# Solvent Deuterium Isotope Effects on Acid-Base Reactions. Part VI. Recalculation of the Ratio of Ionic Products of Light and Heavy Water

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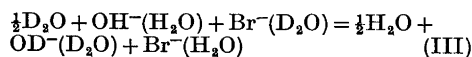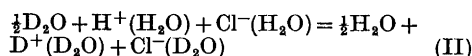*Department of Chemistry, University of Turku, Turku, Finland*

One of the early attempts to determine the ratio of the ionic products of light and heavy water was that Kingerley and LaMer,[1] who combined the results of independent thermodynamic measurements. The value thus obtained, $K_w(H_2O)/K_w(D_2O) = 6.54$ at 25°C (standard states on the mole fraction scale), is definitely lower than the values recently determined by other methods.[2,3]

It was recognized by Kingerley and LaMer [1] that their derivation involved the assumption that the standard free energy change for reaction (I) is zero. However,

$$Cl^-(D_2O) + Br^-(H_2O) = Cl^-(H_2O) + Br^-(D_2O) \quad \text{(I)}$$
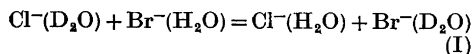
recent solubility measurements on thallium(I) halides carried out in this laboratory [4] indicate that the free energy of transfer of the bromide ion from H_2O to D_2O exceeds that of the chloride ion by 325 ± 70 J/mol at 25°C. This value agrees with that calculated theoretically by Swain and Bader.[5] This agreement is, however, fortuitous as a number of experimental values for electrolytes, such as those for potassium chloride,[6] are not consistent with the calculated values.

In essence, the procedure of Kingerley and LaMer [1] was to add up the standard free energy values of reactions (II) and (III). The sum obtained gives directly a

$$\tfrac{1}{2}D_2O + H^+(H_2O) + Cl^-(H_2O) = \tfrac{1}{2}H_2O + D^+(D_2O) + Cl^-(D_2O) \quad \text{(II)}$$

$$\tfrac{1}{2}D_2O + OH^-(H_2O) + Br^-(D_2O) = \tfrac{1}{2}H_2O + OD^-(D_2O) + Br^-(H_2O) \quad \text{(III)}$$

value for the standard free energy change of reaction (IV), if one ignores the possible free energy change associated with reac-

$$D_2O + H^+(H_2O) + OH^-(H_2O) = H_2O + D^+(D_2O) + OD^-(D_2O) \quad \text{(IV)}$$
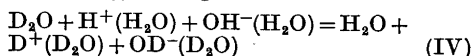
tion (I). The equilibrium constant of reaction (IV) is, of course, the ratio of the ionic products of deuterium and protium oxides.

The most accurate recent values [7] give 3590 J/mol for the standard free energy change of reaction (II) at 25°C (all standard states on the mole fraction scale). Astonishingly, this is consistent with the early value, 3580 J/mol, reported by Kingerley and LaMer.[1] The value for reaction (III) is 1070 ± 40 J/mol at the same temperature;[1] the standard error has been evaluated from the data given in the original paper. From these values and our value for reaction (I), we obtain 4985 ± 80 J/mol for the standard free energy change of reaction (IV).

The above value for reaction (IV) gives 7.47 ± 0.24 for $K_w(H_2O)/K_w(D_2O)$ at 25°C. Comparable values, converted to the mole fraction scale, are 7.35[2] and 7.23.[3] In their original paper, Covington, Bates and Robinson [2] give a ratio of 8.17 instead of 7.35 as cited here. This results from their omitting a factor of two in the equation used to convert the pK values on the molal scale to those on the mole fraction scale. The corrected equation reads: pK (mole fraction) = pK (molal) + 2 log(1000/W), in which W denotes the molecular weight of the solvent. The factor two is a consequence of the fact that the ionic products of the waters involve two ionic activities, the activities of the waters themselves being throughout on the mole fraction scale in pK values expressed in the different units, and no conversion of the latter activities need be made.

It is seen that the values derived from independent sets of measurements show excellent agreement. The definitely smaller ratio, 6.40, determined earlier by Salomaa, Schaleger and Long [8] by means of the glass electrode, included undoubtedly a contribution from a liquid junction potential associated with the cell used. In the very alkaline solutions in which the pK values were measured, this potential may be expected to be different from that in the acidic solutions in which the glass electrode was calibrated. The glass electrode method, as refined by Gold and Lowe,[3] adroitly circumvents these liquid junction difficulties.

The results of the above calculations, along with those reported in the preceding communications,[7,9] serve to illustrate the potential dangers that exist when inter-

preting results derived from electro-chemical cells with liquid junctions, in particular, those involving solutions in two different solvents, such as H_2O and D_2O.

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On the Crystal Structure of a Tetranuclear Hydroxo Complex of Uranyl(VI)

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Hydrolyzed aqueous solutions of ura-nyl(VI) chloride have been found to contain polynuclear complexes.[1] X-Ray diffraction studies on such solutions have shown that the dominating species are prob-ably dinuclear and triangular trinuclear complexes.[2] Crystals containing a dinuclear complex can easily be prepared from solu-tions with $0.3 \lesssim$ bound $OH/U \lesssim 1.0$. The crystal structure of this compound, $[(UO_2)_2(OH)_2Cl_2(H_2O)_4]$, has been solved.[3] An attempt to isolate the trinuclear complex from solutions with near-ly maximum degree of hydrolysis (bound $OH/U \approx 1.0$ for $[UO_2^{2+}]_{total} = 3.1$ M) for a structure determination has resulted in the formation of crystals containing a tetranuclear complex. Tetranuclear hydroxo complexes are most probably present in rather small amounts even in strongly hydrolyzed solutions. It has, however, been considered worthwhile to carry out a complete crystal structure determination of this compound to clarify how the polynuclear complexes are formed.

The crystals have the composition $[(UO_2)_4O_2(OH)_2Cl_2(H_2O)_6].xH_2O$, where x is probably equal to four. The symmetry is monoclinic and the space group is No. 14: $P2_1/n$. The unit cell contains two formula units and has the dimensions: $a = 11.645$ Å, $b = 10.101$ Å, $c = 10.206$ Å $(3\sigma = 0.004$ Å$)$ and $\beta = 105.77°$ $(3\sigma = 0.04°)$. The calculated density is 3.91 g/cm³.

Using the multiple film technique, Weissenberg photographs were taken around the b axis ($h0l$ to $h8l$) and around the c axis ($hk0$) with CuKα radiation ($\lambda = 1.5418$ Å). Intensities were estimated visually by comparison with a calibrated intensity scale and were corrected for Lorentz and polarization factors and for absorption. The number of observed re-flections was 1633. Approximate positions of the uranium atoms were found from the Patterson projections $P(u,0,w)$ and $P(u,v,0)$. The eight uranium atoms in a unit cell occupy two of the general fourfold positions, $\pm (x,y,z)$; $\pm (\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$; in space group $P2_1/n$. The parameters of the uranium atoms were refined in a least squares procedure using the three-dimen-sional data without absorption correction. The positions of the light atoms were found from an electron density map based on $F_{obs} - F_{calc}{}^U$. The least squares refinement of the parameters of all atoms gave an R-value of 0.184 without absorption correc-tion and 0.152 with absorption correction. Individual scale factors for the nine layers and isotropic temperature factors for all atoms were also refined. The positional and thermal parameters at this stage of the crystal structure determination are given in Table 1.

The structure of the tetramer is shown in Fig. 1. The four uranium atoms lie at the corners of two coplanar, approximately equilateral triangles sharing one edge. Each uranyl group is surrounded by one chlorine and four oxygen atoms exactly as in the dinuclear complex.[3] In the