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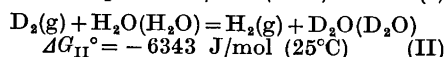
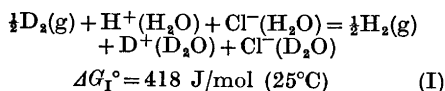
## Solvent Deuterium Isotope Effects on Acid-Base Reactions. Part V. Assignment of Individual Ionic Contributions to Transfer Free Energies of Electrolytes from H<sub>2</sub>O to D<sub>2</sub>O

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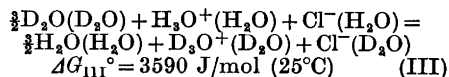
Relative equilibrium and rate constants of ionic and other reactions in light and heavy water include always the free energies of transfer of the reactants and products (or critical complexes) from H<sub>2</sub>O to D<sub>2</sub>O. This fact, which was early recognized by LaMer and his coworkers,<sup>1</sup> has been recently discussed by several authors.<sup>2-6</sup> Although there are no exact thermodynamic methods of estimating single-ion thermodynamic quantities, fairly reasonable assumptions can be made in the present particular case. As shown below, this involves the pooling of data collected by several independent methods.

Accurate values based on careful experimental investigations are available for the standard free energy changes of reactions (I) and (II). Both values refer to standard states on the mole fraction

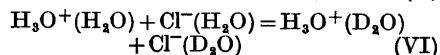
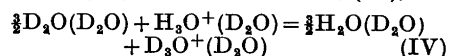


scale. The former value is that derived from EMF data by Gary, Bates and Robinson,<sup>7</sup> the latter has been calculated here from the spectroscopic value for the corresponding gas phase reaction<sup>8</sup> and the critically reevaluated ratio, 1.1483, of the vapor pressures of H<sub>2</sub>O and D<sub>2</sub>O at 25°C.<sup>9</sup> The value thus obtained is seen to be fairly consistent with the early electrochemical value, -6300 J/mol, reported by Kingerley and LaMer.<sup>1</sup>

It has been shown<sup>4,10</sup> that the water molecules hydrogen-bonded to L<sub>3</sub>O<sup>+</sup> (L=H, D) must possess essentially the same isotope composition as the bulk water. Hence the classical H<sub>3</sub>O<sup>+</sup> model is a satisfactory approximation of the aqueous proton in so far as its isotope exchange equilibria are concerned. Adopting this model, the quantity  $\Delta G_I^\circ - \frac{1}{2}\Delta G_{II}^\circ$  represents the standard free energy change of reaction (III).



Reaction (III) can be thought to be composed of three separate processes, (IV), (V) and (VI). The first of these, (IV), the



isotope exchange equilibrium between the hydronium ion and water, does not actually depend on whether this exchange reaction takes place in light or heavy water, owing to cancellation of the respective free energy terms. Experimentally measured values of its equilibrium constant<sup>4,5,10</sup> provide confirmatory evidence on this point. Further, the standard free energy change for (V) must be close to zero as no deviations from the ideal mixture behavior have been detected in the solvent system in question.<sup>4,5,10</sup> The last-mentioned process, (VI), involves the transfer of hydronium and chloride ions from light to heavy water.

The standard free energy change of reaction (IV) is, according to the best estimates of its equilibrium constant,<sup>3,5,10</sup> 2760 J/mol at 25°C. This value and that of reaction (III) yields  $\Delta G_{VI}^\circ = 830$  J/mol for reaction (VI) at the same temperature. The least accurate value involved in the whole derivation is un-

doubtedly that for reaction (IV). When more accurate data for this reaction become available, the above value will improve correspondingly.

When dealing with single-ion thermodynamic quantities, it is usual to assign a zero value to the hydronium ion, although this seems to deviate greatly from the true value in most cases.<sup>11</sup> Yet, in the present context, the assignment of a zero value to the transfer free energy of  $\text{H}_3\text{O}^+$  from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  is fairly well founded. First, this ion is capable of fitting into the surrounding water structure with minimum disturbance.<sup>12,13</sup> Second, in the first coordination sphere of the hydrated  $\text{H}_3\text{O}^+$  ion, the acidic protons are hydrogen-bonded to isotopically similar atoms, oxygen atoms, irrespective of the hydrogen isotope composition of the bulk solvent. Hence only secondary isotope effects of minor magnitude may be involved. Third, independent experimental methods, some though not all of which actually depend on possible transfer effects associated with this ion, give consistent equilibrium constants for (IV).<sup>5</sup>

Indeed, the above assumption has been more or less implicitly made in many studies of acid-base reactions in light and heavy water,<sup>2-5,10</sup> where the possible transfer free energy of the hydronium ion has been ignored. As shown above, it leads to a value of about 800 J/mol for the free energy of transfer of the chloride ion from light to heavy water at 25°C. Transfer free energies for other ions, on the same scale, are then readily calculable in cases where the overall transfer free energies are known for the electrolytes in question. Thus, a value of 890 J/mol has been determined for potassium chloride from measured data for cells without liquid junction,<sup>14</sup> which gives about 100 J/mol for the transfer free energy of the potassium ion.

At first sight, the above assignment is at variance with that made by Arnett and McKelvey,<sup>6</sup> who based their scale on a zero value for the transfer free energy of the lithium ion. Using this scale, they arrived at 96 J/mol for the transfer free energy of the chloride ion, which is only approximately one-eighth of that given above. However, the choice involving the lithium ion is probably not unrealistic;

it seems to the present writer that the grossly different values are more likely due to the circumstance that most of the ionic free energy values listed<sup>6</sup> were derived from data for cells with liquid junction potentials of unknown magnitude. Hence the cation contributions were overestimated and the anion contributions underestimated as illustrated above by the widely divergent values obtained for the chloride ion.

Results of further studies of the thermodynamics of transfer of electrolytes from light to heavy water will be published shortly.

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