta v/v)/(\Delta M/M)$, where Δ stands for isotope differences, v for transport velocities, M for mass numbers] is of the order $a \approx +0.35$.

A year ago it has been reported [1] that if alternating current is passed along a Li metal rod, the ends of which are force-cooled, the temperature gradient causes a considerable flow of Li atoms (thermotransport) away from the hot zone. It was to be expected that, as in all diffusive motion, this flow should be accompanied by an isotope effect. This year the isotopic compositions of three Li rods have been investigated after about one month's thermotransport anneal. Before sectioning for mass analysis, each sample presented a typical "hourglass" appearance. Because of atom transport away from the hottest point, the "waist" diameter had diminished by some 10%. At this portion of each specimen, the change in isotopic composition was found to be greatest, amounting to an enrichment of the *light* isotope by about 2%. The heavy isotope was found to be enriched where the specimens had become thicker.

A convenient way of expressing isotope transport results is by means of the "isotope factor", defined as

$$a = \frac{\Delta v/v}{\Delta M/M}, \tag{1}$$

where v is the atom transport velocity wrt. the lattice, Δv the differences in migration velocity of two isotopes, whose mass difference is ΔM.

This factor can be derived from experimental data according to the following arguments:

Let the concentration of isotope i ($i = 6$ or 7) at a length coordinate x of the metal rod be c_i and the time independent isotope velocity v_i. Let $x + \delta x$ correspond to $c_i + \delta c_i$ and to $v_i + \delta v_i$. The primary results of the

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[1] A. Lodding and P. Thernquist, Z. Naturforschg. **21 a**, 857 [1966].

actual experiments amply prove that the assumptions $\partial \ln c_i/\partial x \ll \partial \ln v_i/\partial x$ and $\Delta c_i \ll c_i$ are justified throughout the typical duration of an experiment (one is found to be of the order of 2% of the other). Under these assumptions, the concentration between the two coordinates will have changed by

$$-\Delta c_i = (\delta v_i/\delta x)\, c_i\, t\,, \tag{2 a}$$

and so

$$-\Delta \ln c_i = (\delta v_i/\delta x)\, t\,. \tag{2 b}$$

Subtracting this equation for $i=7$ from that for $i=6$, one gets, letting δx approach zero,

$$-\Delta \ln Q_x = (\partial (v_6 - v_7)/\partial x)\, t \tag{3 a}$$

where the isotope separation factor Q_x, at the coordinate x, is defined by

$$Q_x = (c_6/c_7)_x/(c_6/c_7)_0\,, \tag{3 b}$$

the suffix zero denoting the original composition.

Thus the separation factor, achieved by thermotransport at any point of the specimen, indicates the variation of the relative isotope velocity along the specimen.

The same kind of treatment can be applied to the (nonisotopic) flow of Li atoms relative to the lattice. If the number n_i of Li atoms in a lattice fixed zone decreases by Δn_{Li} during the time t, and the thermotransport velocity is v_{th} wrt. the lattice, then, analogously with Eq. (2 b)

$$-\Delta \ln n_{\mathrm{Li}} = (\delta v_{\mathrm{th}}/\delta x)\, t\,. \tag{4}$$

Experimentally v_{th} can be found from the observation of the velocity v_{m} of inert lattice markers, if the proportionality factor in $v_{\mathrm{m}} = \alpha\, v_{\mathrm{th}}$ can be found. This factor, which is $-1/3$ if the sample deformation is isotropic, can be measured by comparing the observed marker flow with the relative radial deformation $\Delta r/r$ at any point of the cylindrical sample. The deformation is fairly easily measured by microscope.

As the number of atoms in the little region δx is

$$n_{\mathrm{Li}} = \pi\, r^2\, \delta x\, c \quad (\text{where } c = c_6 + c_7)\,, \tag{5}$$

for small increments one may write

$$\Delta n_{\mathrm{Li}}/n_{\mathrm{Li}} = 2\, \Delta r/r + \Delta(\delta x)/\delta x + \Delta c/c\,. \tag{6}$$

But $\Delta(\delta x)$ is just the observed widening between two lattice markers at x and $(x+\delta x)$, which is, after a time t, totally $\delta v_{\mathrm{m}}\, t$. Substituting into Eq. (6) and comparing with Eq. (4), one obtains

$$-\delta(v_{\mathrm{th}}\, t)/\delta x = 2\, \Delta r/r + \delta(v_{\mathrm{m}}\, t)/\delta x + \Delta c/c\,. \tag{7}$$

If no voids are being formed, the last term can be neglected. Assuming this [2], one obtains

$$-\alpha^{-1} = 1 + \frac{2\, \Delta r/r}{\partial (v_{\mathrm{m}}\, t)/\partial x}\,. \tag{8}$$

With α thus obtained from the sample deformation and from the marker velocity curve, v_{th} is available. Using also Eq. (3), one obtains for the isotope factor in thermotransport at any coordinate x

$$a_{\mathrm{th}} = \frac{(v_6 - v_7)/v_{\mathrm{th}}}{\Delta M/M} = \frac{-\Delta \ln Q_x \cdot \alpha}{(\partial (v_{\mathrm{m}}\, t)/\partial x)(\Delta M/M)}\,. \tag{9}$$

In Table 1, the experimental parameters in Eq. (9) are listed for the hottest point (at the "waist") of each sample, and the corresponding a_{th} values are calculated. As can be seen, the mean value is about $a_{\mathrm{th}} = +0.35$.

Sample	$10^2 \Delta \ln Q$	$-10^2 \dfrac{\partial v_{\mathrm{m}}\, t}{\partial x}$	$-10^2 \dfrac{\Delta r}{r}$	$-\alpha$	a_{th}
XI	1,1	10	9	0,35	0,27 ± 0,15
XIII	1,8	11	10	0,35	0,41 ± 0,15
XVII	2,1	9	15	0,23	0,37 ± 0,15

Table 1. Primary results (at hottest point of sample), and calculation of effective isotope factor.

The positive sign accounts for the fact that the light isotope has been enriched at the hot region, while Li atoms were transported away from it. This is a surprising result. In diffusive transport one would always expect the light isotope to move faster on account of its greater vibration frequency. Thus, if the atoms jumped (jump frequency w) one at a time from one "rigid cage" to another, the mobility would be inversely proportional to the root of isotope mass, and the factor a, written in the form

$$a_w = \frac{\partial \ln w}{\partial \ln M} \tag{10}$$

would be $-\frac{1}{2}$. The isotope factor has been measured for ionic solids and liquids in electrotransport experiments [5, 6], and for solid salts and metals by isotope diffusion [7, 8]. In the diffusion case, BARDEEN–HERRING correlation enters into the discussion via a reasoning first developed by SCHOEN [9], which requires that

$$\partial(\ln D) = f\, \partial(\ln w) \tag{11 a}$$

and consequently

$$a_D = f\, a_w \tag{11 b}$$

if both diffusion and electro- or thermotransport are governed by the same mechanism [10].

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[2] A tendency to "bubble"-formation has in fact been observed in the electrotransport of In [3] and Ag [4] under certain circumstances. However, even where detected, the relative volume occupied by voids has never been greater than a few percent of $\partial (v_{\mathrm{m}}\, t)/\partial x$.

[3] A. LODDING, J. Phys. Chem. Solids **26**, 143 [1965].

[4] P. S. C. HO and H. B. HUNTINGTON, J. Phys. Chem. Solids **27**, 1319 [1966].

[5] A. LUNDÉN, Z. Naturforschg. **17 a**, 142 [1962].

[6] See review in A. KLEMM, Ion Transport Properties of Liquid Salts, in Molten Salt Chemistry, ed. MILTON BLANDER, Interscience, New York 1964.

[7] L. W. BARR and A. D. LECLAIRE, Proc. Brit. Cer. Soc. **1**, 109 [1964].

[8] J. N. MUNDY, L. W. BARR and F. A. SMITH, Phil. Mag. **14**, 785 [1966].

[9] A. H. SCHOEN, Phys. Rev. Letters **1**, 524 [1958].

[10] ΔK, a kinetic energy distribution term often discussed in isotope diffusion work [11, 12], is the same as $(-2\, a_w)$.

[11] J. G. MULLEN, Phys. Rev. **121**, 1649 [1961].

[12] A. D. LECLAIRE, Phil. Mag. **14**, 1271 [1966].

For the nearest related metal of Li, i. e. for Na, a_D has been carefully measured[8], and found to be -0.18. Assuming $f=0.73$, as for a vacancy mechanism, one would expect $a_w \approx -0.25$. If the same mechanism applies $a_{th}=a_w$. The present results in Li give about the expected order of magnitude, but, more important, the wrong sign.

Actually, if vacancies are the dominant mechanism (which appears likely in Na[13–15] and K[16]), then the paradox lies in the direction of Li thermotransport relative to lattice, rather than that of the isotope transport, as has been pointed out in ref. [1]. If simple vacancies are the dominant mechanism, then in the expression

$$-v_{th}=Q^*(D/f\,R\,T)\nabla\ln T \tag{12}$$

one would expect $Q^* \cong E_m - E_f$, i. e. the difference of activation energies of motion and formation. This is for alkali metals definitely negative[15], and thus the thermotransport samples should have become thicker, rather than thinner at the "waist". The observed Q^* was nearly as great as the total activation energy of diffusion, and positive, which would be compatible with interstitials or with very extended local relaxation. The isotope effect, on the other hand, seems qualitatively compatible with vacancies.

Assuming two different mechanisms, I and II (possibly two aspects of the same complex defect), and following a reasoning developed for isotope thermotransport by one of the authors[17], the observed non-isotope results could be described by

$$v_{th}=-(\nabla\ln T/R\,T)\,(\varphi_I\,Q_I^*\,f_I^{-1}\,D_I+\varphi_{II}\,Q_{II}^*\,f_{II}^{-1}\,D_{II}) \tag{13 a}$$

and the isotope transport by

$$\Delta v=-(\nabla\ln T/R\,T)\,(\Delta M/M)\,(a_{wI}\,\varphi_I\,Q_I^*\,D_I + a_{wII}\,\varphi_{II}\,Q_{II}^*D_{II})\,. \tag{13 b}$$

Here $D_I+D_{II}=D$. The φ term, omitted in the derivation of Eq. (12), relates the size of the diffusing species (such as clusters or coupled atoms) to the jump distance, and should be great for certain extended defects. The a_w term, on the other hand, should be small if many atoms cooperate in diffusion. Q^* could reasonably be expected to be negative only for vacancies. If it is therefore inferred that vacancies (with $a_w \approx 0.5$, $\varphi \approx 1$) are mechanism I and mainly responsible for the isotope effect, then a_{wII} must be considerably smaller than 0.5, as the other defect, with Q^* positive, appears to be dominant in bulk thermotransport. The latter dominance implies that either $(D/f)_{II}$ is of the same order as $(D/f)_I$, or the defect is extended (φ great).

If, as seems to be the case, two different mechanisms are operative in comparable degrees, this could be further confirmed by self-diffusion measurements in Li made with sufficient accuracy to detect a possible curvature in the Arrhenius plot. Such measurements are in progress at this laboratory. Even more information in this respect could be obtained by a careful Simmons–Baluffi type[18] dilatometric investigation.

In Na no isotope thermotransport has been measured, but bulk transport data are available[19]. Q^* here turned out to be negative, but much smaller than expected by theory. Possibly the non-vacancy mechanism operates also in Na, although to a smaller extent. The results of precise self-diffusion measurements[8] and dilatometric measurements[14, 15] in Na do not altogether exclude such a possibility.

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[13] N. H. Nachtrieb and G. S. Handler, Acta Met. **2**, 797 [1954].

[14] G. A. Sullivan and J. W. Weymouth, Phys. Rev. A **136**, 1141 [1964].

[15] R. Feder and H. P. Charbnau, Phys. Rev. **149**, 464 [1966].

[16] J. N. Mundy, L. W. Barr, and F. A. Smith, Phil. Mag. **15**, 411 [1967].

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

[18] R. O. Simmons and R. W. Baluffi, Phys. Rev. **117**, 52 [1960].

[19] G. A. Sullivan, Phys. Rev. **154**, 605 [1967].