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A STUDY OF THE SYSTEM: WATER, POTASSIUM IODIDE AND IODINE AT ZERO DEGREES.

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This investigation was undertaken as a necessary preliminary step in the study of the temperature coefficient of the free energy of formation of silver iodide from its elements. The method of procedure in determining this free energy was to measure the electromotive force of cells in which silver iodide is reversibly formed from silver and iodine at 0° and 25°. One-half of these cells consisted of a silver electrode surrounded with solid silver iodide immersed in a dilute potassium iodide solution; the other half consisted of a platinum electrode surrounded by solid iodine immersed in a saturated solution of iodine in dilute potassium iodide solution.

In order to apply a correction for the potential at the boundary of the two solutions and a correction for osmotic work involved in the operation of the cell, it is necessary to know the concentration and mobility of the potassium, iodide and tri-iodide ions present in each half of their cell at two different temperatures.

The necessary information in regard to the ionic mobilities and concentrations at 25° is furnished by the investigation of Bray and MacKay.[1]

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[1] W. C. Bray and G. M. J. MacKay, THIS JOURNAL, **32**, 914 (1910); W. C. Bray, *Ibid.*, **32**, 932 (1910).

No other comprehensive investigation at any other temperature is known to us.[1] It was, therefore, decided to make a study of dilute potassium iodide solutions saturated with iodine at 0°. This study necessarily follows closely the methods used by Bray and MacKay, both in experimental procedure and in the interpretation of the results. It is a pleasure to acknowledge our indebtedness to these authors for many valuable suggestions. We introduced a number of variations in the experimental methods, some of which were required because we were making our measurements at 0°, but with one exception these variations were probably without significant effect on the results. This exception is the determination of the change in viscosity caused by the solution of potassium iodide and of potassium iodide plus iodine in water. As will be shown more in detail in the following pages, a 0.1 *N* solution of potassium iodide has a viscosity only 0.982 of the viscosity of pure water at the same temperature. Therefore, the degree of dissociation of potassium iodide would be overestimated by about 1.8% by the usual method of calculation. After this solution is saturated with iodine at 0°, its viscosity is raised to 0.995 of that of water. Therefore, the change in conductivity when iodine is dissolved in potassium iodide solutions is not due wholly to the replacement of part of the iodide ion by the tri-iodide ion, but partly to a slower motion of all of the ions present. Bray and MacKay neglected this influence, but, fortunately, the error caused thereby at 25°, although greater than the other errors in the work of Bray and MacKay is much less than the errors which would have been caused at 0° by the neglect of this correction. Of course the influence of the change in viscosity is less with the weaker solutions.

Purification of Materials.

Water.—All of the water used in this investigation, either in the purification of chemicals or in making the solutions, was conductivity water obtained from the special still[2] in this laboratory. The distillation was made from alkaline permanganate solution, and only the middle portion was collected for use. It was collected hot in previously steamed bottles of "non-sol" glass. The specific conductance of this water prepared at different times varied from 0.24×10^{-6} to 0.7×10^{-6} at 0°.

Iodine.—Iodine was prepared by dissolving "C. P." resublimed iodine in a very concentrated potassium iodide solution, diluting and distilling off the iodine. It was then washed with water on a Büchner funnel to remove any salts which might have spattered over during distillation,

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[1] H. M. Dawson, *J. Chem. Soc.*, **79**, 239 (1901), has studied the equilibrium $KI + I_2 \rightleftarrows KI_3$ at 13.5°, but his purpose did not require the measurement of the electrical conductivity of his solutions.

[2] Our still was patterned after the one described by Noyes and Coolidge, *Proc. Am. Acad.*, **39**, 190 (1910).

and then reduced to hydriodic acid by adding yellow phosphorus. The reaction went very smoothly; after standing on the steam bath for a short time the solution was completely decolorized. The hydriodic acid was separated from acids containing phosphorus by distillation. The solution being more dilute than the constant boiling mixture, water came off first, and this fraction must have contained all the hydrocyanic acid, if any were formed during the process.[1] Acid boiling from 123° to 135° was collected.

The iodine was liberated from a portion of this acid by action of halogen-free potassium permanganate and sulfuric acid.[2] The precipitated iodine was thoroughly washed with water in a Büchner funnel and dried in a desiccator over sulfuric acid for nearly a year before use. A short time before use this iodine was resublimed in a current of dry air, the condenser consisting of a hard glass tube which fitted into the subliming apparatus by a ground glass joint.

Potassium iodide.—Another portion of the hydriodic acid, prepared as described above, was redistilled, reserving only the portion which distilled over between 125° and 127° for use in making potassium iodide. Kahlbaum's potassium bicarbonate, which contained some normal carbonate but no halogens, and which showed only a trace of sodium by the flame test, was recrystallized by dissolving in hot water, cooling and passing in pure carbon dioxide. This gave a mixture of carbonate and bicarbonate, which was dried centrifugally[3] in platinum Gooch crucibles. It gave no flame test for sodium after this treatment. The hydriodic acid was added in slight excess and the solution concentrated by evaporation. The potassium iodide was then crystallized by cooling and the salt dried centrifugally. The salt had a slight yellow color due to free iodine. It was heated on an electric stove at 60° for twenty-four hours to drive off water, hydriodic acid and iodine. The salt thus prepared was perfectly white and when dissolved in water gave a solution which was neutral and contained no free iodine and no iodate. It was found to be unsafe to heat the salt above 60° because iodine is liberated and it becomes alkaline.

Experimental Methods.

The Preparation of the Standard Potassium Iodide Solutions.

The potassium iodide was dried to constant weight at 60° by reheating for several hours in the weighing bottle on an electric stove. It was then

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[1] Commercial iodine sometimes contains traces of iodine cyanide which may be eliminated as described above. See G. P. Baxter, *Proc. Am. Acad. Arts and Science*, **40**, 421 (1904).

[2] A little manganese peroxide was precipitated with the iodine owing to failure to secure the best proportions of the reagents. It was, however, completely separated later by subliming the iodine.

[3] G. P. Baxter, THIS JOURNAL, **30**, 287 (1908).

weighed and dissolved in a "non-sol" glass bottle in conductivity water to make a solution approximately 0.1 *N* and the exact weight of the solution was determined.[1]

The mols of potassium iodide per thousand grams of solution is called the weight normality of the solution. The density of this solution at 0° was carefully determined in order that the mols per liter or volume normality could be calculated. The density determinations were made in a pycnometer of the familiar Ostwald-Sprengel type, which was modified by the addition of a small bulb in the larger capillary tube beyond the graduation mark, of sufficient capacity to prevent loss of liquid owing to expansion when the solution was warmed to room temperatures for weighing. It was provided with a ground glass cap over the capillary tip to prevent evaporation. It had a volume slightly greater than 26 cc. and its weight when filled to the mark was concordant on successive trials to within 0.5 mg., or about 2 parts in one hundred thousand. A similar pycnometer was used as a counterpoise when weighing.

All solutions weaker than 0.1 *N* were prepared by dilution of a stronger solution by weight rather than by volume. Conductivity water was added to a known weight of a standard solution in a "non sol" bottle and the weight of the more dilute solution determined. The volume normality of the diluted solution at 0° was calculated with the help of the density. This procedure is more accurate than dilution by means of pipets, since the results are not influenced by uncertainties in drainage or temperature. These advantages are especially marked if it is necessary to know the concentration of solutions at temperatures far removed from room temperatures.

Conductance Measurements.

The conductance measurements were made by means of a slide-wire bridge of the roller type made by Leeds & Northrup. The bridge wire was manganin about two meters long with scale divisions of approximately three millimeters. The bridge wire was calibrated against the resistances of two Leeds & Northrup decade boxes, which had been standardized by the Bureau of Standards. The resistances used were made of manganin wire wound according to the Chaperon[2] principle to reduce self-induction and static capacity. These resistances were checked against standard resistance boxes and were found to be free from significant errors. A small condenser was used, when necessary, to balance the capacities of the resistance box and the conductivity cell, as recommended by Kohlrausch and Holborn.

A commutating device on the bridge allowed the ends of the wire to be reversed or commutated, and this was done in every case, although

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[1] All weights have been corrected to vacuum.

[2] Chaperon, *Compt. rend.*, **108**, 799 (1889); Kohlrausch and Holborn, p. 58.

no variation in resistance was found by reversing the position of the resistance box and the conductance cell. Readings on the bridge were reproducible to one part in five thousand. The conductance cells were of the pipet type.[1] The cell constants were determined exactly according to the directions of Kohlrausch and Holborn, "Leitvermögen der Electrolyte." The constant of No. 1 was found by E. K. Strachan to be 4.077 at 0°, using both 1 *N* and 0.1 *N* potassium chloride. We determined the constant of No. 2 using 0.1 *N* potassium chloride and found it to be 0.6222, which agrees exactly with the result of Washburn and MacInnes on the same cell obtained a year before. The constant of cell No. 3 was determined to be 0.06198 by comparison with No. 2 by using the same dilute solution in both cells. This result agreed exactly with that obtained by C. G. Derick, using 0.01 *N* potassium chloride. The conductance of the water used was determined by means of a cell with platinum-iridium electrodes about 3 cm. in diameter and 1 mm. apart. The surfaces of these electrodes were sand-blasted, but not covered with platinum black. The constant of this cell was 0.0294.

The conductance cells were kept during measurement in large Dewar tubes filled with distilled water and finely cracked ice made from distilled water.

An approximate setting having been made on the bridge, sufficient time was allowed to insure that the cell was at 0°, and then the final adjustment was made. This precaution was necessary because the solutions, especially the concentrated ones, became heated by the current from the induction coil, thereby decreasing the resistance. In all cases the ends of the bridge were commutated and readings made with the resistance in the box both higher and lower than the resistance of the solution in the other arm of the bridge. These values agreed within 0.1%.

The specific conductance of the water used in making the solutions was always measured and subtracted from the observed conductance of the solutions. This was never larger than 0.7×10^{-6} at 0°.

Saturation of the Potassium Iodide Solutions with Iodine.

The saturation of the potassium iodide solution with iodine was accomplished by shaking the solution with an excess of iodine in 250 cc. "non sol" glass-stoppered bottles in a shaking machine working in a bath of finely cracked ice and distilled water. The shaking was accomplished by means of a simple reciprocating motion from a crank on a fly wheel, and driven at high speed by a motor. The piston rod was supported

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[1] See E. W. Washburn and D. A. MacInnes, THIS JOURNAL, 33, 1688–9 (1911) for a diagram and description of the type of cell used. These authors point out that this type of cell has important advantages over the usual form. Our cell No. 2 was the same as Washburn and MacInnes' cell No. 2. Our Nos. 1 and 3 were similar to theirs, but not the identical cells.

at an angle in order to secure the greatest efficiency in stirring in the bottle. The machine made about 200 strokes per minute. After the bottle was filled almost full of the solution under investigation, and an excess of solid iodine had been added, the stopper was inserted and a rubber "cap" was then slipped over the stopper and neck of the bottle and wired on to prevent the water of the ice bath from reaching the ground glass joint. The bottle was shaken in the ice bath for one and a half hours or more. Experiments were made which showed that this amount of shaking gave complete saturation.

After saturating with iodine, the electrical conductivity, density and free iodine dissolved were determined. The bottle was first allowed to stand for a short time to allow the iodine to settle and then the conductance cell was filled directly from the bottle without filtering, since the presence of particles of solid iodine could do no harm. A portion for the density determination was forced by air pressure through a tube containing a small bulb filled with tightly packed asbestos, which served as a filter, into a beaker cooled with ice and from this at once transferred to the pycnometer.[1] Several portions of the solution for analysis were forced in the same manner into weighed glass-stoppered flasks. The filtering bulb was below the liquid in the shaking bottle, and so it was always at 0°, thus preventing any warming of the solution while in contact with solid iodine. The flasks containing these samples were allowed to warm up to room temperature, and were then weighed. They were then cooled again with ice to condense the iodine vapors before the flasks were opened for titration, in order to avoid loss of iodine. In the later experiments several grams of solid potassium iodide were added to the flask and weighed with it before the sample was forced into the flask. This reduced the vapor pressure of iodine and thus served to prevent loss.

The free iodine was titrated by means of standard solutions of sodium arsenite containing a large amount of monosodium and disodium phosphates in the proportions recommended by Washburn,[2] who has clearly demonstrated that this is a very accurate titration when carried out under the proper conditions. Two solutions about 0.15 N and 0.007 N, respectively, were used. These titrations were carried out entirely by means of weight burets for the sake of accuracy, the final approach to the end point being accomplished with the dilute solution. In rare cases the end point was passed accidentally and in these cases a dilute iodine solution, approximately 0.006 N, was used. This solution was standardized against the dilute arsenite solution. These arsenite solutions were standardized against known weights of pure dry iodine, the weighing

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[1] The first 5 or 10 cc. which came through were always rejected.

[2] E. W. Washburn, This Journal, **30**, 31 (1908); Washburn and Bates, *Ibid.*, **34**, 1355 (1912).

bottle being opened under the arsenite solution to prevent loss of iodine. These standardizations were concordant within 0.02%, which was ample for the present purpose.

We found that a very satisfactory method of determining when the iodine was all reduced was to titrate until the very faintest yellow color remained. Then about 5 cc. of pure benzene were added and the solution shaken violently. The small trace of iodine dissolved in the benzene gave a pink color, which could be easily seen. Dilute arsenite solution was then added drop by drop until the pink color in the benzene layer had disappeared after shaking.

Viscosity Measurements.

The viscosity measurements were very kindly made for us by G. Y. Williams.[1] The viscosities of potassium iodide solutions approximately 0.1 *N* and 0.05 *N* were measured at 0° (see Table III, Column 5, for the results) and at 25° (Table IV, Column 5) and then these solutions were saturated with iodine at 0° and the viscosity determined again at 0° (Table III, Column 9) and at 25°. Since these solutions were not quite saturated at 25°, a slight correction has been made on the assumption that the small additional amount of iodine had the same proportional effect on the viscosity. The results are given in Table IV, Column 9. It is believed that these viscosity data are accurate within 0.1%.

TABLE I.—THE EXPERIMENTAL DATA.

First Series.

	Potassium iodide.				Saturated with iodine.			
No.	Wt. norm.	Density 0°/4°.	Vol. norm. 0°.	Specific conductance $\times 10^6$.	Density 0°/4°.	Gram iodine per g. sol.	Spec. cond. $\times 10^6$.	Σ K vol. norm. 0°.
1	0.09861	1.01231	0.09982	7340.7	1.02187	0.01199	6412.9	0.09956
2	0.04966	1.00610	0.04996	3765.2	1.01089	0.006083	3308.4	0.04989
3	0.01992	1.00236	0.01997	1549.6	1.00429	0.002535	1365.8	0.019957
4	0.00998	(1.0011)	0.009993	789.2	(1.0020)	0.0013546	694.0	0.009990
						0.0013518	692.0	
5	0.004991	(1.0005)	0.004993	400.1	(1.0011)	0.0007574	352.8	0.004992
						0.0007580	352.9	
6	0.002000	(1.0001)	0.002000	162.31	(1.0004)	0.0004074	142.9	0.002000
						0.0004238*	142.8	
						0.0004099		
7	0.000992	(1.0000)	0.000992	81.19	(1.0002)	0.0002823	71.9	0.000992
						0.0002802*	72.0	

* Not included in summary Table III. Numbers in parentheses are interpolated values.

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[1] See Washburn and Williams, THIS JOURNAL, **35**, 737 (1913) for a description of the method. These measurements were made in the early stages of their investigation described in this paper and before all of the experimental details had been perfected.

TABLE II.—EXPERIMENTAL DATA.

Second Series.

	Potassium iodide.				Saturated with iodine.			
No.	Wt. norm.	Density 0°/4°.	Vol. norm.	Specific conductance $\times 10^6$.	Density 0°/4°.	G. iodine per g. sol.	Spec. cond. $\times 10^6$.	Σ K vol. norm.
8	0.09871	(1.0123)	0.09993	7341.1	(1.0219)	0.01199	6403.6	0.09966
9	0.04969	(1.0061)	0.05000	3753.7	(1.0109)	0.006088	3297.6	0.04992
						0.006100*	3296.5	
10	0.01983	(1.0024)	0.01988	1538.3	(1.0044)	0.002533	1353.5	0.01987
						0.002532	1353.1	
11	0.009992	(1.0011)	0.010003	787.75	(1.0020)	0.001361*	694.2	0.01000
						0.001356	692.2	
12	0.004999	(1.0005)	0.005001	399.90	(1.0010)	0.0007586	352.6	0.005000
						0.0007632	352.6	
13	0.002000	(1.0001)	0.002000	162.16	(1.0004)	0.0004021	143.31	0.002000
						0.0004009	143.5	
14	0.000999	(0.9999)	0.000999	81.72	(1.0002)	0.0002869	72.3	0.000999
						0.0002823	71.9	
						0.0002825	72.0	

* Not included in summary Table III.

The Experimental Data.

The experimental data for the solubility, density and conductance are shown in Tables I and II. The figures for the conductance are the averages obtained by commutating the bridge-wire and changing the resistance used. The figures for the solubility of iodine are the averages obtained by titrating two or three portions of the same solution. When more than one set of data is given for the solutions, saturated with iodine, they represent separate saturations with iodine of the corresponding potassium iodide solutions. Except in a very few cases, the conductance data are concordant within 0.1%. The solubility data do not agree so well, discrepancies of 0.2% being common. In a few cases discrepancies up to 1%, and in one case up to 4%, were encountered, but a repetition of the experiment and a plot of the results at different concentrations enables us to reject the erroneous results. These occasional erratic results were probably due to small particles of solid iodine passing the filters. Bray and MacKay[1] also found it impossible to secure as great conductance in the solubility data as in the conductance data.

The last column gives the volume normality of the solutions saturated with iodine corrected for the change in volume, which occurs when iodine is dissolved.

The solubility of iodine in mols I_2 per liter in potassium iodide solutions at 0° is expressed within the limit of error of our experiments up to and including 0.05 N by the linear equation, $(I_2) = 0.000638 + 0.472\ c$, c being the concentration of the potassium iodide solution. A 0.1 N

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[1] Bray and MacKay, THIS JOURNAL, **32**, 919 (1910).

solution dissolves about 1% more iodine than the result given by this equation.

The density determinations were carried out with the three strongest solutions only, because the density was found to be a linear function of the concentration with an accuracy much surpassing our needs. For potassium iodide solutions

$$d\ ^{0°}/_{4°} = 0.99987 + 0.1246\ c.$$

For the same solutions saturated with iodine,

$$d\ ^{0°}/_{4°} = 0.99987 + 0.2205\ c.$$

The Equivalent Conductance of Potassium Iodide.

In order to simplify the interpretation and use of the experimental data, the results of the two series have been rounded off to even concentrations by volume, as shown in Table III. Experimental results which were known to be in error, and in a few cases data which for some unknown reason were obviously discordant with the other data, have been rejected in deriving this summary table. Column 3 gives the equivalent conductance of potassium iodide solutions at 0°. Similar measurements have been made by Sloan,[1] Kahlenberg,[2] and Harry C. Jones.[3] These results have all been plotted (log C against Λ and by the Noyes method $1/\Lambda$ against $(C\Lambda)^{n-1}$) for comparison. Sloan's measurements extend from 0.04235 *N* to 5.1 *N*. In the small range where our measurements overlap with Sloan's, his values for Λ are about 0.2 higher than ours, and our results may be regarded as an extension of Sloan's curve into more dilute solutions. The curve (log C against Λ) representing Kahlenberg's results is very irregular, having two well-marked points of inflection in marked contrast to the curve representing our results, which has none.[4] Three of Kahlenberg's points (C = 1/32, 1/64, 1/128) fall near our curve, but the others are about 1 to 1.15 units on the conductance lower than ours and Sloan's. The curve representing Harry C. Jones' results is lower than ours by 4 or 5 units of the equivalent conductance or about 6%. The measurements of Harry C. Jones on potassium iodide at 25° are lower than those of Bray and MacKay at 25° by about the same per cent.

The equivalent conductance of potassium iodide at infinite dilution has been found to be 83.5 by the plotting of $1/\Lambda$ against the corresponding value of $(C\Lambda)^{n-1}$, as proposed by A. A. Noyes.[5] The value of n was found by trial plots using several values from $n = 1.3$ to $n = 1.6$, and choosing $n = 1.45$ as the exponent which gave the best straight line through

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[1] W. H. Sloan, THIS JOURNAL, 32, 946 (1910).

[2] L. Kahlenberg, *J. Phys. Chem.*, 5, 348 (1901).

[3] H. C. Jones, *Carnegie Inst. of Washington Pub.*, 170, 21 (1912).

[4] See Noyes and Falk, THIS JOURNAL, 34, 473 (1912), footnote 13.

[5] A. A. Noyes, THIS JOURNAL, 31, 745 and 1010 (1909); Carnegie Publication No. 63.

TABLE III.

This table applies at 0°.

1. Vol. norm. KI.	2. Density 0°/4°.	3 Λ_{KI}.	4. 100γ KI not corrected.	5. η/η_0 KI.	6. $\Lambda\eta/\eta_0$ KI.	7. 100γ KI corr. for viscosity.	8. Λ KI + KI_3.	9. η/η_0 KI + KI_3.	10. $\Lambda\eta/\eta_0$ KI + KI_3.	11. $\Delta\Lambda$.
0.1	1.0124	73.5	88.0	0.982	72.2	86.4	64.35	0.995	64.05	8.15
0.05	1.0061	75.2	90.1	0.991	74.5	89.25	66.2	0.9975	66.05	8.45
0.02	1.0023	77.5	92.8	0.996	77.2	92.45	68.25	0.999	68.2	9.05
0.01	1.0011	78.85	94.5	0.998	78.7	94.3	69.4	0.9995	69.4	9.3
0.005	1.0005	80.05	95.8	0.999	80.0	95.8	70.6	1.000	70.6	9.4
0.002	1.0001	81.1	97.2	0.9996	81.05	97.1	71.55	1.000	71.5	9.55
0.001	1.0000	81.8	98.0	0.9998	81.8	98.0	72.2	1.000	72.2	9.6
0.000	..	83.5	100.0	..	83.5	...	..	..	..	9.8

KI.	12. ΣK.	13. $\Sigma KI_3 + I_2$.	14. ΣI_3.	15. ΣI.	16. $r = \Sigma I_3/\Sigma K$.	17. $\Delta\Lambda/r$.	18. Λ KI_3 corr.	19. γ KI_3 corr.	20. I^-.	21. I_3^-.	22. I^-/I_3^-.	23. $(I^-)(I_2)/I_3^-$.
0.1	0.09973	0.04833	0.04769	0.05204	0.478	17.05	55.15	87.7	0.04498	0.04181	1.076	686 × 10^{-6}
0.05	0.04993	0.02426	0.02362	0.02631	0.473	17.9	56.6	90.0	0.02348	0.02125	1.105	705
0.02	0.01999	0.01006	0.00942	0.01057	0.471	19.1	58.1	92.4	0.00977	0.00870	1.123	716
0.01	0.009996	0.005354	0.004716	0.005280	0.472	19.7	59.0	93.8	0.004976	0.004423	1.125	718
0.005	0.004999	0.002993	0.002355	0.002644	0.471	19.9	60.1	95.4	0.002533	0.002246	1.128	720
0.002	0.002000	0.001582	0.000944	0.001056	0.472	20.2	60.85	96.7	0.001025	0.000913	1.123	717
0.001	0.001000	0.001113	0.000475	0.000525	0.475	20.2	61.6	97.8	0.000514	0.000464	1.108	707
0.000	0.000000	0.000638	....	....	0.472	20.7	62.9	...	....	....	...	..

TABLE IV.

This table applies at 25°. Data from Bray and MacKay, THIS JOURNAL, 32, 914, corrected for viscosity.

1. Vol. norm. KI.	2. Density.	3. Λ_{KI}.	4. 100γ KI not corrected.	5. η/η_0 KI.	6. $\Lambda\eta/\eta_0$ KI.	7. 100γ KI corr. for viscosity.	8. Λ KI + KI_3.	9. η/η_0 KI + KI_3.	10. $\Lambda\eta/\eta_0$ KI + KI_3.	11. $\Delta\Lambda$.
0.1		130.8	86.5	0.994	130.0	85.9	115.25	1.003	115.6	14.4
0.05		137.7	89.1	0.997	134.3	88.8	118.8	1.0015	119.0	15.3
0.02		139.4	92.1	0.999	139.3	92.05	123.45	1.0005	123.5	15.8
0.01		142.3	94.1	0.9995	142.25	94.0	126.0	1.000	126.0	16.25
0.005		144.5	95.5	1.000	144.5	95.5	128.2	1.000	128.2	16.3
0.002		146.7	97.0	1.000	146.7	97.0	130.4	1.000	130.4	16.3
0.001		147.9	97.8	1.000	147.9	97.8	131.7	1.000	131.7	16.2
0.000		151.3	100.0	..	151.3	...	..	..	..	...

KI.	12. ΣK.	13. $\Sigma KI_3 + I_2$.	14. ΣI_3.	15. ΣI.	16. $r = \Sigma I_3/\Sigma K$.	17. $\Delta\Lambda/r$.	18. Λ KI_3 corr.	19. γ KI_3 corr.	20. I^-.	21. I_3^-.	22. I^-/I_3^-.	23. $(I^-)(I_2)/I_3^-$.
0.1	0.09969	0.05135	0.05003	0.04966	0.502	28.7	101.3	87.5	0.04267	0.04377	0.9751	1287×10^{-6}
0.05	0.04992	0.02577	0.02445	0.02547	0.497	30.8	103.5	89.4	0.02261	0.02185	1.034	1366
0.02	0.01999	0.01113	0.00981	0.01018	0.491	32.2	107.1	92.5	0.00937	0.00907	1.033	1363
0.01	0.01000	0.006185	0.004865	0.005135	0.486	33.45	108.8	94.0	0.004827	0.004571	1.056	1394
0.005	0.00500	0.003728	0.002408	0.002592	0.482	33.8	110.7	95.6	0.002475	0.002302	1.075	1420
0.002	0.00200	0.002266	0.000946	0.001054	0.473	34.5	112.2	96.9	0.001022	0.000917	1.115	1472
0.001	0.00100	0.001788	0.000468	0.000532	0.468	34.6	113.3	97.8	0.000520	0.000458	1.136	1499
0.000	....	0.00132	....	....	...	...	115.8	100.0	....	....	..	..

the points. This was also shown to be the best line by calculating the deviations by the method of least squares. The first series gave $\Lambda_0 = 83.47$ and the second series $\Lambda_0 = 83.49$. The rounded-off value 83.5 is accepted.

This method is purely empirical and every one who has used it has recognized that the results obtained with it are open to some doubt. Recently Bates[1] has argued that the values of Λ_0 obtained by this method are too high by about 0.5%. Still more recently Kraus and Bray[2] have proposed a general equation for the relationship between ionization and concentration of solutions, which they consider applicable to all solutions, both dilute and concentrated, aqueous and non-aqueous. This general equation is $c\gamma^2/1 - \gamma = K + D(c\gamma)^m$. Since $\gamma = \Lambda/\Lambda_0$ and the value of Λ_0 must also be selected to fit the data, this is a four constant equation.

An equation having a different form, but mathematically equivalent to the above equation, has been proposed independently by MacDougall.[3]

The argument of Kraus and Bray is based mainly on a discussion of data on non-aqueous solutions. They have applied their equation to a single aqueous solution, namely, potassium chloride, at 18°, using the data of Kohlrausch and Maltby. They reach the conclusion that the equivalent conductance of potassium chloride at infinite dilution at 18° is 128.3 instead of 130.1, which is the value given by Noyes' method and has been commonly accepted. Kraus and Bray's method thus gives a result which is nearly 1.5% lower than Noyes' method in this case. The method of Kraus and Bray requires a knowledge of the conductivity and viscosity of very concentrated solutions (up to several times normal). These data are not available in very many cases. They find it necessary to reject the data for solutions below 0.001 *N*, which by their method of plotting do not fall on the same curves as the data for all the stronger solutions.[4] They conclude that these data are in error owing to the uncertainty in applying the water correction. Bates,[5] on the other hand, lays especial

[1] S. J. Bates, THIS JOURNAL, **35**, 519 (1913).

[2] C. A. Kraus and W. C. Bray, *Ibid.*, **35**, 1315 (1913).

[3] F. H. MacDougall, *Ibid.*, **34**, 855 (1912). MacDougall considers this a three constant equation, and assumes γ known, apparently overlooking the fact that Λ_0 must be selected to fit the data, and does not use the equation as a means of determining Λ_0.

James Kendall, *Proc. Chem. Soc.*, **28**, 255 (1912), has proposed the equation $c\gamma^2/1 - \gamma = K + D(1 - \gamma/\gamma)$ which he derives theoretically from very improbable assumptions. He does not publish any attempts to test his equation by means of the available data. We have, however, convinced ourselves that it is not possible to find a value for Λ_0 which will make this equation agree with Kohlrausch's data on potassium chloride at 18°, and this equation therefore is not generally applicable.

[4] Kraus and Bray, *Loc. cit.*, p. 1413.

[5] Bates, *Ibid.*, p. 528.

emphasis on the data for these extremely dilute solutions. He says, "If these constants (equivalent conductances at infinite dilution) are to be known with a certainty greater than 0.1% it is necessary that accurate conductivity data be determined for solutions more dilute than 0.0001 *N*."

It is evident that a definite solution of this problem must await the collection and publication of much new data on the conductivity of both very dilute and very concentrated solutions and the viscosity of the latter. Pending the collection of the new data and the reinterpretation of the best of the old, and the general adoption of some new method of extrapolating to infinite dilution, it has seemed best to use the Noyes method in interpreting our data. Our results will then be consistent and comparable with the great body of figures in the literature dealing with ionic mobilities and ionization including the similar work of Bray and MacKay at 25°. The results calculated in this way will be equally useful for the calculation of the corrections to the electromotive force of our silver-silver iodide-iodine cells, because we do not need to know the absolute values of the concentration and mobilities of the ions in potassium iodide solutions and in potassium iodide solutions saturated with iodine, provided the ratios of these quantities are correct. We will, therefore, adopt provisionally the value 83.5 for the equivalent conductivity of potassium iodide at infinite dilution at 0°. Noyes and Falk[1] have calculated the identical value for this constant, using Déguisne's[2] data on the temperature coefficient of conductance. Déguisne's thesis does not give the actual conductance measurements but only the temperature coefficients. The most probable value of the equivalent conductance of the potassium ion appears to be 40.1. This is derived from the equivalent conductance[3] of potassium chloride at infinite dilution at 0°, 81.4, and the transference number[4] of the cation in this salt at 0°, 0.493. The equivalent conductance of the iodide ion at 0° is, therefore, 83.5 — 40.1 = 43.4.

Referring again to Table III, Column 4 gives the degree of dissociation calculated by the usual formula $\gamma = \Lambda_c/\Lambda_o$. But since the viscosity of the more concentrated solutions is appreciably different from that of water, it will doubtless be more accurate to write $\gamma = \Lambda_c\eta/\Lambda_o\eta_o$, where η/η_o is the relative viscosity of the solution to that of water at the same temperature, the results being given in Col. 5. Col. 6 gives $\Lambda_c\,\eta/\eta_o$, which is the conductivity to be expected in a solution of unit viscosity. This figure, from which viscosity effects have been eliminated, is a convenient figure to use in studying change in conductivity caused by adding iodine.

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[1] Noyes and Falk, THIS JOURNAL, 34, 468 (1912).

[2] Déguisne, Dissertation, Strassburg (1895); Landolt-Börnstein Tabellen, 1912 ed., p. 1116.

[3] A. A. Noyes and K. G. Falk, THIS JOURNAL, 34, 468 (1912).

[4] *Ibid.*, 33, 1454 (1911).

The Equivalent Conductance of Potassium Triiodide at 0°.

The experimental data concerning potassium iodide solutions saturated with iodine is also summarized in Table III, corrected to even concentrations, and a number of quantities calculated from the experimental data.

When iodine dissolves in potassium iodide, the volume of the solution increases and a correction must be applied, in the case of the stronger solutions, in order to compare them with the solutions of potassium iodide from which they were made. The change in concentration due to this volume increase was calculated for the stronger solutions, using our data for the density and concentration of these solutions. The concentrations expressed in terms of the total potassium salts $(KI + KI_3) = \Sigma K$ in the solutions saturated with iodine are given in Col. 12.

Col. 13 gives the free iodine in the solution, that is, the total amount titrated with the arsenite solution. This includes free iodine dissolved in the water as I_2 and the iodine in the complexes ($I_3^- + KI_3$ and higher complexes if present).

The solubility of iodine in pure water was determined to be 0.000638 mols I_2 per liter (see page 256). Subtracting this amount from the total iodine gives $\Sigma I_3 = I_3^- + KI_3$ (assuming higher complexes absent).

Substracting ΣI_3 from ΣK gives $\Sigma I = (I + KI)$ (Col. 15) the concentration of the iodide in the solution. In Col. 16, the ratio $\Sigma I_3/\Sigma K = r$ is given. This ratio is independent of the degree of dissociation, since it relates only to the total I_3 and total K.

The equivalent conductances of the solutions saturated with iodine are given in Col. 8. These equivalent conductances have been corrected for viscosity, and these corrected conductances are given in Col. 10.

The change in the equivalent conductance due to the solution of iodine to form the slower moving ion I_3^- is found by subtracting the data of Col. 10 from that of Col. 6. These differences are shown in Col. 11 ($\Delta\Lambda$).

If we assume that, when part of the potassium iodide is converted into potassium triodide, there is no change in the degree of dissociation of the remaining potassium iodide.[1] then the ratio $\Delta\Lambda/r$ shown in the 17th column represents the decrease in equivalent conductance which would be

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[1] This is in accord with what is known about the ionization of salts in mixtures.

"In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture;" Arrhenius, *Z. physik. Chem.*, **2**, 285 (1888); Arrhenius, *Ibid.*, **31**, 218 (1899); MacGregor, McIntosh, Archibald and MacKay, *Trans. Nova Scotia Inst. Science*, 9 and 10 (1895–1899); A. A. Noyes, *Z. physik. Chem.*, **52**, 635 (1905); M. S. Sherrill, THIS JOURNAL, **32**, 741 (1910); G. M. J. MacKay, *Ibid.*, **33**, 308 (1911).

obtained if all of the iodide were changed into triiodide, and if the resulting triiodide had the same degree of dissociation that it has in the mixture. This does not involve the assumption that the degree of dissociation of potassium triiodide is identical with the degree of dissociation of potassium iodide. Subtracting this change of conductance from the equivalent conductance of potassium iodide solution gives the equivalent conductance of a solution of potassium triiodide of the concentration $=\Sigma K$, and having a degree of dissociation equal to the triiodide in the mixture. These data have been plotted in the same manner as the potassium iodide solutions, and the extrapolation made to infinite dilution. By this method the equivalent conductance of potassium triiodide at infinite dilution has been found to be 62.9. If the mobility of the potassium ion be taken as 40.1, that of the triiodide becomes 22.8.

The degree of dissociation of the triiodide is given in Column 19. On comparing this with the degree of dissociation of the potassium iodide corresponding, it will be noticed that the triiodide is slightly less dissociated below 0.02 *N* but in the 0.1 *N* and 0.05 *N* solution it is slightly more dissociated. The slightly smaller value for 0.001 *N* solution is probably not significant, since it is difficult to secure the same percentage accuracy in this dilute solution. Perhaps this exceptional behavior of the 0.1 *N* solution is only apparent and would disappear if the proper allowance could be made for the presence of higher complexes. The concentrations of the iodide and the triiodide ions and their ratio are given in the next three columns. This ratio is essentially constant for all the concentrations up to 0.05 *N* and 0.1 *N* and here falls off very slightly. This is somewhat remarkable in view of the previous work of Bray and MacKay at 25°. They found that at 25° the ratio I^-/I_3^- decreased from 1.14 to 0.99 with increasing concentrations from 0.001 to 0.1 *N* and became 0.35 at 1 *N*. No such marked deviation is found from the results of this investigation at 0°, although a slight tendency in that direction appears in the two stronger solutions. If this apparent deviation from the mass law at 25° is to be explained by the obvious assumption that a higher complex than KI_3 is formed, then the data at 0° would show that the formation of these higher complexes is much less at the lower temperature.

In the last column is shown the equilibrium constant for the reaction

$$I^- + I_2 = I_3^-$$

obtained by multiplying the ratio of the preceding column by the solubility of iodine in water, 0.000638 mols per liter.

This equilibrium constant is slightly lower than that obtained by Fedotieff[1] in the study of the reaction,

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[1] Fedotieff, *Z. anorg. Chem.*, 69, 31 (1911).

$$2Cu^+ + I_2 \rightleftarrows 2Cu^{++} + 2I^-.$$

He obtained the constant 735×10^{-6}.

The Solubility and Hydrolysis of Iodine in Water at 0°.

In order to determine to what extent the reaction

$$(1) \qquad I_2 + H_2O \rightleftarrows HIO + H^+ + I^-$$

might interfere with the conductance measurements of the very dilute solutions, some pure water was saturated with iodine by shaking at 0°, and the conductance of the solution measured. The conductance of the water itself was measured after it had been shaken under the same conditions. The average of several determinations showed that the hydrolysis caused an increase of 0.6×10^{-6} mhos in the conductance. The solubility of the iodine was 0.0006383 mols per liter.[1]

The reaction is further complicated by the side reaction

$$I^- + I_2 = I_3^-.$$

Combining the two equations, using the ratio $\Sigma I^-/\Sigma I_3^- = 1.125$ from Table III, gives

$$1.471\ I_2 + H_2O \rightleftarrows H^+ + 0.529\ I^- + 0.471\ I_3^- + HIO.$$

For every molecule of hydrogen ion produced, 1.471 mols of iodine are dissolved in forms other than I_2. If the mobilities of the hydrogen, iodide, and triiodide ions are taken as 240, 43.4 and 22.8, respectively, then for the water solution assuming complete dissociation

$$\Lambda = 240 + 0.529 \times 43.4 + 0.471 \times 22.8 = 273.7$$

$$\text{and } c = \frac{\kappa \times 10^3}{\Lambda} = \frac{(0.6 \times 10^{-6}) \times 10^3}{273.7} = 2.2 \times 10^{-6} \text{ mols } H^+$$

produced. Since every mol of H^+ ion represents 1.471 mols of iodine, there are dissolved 3.2×10^{-6} mols of iodine in the form of HIO, I^- and I_3^- in the water. Subtracting this from the total solubility of iodine in water gives 0.0006380 mols I_2 dissolved.

The hydrolysis constant may now be calculated for reaction (1).

$$K = \frac{(HIO)(H^+)(I^-)}{(I_2)} = \frac{(2.2)(2.2)(2.2 \times 0.53) \times 10^{-18}}{0.000638} = 9 \times 10^{-15}.$$

It is easy to show that hydrolysis is negligible in solutions containing 0.001 *N* KI. The iodide ion concentration in such a solution is 0.000514 and since $(H^+) = (HIO)$ we have

$$9 \times 10^{-15} = \frac{(H^+)^2\ 0.000514}{0.000638}$$

$$(H^+) = 1.05 \times 10^{-7}.$$

The increased conductivity is therefore

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[1] This is lower than the value obtained by Fedotieff (*Z. anorg. Chem.*, 69, 30 (1911), who obtained 1.30 mg. atoms per liter = 0.00065 mols per liter.

$$\frac{1.05 \times 10^{-7} \times 273.7}{1000} = 0.029 \times 10^{-6}$$

which is less than the uncertainty in the water correction and entirely negligible. The increase in free iodine dissolved in the form of HIO and I_3 owing to hydrolysis is 1.05×10^{-7} mols HIO and $0.471 \times 1.05 \times 10^{-7}$ mols I_3 together equivalent to 1.6×10^{-7} mols I_2, which is also negligible.

It is a well-known fact that chlorine water liberates free oxygen, especially in sunlight, and therefore the possibility of a similar reaction occurring with the much weaker oxidizing agent, iodine, was considered. On the other hand, strong potassium iodide solutions when exposed to air and sunlight liberate free iodine. We must, therefore, consider the possibility of the reaction $2I_2 + 2H_2O \rightleftarrows 4H^+ + 4I^- + O_2$. There are no electromotive data which throw light on this question at 0°. A study of the available data on iodine and oxygen electrodes at 25° indicates that under the conditions existing in a water solution of iodine there is a very slight tendency (about 0.04 volts) for oxygen to be liberated. This, however, gives no indication of the velocity of the reaction.

Another conceivable reaction is $3I_2 + 3H_2O \rightleftarrows 6H^+ + 5I^- + IO_3^-$. Since the conductance of water was only increased by 0.6×10^{-6} mhos by saturation with iodine, it is obvious that none of these reactions can occur sufficiently to cause an appreciable error in our results. We have assumed that the increased conductance is caused by the reaction $I_2 + H_2O \rightleftarrows HIO + H^+ + I^-$, as seems most probable. It is evident that none of these reactions occurs to an extent great enough to influence appreciably either the conductivity of our solutions or the amount of iodine dissolved. Therefore, it did not seem necessary to carry out experiments to decide between these alternatives.

A Comparison of the Results at 0° with those of Bray and MacKay at 25°.

The influence of the viscosity on the results having been found to be considerable at 0°, it seemed to us important to determine how great this influence is at 25°, and, if necessary, correct the results of Bray and MacKay.

The viscosities of a 0.1 *N* and 0.05 *N* solution of potassium iodide and the same solutions after saturating with iodine were found at 25° with the help of G. Y. Williams, the results being shown in Cols. 5 and 9 of Table IV.

The viscosities of the weaker solutions were obtained by interpolation. These results have been used to correct the results of Bray and MacKay, the results being shown in Table IV. The weaker solutions are, of course, not influenced by this correction, but it seemed worth while to reprint the figures in order to facilitate a comparison of the results at 0° and at

25°. Col. 7 shows that the degree of dissociation of potassium iodide is greater at 0° than at 25°. Bray and MacKay found the same effect of temperature on comparing their results at 25° with those of Kohlrausch at 18°. The influence of temperature on the dissociation of KI_3, on the other hand, although slight, is in the opposite direction. The solubility of iodine in potassium iodide solutions is somewhat less at 0° than at 25° (Cols. 13 and 14).

The most interesting comparison is found in Cols. 16, 22 and 23, which show a much greater constancy at 0° than at 25°. It is evident that the results conform to the requirements of the mass law much better at 0° than at 25°.

There is a slight deviation in the results at 0° with the two strongest solutions in the same direction as at 25°, but the deviations are comparatively small. The deviation from the mass law at 25° is discussed in considerable detail by Bray and MacKay, who reach the conclusion that the "activity of the ions is not proportional to their concentration."

Summary.

1. The conductances at 0° of potassium iodide solutions and of the same solutions saturated with iodine between 0.1 and 0.001 *N* have been measured.

2. The solubility of iodine in each of the solutions and in pure water has been determined.

3. The degree of dissociation of potassium iodide at 0° and 25° have been corrected for the change of viscosity of the solution.

4. The mobilities of the iodide and triiodide ions were found to be 43.4 and 22.8, respectively, at 0°.

5. The hydrolysis constant of iodine in water at 0° was found to be 9×10^{-15}.

6. The increase of the mass-law constant of the reaction $I_2 + I^- \rightleftarrows I_3^-$ with the concentration of the solutions, which was found by Bray and MacKay at 25°, we now find at 0°.

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ON THE ASSOCIATION OF MERCURIC CHLORIDE IN WATER SOLUTION.

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It is a generally accepted fact that mercuric chloride in solution of a pure indifferent solvent does not associate.[1] The data thus far published are the results obtained from a study of the molecular weight of mercuric chloride in several organic solvents,[2] and seem to justify the above con-

[1] Abegg's *Handbuch der Anorg. Chem.*, II, 2, 615.

[2] Castro, *Gazz. chim. ital.*, 28, II, 317; Salvadori, *Ibid.*, 26, I, 237.