

fer<sup>7</sup>. Since the H and D systems are separately in equilibrium we have the usual relationship between rate constants and concentrations — i. e.,  $k_{wx}^H/k_{xw}^H = H_w/H_x = K_H$ , and similarly for D. Using these relations to eliminate  $H_w$  and  $D_w$  from the defining expressions for the  $\beta$ 's, we get homogeneous algebraic equations for  $H_x$  and  $D_x$ . The condition for a non-trivial solution requires that  $\beta_w/\beta_x = (1-K)\beta_w + K$ , where  $K = K_H/K_D$ . For a dilute solution  $\beta_w$  is very nearly the same as the overall proton fraction ( $\beta$ ). Thus, Eq. (1) becomes

$$T_2^H = (w/nx)(T_{2x} + \tau_{xw})_H[(1-K)\beta + K]. \quad (3)$$

The analogous expression for  $T_2^D$  is obtained by replacing  $K$  by  $K^{-1}$ , and  $\beta$  by  $(1-\beta)$ . The ratio of deuteron to proton relaxation times in the same solution comes out to be  $T_2^D/T_2^H = (T_{2x} + \tau_{xw})_D/K(T_{2x} + \tau_{xw})_H$ , which is not explicitly dependent on  $\beta$ . The ratio  $K = K_H/K_D$  is temperature dependent — i. e.,

$$K = \exp(\Delta G_D - \Delta G_H)/RT,$$

hence the isotope effect will be most pronounced at low temperature.

The experimental results of MAZITOV and RIVKIND<sup>5,6</sup> are in partial agreement with the above conclusions. The observed relaxation times are either constant, or decrease linearly with  $\beta$ . For a 0.1 M solution of  $\text{CrNO}_3$ , at 0 °C, both  $T_2^H$  and  $T_1^H$  data indicate  $K=2$ . For a 0.16 M solution of  $\text{VOSO}_4$ , at 25 °C, the  $T_2^H$

and  $T_2^D$  data are entirely compatible with the above picture, and give  $K=1.6$ . On the other hand,  $T_{1,2}^D$  in the case of  $\text{Cr}^{3+}$ , and  $T_{1,2}^H$  in the case of  $\text{VO}^{2+}$  show at most slight variations with  $\beta$ , contrary to what would be expected from Eq. (3).

The above analysis is based on the assumption of a simple "primary" isotope effect. In contrast, the explanation offered by MAZITOV<sup>5</sup> invokes a dependence of the lifetimes,  $\tau_{xw}^{H,D}$ , upon isotopic composition of the solution. Such a dependence would be classed as a secondary isotope effect<sup>7</sup>, and may well be required for a complete explanation of the experimental results. However, the data presently available do not really permit one to draw definitive conclusions along these lines. This is because recent work has shown that unless the concentrations of proton donors like  $\text{H}_3\text{O}^+$  and  $\text{HSO}_4^-$  are suitably adjusted, the relaxation behavior of the system lies outside the realm of validity of the simple Eq. (1)<sup>8,9</sup>. Nevertheless, it seems clear that experimental studies of this kind will allow one to distinguish between primary and secondary isotope effects, as well as to make inferences regarding mechanisms of proton transfer reactions involving paramagnetic complex ions.

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<sup>7</sup> See, e. g., Chapt. XI, "Isotope Effects in Acid-Base Reactions" in R. P. BELL, *The Proton in Chemistry*, Cornell University Press 1959.

<sup>8</sup> C. E. MANLEY and V. L. POLLAK, *J. Chem. Phys.* **46**, 2106 [1967].

<sup>9</sup> T. J. SWIFT, T. A. STEPHENSON, and G. R. STEIN, *J. Amer. Chem. Soc.* **89**, 1611 [1967].

## Hydrogen Isotope Effect among the Different Dehydration Stages of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

K. HEINZINGER and T. S. RAO

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz  
(Z. Naturforsch. **22 a**, 2111—2112 [1967]; eingeg. am 6. Oktober 1967)

Several investigations are reported in the literature dealing with the fractionation of hydrogen isotopes between salt hydrates and their saturated solutions. The measurements by DAY et al.<sup>1</sup>, TEIS<sup>2</sup>, and UUSITALO<sup>3</sup> showed either no isotope effect or an enrichment of deuterium in the solid phase. BARRER and DENNY<sup>4</sup>, however, found an inverse effect in several chloride and sulphate systems. Their result was a few per cent enrichment of the light isotope in the hydration water of

the crystal. Based on the assumption that hydration effects in the crystal are similar to those of the ions in solution, their results are in agreement with calculations by SWAIN, BADER and THORNTON<sup>5</sup>, concluding that in solutions the hydration water of ions has a smaller D/H ratio than the bulk water. This conclusion has been supported in the case of the hydronium ion by NMR<sup>6,7</sup> as well as by vapor pressure measurements<sup>8</sup>.

Only one investigation is known searching for a difference in the D/H ratio of water liberated on stepwise dehydration of hydrated crystals. ANDERSON et al.<sup>9</sup> used water containing 0.5%  $\text{D}_2\text{O}$  for the hydration of anhydrous  $\text{CuSO}_4$  and found that on dehydration the first four molecules of water liberated were heavier than the fifth. The variations in their data, however, did not enable them to attach a quantitative significance to the results.

<sup>1</sup> J. N. E. DAY, E. D. HUGHES, C. K. INGOLD, and C. L. WILSON, *J. Chem. Soc.* **1934**, 1593.

<sup>2</sup> TEIS, *Dokl. Akad. Nauk SSSR* **99**, 585 [1954].

<sup>3</sup> UUSITALO, *Suomen Kem.* **31 B**, 362 [1958].

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<sup>8</sup> K. HEINZINGER and R. E. WESTON JR., *J. Phys. Chem.* **68**, 744 [1964].

<sup>9</sup> J. S. ANDERSON, R. H. PURCELL, T. G. PEARSON, A. KING, F. W. JAMES, H. J. EMELÉUS, and H. V. A. BRISCOE, *J. Chem. Soc.* **1937**, 1492.



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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<sup>10</sup> 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
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	2	1.000
$\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$	2	$1.002 \pm 0.002$
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	1	$1.025 \pm 0.002$

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.<sup>9</sup> 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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<sup>10</sup> J. BIGEISEN, M. L. PERLMAN, and H. C. GROSSER, *Anal. Chem.* **24**, 1356 [1952].

## Isotope Thermotransport in Liquid Indium Metal

A. OTT, L. LÖWENBERG, and A. LODDING

Physics Department, Chalmers University of Technology  
Gothenburg, Sweden

(Z. Naturforsch. **22 a**, 2112—2113 [1967]; received 16 October 1967)

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<sup>1</sup>, K and Rb<sup>2,3</sup>, and Ga<sup>2</sup>. Proposed theory<sup>4</sup> 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.<sup>2</sup>. 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,  $T_{\text{H}}$  at the top and  $T_{\text{C}}$  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.<sup>2</sup>) and of parameters relevant to a theory put forward to interpret isotope thermotransport<sup>4</sup>.

This theoretical approach predicts, with certain qualitative approximations<sup>5</sup>,

<sup>1</sup> A. OTT and A. LUNDÉN, *Z. Naturforsch.* **19 a**, 822 [1964].

<sup>2</sup> A. LODDING and A. OTT, *Z. Naturforsch.* **21 a**, 1344 [1966].

<sup>3</sup> L. LÖWENBERG, A. NORDÉN-OTT and A. LODDING, *Z. Naturforsch.*, in print.

<sup>4</sup> A. LODDING, *Z. Naturforsch.* **21 a**, 1348 [1966].

<sup>5</sup> The exponential (—1) on extreme right in eq. (13), ref. <sup>4</sup>, is a proof error and is to be omitted.