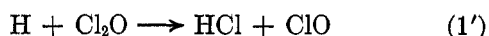


about equal to the estimated error of the measurements. At the beginning of this investigation a large number of measurements of the primary rate were made without poisoning the walls of the reaction vessel with phosphoric acid. All of these measurements gave results which were lower and more scattered than those of Table I. This may have been due to loss of some H atoms by reaction with atomic chlorine adsorbed on the unpoisoned walls.

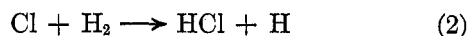
The early appearance of HOCl in the products indicates that we must include, as a primary step, the reaction



which is exothermic to the extent of 63 ± 3 kcal.⁶ However, the alternative reaction path



is 68 kcal exothermic and cannot be ruled out. Thus our measured k_1 must refer to the sum of these two processes. This kind of uncertainty as to the outcome of a simple binary collision recurs throughout any reaction scheme which is devised for this system, most notably in the reactions of H atoms with ClO and HOCl and of Cl atoms with HOCl, and is responsible for our inability to produce a complete mechanism. A number of reaction schemes can account for the observed products and stoichiometry. The consumption of molecular hydrogen at $t = 100$ msec can be explained by the reaction



with H atoms in excess, where $k_2 = 1.4 \times 10^{10}$ cm³ mol⁻¹ sec⁻¹.⁷ With excess Cl₂O this reaction has to compete with the reaction of chlorine atoms with Cl₂O, for which the rate constant has a lower limit of 4×10^{11} cm³ mol⁻¹ sec⁻¹.² However, since the only alternative means of consuming H₂, namely the reaction⁸ of H₂ with ClO, has been shown to be very slow,⁹ it appears that reaction 2 must still be significant under these conditions.

Acknowledgments. C. G. F. is grateful for the award of an I.C.I. (N. Z.) Research Fellowship. This work was supported by the New Zealand Universities Research Committee and by Grants AFOSR-264-65 and AF-AFOSR-1265-67 from the United States Air Force Office of Scientific Research.

(6) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1960-1965.

(7) M. A. A. Clyne and D. H. Stedman, *Trans. Faraday Soc.*, **62**, 2164 (1966).

(8) T. Iredale and T. G. Edwards, *J. Amer. Chem. Soc.*, **59**, 761 (1937).

(9) M. A. A. Clyne and J. A. Coxon, *Proc. Roy. Soc.*, **A303**, 207 (1968).

The Temperature of Maximum Density of Heavy Water Solutions¹

by A. J. Darnell and J. Greyson

*Atomics International Division and the Rocketdyne Division,
North American Rockwell Corporation,
Canoga Park, California 91304 (Received February 19, 1968)*

It is well known that heavy and normal water exhibit density maxima as a function of temperature, heavy water at 11.17° and normal water at 3.98°. These maxima are attributed to the presence in the solvents of both low-density icelike clusters and high-density nonstructured regions.² The temperature of maximum density (T_m) is thought to reflect the point at which, with rising temperature, the volume decrease resulting from the breakdown of the structured part is counterbalanced by the volume increase resulting from thermal expansion.³ The higher value of T_m for heavy water along with its higher melting point, viscosity, and heat capacity, all of which are structure-sensitive parameters has led, furthermore, to the conclusion that heavy water contains a greater amount of structure than normal water.^{4,5} With these points in view, it is interesting to consider the effect of dissolved species with structure-influencing properties² upon the value of the temperature of maximum density of both solvents.

Considering these effects, one would expect structure-breaking species to lower T_m and structure makers to raise it, while the relative influence of each should be manifested by similarly relative effects on T_m . Furthermore, theoretical considerations have indicated that heavy water's enhanced structure results from larger clusters than those present in normal water and that cluster size is more sensitive to temperature in heavy water than in normal water.⁵ Thus one might also expect the effects of structure-influencing species on T_m to be somewhat different in heavy water than those which are observed in normal water.

Although data pertinent to these arguments are available for normal water solutions,⁶ a dearth of data exists for heavy water solutions. It is the purpose of this note, therefore, to report some values of the temperature of maximum density of heavy water solutions of the family of alkali chlorides. The data were ob-

(1) This research was supported by the Office of Saline Water, U. S. Department of the Interior, Washington, D. C.

(2) H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(3) J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, Inc., San Francisco, Calif., 1964.

(4) G. Nemathy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

(5) G. Nemathy and H. A. Scheraga, *ibid.*, **41**, 680 (1964).

(6) "International Critical Tables," E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1933.

tained as part of an over-all program of investigation of the influence of dissolved species on the structure of water and are interesting when compared with values of T_m for normal water solutions of the same salts.

Experimental Procedure

Heavy water was obtained from the U. S. Atomic Energy Commission's Savannah River Operations Office. Its minimum D_2O concentration was 99.75% and its specific resistance was greater than 5×10^5 ohm cm. All salts were analytical reagent grade and were used without further purification.

Measurements of T_m were carried out dilatometrically. The details of the dilatometer and the experimental technique have been described in detail elsewhere.⁷ However, it is appropriate to state here that the estimated precision and accuracy of the reported values of T_m are about $\pm 0.1^\circ$.

Results and Discussion

The results of the measurements on heavy water are shown in Table I. Concentrations are presented in units of aquamolality (mol of salt/55.5 mol of solvent) to maintain consistency with other publications discussing the properties of heavy water solutions.⁸ Both the measured values of T_m and their displacements from the temperature of maximum density of the pure solvent are shown. It is to be noted that in all cases the value of T_m is reduced by the presence of the salts indicating structure-breaking influence. It is also to be noted that T_m is reduced by each of the salts proportionally to its concentration.

Table I: Concentration Dependence of the Temperature of Maximum Density of Heavy and Normal Water Solutions of Alkali Chlorides

Salt	Concn, aquamolality	Heavy water ($T_m^0 = 11.2^\circ$)		Normal water ($T_m^0 = 4.0^\circ$)
		$T_m, ^\circ C$	$(T_m^0 - T_m), ^\circ C$	$(T_m^0 - T_m), ^\circ C$
LiCl	0.11	10.6	0.6	0.1
	0.37	9.0	2.2	2.3
	1.03	4.8	6.4	6.2
NaCl	0.19	8.8	2.3	2.5
	0.33	7.0	4.1	4.4
	0.48	5.2	5.9	6.4
KCl	0.10	10.0	1.2	1.2
	0.21	9.0	2.2	2.4
	0.35	7.4	3.8	4.0
	0.43	6.5	4.7	4.9
RbCl	0.14	9.7	1.5	1.6
	0.30	8.0	3.2	3.5
	0.58	5.1	6.1	6.6
CsCl	0.13	9.8	1.4	1.6
	0.32	7.8	3.4	3.9
	0.54	5.4	5.8	6.6

For comparison with the heavy water data, the displacements of T_m for various normal water solutions of alkali chlorides are also shown. The normal water data were taken from the International Critical Tables⁹ compilation and were interpolated to the solution concentrations of the heavy water measurements shown in Table I. The value of T_m of normal water is seen also to be reduced by the presence of the dissolved salts and exhibits concentration dependence similar to that observed for the heavy water solutions. The slope of the T_m vs. concentration curve has often been called the Despretz⁹ constant for the solution.

It is interesting that LiCl reduces T_m of both solvents. It behaves as a structure breaker, contrary to the behavior it exhibits in normal water solutions at room temperature.⁸ One can also see from the data that the relative order of suppression of T_m by the salts is the same in D_2O as it is in H_2O . With the exception of LiCl, however, each of the salts at any given concentration lowers T_m of H_2O to a somewhat greater extent than T_m of D_2O ; i.e., the absolute value of the Despretz constant is somewhat larger in H_2O than in D_2O .¹⁰ Since a breakdown of structure should result in a reduced value of T_m , one concludes that the salts should disrupt the structure of H_2O to a greater extent than D_2O . These conclusions, however, are contrary to expectations, since room-temperature measurements of entropies of transfer of the alkali chlorides between heavy and normal water have indicated the opposite, that the salts disrupt the structure of D_2O to a greater extent than H_2O .⁸

Work with aqueous solutions of quaternary alkyl ammonium halides has yielded a possible explanation for the apparent discrepant behavior of these systems.⁷ The results of that work indicated that the enhanced structure of the solvents in the neighborhood of the temperature of maximum density overpowers salt structure-influencing properties which are normally observed at room temperature. At temperatures near T_m , the presence of ions within the highly structured framework of the solvent generally resulted in structure disruption, the extent of which was strongly dependent upon ion size. Thus at T_m , LiCl behaves, at least superficially, as a structure breaker.

Furthermore, from theoretical calculations,⁵ it has been concluded that in the vicinity of T_m heavy water has a greater proportion of unbroken hydrogen bonds

(7) A. J. Darnell and J. Greyson, *J. Phys. Chem.*, **72**, 3021 (1968).

(8) J. Greyson, *J. Phys. Chem.*, **71**, 2210 (1967).

(9) M. C. Despretz, *Ann. Chem. Phys.*, **70**, 49 (1839); **73**, 296 (1840).

(10) We recognize that it may not be entirely valid to compare our data with data taken from the International Critical Tables, since the latter is a compilation of the results of different investigations and different experimental techniques. However, the consistency of the differences between heavy and normal water T_m displacements and the estimated accuracy of our data combined with several check measurements of the International Critical Tables data⁹ lead us to believe that the differences are real.

than normal water. That is, there is apparently more structure in D₂O than in H₂O near the point of maximum density of each. Structure disruption resulting primarily from ion-size effects might, therefore, be less effective in heavy water than in normal water and result in a somewhat smaller displacement of $T_m(\text{D}_2\text{O})$. It is noteworthy that LiCl causes T_m displacements of about the same value in both solvents, while the solution of the larger species results in displacement differences. Of course, it should be emphasized that the effect of the difference in T_m for pure H₂O and D₂O of 7.2° may affect the sensitivity of T_m toward ions. However, the extent of this effect is not apparent.

A Modified VWJ Equation for Calculating the Totality of States of a Collection of Harmonic Oscillators

by James C. Tou

Chemical Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

and Austin L. Wahrhaftig

Department of Chemistry, University of Utah, Salt Lake City, Utah 84102 (Received January 29, 1968)

Since Rosenstock, *et al.*, proposed the quasi-equilibrium theory of mass spectra,¹ many approaches have been developed for calculating the totality of states.^{2a} Vestal, Wahrhaftig, and Johnston (VWJ) have derived an improved expression,^{2b} which has been applied in the quantitative treatments of mass spectra of propane³ and sulfides⁴ and of the photoionization data of C₆-C₈ alkanes.⁵

The VWJ equation can be written as

$$W(E) = \sum_{p=0}^p \binom{N}{p} \frac{1}{p!} \left(\frac{\sigma_p E}{h\bar{\nu}} - \frac{p-1}{2} \right)^p \quad (1)$$

where $W(E)$ is the number of states of a collection of N harmonic oscillators with internal energy equal and less than E , $\bar{\nu}$ is the geometric mean of the frequencies for all oscillators, and σ_p is a quantity defined as

$$\sigma_p = \left\langle \prod_{i=1}^p \frac{\bar{\nu}}{\nu_i} \right\rangle_{av}^{1/p}$$

The summation over p in eq 1 is introduced by assuming that 0, 1, 2, ..., p oscillators are excited out of N oscillators and terminated with the last positive term

$$p \leq \frac{2\sigma_p E}{h\bar{\nu}} + 1$$

In a recent study,² it was found that eq 1 always gave a

positive deviation from the exact value except at $E = 0$ eV. However, eq 1 is still superior because of the availability of its extended form including rotors^{5,6} and of its short computing time. The inclusion of internal rotors in the theoretical calculation of mass spectra is found to give a better result and is physically reasonable.^{5,7}

In their derivations, Vestal, *et al.*, has used the arithmetic mean for calculating the number of states, $W_d(E)$, of a collection of N identical oscillators of frequency ν under the restriction that none have the quantum number zero

$$W_d(E) = \binom{E/h\nu}{N} \approx \frac{1}{N!} [(E/h\nu) - 1/2(N-1)]^N$$

The use of the arithmetic mean instead of the geometric mean is the main cause of the positive deviation of the computed results. The result of this approximation falls between the lower and upper bounds obtained from Dirichlet integral over the volume bounded by the surfaces $n_\nu = 1$ and 0 under the same restriction

$$\frac{1}{N!} [(E/h\nu) - N]^N; \quad \frac{1}{N!} [E/h\nu]^N$$

respectively. However, if we carry out the Dirichlet integral over the volume bounded by the surfaces $n_\nu = 1/2$, the expression

$$\frac{1}{N!} [(E/h\bar{\nu}) - (N/2)]^N$$

is obtained, which can be taken as another approximate form for $W_d(E)$.

By using this expression and by following exactly the derivation of Vestal, *et al.*, the final result is the same as that given in eq 1, except the term $(p-1)/2$ is replaced by the term $p/2$. Qualitatively speaking, this replacement will make the p -power term smaller and will make the value of p 1 less than that without the modification if $p < N$. The detail of the calculation is the same as that reported previously.^{2,5} The ratios of the calculated results ($W'(E)$) and the exact values ($W_e(E)$) are plotted in Figure 1, along with those obtained from the original equation ($W(E)$) for three different size molecules with energies between 0 and 2 eV. Figure 2

(1) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

(2) (a) J. C. Tou, *J. Phys. Chem.*, **71**, 2721 (1967), and references therein; (b) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *J. Chem. Phys.*, **37**, 1276 (1962).

(3) M. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965).

(4) B. G. Hobrock, Ph.D. Dissertation, Kansas State University, Manhattan, Kan., 1963.

(5) J. C. Tou, L. P. Hills, and A. L. Wahrhaftig, *J. Chem. Phys.*, **45**, 2129 (1966).

(6) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, Contract AF 33(616)-7638, Project 7023, Task 7023-03, William H. Johnston Laboratories, Inc., Baltimore, Md., Sept 1962.

(7) Z. Prášil and W. Forst, *J. Phys. Chem.*, **71**, 3166 (1967).