water lighter by 9 p. p. m. than Lake Michigan water. When 6.4 p. p. m. are added to 9 p. p. m. to correct for the difference in atomic weight of atmospheric oxygen and aqueous oxygen, the density of D-free water containing normal oxygen is 15.4 p. p. m. lighter than normal water. From this the ratio of deuterium atoms to hydrogen atoms in Lake Michigan water is calculated to be 1:6900. Our density value of $-15.4\ \gamma$ agrees within 1.1 p. p. m. with that of Hall and Jones, $-16.5\ \gamma$, and confirms their belief that the commonly accepted value for the D/H ratio is too high and should be revised downward. Our result indicates, however, that the downward revision should be somewhat more than that recommended by Hall and Jones.

Isotopic exchange equilibrium constants involving D_2O^{16} and D_2O^{18} have been calculated and tabulated.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Solubilities of Potassium Chloride in Deuterium Water and in Ordinary Water from 0 to 180°

BY R. W. SHEARMAN AND ALAN W. C. MENZIES

Published measurements of solubility of salts in deuterium water[1] hitherto have been limited to a few determinations near room temperature. The present work is one of a series of studies over a wide temperature range undertaken in the hope of gaining insight into portions of the general subject of aqueous solubility.

Method and Materials.—For all our experiments with deuterium water, and for most of those with ordinary water, the method used was that described by Menzies.[2] A few experiments requiring much ordinary water in relation to the quantity of solute were carried out by the older synthetic method, where each experiment demands a separate sealed tube. Our method of securing and measuring steady temperatures has already been described;[2] and it may be added that about one-half of the measurements were carried out in the jacketed air-oven referred to in the earlier publication.

The deuterium water was similar to that described elsewhere,[3] with a content of 98.2% D_2O. The relative density of this water compared to ordinary water at 25°·was taken as 1.1059 for the purposes of conversion of measured volumes to masses. In order to apply the small correction for the weight of water vapor present in the gas phase, values of the vapor pressure of saturated solutions of potassium chloride were derived, by extrapolation when necessary, from the work of Leopold and Johnston;[4] and these pressure values could, with adequate approximation, be adapted to suit the case of deuterium water solutions from a knowledge of solubility and of the vapor pressures of deuterium water relative to that of ordinary water.[3]

Potassium chloride is easily obtained of highest purity, and we estimate the impurity of our sample, other than water, as less than five parts per 10,000. Water was removed by slow heating to incipient fusion.[5]

Manner of Stating Solubility.—The solubility of potassium chloride in common water is reported in moles of solute per 1000 g. of water (55.51 moles H_2O), conformably to the practice of "International Critical Tables." To secure a comparable statement of solubility in deuterium water, we state the number of moles of solute per 1111.7 g. of solvent, which is 55.51 moles of D_2O. To arrive at this value from experiments made with 98.2% D_2O, we first computed, from the weights of solvent and solute used, the molal solubility in 1109.7 g. of our sample, which is the weight containing 55.51 moles of mixed D_2O and H_2O. By comparing the value so found with the molal solubility in ordinary water, we were able, by a short linear extrapolation, to arrive at the solubility per 55.51 moles of pure D_2O.

Experimental Results.—For all but the lower temperature experiments the identical solute material, 0.4086 g. of potassium chloride, was employed with both solvents. The total weight of 98.2% deuterium water employed was 1.39 g., and this was completely recovered in its original purity. In the case of deuterium water, the ratio of mass of solute to solvent was reduced for a few of the lower temperature experiments by using a smaller weight of solute in the apparatus described; and, in the case of ordinary water, by increasing the amount of solvent in separate sealed-tube experiments.

Table I records the results observed in ordinary water in the first two columns and in deuterium water in the third and fourth columns.

These observations were graphed in the manner described previously,[2] and solubility values read off for round values of temperature, as recorded in Table II, where, in the fourth column a comparison is made with the solubility values found in "International Critical Tables."

(1) *Cf.* Taylor, Caley and Eyring, THIS JOURNAL, **55**, 4334 (1933).
(2) Menzies, *ibid.*, **58**, 934 (1936).
(3) Miles and Menzies, *ibid.*, **58**, 1067 (1936).
(4) Leopold and Johnston, *ibid.*, **49**, 1974 (1927).
(5) *Cf.* Cohen and Blekkingh, *Proc. Acad. Sci. Amsterdam*, **38**, 843 (1935).

TABLE I

OBSERVED SOLUBILITY OF POTASSIUM CHLORIDE (74.55) IN ORDINARY WATER AND IN DEUTERIUM WATER

M_{H_2O}, M_{D_2O} = moles KCl in 55.51 moles H_2O, D_2O, respectively

Temp., °C.	M_{H_2O}	Temp., °C.	M_{D_2O}
7.5	4.08	5.3	3.44
18.2	4.56	12.5	3.80
21.2	4.64	20.4	4.23
28.5	4.94	24.7	4.37
58.6	6.04	47.8	5.31
62.7	6.18	71.4	6.20
96.0	7.32	98.7	7.21
127.1	8.41	133.0	8.39
147.2	9.16	150.5	9.02
175.6	10.12	177.4	10.11

Extrapolated values are in italics. The fifth column states the percentage of the solubility value in ordinary water by which that in deuterium water falls short.

TABLE II

SOLUBILITIES OF POTASSIUM CHLORIDE IN ORDINARY WATER AND IN DEUTERIUM WATER AT ROUNDED TEMPERATURES

M_{H_2O}, M_{D_2O} = moles KCl per 55.51 moles H_2O, D_2O, respectively

Temp., °C.	M_{H_2O}	% correction to "I. C. T." values	M_{D_2O}	$100 \times (M_{H_2} - M_{D_2O})/M_{H_2O}$
0	*3.78*	+0.5	*3.16*	*16.4*
10	4.20	+ .2	3.68	12.4
20	4.61	.0	4.16	9.8
25	4.80	− .2	4.38	8.7
30	5.00	− 2	4.59	8.2
40	5.37	− .6	5.01	6.7
60	6.09	−1.0	5.79	4.9
80	6.80	−0.4	6.52	4.1
100	7.51	.0	7.25	3.5
120	8.21	+ .1	7.97	2.9
140	8.89	− .1	8.67	2.5
160	9.57	− .3	9.36	2.2
180	*10.24*	− .6	*10.06*	*1.8*

It will be seen from Table II that the solubility in ordinary water diverges most largely from the "I. C. T." values in the region near 60°. Since the latter values were compiled, new measurements have been made by Scott and Durham,[6] who report solubilities at 50.21, 67.91 and 92.23°. Their values, followed by our own in parentheses for these temperatures, are 5.73 (5.75), 6.35 (6.36) and 7.20 (7.24), respectively. The divergencies here are in the opposite direction from those of "I. C. T."

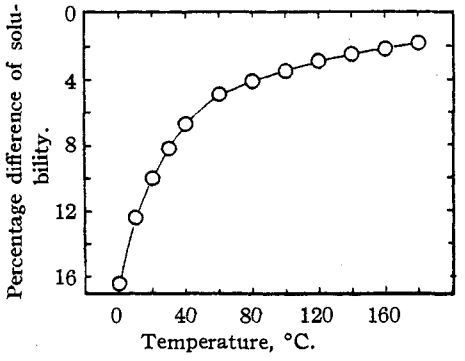

Fig. 1.—Comparison of solubility of potassium chloride in ordinary and in deuterium water.

The error in measurement by the method here used has been discussed elsewhere.[2] The average divergence of the experimentally determined points from our smooth curves was about 0.3% in the present work.

Graphical Comparison.—The diagram, Fig. 1, shows a plot of the values in Table II, column 5, against temperature.

Discussion.—The solubility of potassium chloride increases with temperature faster with deuterium water as solvent than with ordinary water. In addition to the nature of the solvent, another of the factors concerned in this is the heat of ion hydration. This in turn is influenced by the nature and the condition of the solvent.

Inspection of Fig. 1 makes it evident that, passing downward from 180 to about 60°, the change with temperature of the solubility difference is roughly rectilinear. From about 60° downward, the solubility difference increases at a much faster rate than before. This may perhaps be correlated with change with temperature of the average configurations in liquid water.[7] Recalling that the temperature of maximum density for deuterium water is 11.6° as compared with 4.0° for ordinary water, one is led to believe that the forms or structures present in water just above the melting point persist to higher temperatures in the case of deuterium water than of ordinary water.

Contrary to a prevalent belief,[8] in comparing deuterium water with ordinary water as a solvent for salts it must not be thought that the former is a poorer solvent under all circumstances, for such is not the case.[9] Because such facts must be taken into consideration, further discussion will find more appropriate place after the solubility results for other salts have been communicated.

Summary

Values for the solubility of potassium chloride in ordinary water and in deuterium water have been reported in the temperature range 0–180°. The differences in solubility have been briefly discussed.

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(6) Scott and Durham, *J. Phys. Chem.*, **34**, 1434 (1930).
(7) *Cf.* Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).
(8) *Cf.* Hall, Wentzel and Smith, THIS JOURNAL, **56**, 1822 (1934).
(9) *Cf.* Miles, Shearman and Menzies, *Nature*, **138**, 121 (1936).