THE NATURE OF THE STRUCTURE DIFFERENCE BETWEEN LIGHT AND HEAVY WATER AND THE ORIGIN OF THE SOLVENT ISOTOPE EFFECT[1-3]—I

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Abstract—The observed differences in heat content, entropy and free energy of light and heavy liquid water can be calculated within experimental error from measured infrared frequencies, using a model for water with tetrahedral hydrogen bonding and treating the hindered rotations (librations) of the water molecules as three-dimensional isotropic harmonic oscillators. The origin of the solvent isotope effect for monatomic ions in light and heavy water is their effect on the structure difference between light and heavy water. The quantity $\Delta\theta = h\,\Delta\nu/k$ provides a measure of this structure difference, where $\Delta\nu$ is $\nu - \nu'$, the difference in average values of the librational frequencies of H_2O and D_2O, and $\nu' = \nu/1.3815$. Differences in heat content, entropy and free energy for solution of monatomic ions in light and heavy water and individual ionic activity coefficients can be calculated from $\Delta\theta$. Hydronium and hydroxide ions are also discussed.

"Solvent isotope effect" is a term frequently used in discussions of kinetic and equilibrium processes in light and heavy water for the part of the total isotope effect which is attributed to isotopic substitution of the solvent. Solvent isotope effects are of increasing concern to organic chemists studying reaction mechanisms *via* isotope effects. They have been said to be due primarily to differences in structure of the two waters.[4-6] However, no indication was given as to the cause of the structure of either solvent alone, nor any reasons proffered as to why there should be differences in structure. That differences do exist is evident from differences in thermodynamic properties of the two liquids,[7-9] and in heats of hydration[10] and solubilities[4,11] of salts in the two waters.

La Mer[12-16] and Noonan[17], who determined a number of exchange constants for processes conducted in the two media, stressed that these equilibrium measurements unfortunately lump together free energies of both exchange and transfer.

[1] Supported in part by the Atomic Energy Commission Under Contract No. AT(30-1)-905 and by the National Institutes of Health under Research Grant RG-3711(C4).
[2] Cf. Part II: C. G. Swain, R. F. W. Bader and E. R. Thornton Tetrahedron, 10, 200 (1960).
[3] For further details, cf. R. F. W. Bader, Ph.D. Thesis in Organic Chemistry, M.I.T., December, 1957.
[4] R. W. Shearman and A. W. C. Menzies, J. Amer. Chem. Soc. 59, 185 (1937).
[5] K. Wirtz, Angew. Chem. A59, 138 (1947).
[6] P. M. Laughton and R. E. Robertson, Canad. J. Chem. 34, 1714 (1956); R. E. Robertson, Ibid. 35, 613 (1957); R. E. Robertson and P. M. Laughton, Ibid. 35, 1319 (1957).
[7] E. A. Long and J. D. Kemp, J. Amer. Chem. Soc. 58, 1829 (1936).
[8] A. H. Cockett and A. Ferguson, Phil. Mag. 29, 185 (1940).
[9] F. D. Rossini, J. W. Knowlton and H. L. Johnston, J. Res. Nat. Bur. Stand. 24, 369 (1940).
[10] E. Lange and W. Martin, Z. Physik. Chem. A180, 233 (1937).
[11] R. D. Eddy and A. W. C. Menzies, J. Phys. Chem. 44, 207 (1940).
[12] S. Korman and V. K. La Mer, J. Amer. Chem. Soc. 58, 1396 (1936).
[13] C. K. Rule and V. K. La Mer, J. Amer. Chem. Soc. 60, 1974 (1938).
[14] E. C. Noonan and V. K. La Mer, J. Phys. Chem. 43, 247 (1939).
[15] F. Brescia, V. K. La Mer and F. C. Nachod, J. Amer. Chem. Soc. 62, 614 (1940).
[16] R. W. Kingerly and V. K. La Mer, J. Amer. Chem. Soc. 63, 3256 (1941).
[17] E. C. Noonan, J. Amer. Chem. Soc. 71, 102 (1949).

Similarly, the understanding of kinetic isotope effects for reactions involving hydroxide ion in light and heavy water[18] is hampered by difficulty in unraveling the solvent isotope effect from the effect due to the difference between the reactants HO^- and DO^-.

Calculation of thermodynamic differences for light and heavy water

Model for liquid water. Our working model is essentially that of Bernal and Fowler[19]. From a consideration of spectral and X-ray data they proposed structures in which each molecule is tetrahedrally bonded to exactly four others as illustrated in Fig. 1. Hydrogen-bonding with this geometry is not possible for other molecular liquids.
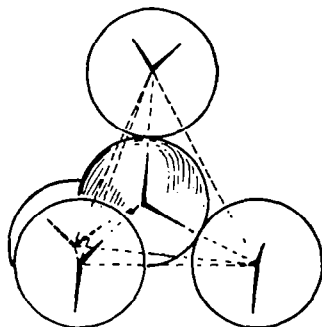

FIG. 1. Structural element of liquid water.

With this model they were able to deduce many of the physical properties of water and ice quantitatively in good agreement with experiment. They also concluded that the dielectric constants of water and ice and their variation with temperature and frequency are explicable only if most of the water molecules are not able to undergo free rotation, and hence not free to respond to an externally applied electric field. The dipole interaction pictured in Fig. 1 thus hinders rotation of the water molecules. Pople[20] quantitatively accounted for the X-ray radial distribution function, the discontinuity in density associated with the melting of ice, and the observed values of the dielectric constant of water, also by using four hydrogen bonds to nearest neighbors and considering the hindered rotation as bond bending. The essential difference between ice and water is that in ice the four bonds from one molecule bend only in such a way that the lattice order is retained, while in water they bend independently. The bond bending in Pople's theory and its associated force constant may be related to the hindered rotation and librational frequency of the present paper. The tetrahedron is not regular because the kinetic energy of the librations (hindered rotations) gives a resultant average OHO angle of less than 180°. Actually the calculations below for H_2O and D_2O do not even require the assumption of four coordination. However, we assume a tetrahedral model for clarity in discussing the kinds of motions involved because the evidence for it is so compelling.

Bernal and Tamm[21] calculated that the librational motion (hindered rotation)

[18] W. E. Nelson and J. A. V. Butler, *J. Chem. Soc.* 957 (1938); S. H. Maron and V. K. La Mer, *J. Amer. Chem. Soc.* **60**, 2588 (1938).

[19] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933); *cf.* J. W. Ellis, *Phys. Rev.* **38**, 693 (1931); S. Katzoff, *J. Chem. Phys.* **2**, 841 (1934); J. Morgan and B. E. Warren, *Ibid.* **6**, 666 (1938); G. W. Brady and W. J. Romanow, *Ibid.* **32**, 306 (1960).

[20] J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.* A **205**, 155 (1951); J. A. Pople, *Ibid.* A **205**, 163 (1951).

[21] J. D. Bernal and G. Tamm, *Nature, Lond.* **135**, 229 (1935).

contributes about 17 per cent to the difference in heat content between light and heavy ice. They stated that a difference of comparable magnitude, again due to libration, should exist between light and heavy water, and that this difference would be affected by added ions. The librational motion clearly plays an important role in determining the differences in thermodynamic properties of H_2O and D_2O. We will show that it plays the predominant role in determining solvent isotope effects.

Calculations for H_2O *and* D_2O. We will first calculate the thermodynamic differences between light and heavy water by treating the librational motion of each water molecule as a three-dimensional isotropic harmonic oscillator. This approximate treatment of the hindered rotation may be justified as follows. Pitzer and Gwinn[22] showed that the quantum partition function for a hindered rotor can be well approximated by $Q_r = Q_{class}Q_q/Q_c$ where Q_{class} is the classical partition function for translation and rotation and Q_q and Q_c are the quantum and classical partition functions for a harmonic oscillator. In the case of isotopic molecules with no translational motion, the ratio Q_r'/Q_r, reduces to Q_q'/Q_q, and Stockmayer[23] has demonstrated that for a system of nearly classical rotors the difference in heat capacities for isotopic hindered rotors will agree with that predicted from the harmonic oscillator approximation as long as the barrier is comparable to or greater than kT. Blue[24] showed that the observed differences in the heat capacities of solid H_2O and D_2O can be accounted for in the above manner.

The barrier to free rotation of the water molecules in liquid water at 25° is considerably greater than kT since it gives rise to a vibration with an average frequency of 667 cm^{-1}. The water molecule is an asymmetric top and thus possesses three different principal moments of inertia. However, only one broad band with one maximum is observed due to the thermal motions of the molecule. Accordingly we will use an *average librational frequency*. Although we will see below that the use of the observed maximum for this average frequency for light water with no adjustable parameter actually does give good agreement of calculated and observed thermodynamic quantities, there is no *a priori* reason to expect or require agreement of this average frequency with any observed frequency. The average librational frequency could have been used as an adjustable parameter in our theory, although in fact it was not.

The three librational isotopic frequency ratios should equal the inverse ratios of the corresponding moments of inertia to the one-half power. We employ, as did Blue[24], the mean of the three ratios to calculate the isotopic shift in the librational frequency, since none of the three ratios differs by more than 5·8 per cent from the mean. Thus the librational frequency ratio ω_r/ω_r' is $(1·9083)^{1/2}$ or 1·3815, and this is the isotopic shift which should be employed in calculations using the harmonic oscillator approximation.[23] There is a close correspondence between this value and the observed value of 1·35 in Table 1, which lists the librational frequencies observed for water and ice at various temperatures. For the librational frequency the observed value of ω_r (Table 1) was used, but ω_r' for heavy water was taken as $\omega_r/1·3815$.

Since rotation and translation are inextricably bound together, Q_{class} of the Pitzer–Gwinn approximation will involve both the rotational and translational degrees of freedom.[3] Since light and heavy water form nearly ideal solutions[25] the configurational

[22] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942); K. S. Pitzer, *Ibid.* **14**, 239 (1946); J. E. Kilpatrick and K. S. Pitzer, *Ibid.* **17**, 1064 (1949).
[23] W. H. Stockmayer, *J. Chem. Phys.* **27**, 321 (1957).
[24] R. W. Blue, *J. Chem. Phys.* **22**, 280 (1954).
[25] I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water*. McGraw-Hill, New York (1951).

integrals contained in Q_{class} may be equated. The result is that the external degrees of freedom contribute the factor $(Q_q'/Q_q)(M'/M)^{3/2}$ to the total partition function ratio Q'/Q where primes denote the heavier molecule and M is molecular weight. The hindered translations are of such low frequency (approximately 170 cm^{-1})[26] that this classical treatment of them is justifiable.

TABLE 1. LIBRATIONAL FREQUENCY OF WATER AND ICE[a]

T, °C	ω_r, cm^{-1}	ω_r', cm^{-1}	ω_r/ω_r'
43	667	—	—
40	667	—	—
32	667	—	—
25	667	—	—
10	710	530	1·34
−15	800	590	1·36
−55	820	610	1·35
−170	850	630	1·35

[a] The values in Table 1 for 25° and above were determined in the present investigation. The remaining figures are those of Giguère[26]. The uncertainty in ω_r is of the order of ± 10 cm^{-1}.

The internal vibrations were treated as independent harmonic oscillators. The internal vibrational frequencies observed in this study (see Experimental section) are listed in Table 2. These values have also been reported by other observers.[26] The bands for the two stretching modes ω_1 and ω_3 are completely merged. In the gas phase, ω_1 and ω_3 are 3825 and 3935 for H_2O and 2758 and 2883 for D_2O.[25] For the internal vibrations, observed values of ω and ω' (Table 2) were used. The internal vibrations contribute the factor Q_v'/Q_v to the total partition function ratio Q'/Q. Thus for the six degrees of freedom for rotation and vibration of liquid H_2O we use three equal librational frequencies (667, 667, 667 cm^{-1}) from Table 1 and three vibrational frequencies (3400, 1645 and 3400 cm^{-1}) from Table 2.

The calculations were based on the equations

$$Q_q \text{ (or } Q_v) = \prod^3 e^{-u/2}/(1 - e^{-u})$$

$$u = h\nu/kT = hc\omega/kT$$

$$Q'/Q = (M'/M)^{3/2} Q_q'Q_v'/Q_qQ_v$$

$$\Delta F = \Delta A = A' - A = -RT \ln Q'/Q$$

$$= -\frac{3}{2} RT \ln (M'/M) - RT \sum^{u'} \ln \frac{e^{-u'/2}}{1 - e^{-u'}} + RT \sum^{u} \ln \frac{e^{-u/2}}{1 - e^{-u}}$$

$$\Delta H = \Delta E = RT^2 \partial \ln (Q'/Q)/\partial T$$

$$= RT \sum^{u'} \left(\frac{u'}{e^{u'} - 1} + \frac{u'}{2}\right) - RT \sum^{u} \left(\frac{u}{e^u - 1} + \frac{u}{2}\right)$$

$$\Delta S = (\Delta H - \Delta F)/T$$

$$\Delta C_p = \partial \Delta H/\partial T = R \sum^{u'} \frac{u'^2 e^{u'}}{(e^{u'} - 1)^2} - R \sum^{u} \frac{u^2 e^u}{(e^u - 1)^2}$$

$$\Delta L = \Delta H_{gas} - \Delta H$$

[26] P. A. Giguère and K. B. Harvey, *Canad. J. Chem.* 34, 798 (1956).

where Δ before a thermodynamic symbol denotes the quantity for heavy water minus the quantity for light water, h is the Planck constant, k is the Boltzmann constant, T is the absolute temperature (°C + 273·2) and ν or ω is a frequency in sec^{-1} or cm^{-1}.[3,27] The standard states are the liquid waters at 25° and 1 atm pressure, except for ΔH_{gas}, which refers to the gaseous waters under the same conditions. The heat contents are

TABLE 2. Internal frequencies of liquid water at 25°

Vibrational mode	H_2O, cm^{-1}	D_2O, cm^{-1}
ω_1 stretching	3440	2500
ω_2 bending	1645	1208
ω_3 stretching	3440	2500

referred to the electronic energy minima, *i.e.* zero-point energies are included. The entropies are practical entropies, *i.e.* not including nuclear spin. The calculated ΔH_{gas} of -3549 cal mole^{-1} includes a 103 cal contribution from anharmonicity factors.[3] The uncertainty in the calculated value of ΔH is ± 14 cal mole^{-1} associated with a ± 10 cm^{-1} uncertainty in ω_r.

*Comparison with calorimetrically determined thermodynamic differences for* H_2O *and* D_2O

Table 3 offers a comparison of calculated and found thermodynamic differences of

TABLE 3. Comparison of calculated and calorimetrically determined thermodynamic differences for H_2O and D_2O at 25°

ΔG^a	Internal vibrations	Librations[a] ΔG_w	Translations	Calc. value	Found[7-9,25] value
ΔH	$-3303\cdot1$	$-581\cdot9$	—	-3885	-3866 ± 23
ΔS	$0\cdot034$	$1\cdot0665$	$0\cdot3164^b$	$1\cdot417$	$1\cdot439 \pm 0\cdot031$
ΔF	$-3313\cdot2$	$-900\cdot1$	$-94\cdot3$	-4308	-4295 ± 24
ΔC_p	$0\cdot1550$	$1\cdot166$	$(0\cdot03)^b$	$1\cdot32$	$1\cdot70$
ΔL	—	—	—	336	318

[a] Units of cal mole^{-1} for ΔH, ΔF, and ΔL, and cal deg^{-1} mole^{-1} for ΔS and ΔC_p. ΔG_w will refer to that portion of any thermodynamic difference ΔG_{H_2O} arising from librational (Q_o) differences alone. A Δ before a thermodynamic symbol will designate the quantity for heavy water minus the quantity for light water. [b] The contribution to the entropy from the translations is the same to three figures if they are treated as low frequency oscillations. Their contribution to the heat capacity if treated as such is as shown.

H_2O and D_2O at 25°, and shows the contributions from the different degrees of freedom. The found ΔH is the heat of the reaction

$$D_{2\ gas} + H_2O_{liq} \rightleftharpoons H_{2\ gas} + D_2O_{liq}$$
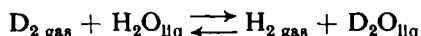
at 25° (-2096 cal mole^{-1}) plus the difference in heat contents $[(H_{298} - H_0)_{D_2} - (H_{298} - H_0)_{H_2} = 24$ cal mole$^{-1}]^9$ and the difference in zero-point vibrational energies (-1794 cal mole^{-1})[9] of D_2 and H_2 at 1 atm and 25°. The agreement with the calculated

[27] For a discussion of partition functions and thermodynamic functions of harmonic oscillators, *cf.* M. Dole, *Introduction to Statistical Thermodynamics* pp. 113f. and 163f. Prentice-Hall, New York (1954). *Cf.* section on *Calculation of isotope effects for ionic hydration* and footnote 34 for practical details of calculations.

values of ΔH, ΔS, ΔF and ΔL (the difference in latent heats of evaporation) is excellent. The value of ΔC_p (the difference in heat capacity) is undoubtedly too small as calculated here and the error is probably due primarily to equating the configurational integrals.

Comparison of the structures of light and heavy water

The water molecule in the liquid phase is prevented from undergoing unrestricted rotational motion due to its coordination with the four surrounding water molecules which make up the solvent "cage". This is the source of the "structure" of liquid water. The stronger the potential interaction between the water molecule within the cell and its neighbors, the greater is the structure, and the higher the value of the librational frequency, which is, therefore, a qualitative measure of the structure. Because of the key importance of the librational frequency it is convenient to define a libration temperature θ as $\theta = hc\omega_r/k = 1\cdot439\ \omega_r$ and the difference in libration temperatures between light and heavy water (or solutions in light and heavy water) as $\Delta\theta = hc\ \Delta\omega_r/k = hc(\omega_r - \omega_r')/k$ where $\omega_r' = \omega_r/1\cdot3815$.

The structure of heavy water is always greater than that of light water under similar conditions due to its lesser librational thermal energy. Although its potential energy of interaction with other water molecules or solutes is the same as that of light water, the amplitudes of librational oscillations are smaller and thus the kinetic energy is less for heavy water.

Any decrease in structure, e.g. one caused by the addition of solutes, always decreases the librational frequency ω_r and θ and $\Delta\theta$. The quantity θ therefore gives a useful qualitative indication of the structure of H_2O under given conditions. The quantity $\Delta\theta$ always changes in the same direction as the structure difference between light and heavy water (or solutions); therefore, it is a measure of the structure difference. Furthermore, $\Delta\theta$ is a quantitative measure of the structure difference because the thermodynamic differences which arise from the difference in structure can be calculated from it as the only variable. With the introduction of a solute molecule one can determine the new value of the librational frequency to see whether the introduction of the solute molecule has increased or decreased the structure of the water. One may then assign a new structure difference $\Delta\theta$. From values for final and initial states, thermodynamic differences and hence isotope effects may be calculated. The origin of solvent isotope effects observed in light and heavy water is the change in the structure difference $\Delta\theta$ of the two waters from initial to final state.

The librational frequency as a function of the temperature is given in Table 1. In ice the intermolecular forces are very strong and the structure is very ordered. This rigidity is reflected in the high value of the librational frequency and in its slow decrease with increasing temperature. It is obvious that a sharp decrease occurs near the melting point. It has been assumed that the structure difference is independent of temperature in the region of 25° (in accord with the observed constancy of the librational frequency ω_r and $\Delta\theta$ from 25 to at least 43°). Pople's theory of water also points to the fact that while the average value of the angle measuring the extent of bending of the hydrogen bonds increases with rising temperature, the force constant govering this motion is practically constant.[20] There is much independent evidence that the structure difference between the two waters is independent of temperature from approximately 18° to 70°. Wirtz[5], from a consideration of the molecular volumes of the two

liquids and other physical data, concluded that their structure difference was constant over a considerable range of temperature. Baker[28] noted that the viscosity of heavy water equals that of light water at a temperature $8 \cdot 5°$ less, from $15°$ to the highest temperature studied, $35°$. A calculation of the heat content differences at temperatures up to $60°$, assuming the frequencies to be independent of temperature, closely duplicates the experimentally determined values. One of the most striking features of equilibrium or kinetic isotope effects observed in light and heavy water is the very small or zero value of ΔC_p in the temperature range from approximately $18°-70°$ as noted by La Mer[15,16] and Robertson[6], although the heat of reaction is not independent of temperature for reactions in either solvent alone, and the isotope effect on the heat of reaction is not constant below $15°$. This behavior is explicable only in terms of a structure for water which changes rapidly in the low temperature region and then becomes relatively constant from $18°$ to $70°$.

Ionic hydration equilibria in light and heavy water

The structure of water is controlled by the potential energy of interaction of the water dipoles. The introduction of a charged ion will exert a pronounced effect on this potential energy. Bernal and Fowler[19] concluded that not only water but also all singly charged ions are 4-coordinated in water solution. They defined hydration as occurring only when the potential energy for the ion–water interaction was more negative than that for the water–water interaction. In this sense they concluded that H^+, Li^+, Na^+, all multiply charged ions and OH^- and F^- are hydrated, while the remaining cations and anions are not.

The infrared spectra of ionic solutions. The structure of water is characterized by the frequency of its librational motions. It is natural to determine what effect the addition of ions has on this frequency and hence on the structure of water. Ions exert a pronounced effect upon the librational band of liquid water as can be seen from typical actual spectra in Fig. 2, or more readily from the derived averaged curves in Fig. 3, which were generated by correcting percent absorption for absorption by the empty silver chloride cell and multiplying the resulting percent transmissions by a different scale factor for each solution to obtain equal vertical spreads to facilitate comparison. Due to the broad nature of the librational band, even for pure water itself, one cannot hope to locate new points of maximum absorption with any great certainty or to detect any fine structure. The qualitative conclusions are, however, inescapable. The anions effect the greatest changes. Fluoride ion increases the frequency at which maximum absorption occurs. Chloride, bromide and iodide ions give rise to new regions of maximum absorption at lower frequencies. Lithium ion does not significantly alter the band, but the other singly charged cations absorb at slightly lower frequencies, lower the larger the ion. The internal vibrations undergo no noticeable shifts in frequency. Falk and Giguère[29] have also noted that the addition of simple salts to water solutions brings about a shift in the ω_r band but has little effect on the internal frequencies. The effect of added ions is thus to change the structure difference (and $\Delta\theta$) between light and heavy water. Fluoride ion increases the structure difference, the remaining ions (with the possible exception of lithium ion) decrease it.

[28] W. N. Baker, *J. Chem. Phys.* **4**, 294 (1936).
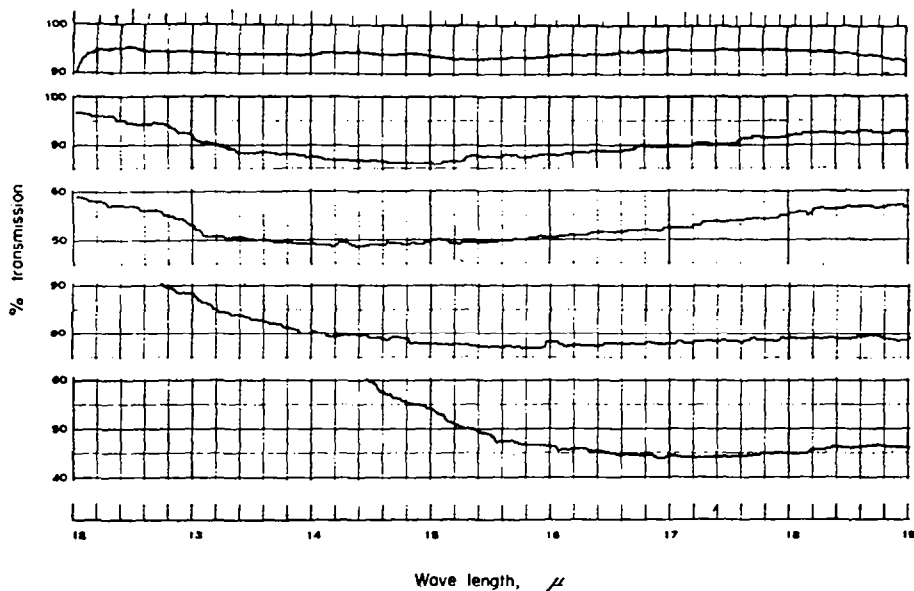[29] M. Falk and P. A. Giguère, *Canad. J. Chem.* **35**, 1195 (1957).

FIG. 2. Typical actual spectra at 25° of (from top to bottom) the empty silver chloride cell, water, sodium fluoride, sodium chloride and lithium bromide solutions.
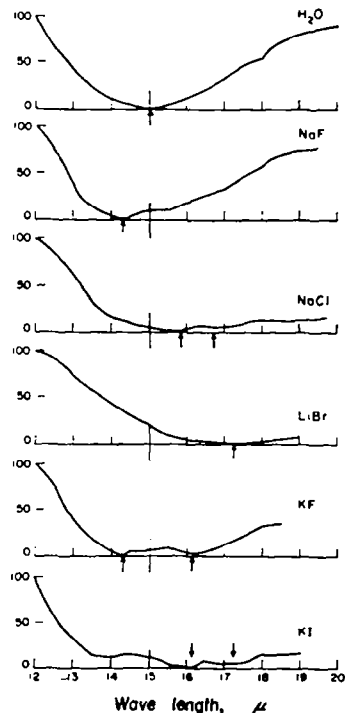

FIG. 3. The librational bands of water and ionic solutions at 25°. Ordinate is percentage of total observed change in percent transmission from maximum to 12 microns.

The librational frequencies observed for water molecules solvating ions should be practically the same at infinite dilution as in the moderately concentrated solutions where they were measured because they are for the relatively tightly held water molecules in the immediate coordination shell. The frequency of the maximum was found to be practically independent of concentration over the range where it was observable. At higher concentrations of salt, the structure of the more remote water molecules also became broken down as evidenced by a wide range of libration frequencies which exhibited no maximum before the cut-off region of the instrument. For example, fluoride ion exhibited the same maximum in solutions of sodium fluoride and potassium fluoride where the ion/water mole ratios were 1/27 and 1/4 respectively. A sodium chloride solution with a chloride/water mole ratio of 1/6 gave a maximum at 596 cm^{-1}, but a more concentrated solution, 1/4·5, gave no maximum, only a continuous increase in absorption down to the cut-off point of the instrument. A lithium chloride solution with a chloride/water mole ratio of 1/9 gave a broad flat maximum from 625–596 cm^{-1}, while a 1/8 solution gave a maximum at 600 cm^{-1} and a 1/4 solution gave a slight maximum at 596 cm^{-1}.

Model for an ion in solution. Consider the replacement of a water molecule in its tetrahedral cell by an ion. Two of the four coordinated water molecules will have to be reoriented in the field of the ion so that each of the four will have one of its hydrogens directed toward the ion if it is an anion or so that each will have its oxygen toward the ion and both hydrogens away if it is a cation. If the ion has a small radius the polarization effect will be large enough to bind the water molecules more tightly than they were previously bound when coordinated about a water molecule. If the ion replacing the central water molecule is large, the water molecules forming the coordination shell are now more loosely bonded than previously in pure water. It is important to note that the orientation and mode of attraction between an ion and a water molecule are different than that of water–water interaction. Thus it does not necessarily follow because a Na^+ ion shows a small decrease in the librational frequency that the water molecules forming the coordination shell are more loosely held than in the absence of the ion. However, a large decrease in the librational frequency such as that noted for the Cl^- ion undoubtedly does imply looser binding.

Calculation of isotope effects for ionic hydration. The present goal is to calculate the differences in thermodynamic quantities associated with the introduction of a gaseous ion into light and heavy water at infinite dilution. This is to be attempted in the following fashion. Within the radius of the coordination shell of four water molecules, water does not behave as a dielectric medium.[19,30] The heat and entropy differences for the coordinated water molecules will be calculated by the statistical mechanical method from the pure water and solution librational frequencies. Beyond the coordination sphere the field due to the ion is less than the saturation value for water, normal dielectric properties are again assumed for the solvent, and the thermodynamic changes are derived from "Born charging" effects.

Dielectric constants were determined for light and heavy water over a range of temperatures by Wyman and Ingalls[31], who noted that they were much too similar to explain differences in ionic heats of solution. Employing a radius equal to that of the ion[32]

[30] D. D. Eley and M. G. Evans, *Trans. Faraday Soc.* **34**, 1093 (1938).
[31] J. Wyman, Jr. and E. N. Ingalls, *J. Amer. Chem. Soc.* **60**, 1182 (1938).
[32] All ionic radii employed in this paper are those given by V. M. Goldschmidt, *Trans. Faraday Soc.* **25**, 253 (1929).

plus the diameter of the water molecule (2·76 Å) in the formulas for Born charging effects gives heat differences between D_2O and H_2O of only 7 cal mole^{-1} and free energies of only 2 cal mole^{-1} for the ions considered in this paper. A difference of ·7 cal mole^{-1} is equivalent to an error of 1 cm^{-1} in the librational frequencies. It does not seem realistic to retain a value which is small relative to the differences arising from the innermost shell and is actually less than the uncertainties of both the experimental and calculated values.

Therefore essentially all of the isotope effect on a heat or entropy of ionic solution at infinite dilution must have its origin in the motions of the four coordinated water molecules. The internal vibrations of the water molecules are taken as unchanged in the resulting solution,[33] and since there are practically identical potential fields for isotopic molecules there will be no direct contribution to the isotope effect from the monatomic ion itself. All of the thermodynamic differences for ionic solution in light and heavy water will arise from differences in the librational frequencies alone, i.e. from changes in $\Delta\theta$. Therefore, the difference in free energy of the four coordinated light and heavy water molecules upon changing coordination from a central water molecule to an ion is
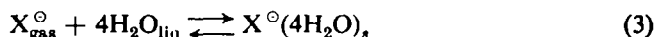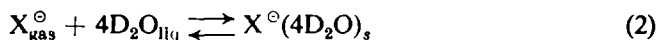
$$\Delta F_i = 4RT \ln \left(\frac{Q_q}{Q_q'}\right)_i \left(\frac{Q_q'}{Q_q}\right)_w \tag{1}$$

where the partition function ratio $(Q_q/Q_q')_i$ is determined by the $\Delta\theta$ between the two ionic solutions, $(Q_q'/Q_q)_w$ is determined by the $\Delta\theta$ between the two pure waters, and the factor of four arises from the assumption that four water molecules are coordinated.
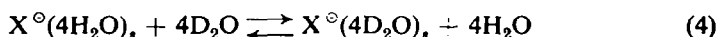
Thus the librational frequency is to be employed to determine all of the thermo-dynamic differences. The calculations will of course be carried out for individual ions. Since the maximum for the librational band in an observed spectrum is difficult to pin down exactly due to the broad nature of the band and overlapping effects, it will be more practical to begin with the observed frequency for one ion with a clear maximum in its spectrum. From this value and observed[10] differences in heats of solution of salts in light and heavy water (Table 4), the individual heats of all of the other ions may be tabulated (Table 5). The corresponding values for the librational frequencies may then be determined for these remaining ions by performing the calculation in reverse, and the values for the librational frequencies thus obtained compared with the experimental observations (Table 6). By proceeding in this manner the theory may be compared with experiment and at the same time the best values for the corresponding entropies obtained. The fluoride ion exhibits a maximum in the librational band at 698 cm^{-1} in solutions of both sodium fluoride and potassium fluoride (see Fig. 3). The librational frequency for this ion and that for pure water (667 cm^{-1}) are taken as the basis for the calculations. The quantities ΔH_w, ΔS_w and ΔF_w (Table 3 footnote a) are calculated for three-dimensional isotropic harmonic oscillators of frequencies ω_r and $\omega_r' = \omega_r/1\cdot3815$. The quantities ΔH_i, ΔS_i and ΔF_i are determined in a similar fashion from $\Delta\theta_i$, the new value of $\Delta\theta$ for the ionic solution in H_2O. For example, the isotope effect on the heat of solution of a gaseous ion in light and heavy water is $\Delta H_i = 4 \Delta H_i - 4 \Delta H_w$ where $4 \Delta H_i$ is the difference in *librational* heat contents of four heavy and four light water molecules coordinated to an ion in solution

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[33] A small change in value of an internal frequency will not sensibly affect the zero-point energy difference, and the Einstein contributions from these frequencies are negligible. Furthermore, a structure-breaking ion would tend to raise ω_1 and ω_3 but lower the bending mode ω_2. The reverse would be true for a structure-forming ion. Thus for any one ion the small changes in frequency would tend to compensate.

and 4 ΔH_w is the difference in librational heat contents of four heavy and four light water molecules coordinated to a water molecule in pure liquid water. The quantity ΔH_s is the difference in the heats of the two reactions

$$X_{gas}^{\ominus} + 4D_2O_{liq} \rightleftharpoons X^{\ominus}(4D_2O)_s \qquad (2)$$

$$X_{gas}^{\ominus} + 4H_2O_{liq} \rightleftharpoons X^{\ominus}(4H_2O)_s \qquad (3)$$

and is therefore the heat of the reaction

$$X^{\ominus}(4H_2O)_s + 4D_2O \rightleftharpoons X^{\ominus}(4D_2O)_s + 4H_2O \qquad (4)$$

for transfer of an ion from light to heavy water.[34]

TABLE 4. Isotope effects[10] for heat
of solution at 25°

Salt	ΔH_s cal mole^{-1}
LiCl	400
NaCl	560
KF	60
KCl	615
KBr	750
KI	890
RbBr	790
CsBr	815

TABLE 5. Calculated isotopic differences for individual ionic heats, entropies and free energies of solution in light and heavy water at 25°[a]

Ion	Radius Å	ω_r cm^{-1}	$-4\,\Delta H_i$	$4\,\Delta S_i$	ΔH_s	ΔS_s	ΔF_s	$\log \dfrac{\gamma_{D_2O}}{\gamma_{H_2O}}$
F$^-$	1·35	(698)[b]	2503	4·048	-175	$-0\cdot218$	-110	$-0\cdot0806$
Cl$^-$	1·81	598	1948	4·758	$+380$	$+0\cdot492$	$+233$	$+0\cdot171$
Br$^-$	1·96	573	1813	4·949	515	0·683	311	0·228
I$^-$	2·20	546	1673	5·138	655	0·872	395	0·290
		587[c]	2830[c]	7·240[c]	662[c]	0·841[c]	411[c]	0·308[e]
Li$^+$	0·78	664	2308	4·285	20	0·019	14	0·00103
Na$^+$	0·98	635	2148	4·491	180	0·225	113	0·0828
K$^+$	1·33	625	2093	4·571	235	0·305	144	0·106
Rb$^+$	1·49	618	2053	4·615	275	0·349	171	0·125
Cs$^+$	1·65	613	2028	4·652	300	0·386	185	0·136

[a] Units of cal mole-ion^{-1} for all ΔH and ΔF, and cal deg^{-1} mole-ion^{-1} for all ΔS. Data for water: $\omega_r' = 667$ cm^{-1}; $4\,\Delta H_w = -2328$ cal mole^{-1}; $4\,\Delta S_w = 4\cdot266$ cal deg^{-1} mole^{-1}; $4\,\Delta F_w = -3600$ cal mole^{-1}. [b] This frequency is the observed one. All others are calculated as explained in the text. [c] The second set of values for I$^-$ is calculated assuming a coordination number of 6.

[34] The isotope effects are easily calculated using the tabulated values of the Einstein functions given in Dole[27]. For each value of θ/T the values of

$$\frac{H^\circ}{RT} = \left(\frac{\theta/T}{e^{\theta/T}-1}\right); \quad \frac{S^\circ}{R} = \left(\frac{\theta/T}{e^{\theta/T}-1}\right) - \ln(1 - e^{-\theta/T}); \quad \frac{F^\circ}{RT} = -\ln Q^\circ = \ln(1 - e^{-\theta/T})$$

are tabulated. The quantities H°, F°, and Q° as calculated from Dole's tables do not include the zero-point energy contribution, which for three degrees of freedom is $3R\theta/2$, or $-3R\,\Delta\theta/2$ for the difference between heavy and light water. For example, the isotope effect on the heat of solution is

$$\Delta H_s = 4\,\Delta H_i - 4\,\Delta H_w = 4\left(-\frac{3}{2}R\,\Delta\theta_i + 3\,\Delta H_i^\circ\right) - 4\left(-\frac{3}{2}R\,\Delta\theta_w + 3\,\Delta H_w^\circ\right)$$

A graph was constructed giving $4\,\Delta H_i$ vs. ω_r for convenience in deriving Table 5.

Isotopic differences in heats of solution, listed in Table 4, were shown[10] to be independent of concentration below 0·5 moles of salt per 100 moles of water and so are valid for infinite dilution. The results of the calculations are given in Table 5. Although the band maxima cannot be located accurately, we have listed in Table 6 the observed regions (± 10 cm^{-1}) of maximum absorption (cf. Fig. 3). In every case the band extends to the frequencies calculated for the different ions. Spectra of lithium chloride solutions show that the lithium ion leaves the water band undisturbed. No new

TABLE 6. COMPARISON OF CALCULATED AND
OBSERVED LIBRATIONAL FREQUENCIES

Ion	Calc. ω_r, cm^{-1}, for		Obs cm^{-1}
	4-coord	6-coord	
F$^-$	(698)	—	698
Cl$^-$	598	621	600
Br$^-$	573	604	580
I$^-$	546	587	580
Li$^+$	664	—	(667)
Na$^+$	635	—	630
K$^+$	625	—	620
(H$_2$O)	—	—	(667)

maximum was observable for this ion in lithium chloride or lithium bromide solutions. Therefore, the value for pure water has been entered in parentheses for this ion in Table 6. The agreement between the second and fourth columns in Table 6 (with the exception of the iodide ion which is discussed below) is very satisfactory. The agreement provides some *a posteriori* justification for the approximations which have been made and suggests that the isotope effect for the heat of solution of an ionic solute in light and heavy water is indeed due to changes in the structure difference between the two waters. The agreement in Table 6 is very dependent upon the number of water molecules which are assumed to be coordinated to the ion. The calculated values of the librational frequencies were arrived at by assuming a coordination number of four. Table 6 also shows the results of calculations of the librational frequency for the largest ions (Cl$^-$, Br$^-$ and I$^-$) if coordination numbers of six are assumed. This change in coordination number produces a change in the calculated librational frequency large enough to be detected experimentally. The results suggest that while the chloride and bromide ions are four-coordinated in aqueous solution, the iodide ion may well be six-coordinated, a reasonable result since it is the largest of these anions.

Multiply-charged ions. Although no measurements were made with multiply-charged ions in this study, one can calculate in the same way from heats of solution[10] that the water molecules coordinated to Mg^{++} and the heavier alkaline earth ions would also have very slightly decreased librational frequencies, structures and structure differences $\Delta\theta$. These calculations were made assuming a coordination number of 6. If the coordination number were 4 the shifts would still be in the same direction, but slightly larger.

Heats of solution. Addition of the values ΔH_s for any anion-cation pair gives the isotopic difference for heat of solution of the salt in light and heavy water. Only the

fluoride ion increases the librational frequency of the water molecules and hence the structure difference. Therefore, it is the only singly charged ion for which more heat is evolved in heavy than in light water. All of the other singly-charged ions decrease the librational frequency of water and hence more heat is evolved from their solution in light than in heavy water. Fig. 4 shows a plot of ΔH_s vs. the ionic radius. There is a sharp break between Na^+ and K^- in the ΔH_s curve. This agrees with the calculations of Bernal and Fowler[19] that Li^+ and Na^+ are more strongly bonded to their coordinated water molecules than water itself whereas K^+, Rb^+ and Cs^+ are not. Once the
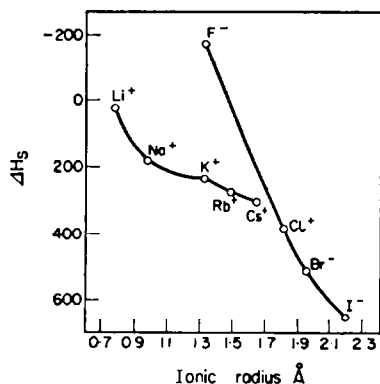
FIG. 4. The isotope effect for the ionic heat of solution in light and heavy water ΔH_s in cal mole-ion^{-1} vs. the ionic radius, at 25°.

bonding becomes weaker, any further structure breaking is due more to the mere increase in size of the ions and less to the polarization changes, which become relatively small as the ionic radius is increased. This same change in slope with increasing ionic radius is exhibited in a curve of mutual potential energy for water molecules and singly-charged ions.[19] This parallelism is to be expected because the isotope effects refer to differences in kinetic energy of the coordinated water molecules, and these kinetic motions are determined by the potential energy.

Entropies of solution. The changes in ΔS_s parallel those for ΔH_s. Only the fluoride ion increases the librational frequency and thus leads to a greater loss of entropy for its solution in heavy water as opposed to its solution in light water. The remaining singly-charged ions, with the possible exception of the lithium ion, break down the structure of the water (decrease $\Delta\theta$) and lead to a smaller loss in entropy in heavy water. Frank[35] has pointed out that an ionic solution appears to have too much entropy. Solution of two argon gas molecules in water leads to a greater entropy loss than when potassium chloride is dissolved in water. Potassium and chloride ions have the same electronic structure as an argon atom. The effect of the charge is thus to *lessen* the entropy decrease. The explanation of this seemingly contrary result given by Frank is now generally accepted. A large part of the entropy decrease arises from the restriction of the ion in its "box" in solution as opposed to its complete freedom in the gas phase. This is a free volume effect. There is a smaller contribution from the Born charging effect which Frank also considers as arising only outside of the primary coordination shell. Frank employed the geometric model of Bernal and Fowler and

³⁵ H. S. Frank and M. W. Evans, *J. Chem. Phys.* 13, 507 (1945).

considered each ion as coordinated with four water molecules. However, this is as far as he accepted the model, for he always considered water as coordinated more tightly to the ion than to water in pure water no matter what the ionic radius. For the entropy change of the water molecules coordinated to the ion, he used 4 times one half of the entropy decrease of a water molecule changing from liquid to ice. Thus he always considered the water as more tightly bound and more restricted in its movement when bound to the ion than when bound to water. Adding these contributions he finds that he has too little entropy, i.e. his result is too negative. To bring the quantities back into line he postulates a "fluctuation entropy" which arises in the outer layers of the water molecules surrounding the primary coordination shell. The presence of the ion and the reorientation of the water molecules about the ion disrupts the structure of the sur- rounding water molecules in the immediate vicinity. In this boundary layer the struc- ture of water will be broken down because the ion with its coordination sphere no longer fits in with the general structural pattern of water. Inserting values for the known results and all of the other factors but the fluctuation entropy, he has solved for and tabulated the latter quantity.

From the spectra of ionic solutions and from the isotope effects it would seem that, aside from the fluoride ion, all of the singly-charged ions decrease the librational frequency of the water molecules coordinated to the ion. These water molecules must have more kinetic freedom since the energy levels for water molecules bound to ions other than fluoride are closer together than for pure water; otherwise the heat and entropy effects for the solution of ions in water would show an isotope effect in the other direction, as they do for the fluoride ion. Thus the assumption of Frank that the water molecules in the coordination sphere undergo one half of the entropy of freezing to ice is seemingly invalid. When one removes this negative contribution of approximately 12 cal deg^{-1} mole-ion^{-1} and replaces it with a positive one which repre- sents the fact that for all of the ions but fluoride the water molecules in the coordination shell actually possess more kinetic freedom than previously, then the discrepancy that ions seem to have too much entropy disappears and with it the need to postulate a fluctuation entropy. The values tabulated by Frank for the fluctuation entropy paral- lel the isotope effects and spectral results perfectly. Thus, fluoride ion is the only anion with a negative fluctuation entropy, lithium ion has one close to zero and other ions have positive fluctuation entropies increasing with ionic radius.[36]

Probably, at least for the larger ions, a structure breaking effect does occur beyond the primary coordination shell but the effect is much smaller than supposed (by at least 12 cal deg^{-1} deg^{-1} mole-ion^{-1}).

Free energies of solution. The free energies illustrate that solution in light water is favored over solution in heavy water for all the singly charged ions except fluoride ion. The ΔF_s values are the free energy differences between reactions 2 and 3 at infinite dilution
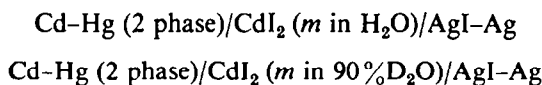
$$\Delta F_s = F_s^{D_2O} - F_s^{H_2O} = -RT \ln K_{D_2O}/K_{H_2O} = RT \ln \gamma_{D_2O}/\gamma_{H_2O}$$

where the standard state for the ion is an ideal gas at 1 atm pressure, and $F_s^{D_2O}$ and $F_s^{H_2O}$, K_{D_2O} and K_{H_2O}, and γ_{D_2O} and γ_{H_2O} are the corresponding free energies of solution, equilibrium constants and individual ionic activity coefficients for equations

[36] Frank and Evans have tabulated values for the process of vaporization of the ion from solution. Since we are considering the reverse of this process the algebraic sign of the fluctuation entropies is reversed.

2 and 3 respectively. Therefore ΔF_s is the free energy of transfer of an anion from light to heavy water at infinite dilution (the free energy of equation 4).

Although this activity coefficient ratio is defined for infinite dilution, it is probable that it generally changes very little at higher concentrations. For example, the difference in voltages of the cells

$$\text{Cd–Hg (2 phase)/CdI}_2 \ (m \text{ in H}_2\text{O})/\text{AgI–Ag}$$

$$\text{Cd–Hg (2 phase)/CdI}_2 \ (m \text{ in } 90\%\text{D}_2\text{O})/\text{AgI–Ag}$$

changes by only 0·00451 volts over the range from 0·00573m (moles of salt per 55·51 moles of solvent) to 1·359m, showing that even with ions as large as Cd^{++} and I^-, $\Delta F_s^{Cd^{+-}}$ $+ 2 \Delta F_s^{I^-}$ does not change by more than −208 cal per mole of salt and log $(\gamma_{D_2O}/\gamma_{H_2O})$ does not change by more than 0·153.[17]

The ΔF_s values should parallel the solubility ratios of the ions in the two waters. A number of solubilities were determined in light and heavy water by Menzies[4,11]. The solubility ratios m_{H_2O}/m_{D_2O}, expressed in moles of solute per 55·51 moles of solvent are all greater than unity for the salts studied and increase as the ionic radii of the ions comprising the salt increase: e.g. m_{H_2O}/m_{D_2O} is 1·07 for NaCl, 1·10 for KCl and 1·12 for KBr. This order is in accord with the calculated values of ΔF_s.

The ratios of the molalities will not give the ΔF_s values precisely because at saturation the unequal solubility of a salt in the two waters will require an activity coefficient correction

$$\Delta F_s = RT \ln \left(\frac{\gamma_{D_2O}^+ \gamma_{D_2O}^-}{\gamma_{H_2O}^+ \gamma_{H_2O}^-} \right) = RT \ln \left(\frac{m_{H_2O} \beta_{H_2O}}{m_{D_2O} \beta_{D_2O}} \right)^2 \tag{5}$$

where the mean ionic activity coefficients β calculated from the Debye–Hückel theory reduce to unity at infinite dilution. The dielectric properties of the two waters are so nearly identical that β_{D_2O} equals β_{H_2O} when the molalities of the salt are the same in the two solvents at low concentrations. Due to the high solubility of the salts referred to above, no satisfactory estimate of $\beta_{H_2O}/\beta_{D_2O}$ may be made. However, it is possible to make this correction in the case of the much less soluble salt lithium fluoride, which according to the calculations should be the only uni-univalent salt to be more soluble in heavy water than in light water. The relative solubility of lithium fluoride has been determined in the two waters[37] and it is indeed more soluble in the heavy solvent. Using

$$-\log \beta = \frac{0\cdot509\sqrt{\mu}}{1 + 1\cdot45\sqrt{\mu}}$$

where μ is the ionic strength to calculate the β values, the solubility ratio m_{D_2O}/m_{H_2O} is calculated to be 1·11. The experimental value is 1·15.

Kinetic solvent isotope effects

The direction and magnitude of kinetic solvent isotope effects (not due to transfer of a proton in the rate-controlling step) are determined by the difference in $\Delta\theta$ between the transition state and the reactants. A reaction which destroys the structure of the water in the formation of the transition state (by the creation of charge) will proceed

[37] H. W. Birnthaler and E. Lange, Z. Electrochem. 43, 649 (1937).

more rapidly in light water. A reaction which returns structure to the solvent when the transition state is reached (by neutralization or distribution of charge) will exhibit an enhanced rate in heavy water. These concepts will be expanded and exemplified in later papers.[38]

Hydronium and hydroxide ions

Hydronium and hydroxide ions contain exchangeable hydrogen atoms and therefore the degrees of freedom of the ions themselves will contribute to their thermodynamic differences when they are solvated by the two waters.
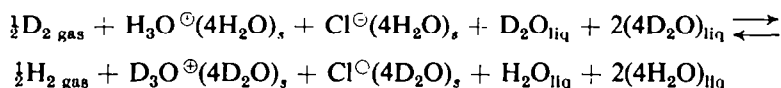
Noonan and La Mer[14] studied the two cells

$$D_2 \,|DCl \,(m \text{ in } D_2O)|\, AgCl\text{-}Ag$$

$$H_2 \,|HCl \,(m \text{ in } H_2O)|\, AgCl\text{-}Ag$$
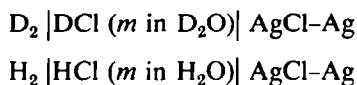
over a range of temperatures. They were thus able to determine the free energy, heat content and entropy changes for the reaction

$$\tfrac{1}{2}D_2 + HCl(H_2O) \rightleftharpoons \tfrac{1}{2}H_2 + DCl(D_2O) \tag{6}$$

As they noted, equation 6 and its measured thermodynamic properties do not allow one to determine any of the differences between the two hydronium ions since the reaction involves the transfer of the chloride ion from light to heavy water. Experimental thermodynamics yields information pertaining to a pair of ions only. However, the present theory permits one to determine individual ionic differences for the transfer of an ion between the two waters and thus equation 6 may be employed in conjunction with the theory for the determination of the thermodynamic differences between D_3O^+ and H_3O^+. By proceeding in this fashion the values obtained will be based on the same scale as all of the others ions as originally fixed by the frequency value assigned to fluoride ion and the heat data for the monatomic ions. Equation 6 may be written as

$$\tfrac{1}{2}D_{2\,gas} + H_3O^{\ominus}(4H_2O)_s + Cl^{\ominus}(4H_2O)_s + D_2O_{liq} + 2(4D_2O)_{liq} \rightleftharpoons$$

$$\tfrac{1}{2}H_{2\,gas} + D_3O^{\oplus}(4D_2O)_s + Cl^{\ominus}(4D_2O)_s + H_2O_{liq} + 2(4H_2O)_{liq}$$

Employing values determined above for the thermodynamic differences for chloride ion (ΔG_i) and for the pure waters (ΔG_w), and measured[9] differences for the pure waters (ΔG_{H_2O}) and the two forms of hydrogen gas, one obtains $\Delta H_i = -7579$ cal mole-ion^{-1}, $\Delta S_i = 6\cdot173$ cal deg^{-1} mole-ion^{-1} and $\Delta F_i = -9419$ cal mole-ion^{-1} for H_3O^+ at 25°.

Furthermore, it is possible through the use of infrared and Raman techniques to obtain sufficient spectroscopic data on the hydronium and deuteronium ions in light and heavy water solutions respectively to calculate ΔH_i, ΔS_i and ΔF_i from first principles. The values determined in this manner are completely independent of those determined above. The values of the internal vibrations employed in the calculations were those obtained by Ferriso and Hornig[39] from their investigation of the infrared spectra of H_3O^+ Cl^- and $D_3O^+Cl^-$. We have observed essentially the same spectra for solutions of HCl and DCl in light and heavy water respectively, as have Falk and

[38] E.g. C. G. Swain, A. D. Ketley and R. F. W. Bader, *J. Amer. Chem. Soc.* **81**, 2353 (1959).
[39] C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.* **23**, 1464 (1955).
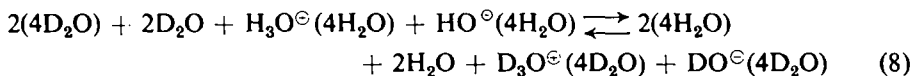
Giguère[29]. The only change from the solid state was a broadening of the bands. Investigations of acidic solutions in the potassium bromide region of the infrared indicated that the hydronium ion leaves the structure of water undisturbed since it leaves the libration band of water unchanged. The rotational motions of the hydronium ion as well as those of the coordinated water molecules will be restricted in solution. Ferriso and Hornig noted a band at 770 cm^{-1} in solid $H_3O^+Cl^-$ which they ascribed to a librational motion of the ion. We found a Raman band for the ion in solution at 643 cm^{-1} for HCl and 465 cm^{-1} for DCl. These may be treated like the hindered rotations of the water molecules. From these data one calculates the following thermodynamic differences: $\Delta H_i = -7456$ cal mole-ion^{-1}, $\Delta S_i = 6{\cdot}082$ cal deg^{-1} mole-ion^{-1} and $\Delta F_i = -9270$ cal mole-ion^{-1}. These values differ from the corresponding ones determined with the aid of the theory by only small amounts. This agreement is evidence for the reasonableness of the values so determined and a check on the assignment of the individual ionic heat and entropy differences.

It is now possible to calculate the equilibrium constant for the exchange process

$$2D_3O^{\oplus}(4D_2O) + 2(4H_2O) + 3H_2O \rightleftharpoons 2H_3O^{\oplus}(4H_2O) + 2(4D_2O) + 3D_2O \quad (7)$$
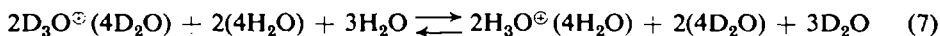
using the experimental value for ΔF_{H_2O}.[9] The free energy change for this reaction is calculated to be -1247 cal and hence the equilibrium constant is $8{\cdot}200$ at 25°.[2] This value indicates that the deuteronium ion in heavy water is a stronger acid than the hydronium ion in light water. The significance of this result in relation to both equilibrium and kinetic studies is fully discussed in part II.[2]

Wynne-Jones[40] determined the ionization constant for heavy water at a number of temperatures. His value for this constant at 25° agrees with that obtained by Abel *et al.*[41] The ratio of the ionization constants for light and heavy water K_{H_2O}/K_{D_2O} determines the equilibrium constant for the exchange reaction

$$2(4D_2O) + 2D_2O + H_3O^{\ominus}(4H_2O) + HO^{\ominus}(4H_2O) \rightleftharpoons 2(4H_2O)$$
$$+ 2H_2O + D_3O^{\ominus}(4D_2O) + DO^{\ominus}(4D_2O) \quad (8)$$

The values of ΔH and ΔS for this change in state as determined by Wynne-Jones at 25° are 970 ± 50 cal and $0{\cdot}0054$ cal deg^{-1} respectively. Since the thermodynamic differences between D_3O^+ and H_3O^+ have been calculated from the theory previously, equation 8 may be used to determine the thermodynamic differences between DO$^-$ and HO$^-$. These values for the hydroxide ion are $\Delta H_i = -3839$ cal mole-ion^{-1}, $\Delta S_i = 5{\cdot}242$ cal deg^{-1} mole-ion^{-1} and $\Delta F_i = -5402$ cal mole-ion^{-1}.

Aqueous solutions of sodium hydroxide were examined in the potassium bromide region of the infrared. The results indicated that the hydroxide ion leaves the librational band of liquid water undisturbed. Thus the hydroxide ion, like the hydronium ion, does not exert a solvent isotope effect by changing the structure of liquid water, and differences between DO$^-$ and HO$^-$ are due principally to differences in vibrations and rotation of the ions themselves. An *a priori* calculation of the thermodynamic differences for deuteroxide and hydroxide ions similar to that performed for the deuteronium and hydronium ions suggests that the hydroxide ion also experiences a barrier to free rotation in aqueous solution. The hindering potential in this case is

[40] W. F. K. Wynne-Jones, *Trans. Faraday Soc.* 32, 1397 (1936).
[41] E. Abel, E. Bratu and O. Redlich, *Z. Physik. Chem.* A173, 353 (1935).

much smaller than those encountered for water or the hydronium ion since the librational frequency in this case is judged to be in the region of 475 cm^{-1}.

The relative basicity of the two ions is determined by the equilibrium

$$2DO^{\ominus}(4D_2O) + 2(4H_2O) + H_2O \rightleftharpoons 2HO^{\ominus}(4H_2O) + 2(4D_2O) + D_2O \qquad (9)$$
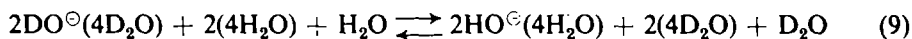
for which ΔF is calculated to be -691 cal. The value of the equilibrium constant is therefore 3·21. Deuteroxide ion in heavy water is thus a stronger base than hydroxide ion in light water. This result is in agreement with observations obtained from kinetic studies. Basic hydrolyses and reactions which are base-catalyzed proceed more rapidly in heavy water than in light water.

EXPERIMENTAL

The infrared spectra of liquid light and heavy water and ionic solutions were obtained by pressing thin films of the liquids between two silver chloride plates, each 1 mm thick. A Baird Model AB-2 double-beam recording spectrophotometer fitted with a sodium chloride prism was used to observe the three internal frequencies of the water molecules. The values thus obtained are listed in Table 1. The librational frequency of liquid water was observed with a potassium bromide prism (which transmits down to 360 cm^{-1}). Frequencies for maximum absorption ranging from 725 cm^{-1} to 550 cm^{-1} were observed depending upon the temperature and the nature of added solute molecules.

The temperature was controlled by circulating a stream of water from a constant temperature bath through metal tubing attached directly to the metal micro-cell holder. The silver chloride plates were clamped in a metal frame which in turn was held flush against the metal holder within the instrument. The temperature of the cell was determined by placing an iron-constantan thermocouple lead in a small hole drilled through one of the silver chloride plates. The thermocouple lead was thus in intimate contact with the cell window and with the film of liquid. Since the film was very thin, the transfer of heat between it and the cell windows was almost instantaneous. Sufficient time was allowed for the complete system to attain temperature equilibrium. Thermocouple voltages were measured with a Leeds and Northrup K-2 potentiometer. The results obtained are listed in Tables 1, 2 and 6. Further details on the spectroscopic equipment and procedure used have been published in the third paper of this series.[38]