On the basis of these observations and with improved methods of isotopic analysis it seemed to be of interest to mutually compare again the D/H ratios in the water that would be liberated in the successive steps of dehydration of copper sulphate pentahydrate.

The study was carried out with copper sulphate pentahydrate freshly crystallised out of water of natural D/H ratio. For purposes of dehydration it was found by preliminary trials that water equivalent to two moles per mole of pentahydrate could be liberated by warming the powdered crystals spread in a thin layer at 60 °C for 120 minutes under vacuum. The water released was condensed in a trap cooled by liquid nitrogen. Similarly by heating further at 110 °C for 90 minutes two more moles of water could be liberated and separately collected. Lastly by heating at 180 °C for 60 minutes, the fifth mole of water could be released and condensed. The dehydrations were carried out with several equal quantities of the copper sulphate crystals and each time the three samples of water were separately collected. All the samples of water were reduced to hydrogen over uranium turnings[10] and the D/H ratios measured in an Atlas mass spectrometer M86.

From the data collected for a number of trials the results for the D/H ratios for the water liberated at different stages of dehydration of copper sulphate are summarized in the Table. All the ratios are expressed relative to that in the two moles of water liberated from the pentahydrate.

Hydrate	Moles of water liberated per mole of hydrate	Relative D/H ratio
$CuSO_4 \cdot 5\,H_2O$	2	1.000
$CuSO_4 \cdot 3\,H_2O$	2	1.002 ± 0.002
$CuSO_4 \cdot H_2O$	1	1.025 ± 0.002

It is observed that the D/H ratio in the two moles of water from the trihydrate is virtually the same as that in the two moles from the pentahydrate. Contrary to the results of ANDERSON et al.[9] the water from the monohydrate is enriched in deuterium by 2.5%. The near identity of the D/H ratios for the two moles each from the pentahydrate and the trihydrate suggests that the binding of the four water molecules in copper sulphate crystals is nearly the same but clearly different from that of the fifth water molecule. Since it is generally accepted that in crystalline copper sulphate pentahydrate four water molecules are coordinated with the cation and one with the anion, it may be inferred that the four molecules for which the D/H ratios are practically the same are the cationic water molecules while the one for which it is different, is the anionic water molecule.

Further work on various aspects of the problem is in progress.

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Isotope Thermotransport in Liquid Indium Metal

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The isotope effect, induced by a temperature gradient along a column of liquid metal, has been measured in indium. The steady-state isotope separation between 165 and 500 °C was about 1 per cent, corresponding to a thermal diffusion factor $\alpha_{\text{In}} = 2.0 \times 10^{-2}$. According to a theoretical model, the mean diffusive displacement is about 10 per cent of the effective atom or cluster diameter.

Isotope thermotransport has hitherto been demonstrated in the following liquid metals: Li[1], K and Rb[2,3], and Ga[2]. Proposed theory[4] requires further measurements, and the present paper reports the investigation of the effect in liquid In.

The experimental technique was identical to that employed in ref.[2]. The mass spectrometer analysis was somewhat more difficult than for the earlier analysed metals, as the sample (in nitrate form) had a tendency to evaporate away before a representative number of mass peaks had been obtained. The difficulty was obviated by very careful control of the filament temperatures and of the heating rates. The small isotope enrichments obtained, only about one per cent, necessitated three analyses for each sample, so as to achieve an accuracy of 0.2 per cent in the relative isotope ratio readings.

As in the earlier work, the steady state separation factor, Q, was measured, i. e. the quotient of the isotope abundance ratios at two temperatures, T_H at the top and T_C at the bottom of the separation capillary. The results for the four cells are shown in Table 1, where they have also been expressed in terms of thermal diffusion factors (for definition see, e. g., ref.[2]) and of parameters relevant to a theory put forward to interpret isotope thermotransport[4].

This theoretical approach predicts, with certain qualitative approximations[5],

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[5] The exponential (−1) on extreme right in eq. (13), ref.[4], is a proof error and is to be omitted.

Cell nr.	T_{C} (°K)	T_{H} (°K)	$(Q-1)\cdot 10^2$	$\alpha\cdot 10^2$	φ_{min}
I	438 ± 5	805 ± 8	1.20 ± 0.25	2.03 ± 0.42	5.4 ± 1.1
II	438 ± 5	788 ± 8	1.20 ± 0.23	2.10 ± 0.40	5.5 ± 1.1
III	437 ± 5	754 ± 8	1.12 ± 0.21	2.10 ± 0.40	5.4 ± 1.1
IV	437 ± 5	692 ± 8	0.81 ± 0.20	1.87 ± 0.46	4.4 ± 1.2

Table 1. Separation factors, thermal diffusion factors, cluster parameters.

Metal	Ref.	ψ_{max} (%)
Li	1	10.4
K	3	12.5
Rb	3	10.0
Ga	2	4.9
In	This work	**9.7**

Table 2. Theoretically estimated relation of displacement length to cluster diameter.

$$\varphi(E_{\mathrm{m}}-E_{\mathrm{f}}) = -20(M/\Delta M)\,\frac{Q-1}{T_{\mathrm{C}}^{-1}-T_{\mathrm{H}}^{-1}}\,. \tag{1}$$

Here E_{f} is the energy of void formation and E_{m} of diffusive motion. M and ΔM denote atomic mass and the isotopic mass difference, respectively. The factor φ expresses the ratio of the effective radius of the diffusing species (an atom or a "cluster") to the mean diffusive displacement length. E_{m} is probably much smaller than E_{f}. Neglecting E_{m}, and thus substituting the entire "activation energy" E_{D} of diffusion for the energy difference on LHS of Eq. (1), is thus a reasonable approximation and at any rate gives a minimum limit of φ. When computing φ_{min} in Table 1, the experimental value $Q_{\mathrm{D}}=2430$ cal/mole was used [6]. The result, $\varphi_{\mathrm{min}}=5.15\pm 0.45$, is in qualitative agreement with the results for other metals. This is shown in Table 2, where the obtained values of $\psi_{\mathrm{max}}=100/2\,\varphi_{\mathrm{min}}$, i. e. the mean displacements in percent of cluster diameters, are compared.

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Diffusion of Sodium in Lithium

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The diffusion of ^{22}Na in solid lithium has been measured between 50 and 176 °C. The data fit the Arrhenius relation $D=D_0\exp(-Q/R\,T)$, where $D_0=(0.41\pm 0.09)$ cm^2 sec^{-1} and $Q=(12.61\pm 0.15)$ kcal mol^{-1}. Similarities with other alkali metal diffusion data allow the conclusion that diffusion is by a vacancy mechanism.

A number of theories of impurity diffusion have been proposed, the most successful of which is based on a screened interaction model. This theory, proposed by Lazarus [1] and further developed by LeClaire [2], has accounted particularly well for impurity diffusion in metals with close packed structure. In b.c.c. metals the same success has not been achieved. While much of the data on such metals refer to the transition metals, for which the screened interaction model is unsatisfactory, the theory proved similarly unsuccessful in accounting for the alkali metal diffusion data of Barr, Mundy and Smith [3]. In order to carry out a further check of the theory we have measured the diffusion of ^{22}Na in lithium.

Experimental Method

The method used was to observe the diffusion out of a thin layer of radioactive ^{22}Na by sectioning. The techniques are essentially the same as those used by Mundy, Barr and Smith [4]. The ^{22}Na was prepared by means of ion exchange from ^{22}NaCl obtained from R.C.C. Amersham. The lithium (3N8) was obtained from Foote Comp., and cleaned by forcing the molten lithium through a stainless steel sinter (pore size ∼ 25 μ). The lithium specimen was cast into a microtome holder and slowly cooled in order to obtain a large grain size (∼5 mm diameter). The thin surface layer was made by vacuum evaporation. The diffusion anneals were carried out in an oil bath controlled to ±0.05 °C. A chromel-alumel thermocouple was used to record the temperature continuously and the plot was used to calculate the "warm up" and "quench" time corrections. The specimens were sectioned using a hand microtome and the section thickness determined by weighing. Allowance was made for the thermal expansion of the lithium at the anneal temperature using data from the American Institute of Physics Handbook. The ^{22}Na activity was determined using a NaI(Tl) well type scintillation counter and standard counting equipment.

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