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THE SOLUBILITIES OF CERTAIN INORGANIC COMPOUNDS IN ORDINARY WATER AND IN DEUTERIUM WATER[1]

ROBERT D. EDDY[2] AND ALAN W. C. MENZIES

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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INTRODUCTION

In the field of solubility in deuterium water, little work has hitherto been published (32, 28, 21). In the present article we contribute the results of solubility measurements, with a 1 per cent accuracy, of fifteen solids in deuterium water, with a comparison of analogous systems in ordinary water, embracing temperatures in the range from near 0°C. to 105–180°C. It is hoped that the collection of such data of reasonably good precision and through a wide temperature range may help in throwing light on the general question of solubility in non-ideal solutions.

METHOD

The method used was that described by Menzies (20), which uses about 1 g. of solvent (later completely recovered), gives an accuracy of the order of 1 per cent, and is adaptable to both high and low solubilities and to high

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[1] This article reports essential portions of the dissertation presented by Robert D. Eddy to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1938.

[2] Present address: Department of Chemistry, Tufts College, Massachusetts.

and low temperatures. The details of the apparatus have been set forth in earlier publications (20, 21), but, in order to assist others who may wish to use this method, certain comments are here added to the earlier descriptions.

(*a*) Before opening the seal after the apparatus has been charged, it is well to reduce the aqueous pressure above the water by cooling it. Otherwise a portion of the seal when melted may be carried over into and admixed with the solid under investigation. (*b*) It is better to place the constriction for the seal on the side of the apparatus distant from, rather than next to, the part containing the solute. (*c*) A mixture of silver chloride with silver iodide containing 43.9 molecular per cent of the former was found most satisfactory. (*d*) Silver iodide containing, as here used, a low concentration of silver chloride in solid solution undergoes enantiomorphic change somewhat below 135°C. The (cubic) high-temperature form has a smaller specific volume than the (hexagonal) low-temperature form. For this reason, the seal is particularly close-fitting below 135°C. In order that leakage shall not occur immediately above 135°C., it is essential that the constriction in the glass which is to be closed by the silver salts shall be of hour-glass shape, and not merely tubular. Consideration of the adjacent schematic diagram (figure 1) will show that, if the plug of silver halides occupies the volume *AABB* at 130°C., it may be expected to occupy the new volume *A'A'B'B'* at 140°C. and that the plug will still be tight because it shrinks alike in each dimension. (*e*) Because of the considerable increase in volume of silver iodide (3) as it passes upon cooling through its inversion point above 135°C., mixtures of the chloride and iodide that are too rich in iodide may cause fracture of a thick-walled cylindrical Pyrex capillary when the temperature falls below 135°C. (*f*) Complete assurance of absence of leakage through the seal is furnished by identity of the volume of unused water before and after each experiment. (*g*) Because of the high viscosity exhibited by certain of the solutions encountered in the present work, the dimensions of the tube containing

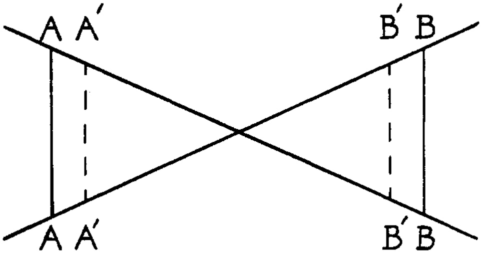

FIG. 1. Contraction of a solid in an hour-glass container

the solute were modified from their former values to a length of 6 cm. and a bore of 8 mm. This tube was attached to the rest of the apparatus through an upright tube of 6-mm. bore. (*h*) A few graduations were etched upon the tube that contained the solution, so that its volume at any temperature could be measured as an aid in determining the volume of water present above the solution in the vapor phase.

Securing and measuring temperatures for equilibrium

For temperatures below 25°C., the apparatus was, in a few cases, immersed in a stirred water thermostat of 320-liters capacity. More usually, for all temperatures below 85°C., the apparatus was submerged in a 4-liter beaker of water, suitably jacketed and adequately stirred. Heat was supplied either by the air of the room (when this was warmer than the experimental vessel), by the lamp bulb used for illumination, suitably screened, or by the additional aid of two knife-form resistance heaters supplied with regulated and metered current. For temperatures above 85°C., the apparatus was placed in a well-insulated air oven, of 1-cu. ft. capacity, with strong internal illumination, distributed heating elements supplied with metered and controlled current, and fan stirring.

Temperatures were measured as previously described (20) but in certain cases with an accuracy of ±0.02°C. instead of ±0.1°C. in the region below 85°C., as controlled by certificated thermometers.

Correction for weight of water in the vapor phase

The volume of such water vapor, which is obviously absent from the liquid solution, was readily obtained from the known volume of the apparatus. But recorded values for the aqueous pressure over the saturated salt solutions at various temperatures are scanty in the case of solutions in ordinary water and entirely lacking for solutions in deuterium water. The value of such correction becomes significant only above 70°C. In the present work, the correction exceeded 2.7 per cent of the solubility value only in one case, an observation at 203.8°C. It can thus be understood that a knowledge of the aqueous pressure over the saturated solutions need not usually be more accurate than 5 per cent, and this only for temperatures above 150°C. A sufficiently accurate value of the aqueous pressures over saturated solutions in deuterium water could be obtained by reducing the values for solutions of like concentration in ordinary water in the ratio of the vapor pressure of pure deuterium water to that of ordinary water at the temperature concerned. These ratios are known (22).

In order to obtain estimates of the aqueous pressure over our solutions in ordinary water, we employed the method of plotting R, relative molal lowering, against molal concentration (18), utilizing the values of R for 100°C. found in the *International Critical Tables* (16 (b)). When the change of R with temperature for identical solutions was known it was small in amount, but due correction was applied for such departure from Babo's law. In case better values for these aqueous pressures should later become available, we have been careful to state in the "a" tables below the actual values of the pressures as used by us for this correction in each case.

In the case of sodium sulfate, direct measurements of the aqueous pressure over its saturated solutions were available. In the cases of cadmium iodide and mercuric chloride we were able with some confidence to utilize Raoult's law to obtain approximate values. The work of Beckmann (1) and of Landsberger (17) has shown that aqueous solutions of these salts are little abnormal.

PURITY OF MATERIALS

Ordinary water. Water from a block-tin still of 350-gallons capacity was boiled in a Pyrex flask for 10 min., and then the flask was stoppered, to keep out air. Investigation had previously shown that the specific conductivity of water thus treated is 5.3×10^{-6} mhos.

Deuterium water. Thirty cubic centimeters of a 2 per cent solution of sodium deuteroxide in 92 per cent deuterium water was electrolyzed to one-sixth of its volume. This was normalized with dried carbon dioxide and distilled twice under reduced pressure at 60°C. The resulting water had a freezing point of 3.80°C.±0.02°, corresponding to a purity of 99.4 per cent. Of the original 5 cc. prepared, but 1 cc. remained at the end, the rest having been lost by accidental dilution during the course of the investigation.

Sodium chloride. Merck's "reagent" sodium carbonate was recrystallized twice above 36°C., and sodium chloride was obtained from this by precipitation from a concentrated solution with an excess of redistilled Grasselli "reagent" hydrochloric acid. This was twice recrystallized from distilled water, and dried by heating to incipient fusion for 20 min.

Sodium bromide. Baker's C.P. sodium bromate was recrystallized twice from water and then decomposed by fusion to sodium bromide. Fusion was continued until the addition of a few drops of sulfuric acid to a solution of the salt failed to give a brown coloration. This salt was recrystallized twice from distilled water and dried at 400°C. for 2 hr.

Sodium iodide. Baker's C.P. ammonium iodide and Merck's "reagent" sodium carbonate were recrystallied twice from water solution, the latter above 36°C. An excess of the ammonium iodide was added to a concentrated solution of the sodium carbonate, the resulting solution evaporated, and the solid material heated to fusion. The salt was then recrystallized three times from water, and dried for 3 hr. at 350°C. A solution of this salt was found to be colorless and neutral to litmus.

Sodium sulfate. Merck's "reagent" sodium sulfate was recrystallized three times above 35°C. and dried for 2 hr. at 500°C.

Potassium bromide. Merck's "reagent" potassium bromate was twice recrystallized from water and then decomposed by fusion in the same manner as was the sodium bromate. The resulting potassium bromide was recrystallized twice from water and dried by heating to 500°C. for 2 hr.

Potassium iodide. Baker's C.P. potassium iodide was recrystallized three times from water and dried for 3 hr. at 350°C.

Barium chloride. Baker's "reagent" barium chloride was recrystallized once from water alone and twice by dissolving it in a minimum amount of water and precipitating it by the addition of alcohol. It was again recrystallized from water and dried for 3 hr. at 350°C.

Cadmium iodide. Merck's "reagent" cadmium iodide was recrystallized once from water solution, once from 95 per cent ethyl alcohol solution, and again from water solution. It was then dried for 2 days at 150°C.

Mercuric chloride. Baker's "reagent" mercuric chloride was tested for impurities and used without further purification. It was dried for 2 days at 150°C.

MANNER OF CALCULATING AND OF STATING RESULTS, AND THEIR ESTIMATED ACCURACY

Solubilities are here stated in number of moles of anhydrous salt per 55.51 moles of water considered as H_2O or D_2O, respectively, conformably to the practice of *International Critical Tables.* This we shall call the molal solubility. The method of reducing the experimental results has been already described elsewhere (28). The density of our (99.4 per cent) deuterium water was taken as $d_{25^\circ}^{25^\circ} = 1.1076$. The molecular weight of H^1 was taken as 1.0081 and of H^2 as 2.0134.

For each salt two tables are given; those lettered "a" stating experimental values and those lettered "b" stating values at rounded temperatures obtained by the graphic method outlined elsewhere (20).

In both "a" and "b" tables, T signifies temperature Centigrade, M molal solubility as above defined; m following a value of M means that the solid phase is metastable.

In "a" tables, S refers to the grams of anhydrous salt used in the apparatus, W to the number of grams of water measured into the solution side of the apparatus, V to the estimated volume of the vapor phase in cubic centimeters, P to the estimated pressure of the water vapor in millimeters of mercury, C to the number of grams of water calculated to be present as vapor. The letter "a" following a few values of S in tables 4a, 5a, and 9a indicates that these points were obtained by measurements made in individual sealed Pyrex tubes by the customary synthetic method.

In "b" tables, in which the style and symbology of *International Critical Tables* have been followed, the heading "I.C.T." designates values of M_{H_2O} extracted from these tables, an asterisk * indicates a value of M_{H_2O} derived from other work not our own, D represents $M_{H_2O} - M_{D_2O}$, $\%D$ represents $D \times 100/M_{H_2O}$, and U placed after a value of M indicates that a transition in the solid phase occurs at this concentration and temperature.

A discussion of error in this method of solubility determination has been given elsewhere (20). It may be stated broadly that molal solubilities are estimated to be accurate within 1 per cent. Since the difference values tabulated under D and $\%D$ are arrived at by subtraction of two much larger quantities, their percentage error is much higher and can be estimated by inspection of the molal solubilities from which they are derived. The terminal digits of these values therefore often lack rigid significance.

TABLE 1a

Observed solubility of sodium chloride (58.454) in ordinary water and in deuterium water

(1) Ordinary water

T	*S*	*W*	*V*	*P*	*C*	*M*
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
101.9	0.3394	0.8691	3.21	601.	0.0015	6.69
168.3	0.3394	0.7780	3.17	3968.	0.0082	7.54

(2) Deuterium water

T	*S*	*W*	*V*	*P*	*C*	*M*
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
−3.8	0.3040	1.0454				5.53
1.7	0.3040	1.0356				5.58
11.7	0.3040	1.0181				5.68
19.7	0.2753	0.9134				5.73
28.2	0.3040	0.9957				5.81
61.5	0.2753	0.8679				6.04
110.8	0.2753	0.8007	3.51	787.	0.0023	6.55
144.1	0.3040	0.8400	3.33	2166.	0.0055	6.92
180.3	0.3040	0.7910	3.40	5258.	0.0127	7.42

The accuracy of transition temperatures arrived at from points of intersection of solubility curves is dependent on their angle of intersection, and absolute values can seldom be expected to be better than ±0.2°C. in the present work.

COMMENTS UPON THE INDIVIDUAL SALTS

Sodium chloride. The values for the molal solubility of this salt in ordinary water as given in *International Critical Tables* are stated to have an estimated accuracy of 0.2 per cent below 55°C., and of 0.5 per cent in the range 60°C. to 110°C., above which the accuracy is unknown. As tests in the higher temperature ranges we made the two measurements recorded in table 1a. At 101.9°C. and 168.3°C. the molal solubilities found were

6.69 and 7.54, respectively, while interpolation from I.C.T. values yields 6.72 and 7.55. This concordance was sufficiently satisfactory to warrant our utilizing unchanged the I.C.T. values for the solubility of sodium chloride in ordinary water.

TABLE 1b

Solubilities of sodium chloride in ordinary water and in deuterium water at rounded temperatures

T	I.C.T.	M_{D_2O}	D	% D
°C.				
−5		(5.53)		
0	6.10 m	5.56	0.54	$8._9$
0.15	6.10 U	5.56	0.54	$8._9$
5	6.10	5.60	0.50	$8._2$
10	6.11	5.64	0.47	$7._7$
15	6.12	5.68	0.44	$7._2$
20	6.13	5.72	0.41	$6._7$
25	6.145	5.76	0.385	$6._3$
30	6.165	5.79	0.375	$6._1$
35	6.18	5.83	0.35	$5._7$
40	6.215	5.87	0.345	$5._6$
45	6.24	5.91	0.33	$5._3$
50	6.26	5.95	0.31	$5._0$
55	6.29	5.99	0.30	$4._8$
60	6.33	6.03	0.30	$4._7$
65	6.37	6.07	0.30	$4._7$
70	6.41	6.12	0.29	$4._5$
75	6.45	6.16	0.29	$4._5$
80	6.50	6.21	0.29	$4._5$
85	6.55	6.26	0.29	$4._4$
90	6.60	6.31	0.29	$4._4$
95	6.65	6.36	0.29	$4._4$
100	6.70	6.42	0.28	$4._2$
105		6.47		
110	6.81	6.52	0.29	$4._3$
115		6.58		
120	6.93	6.64	0.29	$4._2$
125		6.70		
130	7.06	6.76	0.30	$4._2$
135		6.82		
140	7.19	6.88	0.31	$4._3$
145		6.95		
150	7.32	7.01	0.31	$4._2$
155		7.08		
160	7.45	7.14	0.31	$4._2$
165		7.21		
170	7.58	7.28	0.30	$4._0$
175		7.35		
180	7.71	7.42	0.29	$3._8$

One determination of the solubility of sodium chloride in 92 per cent deuterium water at 25°C. is to be found in the literature (32). Converted to molal solubility in 100 per cent deuterium water on the assumption that divergencies in solubility are linear with the change in solvent, this determination gives $M_{D_2O} = 5.72$ at 25°C., with which our value, 5.76, is in satisfactory concordance.

Sodium bromide. Values for the solubility in ordinary water of this salt are reported in I.C.T. up to 120°C. only, and with an estimated accuracy of 2 per cent. We believe their accuracy is higher than this, for no one of these values differs by as much as 2 per cent from the values reported by us in table 2b. Intersection of our solubility curves for the dihydrate and the anhydrous salt occurs at 50.8°C. Richards and Wells (26) reported 50.67°C. for this transition temperature.

In the case of the corresponding system with deuterium water, our value of 47.4°C. for the transition temperature may be compared with that of Bell (2), 47.7°C.

Sodium iodide. I.C.T. reports values for solubility in ordinary water only to 100°C., with an accuracy estimated at 2 per cent. We believe the degree of accuracy is here again understated, for our values, reported in table 3b, in no case diverge by as much as 2 per cent. The temperature of the transition from dihydrate to anhydrous sodium iodide is given by Panfilow (23) as 64.3°C. and by I.C.T. as 68.9°C. Our solubility curves for these salts intersect at 68.2°C. For the analogous system with deuterium water our value is 66.0°C.

While seeking for metastable points on the solubility curves of the anhydrous salts below these transition temperatures, we discovered the existence of a metastable hydrate which has not hitherto been reported. Three experimental points on the solubility curve of this new hydrate are shown in table 3a, as are also three points on the solubility curve of the analogous deuterate. The temperatures of transition to anhydrous salt, as shown by the points of intersection of the appropriate solubility curves, are 60.0°C. and 58.2°C. for hydrate and deuterate, respectively. We were unable to determine with certainty the formulae of these new compounds because of their instability when removed from a closed glass system.

Sodium sulfate. At temperatures below 50°C. the viscosity of the solutions caused some inconvenience. Since the solubility of the decahydrate has been much studied, the values of I.C.T. are there stated to have a 1 per cent accuracy. We therefore confined ourselves to a single measurement at 24.8°C., which showed concordance to 0.5 per cent with these values.

In the case of the metastable heptahydrate, the experimental work has been scanty (10, 19, 24) and has been interpreted very differently by different tabulators. As a consequence of this, the transition temperature

TABLE 2a

Observed solubility of sodium bromide (102.913) in ordinary water and in deuterium water

(1) Ordinary water

T	S	W	V	P	C	M
$NaBr\cdot 2H_2O$						
°C.	grams	grams	cc.	mm.	grams	
−3.1	1.0074	1.2852				7.62
8.4	1.0074	1.1912				8.22
24.3	1.0074	1.0681				9.16
40.5	1.0074	0.9443				10.37
49.0	1.0074	0.8771				11.16
50.1_5	1.0074	0.8658				11.31
50.9_5	1.0074	0.8578				11.41 m
NaBr						
47.1	1.0074	0.8605				11.38 m
53.9	1.0074	0.8578				11.41
72.9	1.0074	0.8465				11.56
97.3	1.0074	0.8278	3.21	348.	0.0009	11.84
120.1	1.0074	0.8059	3.25	730.	0.0017	12.17
144.6	1.0074	0.7739	3.30	1440.	0.0033	12.70
171.2	1.0074	0.7380	3.38	2599.	0.0057	13.37

(2) Deuterium water

T	S	W	V	P	C	M
$NaBr\cdot 2D_2O$						
°C.	grams	grams	cc.	mm.	grams	
−2.3	0.6817	0.9814				7.50
10.1	0.6817	0.9038				8.15
23.4	0.6817	0.8241				8.94
35.4	0.6817	0.7475				9.85
39.9_5	0.9892	1.0438				10.24
44.0	0.6817	0.6911				10.66
46.6	0.6817	0.6731				10.94
47.5	0.6817	0.6699				10.99 m
NaBr						
35.0	0.6817	0.6731				10.94 m
50.2	0.6817	0.6699				10.99
57.9	0.6817	0.6667				11.05
75.7	0.6817	0.6581				11.19
99.7	0.6817	0.6395	3.50	369.	0.0011	11.53
122.9	0.9892	0.8979	3.20	786.	0.0020	11.92
132.9	0.6817	0.6093	3.56	1023.	0.0029	12.14
164.9	0.6817	0.5774	3.63	2297.	0.0061	12.88

TABLE 2b

Solubilities of sodium bromide in ordinary water and in deuterium water at rounded temperatures

T	M_{H_2O}	I.C.T.	M_{D_2O}	*D*	% *D*
			$NaBr \cdot 2Aq$		
°*C.*					
−5	(7.53)		(7.37)	0.16	2.$_1$
0	7.77	7.71	7.61	0.16	2.$_1$
5	8.03		7.86	0.17	2.$_1$
10	8.30	8.17	8.13	0.17	2.$_0$
15	8.59		8.42	0.17	2.$_0$
20	8.89	8.77	8.73	0.16	1.$_8$
25	9.20		9.07	0.13	1.$_4$
30	9.54	9.46	9.44	0.10	1.$_0$
35	9.91		9.84	0.07	0.$_7$
40	10.32	10.31	10.27	0.05	0.$_5$
45	10.78		10.75	0.03	0.$_3$
47.4	10.98		10.98 U	0.00	0.$_0$
50	11.29	11.29 U			
50.8	(11.39) U				
			NaBr		
35			10.93 m		
40			10.95 m		
45	(11.37)		10.97 m	0.40	3.$_5$
50	11.38	11.29	11.00	0.38	3.$_3$
55	11.41		11.03	0.38	3.$_3$
60	11.44	11.38	11.07	0.37	3.$_2$
65	11.48		11.11	0.37	3.$_2$
70	11.52		11.16	0.36	3.$_1$
75	11.57		11.21	0.36	3.$_1$
80	11.62	11.60	11.27	0.35	3.$_0$
85	11.67		11.33	0.34	2.$_9$
90	11.73		11.40	0.33	2.$_8$
95	11.80		11.47	0.33	2.$_7$
100	11.87	11.84	11.54	0.33	2.$_8$
105	11.94		11.62	0.32	2.$_7$
110	12.02		11.70	0.32	2.$_7$
115	12.10		11.78	0.32	2.$_6$
120	12.19	12.13	11.87	0.32	2.$_6$
125	12.28		11.96	0.32	2.$_6$
130	12.38		12.06	0.32	2.$_6$
135	12.49		12.16	0.33	2.$_6$
140	12.60		12.27	0.33	2.$_6$
145	12.71		12.38	0.33	2.$_6$
150	12.83		12.49	0.34	2.$_7$
155	12.96		12.61	0.35	2.$_7$
160	13.08		12.74	0.34	2.$_6$
165	13.22		(12.87)	0.35	2.$_6$
170	13.35		(13.01)	0.34	2.$_5$

TABLE 3a

Observed solubility of sodium iodide (149.92) in ordinary water and in deuterium water

(1) Ordinary water

T	S	W	V	P	C	M
			$NaI \cdot 2H_2O$			
°C.	grams	grams	cc.	mm.	grams	
2.3	1.4218	0.8777				10.81
13.0_8	2.2352	1.2976				11.49
37.6_7	2.2352	1.0991				13.56
47.9_7	2.2352	0.9986				14.93
58.9_3	2.2352	0.8808				16.93
62.7_8	2.2352	0.8343				17.87
64.5_7	2.2352	0.8136				18.32
65.6_8	2.2352	0.7957				18.74
67.6_3	2.5465	0.8802				19.30
68.4_3	2.5465	0.8667				19.60 m
			$NaI \cdot xH_2O$			
46.1_6	2.2352	0.8136				18.32 m
51.6_4	2.2352	0.7957				18.74 m
58.3_0	2.5465	0.8802				19.30 m
			NaI			
72.2_9	2.5465	0.8667				19.60
85.2	2.5465	0.8567				19.83
103.0	2.5465	0.8437				20.13
126.9	2.5465	0.8161	2.75	384.	0.0008	20.83
147.7	2.5465	0.7901	2.77	680.	0.0013	21.53
182.9	2.5465	0.7410	2.80	1733.	0.0031	23.02

(2) Deuterium water

T	S	W	V	P	C	M
			$NaI \cdot 2D_2O$			
12.4	1.5440	1.0204				11.22
27.7_8	1.5440	0.9211				12.43
42.5_0	1.5440	0.8140				14.07
54.0_4	2.2352	1.0427				15.89
60.4_5	2.2352	0.9511				17.43
64.0_2	2.4085	0.9657				18.49
64.0_7	2.2352	0.8958				18.49
65.4_4	2.2352	0.8746				18.95
65.5_5	2.4085	0.9400				19.00
			$NaI \cdot xD_2O$			
46.4_5	2.4085	0.9861				18.11 m
51.7	2.2352	0.8958				18.50 m
56.9_0	2.2352	0.8746				18.95 m
			NaI			
62.1	2.4085	0.9337				19.13 m
77.7	2.4085	0.9237				19.33
112.2	2.4085	0.8917				20.03

TABLE 3b

Solubilities of sodium iodide in ordinary water and in deuterium water at rounded temperatures

T	M_{H_2O}	I.C.T.	M_{D_2O}	D	% D
NaI·2Aq					
°C.					
0	(10.68)	10.72	(10.47)	0.21	$2._0$
5	10.96		(10.75)	0.21	$1._9$
10	11.26	11.31	(11.05)	0.21	$1._9$
15	11.59		11.39	0.20	$1._7$
20	11.95	11.98	11.77	0.18	$1._5$
25	12.34		12.18	0.16	$1._3$
30	12.78	12.75	12.64	0.14	$1._1$
35	13.28		13.15	0.13	0.9_8
40	13.85	13.75	13.73	0.12	0.8_7
45	14.50		14.40	0.10	0.6_9
50	15.24	15.13	15.17	0.07	0.4_6
55	16.10		16.09	0.01	0.0_6
60	17.15	17.18	17.23	−0.07	-0.4_1
65	18.47		18.80	−0.33	$-1._8$
66.0	18.78		(19.15) U	−0.37	$-2._0$
68.2	19.56 U				
68.9		19.59 U			
NaI·xAq					
45	(18.24) m		(18.00) m	0.24	$1._3$
50	18.61 m		18.39 m	0.22	$1._2$
55	19.01 m		18.80 m	0.21	$1._1$
58.2	19.26 m		(19.06) m U	0.20	$1._0$
60.0	(19.43) m U				
NaI					
55	(19.38) m		(19.02) m	0.36	$1._9$
60	(19.44) m		(19.08) m	0.36	$1._9$
65	(19.51) m		19.14	0.37	$1._9$
70	(19.58)	19.60	19.21	0.37	$1._9$
75	19.65		19.28	0.37	$1._9$
80	19.72	19.80	19.36	0.36	$1._8$
85	19.80		19.45	0.35	$1._8$
90	19.89	20.00	19.54	0.35	$1._8$
95	19.99		19.64	0.35	$1._8$
100	20.10	20.24	19.75	0.35	$1._7$
105	20.22		19.87	0.35	$1._7$
110	20.35		19.99	0.36	$1._8$
115	20.48		(20.12)	0.36	$1._8$
120	20.63				
125	20.77				

TABLE 3b—*Concluded*

T	M_{H_2O}	I.C.T.	M_{D_2O}	D	% D
		NaI—*Continued*			
°C.					
130	20.92				
135	21.09				
140	21.27				
145	21.45				
150	21.63				
155	21.82				
160	22.02				
165	22.23				
170	22.45				
175	22.67				
180	22.89				

to anhydrous salt found as 24.4°C. from the data of Loewel (19) has been incorporated unchanged in numerous tables, while I.C.T. prefers 28.2°C. The appropriate intersection of our solubility curves lies at 23.7°C. Since our work was completed, an accurate redetermination of this point has been undertaken by Washburn and Clem (34), who find 23.465°C.

The solubility of the anhydrous salt has been much studied, and the values of I.C.T. are therein estimated as accurate to 1 per cent. We found this salt difficult to work with because of its small change in solubility with temperature, and, in this instance, do not prefer our values to those of I.C.T. Only one of our experimental points (at 82.2°C.) gives, however, a solubility differing from these by more than 1 per cent. In comparing solubilities in deuterium water, we have, nevertheless, utilized our own values for solubility in ordinary water, since both our sets of experiments would be subject to similar systematic error (see table 4a). Our solubility curve for the anhydrous salt intersects the solubility curve for decahydrate based upon I.C.T. values at 32.5°C., while I.C.T. reports this intersection at 32.48°C. (16(c)). The accepted value is 32.384°C. (11, 25), which is raised only 0.01°C. by 35 additional atmospheres of pressure.

In the case of the systems with deuterium water, we found the transition temperatures of deca- and hepta-deuterate to anhydrous salt as 34.2°C. and 26.7°C., respectively, from the points of intersection of the appropriate solubility curves. The former point has been reported by others at 34.48°C. (31), 34.5°C. (2), and 34.6-34.9°C. (14); and the latter at 26.6-27.0°C. (14).

Potassium chloride. The solubility of this salt in ordinary water and in deuterium water has already been studied in this laboratory (28). Because

TABLE 4a

Observed solubility of sodium sulfate (142.05) in ordinary water and in deuterium water

(1) Ordinary water

T	S	W	V	P	C	M
			$Na_2SO_4 \cdot 10H_2O$			
°C.	grams	grams	cc.	mm.	grams	
24.8	0.3093	1.1268				1.93_2
			$Na_2SO_4 \cdot 7H_2O$			
2.9	0.2303 a	1.0994				1.47_5 m
8.1	0.3093	1.1268				1.93_2 m
13.4	0.3093	0.8885				2.45_1 m
17.8	0.3864	0.9296				2.92_6 m
20.8	0.3864	0.8258				3.29 m
21.4	0.3093	0.6526				3.34 m
24.1	0.3864	0.7326				3.71 m
			Na_2SO_4			
21.0	0.3093	0.5810				3.75 m
47.5	0.3864	0.8258				3.29
82.2	0.4025 a	0.9486				2.99
114.0	0.3864	0.9296	3.48	1097.	0.0028	2.93_5
134.5	0.3864	0.9296	3.46	2119.	0.0052	2.94
165.8	0.4025 a	0.9486	0.54	5020	0.0018	2.99

(2) Deuterium water

T	S	W	V	P	C	M
			$Na_2SO_4 \cdot 10D_2O$			
°C.	grams	grams	cc.	mm.	grams	
8.7	0.0499	0.8389				0.466
11.5	0.0776	1.0878				0.558
16.2	0.0499	0.4721				0.827
22.4	0.0499	0.2903				1.34_5
26.2	0.2564	1.1124				1.80_4
29.0	0.2564	0.9134				2.19_7
30.5_5	0.2564	0.7933				2.52_9
			$Na_2SO_4 \cdot 7D_2O$			
7.7	0.0499	0.2509				1.55_6 m
10.3	0.2564	1.1124				1.80_4 m
14.3	0.2564	0.9134				2.19_7 m
17.9	0.2564	0.7933				2.52_9 m
24.7	0.4709	1.1124				3.31 m
27.0	0.4709	1.0101				3.65 m
			Na_2SO_4			
24.8	0.4709	1.0101				3.65 m
42.8	0.4709	1.1124				3.31
124.2	0.2564	0.6943	2.35	1468.	0.0028	2.90
152.0	0.2564	0.6950	2.35	3500.	0.0062	2.91
192.7	0.2564	0.6943	2.30	9280.	0.0147	2.95

TABLE 4b

Solubilities of sodium sulfate in ordinary water and in deuterium water at rounded temperatures

T	m_{H_2O}	I.C.T.	m_{D_2O}	*D*	% *D*
$Na_2SO_4\cdot 10Aq$					
°*C.*					
0	0.342*	0.342	(0.267)	0.075	$2_2.$
5	0.428*	0.428	(0.350)	0.078	$1_8.$
10	0.628*	0.628	0.512	0.116	$1_8.$
15	0.920*	0.920	0.770	0.150	$1_6.$
20	1.33*	1.33	1.12	0.21	$1_6.$
25	1.96*	1.96	1.65	0.31	$1_6.$
30	2.88*	2.88	2.42	0.46	$1_6.$
32.48		3.50 U	2.95	0.55	$1_6.$
32.5	3.52 U*		2.97	0.55	$1_6.$
34.2			3.45 U		
$Na_2SO_4\cdot 7Aq$					
0	(1.25) m	1.34 m	(0.99) m	0.26	$2_1.$
5	1.64 m		(1.36) m	0.28	$1_7.$
10	2.10 m	2.14 m	1.77 m	0.33	$1_6.$
15	2.62 m		2.24 m	0.38	$1_5.$
20	3.18 m	2.94 m	2.76 m	0.42	$1_3.$
23.7	3.69 m U		3.20 m	0.49	$1_3.$
25			3.36 m		
26.7			3.60 m U		
28.2		3.59 m U			
Na_2SO_4					
25	3.67 m		3.66 m	0.01	$0._3$
30	3.57 m		3.55 m	0.02	$0._6$
35	3.47	3.45	3.44	0.03	$0._9$
40	3.39	3.40	3.36	0.03	$0._9$
50	3.26	3.28	3.22	0.04	$1._2$
60	3.16	3.19	3.12	0.04	$1._3$
70	3.07	3.11	3.03	0.04	$1._3$
80	3.01	3.05	2.98	0.03	$1._0$
90	2.96	3.00	2.94	0.02	$0._7$
100	2.94	2.97	2.92	0.02	$0._7$
110	2.93	2.96	2.91	0.02	$0._7$
120	2.92	2.95	2.90	0.02	$0._7$
130	2.93	2.95	2.91	0.02	$0._7$
140	2.95	2.96	2.92	0.03	$1._0$
150	2.97		2.92	0.05	$1._7$
160	2.99	3.01	2.93	0.06	$2._0$
170	(3.01)		2.94	0.07	$2._3$
180	(3.02)	3.09	2.95	0.07	$2._3$

of the unexpected position of the curve for potassium chloride in figure 3 below, in relation to the curves for the bromide and iodide of potassium, solubilities in deuterium water were redetermined for potassium chloride at the three temperatures 13.1°, 33.85°, and 151.9°C. In each case the molal solubility found was about 0.5 per cent lower than that of the earlier work. As this falls within the error of experiment, no change in the earlier values was required.

TABLE 5a

Observed solubility of potassium bromide (119.012) in ordinary water and in deuterium water

(1) Ordinary water

T	*S*	*W*	*V*	*P*	*C*	*M*
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
5.0_7	0.7033 a	1.2553				4.71
11.3_6	0.7896 a	1.3168				5.04
18.1_2	1.0975 a	1.7218				5.36
25.2_5	0.6791	0.9968				5.72
34.5_2	0.4683 a	0.6385				6.16
44.6_0	0.6851	0.8736				6.59
60.9	0.6851	0.7961				7.23
76.8	0.7352 a	0.7837				7.88
94.2	0.6851	0.6715	2.48	430.4	0.0008	8.58
101.5	0.3753 a	0.3553	1.58	552.3	0.0007	8.89
129.7	0.8090 a	0.6823	1.55	1306.	0.0015	9.98
159.3	1.0959 a	0.8226	0.81	2717.	0.0015	11.21
193.7	0.7325	0.4948	3.64	5507.	0.0124	12.76

(2) Deuterium water

T	*S*	*W*	*V*	*P*	*C*	*M*
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
8.0	0.4599	1.0321				4.16
12.2	0.4102	0.8678				4.42
20.1	0.4599	0.8847				4.86
31.1_0	0.4102	0.7085				5.41
48.9_8	0.3817	0.5753				6.20
68.7	0.4599	0.6097				7.05
82.7	0.4599	0.5641				7.62
96.2	0.3817	0.4360	2.90	447.4	0.0011	8.19
126.9	0.4599	0.4609	2.88	1198.	0.0022	9.36
167.2	0.4599	0.3975	2.93	3296.	0.0070	11.00
203.8	0.4599	0.3459	2.97	6686	0.0134	12.91

Potassium bromide. The solubility values for this salt found in I.C.T. are therein estimated to have accuracy within 1 per cent below 100°C. and within 5 per cent above 100°C. We believe their accuracy above

100°C. is better than estimated, for our results between 0° and 170°C. nowhere diverge by as much as 1 per cent from their values. We have not carried our table 5b higher than 170°C., because our experimental points above this temperature indicate a change of slope of the solubility curves for both varieties of water which our experimental values are not sufficiently numerous to define. According to Kracek (15) and others, potas-

TABLE 5b

Solubilities of potassium bromide in ordinary water and in deuterium water at rounded temperatures

T	M_{H_2O}	I.C.T.	M_{D_2O}	D	% D
°C.					
0	(4.44)	4.49	(3.63)	0.81	$1_8.$
5	(4.71)		(3.97)	0.74	$1_6.$
10	4.97	4.97	4.28	0.69	$1_4.$
15	5.23		4.57	0.66	$1_3.$
20	5.48	5.42	4.84	0.64	$1_2.$
25	5.71		5.10	0.61	$1_1.$
30	5.94	5.88	5.35	0.59	$9._9$
35	6.16		5.59	0.57	$9._3$
40	6.38	6.31	5.83	0.55	$8._6$
45	6.59		6.05	0.55	$8._3$
50	6.80		6.27	0.53	$7._8$
55	7.01		6.48	0.53	$7._6$
60	7.21		6.69	0.52	$7._2$
65	7.41		6.90	0.51	$6._9$
70	7.61		7.11	0.50	$6._6$
75	7.81		7.31	0.50	$6._4$
80	8.01		7.51	0.50	$6._2$
85	8.21		7.71	0.50	$6._1$
90	8.41		7.91	0.50	$5._9$
95	8.61		8.11	0.50	$5._8$
100	8.81	8.84	8.31	0.50	$5._7$
105	9.01		8.51	0.50	$5._5$
110	9.21	9.2	8.71	0.50	$5._4$
115	9.41		8.91	0.50	$5._3$
120	9.61	9.7	9.11	0.50	$5._2$
125	9.81		9.31	0.50	$5._1$
130	10.01		9.51	0.50	$5._0$
135	10.21		9.71	0.50	$4._9$
140	10.41	10.5	9.91	0.50	$4._8$
145	10.61		10.11	0.50	$4._7$
150	10.81		10.31	0.50	$4._6$
155	11.01		10.51	0.50	$4._5$
160	11.21	11.3	10.71	0.50	$4._5$
165	11.41		10.91	0.50	$4._4$
170	11.61		11.11	0.50	$4._3$

sium iodide likewise shows at higher temperatures a faster increase with temperature of solubility in ordinary water.

Potassium iodide. In the region above 100°C., the solubility values in I.C.T. have been found to be seriously in error by Kracek (15), whose measurements, however, did not embrace temperatures below 50°C. We considered it unnecessary to repeat the work of Kracek, but made the three measurements recorded in table 6a, which agree within 1 per cent with I.C.T. values, in order to extend Kracek's results to 0°C.

TABLE 6a

Observed solubility of potassium iodide (166.02) in ordinary water and in deuterium water

(1) Ordinary water

T	S	W	V	P	C	M
°C.	grams	grams	cc.	mm.	grams	
6.2	1.0154	0.7655				7.99
11.2	1.0154	0.7434				8.23
56.6_5	1.0154	0.5866				10.4_3

(2) Deuterium water

T	S	W	V	P	C	M
°C.	grams	grams	cc.	mm.	grams	
2.6	1.0130	1.0136				6.69
10.7	1.0130	0.9391				7.22
17.8	1.0130	0.8860				7.65
34.0	1.0130	0.7925				8.55
60.3	1.4968	1.0167				9.86
62.7	1.0130	0.6788				9.99
88.6	1.4968	0.8907				11.2_5
118.1	1.4968	0.7894	2.98	744.	0.0018	12.7_2
146.1	1.4968	0.7169	3.01	1597.	0.0037	14.0_5

Barium chloride. No estimate is given in I.C.T. of the accuracy of the stated values of solubility of barium chloride dihydrate. Their maximum discrepancy from our values is little over 1 per cent. We have not tabulated the values of Etard (13) for the monohydrate, because of their lack of precision. Our solubility curves for these two hydrates intersect in the neighborhood of 102°C. Collins and Menzies (9) found this transition at 101.94°C. ± 0.05°.

Taylor, Caley, and Eyring (32) measured the solubility of barium chloride in 92 per cent deuterium water at 20°C. Converted, as described for the similar case of sodium chloride, to solubility in 100 per cent deuterium water, their value for molal solubility is 1.51, as compared with 1.48 found in the present work. The transition temperature of di- to mono-deuterate is found near 93.3°C. Since the two solubility curves intersect at a very unfavorable angle, this temperature is uncertain by 2°C.

Cadmium iodide. Since the solubility values in I.C.T. up to 40°C. taken from the data of Cohen and coworkers (6, 7), are estimated to have an accuracy of ±0.1 per cent, we did not repeat any measurements in this range. Our experimental values for higher temperatures show wide discordance from the values in I.C.T., amounting to 10 per cent at 140°C. (see table 8a). These values are based, apparently, on the work of Etard (13) and on two values of Dietz (12), whose preparations may have differed from ours (5, 29, 8).

TABLE 6b

Solubilities of potassium iodide in ordinary water and in deuterium water at rounded temperatures

T	M_{H_2O}	Kracek (15)	M_{D_2O}	*D*	% *D*
°C.					
0	(7.66)	7.78	(6.52)	1.14	1_5.
5	(7.92)		6.85	1.07	1_4.
10	8.17	8.24	7.17	1.00	1_2.
15	8.42		7.48	0.94	1_1.
20	8.66	8.70	7.78	0.88	1_0.
25	8.90		8.07	0.83	$9._3$
30	9.14	9.17	8.34	0.80	$8._8$
35	9.38		8.60	0.78	$8._3$
40	9.62	9.63	8.85	0.77	$8._0$
45	9.85		9.09	0.76	$7._7$
50	10.09*	10.09	9.34	0.75	$7._4$
55	10.32*		9.59	0.73	$7._1$
60	10.56*	10.56	9.84	0.72	$6._8$
65	10.79*		10.09	0.70	$6._5$
70	11.02*	11.02	10.33	0.69	$6._3$
75	11.25*		10.58	0.67	$6._0$
80	11.49*	11.49	10.82	0.67	$5._8$
85	11.72*		11.06	0.66	$5._6$
90	11.96*	11.96	11.31	0.65	$5._4$
95	12.20*		11.55	0.65	$5._3$
100	12.43*	12.43	11.80	0.63	$5._1$
105	12.67*		12.04	0.63	$5._0$
110	12.91*	12.91	12.29	0.62	$4._8$
115	13.15*		12.53	0.62	$4._7$
120	13.39*	13.39	12.77	0.62	$4._6$
125	13.63*		13.02	0.61	$4._5$
130	13.87*	13.87	13.26	0.61	$4._4$
135	14.12*		13.51	0.61	$4._3$
140	14.37*	14.37	13.75	0.62	$4._3$
145	14.61*		13.99	0.62	$4._2$
150	14.86*	14.86	(14.24)	0.62	$4._2$

Mercuric chloride. Values for M_{H_2O} for this salt differ widely from those in I.C.T. While the accuracy claimed for these latter is but 10 per cent over the whole range 0–100°C., we find closer agreement over most of the range. Nevertheless even wider deviation is found at 60°, 70° and 80°C.,

TABLE 7a

Observed solubility of barium chloride (208.27) in ordinary water and in deuterium water

(1) Ordinary water

T	*S*	*W*	*V*	*P*	*C*	*M*
			$BaCl_2 \cdot 2H_2O$			
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
9.7	0.3053	0.9223				1.59
29.2	0.3053	0.8078				1.81
53.1	0.3053	0.6946				2.11
65.1	0.5200	1.0935				2.28
78.3	0.3053	0.5895				2.49
98.5	0.5200	0.8911	2.81	612.9	0.0013	2.81
			$BaCl_2 \cdot H_2O$			
102.8	0.5200	0.8672	2.82	711.2	0.0015	2.88
113.1	0.5200	0.8499	2.85	1001.	0.0021	2.95
127.8	0.5200	0.8259	2.87	1585.	0.0033	3.04
153.0	0.5200	0.7807	2.92	3193.	0.0063	3.22
168.7	0.5200	0.7567	2.94	4718.	0.0091	3.34
180.0	0.5200	0.7328	2.96	6111.	0.0115	3.46

(2) Deuterium water

T	*S*	*W*	*V*	*P*	*C*	*M*
			$BaCl_2 \cdot 2D_2O$			
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
4.1	0.2046	0.8766				1.24
21.2	0.2046	0.7299				1.50
21.6	0.3074	1.0879				1.51
37.0	0.3074	0.9463				1.73
53.1	0.3074	0.8400				1.95
77.1	0.3402	0.7900				2.30
80.7	0.3074	0.6954				2.36
			$BaCl_2 \cdot D_2O$			
95.5	0.3402	0.7092	3.35	528.1	0.0015	2.56
104.8	0.3402	0.7006	3.37	739.3	0.0021	2.60
119.8	0.3402	0.6751	3.39	1217.	0.0034	2.70
135.0	0.3402	0.6539	3.42	1936.	0.0052	2.80
159.3	0.3402	0.6178	3.47	3751.	0.0097	2.98
179.7	0.3402	0.5869	3.50	6075.	0.0151	3.17

TABLE 7b

Solubilities of barium chloride in ordinary water and in deuterium water at rounded temperatures

T	m_{H_2O}	I.C.T.	m_{D_2O}	D	% D
$BaCl_2 \cdot 2Aq$					
°C.					
0	(1.50)	1.52	(1.19)	0.31	2_1.
5	(1.55)		1.26	0.29	1_9.
10	1.61	1.61	1.33	0.28	1_7.
15	1.66		1.41	0.25	1_5.
20	1.72	1.72	1.48	0.24	1_4.
25	1.78		1.55	0.23	1_3.
30	1.83	1.83	1.62	0.21	1_1.
35	1.89		1.70	0.19	1_0.
40	1.96	1.94	1.77	0.19	$9._7$
45	2.02		1.84	0.18	$8._9$
50	2.08		1.92	0.16	$7._7$
55	2.15		1.99	0.16	$7._4$
60	2.22		2.06	0.16	$7._2$
65	2.29		2.14	0.15	$6._6$
70	2.37		2.21	0.16	6.[illegible]
75	2.44		2.28	0.16	6.[illegible]
80	2.52		2.35	0.17	$6._7$
85	2.60		2.43	0.17	$6._5$
90	2.68		2.50	0.18	$6._7$
93.3	2.74		2.54 U	0.20	$7._3$
95	2.76				
100	2.85	2.82			
102.1	2.88 U				
$BaCl_2 \cdot Aq$					
95			2.55		
100			2.58		
105	2.89		2.61	0.28	$9._7$
110	2.92		2.64	0.28	$9._6$
115	2.95		2.67	0.28	$9._5$
120	2.98		2.70	0.28	$9._4$
125	3.01		2.73	0.28	$9._3$
130	3.04		2.76	0.28	$9._2$
135	3.07		2.79	0.28	$9._1$
140	3.11		2.83	0.28	$9._0$
145	3.15		2.87	0.28	$8._9$
150	3.19		2.91	0.28	$8._8$
155	3.23		2.95	0.28	$8._7$
160	3.27		2.99	0.28	$8._6$
165	3.31		3.03	0.28	$8._5$
170	3.36		3.08	0.28	$8._3$
175	3.41		3.12	0.29	$8._5$
180	3.46		(3.17)	0.29	$8._4$

temperatures for which other experimental data are scarce. The solubility of this salt changes fifteenfold in the range studied. When this is represented on a single graph, error in graphing causes the greatest percentage error at low solubility, where also the percentage error of experiment is greatest. In the neighborhood of 70°C., however, such error is no longer excessive. Our value is there about 16 per cent higher than that of I.C.T. and about 2 per cent lower than a value published by Sugden (30) in 1929.

TABLE 8a

Observed solubility of cadmium iodide (366.25) in ordinary water and in deuterium water

(1) Ordinary water

T	S	W	V	P	C	M
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
76.9	1.0513	0.9642				2.98
99.1	0.6024	0.4813	3.30	708.0	0.0018	3.43
131.2	1.0513	0.7009	3.42	1950.	0.0048	4.12
155.1	1.0513	0.6012	3.51	3801.	0.0090	4.85

(2) Deuterium water

T	S	W	V	P	C	M
°C.	*grams*	*grams*	*cc.*	*mm.*	*grams*	
1.7	0.4266	0.8491				1.52
11.1	0.4266	0.8026				1.61
24.4	0.4266	0.7395				1.75
44.4	0.3900	0.6008				1.97
57.7	0.7027	1.0104				2.11
78.9	0.7027	0.8800				2.42
96.9	0.7027	0.7708	3.64	653.0	0.0019	2.77
115.0	0.7027	0.6893	3.70	1175.	0.0035	3.11
125.9	0.7027	0.6289	3.76	1652.	0.0048	3.42
137.4	0.7027	0.5812	3.85	2333.	0.0068	3.71
149.4	0.7027	0.5356	3.94	3251.	0.0095	4.05

EXPRESSION OF SOLUBILITY DIFFERENCES

One may, for example, plot the values of $\%D$ for each salt either (*a*) against temperature or (*b*) against M_{H_2O}, the molal solubility of the saturated solution in ordinary water at the temperature of comparison. With the salts here studied, a more open diagram is obtained by method (*b*), which we have employed for figure 2. On this are included for comparison, in addition to salts described above, cupric sulfate pentaquate, strontium chloride hexaquate and diaquate, and potassium chloride from other work in this laboratory (21, 28). Figure 3 shows a plot by method (*a*) for halides of potassium and sodium.

It should be emphasized that the smaller the values of %*D*, the more subject are they to inevitable uncertainty.

TABLE 8b

Solubilities of cadmium iodide in ordinary water and in deuterium water at rounded temperatures

T	M_{H_2O}	I.C.T.	M_{D_2O}	*D*	% *D*
°*C.*					
0	2.16	2.155	(1.50)	0.66	3_1.
5	2.19		1.54	0.65	3_0.
10	2.23	2.230	1.59	0.64	2_9.
15	2.27		1.64	0.63	2_8.
20	2.31	2.312	1.69	0.62	2_7.
25	2.35		1.74	0.61	2_6.
30	2.40	2.404	1.79	0.61	2_5.
35	2.45		1.84	0.61	2_5.
40	2.51	2.506	1.90	0.61	2_4.
45	2.56		1.96	0.60	2_3.
50	2.62		2.02	0.60	2_3.
55	2.68		2.09	0.59	2_2.
60	2.74	2.77	2.16	0.58	2_1.
65	2.81		2.23	0.58	2_1.
70	2.88		2.30	0.58	2_0.
75	2.95		2.38	0.57	1_9.
80	3.03	3.09	2.46	0.57	1_9.
85	3.11		2.54	0.57	1_8.
90	3.19		2.63	0.56	1_8.
95	3.28		2.72	0.56	1_7.
100	3.38	3.48	2.81	0.57	1_7.
105	3.48		2.91	0.57	1_6.
110	3.59		3.01	0.58	1_6.
115	3.70		3.12	0.58	1_6.
120	3.82	3.96	3.24	0.58	1_5.
125	3.94		3.36	0.58	1_5.
130	4.07		3.48	0.59	1_4.
135	4.21		3.61	0.60	1_4.
140	4.35	4.74	3.75	0.60	1_4.
145	4.50		3.89	0.61	1_4.
150	4.67		(4.04)	0.63	1_3.
155	4.84				
160	(5.02)				

TRANSITION TEMPERATURES AND MELTING POINTS

In table 10 we have set down data for nine transitions studied in this laboratory. In comparing, in column 4, by difference in temperature the transition points in systems with ordinary and dueterium water, we have utilized values for each obtained by like methods, when two such values were available.

Inspection of table 10 makes clear that the differences of temperature for analogous transitions may be in either direction. Pure water, sodium sulfate heptahydrate, and sodium sulfate decahydrate show difference values of −3.82°, −3.0°, and −2.1°C. at 0°, 23.7°, and 32.4°C., respectively, an orderly succession not out of harmony with a suggestion of Bernal and Fowler (4) that water in certain hydrates is in an ice-like arrangement.

TABLE 9a

Observed solubility of mercuric chloride (271.524) in ordinary water and in deuterium water

(1) Ordinary water

T	S	W	V	P	C	M
°C.	grams	grams	cc.	mm.	grams	
0.9	0.1344 a	2.8674				0.173
20.9$_3$	0.0627	0.9477				0.244
39.2$_5$	0.0627	0.6082				0.380
55.8$_5$	0.0627	0.4078				0.566
62.7	0.1766	0.9467				0.687
75.4	0.1766	0.6539				0.995
91.6	0.4132	0.9457	3.15	542.	0.0014	1.612
99.7	0.4132	0.7230	3.36	724.	0.0019	2.110
105.6	0.4132	0.5511	3.60	880.	0.0024	2.773

(2) Deuterium water

T	S	W	V	P	C	M
°C.	grams	grams	cc.	mm.	grams	
8.1	0.0279	0.8831				0.129
18.7	0.0279	0.6733				0.170
27.2	0.0279	0.5366				0.213
48.9	0.0796	0.8831				0.369
57.4	0.0796	0.7037				0.463
67.3	0.0796	0.5382				0.605
91.2	0.2612	0.8831	3.30	510.	0.0015	1.212
105.1	0.2612	0.5308	3.73	835.	0.0028	2.024

These transition temperatures are points of incongruent melting. The congruent melting points for these hydrates would lie at concealed maxima on the solubility–temperature curves. The molecular composition of corresponding hydrates and deuterates is, of course, identical. Thus the maxima, for corresponding salts, fall at the same position on the composition axis. The relative positions and slopes of the two analogous solubility curves, as they approach this identical composition, will indicate which will cross this composition at the lower temperature, that is, which will have the lower congruent melting point. Inspection of figure 2 shows if and where any two analogous solubility curves cross, thus making it possible to predict which of the two curves will be at the higher temperature when it reaches its maximum at the composition of the hydrate. Consequently we see that the congruent melting points of $SrCl_2 \cdot 6D_2O$, $SrCl_2 \cdot 2D_2O$, $NaBr \cdot 2D_2O$ and $NaI \cdot 2D_2O$ must lie at lower temperatures than do those of the corresponding hydrates. For example, if one extrapolates the solubility curves of $NaI \cdot 2H_2O$ and $NaI \cdot 2D_2O$ to maxima at the composition $M = 27.75$ (which corresponds to the formula), one finds that the congruent melting points should lie near 80°C., with the deuterate melting point a degree or two lower than that of the hydrate.

TABLE 9b

Solubilities of mercuric chloride in ordinary water and in deuterium water at rounded temperatures

T	M_{H_2O}	I.C.T.	M_{D_2O}	D	$\%D$
°C.					
0	(0.172)	0.170	(0.100)	0.072	4_2.
5	0.184		(0.120)	0.064	3_6.
10	0.200	0.204	0.140	0.060	3_0.
15	0.220		0.160	0.060	2_7.
20	0.243	0.246	0.180	0.063	2_6.
25	0.269		0.202	0.067	2_5.
30	0.300	0.300	0.226	0.074	2_5.
35	0.335		0.253	0.082	2_4.
40	0.376	0.366	0.284	0.092	2_4.
45	0.426		0.321	0.105	2_5.
50	0.486	0.466	0.367	0.119	2_4.
55	0.557		0.426	0.131	2_4.
60	0.640	0.554	0.496	0.144	2_3.
65	0.738		0.569	0.169	2_3.
70	0.853	0.714	0.651	0.202	2_4.
75	0.985		0.748	0.237	2_4.
80	1.140	0.980	0.865	0.275	2_4.
85	1.325		1.006	0.319	2_4.
90	1.546	1.41	1.177	0.369	2_4.
95	1.801		1.378	0.423	2_3.
100	2.151	2.06	1.637	0.514	2_4.
105	2.705		2.018	0.687	2_5.

The contrary case is exhibited by $Na_2SO_4 \cdot 10Aq$. Inspection of figure 2 shows that the solubility curve of $Na_2SO_4 \cdot 10D_2O$ is quite unlikely to lie lower in temperature than the curve for $Na_2SO_4 \cdot 10H_2O$ as they pass through their maxima at $M = 5.55$, for there is no indication that the curves will cross before reaching that composition. The graph on figure 2 will approach nowhere near the zero per cent horizontal if extrapolated to $M = 5.55$.

It thus appears that, when deuterium water forms compounds with salts entirely analogous to compounds with ordinary water, the congruent melt-

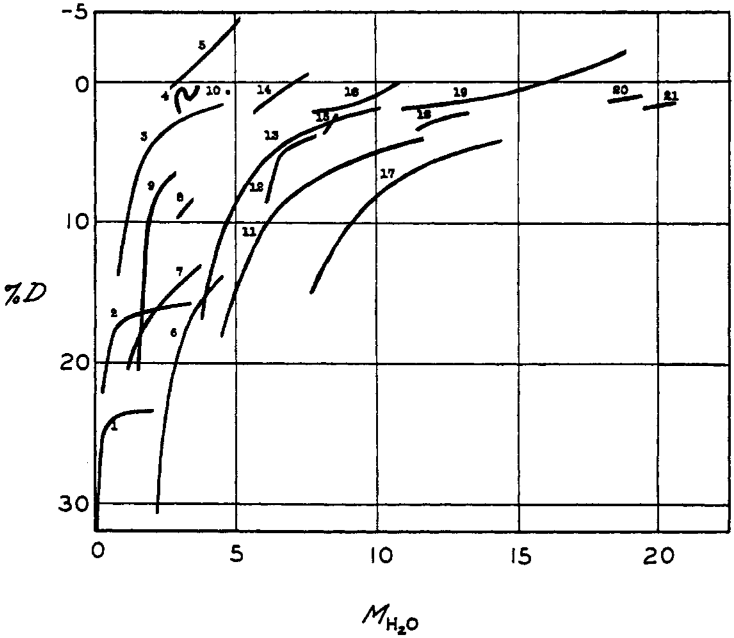

FIG. 2. Graph of %D against M_{H_2O} for certain salts and salt aquates

NO.	SOLID PHASE	RANGE IN °C.	NO.	SOLID PHASE	RANGE IN °C.
1	$HgCl_2$	10–105	11	KBr	0–170
2	$Na_2SO_4 \cdot 10Aq$	0–32	12	NaCl	0–180
3	$CuSO_4 \cdot 5Aq$	3–95	13	KCl	0–180
4	Na_2SO_4	25–180	14	$SrCl_2 \cdot 2Aq$	62–128
5	$SrCl_2 \cdot 6Aq$	0–56	15	$SrCl_2 \cdot Aq$	135–145
6	CdI_2	0–150	16	$NaBr \cdot 2Aq$	45–170
7	$Na_2SO_4 \cdot 7Aq$	0–23	17	KI	0–150
8	$BaCl_2 \cdot Aq$	105–180	18	NaBr	45–170
9	$BaCl_2 \cdot 2Aq$	0–93	19	$NaI \cdot 2Aq$	0–66
10	$CuSO_4 \cdot 3Aq$	100–110	20	$NaI \cdot xAq$	45–60
			21	NaI	55–115

ing points of the deuterium compounds may be either higher or lower than those of their analogues. Such congruent melting points may doubtless be realized, and not merely predicted for metastable phases, in suitably chosen cases.

An examination of merely the few cases before us might make it appear that the relative temperatures of the (unrealized) congruent melting points were always in the same sense as those of the (realized) incongruent melting points. This is not necessarily the case, for the extrapolated

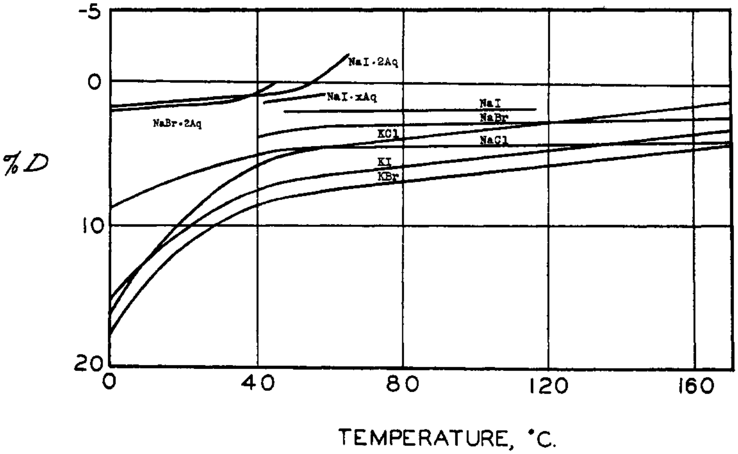

FIG. 3. Graph of %D against temperature in °C. for halides of sodium and potassumi

TABLE 10

The transition temperatures of some salt deuterates and their corresponding hydrates

TRANSITION	TEMPERATURES		
	Hydrates	Deuterates	Difference
	°C.	°C.	°C.
$NaBr\cdot 2Aq \rightleftharpoons NaBr + 2Aq$	50.8	47.4	3.4
	50.674 (26)	47.7 (2)	
$NaI\cdot 2Aq \rightleftharpoons NaI + 2Aq$	68.2	66.0	2.2
	64.3 (23)		
$NaI\cdot xAq \rightleftharpoons NaI + xAq$	60.0	58.2	1.8
$Na_2SO_4\cdot 10Aq \rightleftharpoons Na_2SO_4 + 10Aq$	32.5	34.2	
	32.384 (11)	34.48 (31)	−2.1
		34.5 (2)	
		34.6–34.9 (14)	
$Na_2SO_4\cdot 7Aq \rightleftharpoons Na_2SO_4 + 7Aq$	23.7	26.7	−3.0
	23.46 (34)	26.6–27 (14)	
$CuSO_4\cdot 5Aq \rightleftharpoons CuSO_4\cdot 3Aq + 2Aq$	95.9 (9)	96.2 (21)	−0.3
$BaCl_2\cdot 2Aq \rightleftharpoons BaCl_2\cdot Aq + Aq$	102.1	93.3	8.8
	101.94 (9)		
$SrCl_2\cdot 6Aq \rightleftharpoons SrCl_2\cdot 2Aq + 4Aq$	61.4 (20)	56.4 (21)	5.0
	61.34 (27)	56.5 (2)	
$SrCl_2\cdot 2Aq \rightleftharpoons SrCl_2\cdot Aq + Aq$	134.4 (20)	128.5 (21)	5.9

graph for $CuSO_4 \cdot 5Aq$ in figure 2 may, for example, cross the zero line before reaching the composition $M = 11.1$ (which corresponds to the formula).

Further discussion will find place in the light of additional experimental facts.

SUMMARY

1. The solubilities in ordinary water of NaCl, $NaBr \cdot 2H_2O$, NaBr, $NaI \cdot 2H_2O$, $NaI \cdot xH_2O$, NaI, $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot 7H_2O$, Na_2SO_4, KBr, KI, $BaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot H_2O$, CdI_2, and $HgCl_2$ have been studied, chiefly by a method proposed by Menzies, over their ranges of existence within the interval 0°C. to 105–180°C.

2. A similar study has been made of the analogous systems in deuterium water.

3. The resulting molal solubility values and their differences in the two systems have been tabulated for rounded temperatures at intervals of 5°C. Differences were found to range from −2.0 to +42 per cent.

4. From the intersection of solubility curves, the transition temperatures of six hydrates and six analogous deuterates have been evaluated and compared. These were all incongruent melting points, and were sometimes lower and sometimes higher for deuterates than for their analogous hydrates. It is predicted that the same will be true for congruent melting points of such compounds.

5. The existence has been uncovered of a new hydrate of sodium iodide, and of the analogous deuterate.

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THE CATALYTIC OXIDATION OF HYDROGEN ON PLATINUM. A SEARCH FOR CHEMILUMINESCENCE AND IONIZATION

R. POTVIN and C. OUELLET

Laboratory of Physical Chemistry, Laval University, Quebec, Canada

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INTRODUCTION

Numerous investigations have shown that the radiation and ionization in hot flames can be accounted for by a purely thermal mechanism. Although part of the energy responsible for these phenomena could be derived directly from the chemical reaction, as in cold chemiluminescence, it is difficult to obtain direct evidence of such chemical excitation in the presence of the intense thermal excitation in hot flames of hydrogen, hydrocarbons, and carbon monoxide, as shown by Bonhoeffer (2), Konradjew (7), Garner and Saunders (4), and Gill (5). The present paper describes an attempt to eliminate the thermal background by causing the reaction to proceed at low temperatures on a catalyst. Any effect detected under such conditions should be ascribed a chemical origin.

The oxidation of hydrogen on platinum at temperatures ranging from 80°C. to 170°C. has been investigated, and the light measurements have been limited to the ultraviolet part of the spectrum. Although the net reaction heat is only 57 kg-cal., a number of intermediate steps involving